



EUROPEAN PATENT APPLICATION

Application number : **95302141.7**

Int. Cl.⁶ : **G03C 1/95, G03C 1/79**

Date of filing : **30.03.95**

Priority : **01.04.94 JP 65131/94**

Date of publication of application :
04.10.95 Bulletin 95/40

Designated Contracting States :
DE FR GB NL

Applicant : **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome
Shinjuku-ku
Tokyo 163 (JP)

Inventor : **Masumi, Satoshi, c/o Konica Corp.**
28 Horinouchi
Odawara-shi, Kanagawa-ken (JP)
Inventor : **Ohkawachi, Susumu, c/o Konica Corp.**
28 Horinouchi
Odawara-shi, Kanagawa-ken (JP)

Representative : **Ellis-Jones, Patrick George**
Armine
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

Image forming process.

- Disclosed is an image forming method containing the steps of :
- (1) exposing a silver halide color photographic light-sensitive material with scanning laser-light ; and
 - (2) developing said exposed silver halide color photographic light-sensitive material comprising a support having a resin layer, provided thereon at least one of light-sensitive layers including silver halide grains and at least one of layers other than said light-sensitive layers provided under the lowermost layer of said light-sensitive layers, wherein at least one of said layers other than said light-sensitive layers or said resin layer contains a white pigment in an amount of not less than 20 % by weight.

FIELD OF THE INVENTION

This invention relates to a silver halide color light-sensitive material and a color image forming process in which the above-mentioned color light-sensitive material is used and, particularly, to a silver halide color light-sensitive material suitable for forming a color image for proofing use (that is so-called a color proof) in such a manner that a transmission type black-and-white half tone dot information color separated from a color original document.

BACKGROUND OF THE INVENTION

In recent printing and plate-making industry, such a work as an editing work, a retouching work, a contrast changing work, an enlarging work and a reducing work has been easily performed by reading an original picture and then while seeing a color display, because the hardware and soft ware each for image processing use have been advanced. To record and process an image in the form of an electric signal, it is effective means for solving such a problem as a working speed-up, a distant transfer, a raveling out of short-handed and so forth.

However, for checking up a delicate color shade or a detailed image portion, it is still not satisfactory only to screen an image on a display. It has, therefore, been required to have an image recorded on a support such as a sheet of paper. A variety of systems such as a thermal transfer system, an ink-jet system, an electrophotographic system and a silver-salt photographic system have already been put into practical use. Among these fields, a silver halide photographic light-sensitive material is excellent in easy handling and image quality.

Heretofore, in color plate-making and printing processes, an over-lay method and a surprint method have been used as a method for obtaining a color proof from a plurality of black-and-white half tone dot images obtained by carrying out a color separation and a half tone dot conversion. As a method of improving the defects of the above-mentioned over-lay method and a surprint method, a method using a silver halide color light-sensitive material is disclosed in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP OPI Publication) Nos. 62-280747/1987 through 62-280750/1987 and 62-280849/1987. The silver halide emulsions used therein are silver chlorobromide emulsions having a high silver bromide content, and there is no description of a high silver chloride containing emulsion having a rapid developability and an environmental aptitude, which are satisfiable to put into practical use.

For a light-sensitive material, it has been required to practically use a highly silver chloride containing emulsion capable of realizing the improvements of working environment and environmental aptitude. And, a light-sensitive material has recently been used not only for layout proof to confirm the positions of letters and drawings, but also for tone proof to confirm a color tone, as the fields of utilizing the light-sensitive materials, so that the quality thereof required by the market has been increased.

Japanese Patent Open to Public Inspection Publication Nos. 197069/1993 discloses an image forming process in which a silver halide color photographic light-sensitive material is exposed to light in a scanning-exposure system to form a proof. In this disclosure, however, there is no suggestive description of an amount of a white pigment to be filled.

SUMMARY OF THE INVENTION

To solve the above-mentioned problems, the object of the invention is to provide an image forming method in which a proof is rapidly prepared by making a scanning-exposure when a color-separation and a half tone dot image conversion are made by using a silver halide color photographic light-sensitive material and a color proof is so prepared as to be based on the resulting half tone dot image information.

Item 1: An image forming method comprising the steps of:

- (1) exposing a silver halide color photographic light-sensitive material with scanning laser-light; and
- (2) developing said exposed silver halide color photographic light-sensitive material comprising a support having a resin layer, provided thereon at least one of light-sensitive layers including silver halide grains and at least one of layers other than said light-sensitive layers provided under the lowermost layer of said light-sensitive layers, wherein at least one of said layers other than said light-sensitive layers or said resin layer contains a white pigment in an amount of not less than 20 % by weight.

Item 2: The image forming method of item 1, wherein at least one of said layers other than said light-sensitive layers or said resin layer contains a white pigment in an amount of from 20 % to 80 % by weight.

Item 3: The image forming method of item 1, wherein at least one of said layers other than said light-sensitive layers has a percentage of voids within the range of 5 to 35 % by weight.

Item 4: The image forming method of item 1, wherein a silver chloride content of said silver halide grains

is not less than 80 mol %.

Item 5: The image forming method of item 1, wherein a silver chloride content of said silver halide grains is not less than 95 mol %.

Item 6: The image forming method of item 1, wherein said white pigment is selected from the group consisting of a rutile titanium dioxide, an anatase titanium dioxide, a barium sulfate, a barium stearate, a silica, an alumina, a zirconium oxide and a kaolin.

Item 7: The image forming method of item 1, wherein said white pigment is selected from the group consisting of a rutile titanium dioxide and an anatase titanium dioxide.

Item 8: The image forming method of item 1, wherein said resin layer comprises a organic compound hardened by applying electron beam, and said organic compound has not less than two carbon-carbon double bonds in one molecule thereof.

Item 9: The image forming method of item 8, wherein said organic compound is selected from the group consisting of an acrylic oligomer, a methacrylic oligomer, an acrylic monomer, an methacrylic monomer, a multifunctional acrylic monomer, a multifunctional methacrylic monomer.

Item 10: The image forming method of item 1, wherein said silver halide color photographic light-sensitive material is exposed with scanning laser-light according to a halftone dot image information color-separated into a yellow, magenta, cyan and black image information.

A preferable embodiment of the invention is that the above-mentioned silver halide color photographic light-sensitive material is to contain a white pigment in an amount of not less than 20% by weight in the above-mentioned white pigment layer and that at least one of the above-mentioned silver halide emulsion layers is to contain an silver halide emulsion having a silver chloride content of not less than 80 mol%.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The white pigments employed preferably in the invention include, for example, a rutile type titanium dioxide, an anatase type titanium dioxide, barium sulfate, barium stearate, silica, alumina, zirconium oxide and kaolin. Among them, titanium dioxide is more preferable. A white pigment can be dispersed in a water-soluble binder of a hydrophilic colloid such as gelatin that can make a processing solution permeable thereto so that the white pigment can be coated to form a white pigment layer. When the white pigment is contained in at least one of layers other than light-sensitive layers, a coated amount of the white pigment is preferably within the range of 0.5 g/m² to 50 g/m² and, more preferably, 1 g/m² to 20 g/m².

When a layer other than light-sensitive layers contains a white pigment, the layer is provided under the lowermost layer of the light-sensitive layers. However, between a support and the lowermost layer of the light-sensitive layers, it is allowed, if required, to provide, besides the layer containing a white pigment, a sublayer on the support, or a light-insensitive hydrophilic colloidal layer such as an intermediate layer to any preferable position.

It is preferable that a layer containing a white pigment other than light-sensitive layers is to have a percentage of voids within the range of 5 to 35 % by weight.

In the present invention, a percentage of void is defined as the following formula.

A percentage of void (%) = (a measured layer thickness - a theoretical layer thickness)/(a measured layer thickness) * 100.

The theoretical layer thickness is calculated based upon each of addition amounts and each of density values of compositions contained in a layer.

It is preferable to contain a hollow polymer grain in a layer containing a white pigment other than light-sensitive layers, because the effects of the invention can be enhanced. A hollow polymer grain means that a grain has a hollow inside, but has no polymer inside. A polymer having a hollow inside is preferable, because a fine bubble grain can stably be made present and a light reflectance can also be improved. The hollow polymers applicable thereto include, for example, a hollow polymer of styrene-acrylic resin produced by Japan Synthetic Rubber Co.

The methods for providing a white pigment layer to a support include, for example, a method of making use of a paper sheet laminated with plastic film containing a white pigment as described in JP OPI Publication No. 1-177536/1989, another method of making use of a polyester film containing a white pigment as described in JP OPI Publication No. 2-235045/1990, and a further method of making use of a paper sheet prepared in such a manner that a polyethylene layer containing a white pigment is hardened by making use of electron beam as described in JP OPI Publication No. 2-176648/1990. It is particularly preferable to use a method of using a paper sheet laminated with a plastic film, and another method of using a paper sheet prepared in such a manner that a polyethylene layer is hardened by using electron beam.

In a paper sheet prepared in such a manner that a polyethylene layer is hardened by using electron beam,

an electron beam hardening coatable coating solution is comprised of at least one kind of an organic compound capable of producing a hardened resin by applying electron beam, and a pigment including preferably an inorganic pigment each as the principal components thereof and, if required, other additives. The organic compounds polymerized and hardened by irradiating electron beam include, for example; an unsaturated compound having not less than two carbon-carbon double bond in one molecule thereof, such as an acrylic or methacrylic type oligomer and a multifunctional acrylic or methacrylic type monomer; an unsaturated compound having at least one carbon-carbon double bond in one molecule thereof, such as a monofunctional acrylic monomer; and a vinyl monomer. These unsaturated organic compounds are polymerized by the radicals produced by irradiating electron beam and then hardened by a crosslinkage produced in an intermolecular or intramolecular crosslinking reaction, so that a hardened resin can be produced.

The acryl and methacryl types oligomers include, for example, a polyurethane acrylic or methacrylic acid ester, a polyether alcohol acrylic or methacrylic acid ester, a acrylic or methacrylic acid ester of bisphenol A and maleic or fumaric acid ester type polyester. The multifunctional acrylic or methacrylic monomers include, for example, 1,6-hexanediol diacrylate, neopentyl diacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, tetraethylene glycol diacrylate, glycerol trimethacrylate, stearyl acrylate, polyethylene glycol diacrylate, butoxyethyl acrylate, 1,4-butanediol diacrylate, ethylene glycol dimethacrylate, glycidyl methacrylate, trimethylolpropane triacrylate, pentaerythritol acrylate and pentaerythritol pentacrylate. The monofunctional acrylic or methacrylic monomers and the vinyl monomers include, for example, styrene, N-vinylpyrrolidone, a polyoxyethylene phenyl alcohol acrylic acid ester and 2-ethylhexyl acrylate.

A coating solution of the invention contains a pigment uniformly mixed with an electron-hardenable organic compound including, commonly, a white inorganic pigment. The white inorganic pigments applicable thereto include, for example, titanium dioxide (of the anatase or rutile type), barium sulfate, calcium carbonate, aluminium oxide and magnesium oxide. It is also allowed that the surface of a titanium dioxide grain is processed with a metal oxide such as moisture-containing alumina oxide so that the dispersibility thereof can be improved.

It is preferable to determine an amount of a white pigment to be contained in a coating solution so as to be within the range of 20 to 80% by weight of the whole weight of the solids contained in a layer other than light-sensitive layers or a resin layer. When the amount thereof is less than 20% by weight, the resulting photographic image sharpness on a print leaves something to be desired. When exceeding 80% by weight, the plasticity of the resulting hardened resin-coated layer is lowered, so that a layer fracture may be produced. A white inorganic pigment can be dispersed in an electron-hardenable unsaturated organic compound by making use of a three-roll mill, a two-roll mill, a homomixer, a sand grinder, a supersonic dispersing machine and so forth.

The organic solvents applicable thereto include, for example, acetone, methylethyl ketone, ethyl acetate, butyl acetate, ether, glycol monoethyl ether, dioxane, benzene, toluene, xylene, ethylene chloride, carbon tetrachloride, chloroform and dichlorobenzene.

As for the coating method, a roller coating method may be used. Or, it is also allowed to use any one of commonly known sheet-coating methods such as a bar coating method, an air-doctor coating method, a blade coating method, a squeeze coating method, an air-knife coating method, a reverse-roll coating method and a transfer coating method. It is further allowed to use a fountain coater system or a slit-orifice coater system.

There is no special limitation to an electron-beam irradiator applicable to a process of the invention. As for the electron-beam accelerators for irradiating an electron beam, generally, those of the curtain-beam system may effectively be used, because they are comparatively inexpensive and have a high power output. When irradiating an electron beam, the acceleration voltage is, preferably, within the range of 100 to 300kv.

The suitable thickness of a coated layer is to be within the range of 3 to 100 μ m and, preferably, 5 to 50 μ m. When the thickness thereof is out of the above-given range, it is not preferable from the viewpoint of quality, because a coating unevenness is produced or a layer is a plenty of energy is required for hardening a layer, so that the hardening result may leave something to be desired. After a layer is coated or hardened, it is also allowed, if required, to apply a surface smoothing treatment with the use of a mirror-finished roll or a surface matting treatment with the use of a mat-finished roll such as a silk-finished roll.

As for the base members applicable to the invention, every one of them can be used for, provided that they may be used generally to a support for photographic use. Such a support base member as mentioned above is commonly made of paper. The paper sheets applicable to a sheet-shaped base member include, for example, a natural pulp paper, a synthetic pulp paper, a paper mixedly made of natural pulp and, besides, various combination paper boards. Into such a paper-made base member as mentioned above, it is allowed to compound therein an additive having generally been used for making paper, such as a sizing agent, a paper-strength reinforcing agent, a fixer, an antistatic agent, a pH controller, a pigment and a dyestuff. It is further allowed to apply a surface-coating with a surface sizing agent, a paper surface reinforcing agent and an antistatic agent.

A scanning type exposure apparatus relating to the invention will now be detailed.

As for the scanning type exposure apparatuses, those having three light sources, B, G and R have been known. The well-known light sources thereof include, for example, a combination of a filter and a lamp serving as a white light-source, such as a glow lamp, a xenon lamp, a mercury lamp and a tungsten lamp; a light emitting diode, a gas-laser, a solid-laser, a conductive-laser and so forth. Among them, a laser beam having a substantially narrow light-output intensity distribution is particularly preferred. A combination of various laser beams and a wavelength conversion element may also be used. From the viewpoint of compactness, a combination of an infra-red semiconductive laser and an SHG element is preferred.

The concrete examples of the above-given light sources may be given as follows; blue-light sources include, for example, a He-Cd gas-laser (with 441.6nm), an Ar⁺ laser (with 488.0nm), and a He-Ne gas-laser (with 442.0nm); green-light sources include, for example, a He-Ne gas-laser (with 543.5nm), an Ar⁺ gas-laser (with 514.5nm), a Kr⁺ gas-laser (with 520.8nm), a YAG laser, and a combination of an infra-red semiconductive laser and an SHG element; and red-light sources include, for example, a He-Ne gas-laser (with 632.8nm), a Kr⁺ gas-laser (with 647.1nm) and a semiconductive laser (with 678nm, 750nm or 780nm). When a He-Ne gas-laser is used particularly as a light-source, a stable, inexpensive and compact apparatus may be provided. It is also advisable that a plurality of oscillations are obtained from a single He-Ne gas-laser and may then be used upon separating the oscillations each other by making use of a dichroic mirror. For example, from a single He-Ne gas-laser, four lines of oscillations (442nm, 543.5nm, 594.1nm and 632.8nm) may be obtained.

Silver halide applicable to a light-sensitive material of the invention include any one of silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide, silver chloride and so forth which may be ordinarily applied to a silver halide emulsion. From the viewpoint of a rapid processing, it is advisable to use a highly silver chloride containing emulsion having a silver chloride content of, preferably, not less than 80 mol% and, more preferably, not less than 95 mol%.

The couplers applicable to a silver halide light-sensitive material relating to the invention also include any compound capable of producing a coupling product having a maximum spectral absorption wavelength in a long wavelength region longer than 340nm, upon making a coupling reaction with a color developing agent. Among them, the particularly typical couplers include, for example, those having been known as a yellow coupler having a spectral absorption maximum in a wavelength region within the range of 350 to 500nm, a magenta coupler having a spectral absorption maximum in a wavelength region within the range of 500 to 600nm and a cyan coupler having a spectral absorption maximum in a wavelength region within the range of 600 to 750nm.

The cyan couplers preferably applicable to a silver halide photographic light-sensitive material relating to the invention include, for example, a coupler represented by Formulas (C-I) or (C-II) given in JP OPI Publication No. 4-114154/1992, p. 5 in the lower left column. The typical compounds thereof include, for example, those given in the above-given JP OPI Publication, in the lower right column of p. 5 to the upper left column of p. 6.

Magenta couplers preferably applicable to a silver halide photographic light-sensitive material relating to the invention include, for example, a coupler represented by Formula (M-I) given in JP OPI Publication No. 4-114154/1992, p. 4, in the upper right column. The typical compounds thereof include, for example, those denoted by MC-1 through MC-7 given on p. 5 in the upper left column to the upper right column.

Yellow couplers of a yellow color developable blue light-sensitive layer, preferably applicable to a silver halide photographic light-sensitive material relating to the invention include, for example, a coupler represented by Formula (Y-1) given in JP OPI Publication No. 4-114154/1992, p.3 in the upper right column. The typical compounds thereof include, for example, those denoted YC-1 through YC-9 given in p. 3 in the lower left column to p. 4 in the upper left column. Among them, YC-8 and YC-9 given on, *ibid.*, p. 4 in the upper left column are preferable, because they can reproduce a desirable yellow tone.

When an oil-drop-in-water type emulsification-dispersion method is carried out for adding a coupler applicable to a silver halide photographic light-sensitive material relating to the invention, the following procedures are usually taken. the coupler is dissolved in a water-insoluble high boiling organic solvent having a boiling point of not lower than 150°C and, if required, with a low boiling and/or a water-soluble organic solvent in combination, and the resulting solution is emulsified and dispersed in a hydrophilic binder such as an aqueous gelatin solution by making use of a surfactant. The dispersion means applicable thereto include, for example, a stirrer, a homogenizer, a colloid mill, a flow-jet mixer and a supersonic disperser. It is also allowed to add a step of removing the low boiling organic solvent, after or at the same time when completing the dispersion,

A high boiling organic solvent applicable to dissolve and disperse a coupler (and a photographically useful organic compound such as a UV absorbent and a color stain preventive of which will be detailed later), such a solvent as mentioned above include, preferably, a high boiling organic solvent having a vapor pressure of not higher than 0.5 mmHg at 100°C. The typical compounds thereof include, for example, the examples of the compounds, II-1 through II-9 and III-1 through III-6, given in JP OPI Publication No. 63-103245/1988, the examples of the compounds, H-1 through H-22, given in JP OPI Publication No. 1-196048/1989, the examples

of the compounds, II-1 through II-38, given in JP OPI Publication No. 64-66646/1989, or such a phosphine oxide as given below. A phosphoric acid ester and a phosphine oxide are preferably used for.

Besides the above-mentioned method of using a high boiling organic solvent, it is also allowed to use such a method that a coupler and a water-insoluble and organic solvent-soluble polymer compound are dissolved, if required, in a low boiling and/or water-soluble organic solvent, and the resulting solution is emulsified and dispersed in a hydrophilic binder such as an aqueous gelatin solution by making use of a surfactant. The water-insoluble and organic solvent-soluble polymers include, for example, poly(N-t-butyl acrylamide).

Ethyl acetate is preferably used as a low boiling organic solvent. A surfactant preferably applicable when making a dispersion include, for example, a compound having collectively a hydrophobic group having 8 to 30 carbon atoms and either -SO₃M group or a -OSO₃M group (in which M represents a hydrogen atom or a cation) in a molecule thereof. The typical examples of the surfactant compounds preferably applicable thereto include the anionic surfactants, A-1 through A-11 and, more preferably, A-1 and A-8, given in JP OPI Publication No. 64-26854/1989, p. 15, in the upper left column to the upper right column. It is also preferable to use a surfactant in which a fluorine atom is substituted to an alkyl chain.

It is also preferable to add the above-mentioned surfactant to a coating solution. The resulting dispersed solution thereof is usually added to a coating solution containing a silver halide emulsion or the like and the resulting solution is then coated. However, the dispersed solution is to be added to a coating solution, preferably within 10 hours, more preferably, within 3 hours and, most preferably, within 20 minutes after completing the dispersion.

For the purpose of shifting the absorption wavelength of a color developing dye, it is also allowed to use such a compound as a compound (d-11) given in JP OPI Publication No. 1-114154/1992, p. 10, in the upper left column or a compound (A'-1) given in, *ibid.*, p. 35. Besides the above, a fluorescent dye-releasable compound given in US Patent No. 4,774,187 may also be used.

There is no special limitation to the amounts of the couplers to be added, provided that a satisfactorily high density can be obtained. However, they may be used within the range of 1×10^{-3} to 5 mols per mol of silver halide used and, preferably, 1×10^{-2} to 1 mol.

The magenta couplers applicable to the invention may also be used with a color-fading preventive in combination. The first example of the color-fading preventives is a phenylethyl ether represented by Formulas I and II given in JP OPI Publication No. 2-66541/1990, p. 3, in the upper left column to the upper right column. The typical compounds thereof include, for example, the compounds, I-1 through I-32 and II-1 through II-18, given in, *ibid.*, p. 3, in the lower right column to p. 5, in the upper right column. Among them, the preferable compounds are those respectively denoted by I-13 and II-9.

The second example of the color-fading preventives preferably used in combination include a phenol compound represented by Formula IIIB given in JP OPI Publication No. 3-174150/1991. Among them, compounds III-1, III-12, III-13 and III-14 given therein are more preferable and compound denoted by III-14 is particularly preferable.

The third example of the color-fading preventives preferably used in combination include an amine type compound represented by Formula A given in JP OPI Publication No. 64-90445/1989. The typical examples of the compounds include A-1 through A-15 given in, *ibid.*, p. , in the upper right column. Among them, a further preferable compound is denoted by A-3.

The yellow couplers and cyan couplers each relating to the invention are preferable to be used with a color-fading preventive in combination. Among the color-fading preventives, the preferable compounds thereof include, for example, the compounds represented by Formula I' given in JP OPI Publication No. 1-196049/1989, p. 8, in the upper left column, and the compounds given in JP Application No. 3-185113/1991. The further preferable compounds include, for example, those denoted by I-10 to I-13 each given on p. 9, in the upper left column to the upper right column. A color-fading preventive used with the above-mentioned magenta, yellow or cyan coupler in combination is to be added, together with a coupler, in a proportion within the range of, preferably, 0.1 to 3 mols per mol of the coupler in one and the same oil drop and, more preferably, 0.5 to 1.5 mols. It is preferable that a color-fading preventive is used with a different kind of compound in combination. The preferable examples thereof include a combination use of a phenol type compound represented by Formula IIIB given in JP OPI Publication No. 3-17450/1991 and a phenyl ether type compound represented by Formula I or II given in JP OPI Publication No. 2-66541/1990, p. 3, in the upper right column. The preferable examples thereof also include a combination use of a phenol type compound represented by Formula IIIB given in JP OPI Publication No. 3-17450/1991 and an amine type compound represented by Formula A given in JP OPI Publication No. 64-90445/1989.

A UV absorbent applicable to the invention include, for example, a compound having the maximum spectral absorption wavelength in the ultra-violet region (of not higher than 400nm) and a spectral absorption coefficient of not less than 5000. The preferable compounds thereof include, for example, a compound represented by

Formula III-3 given in JP OPI Publication No. 1-250944/1989 and a compound represented by Formula I given in JP OPI Publication No. 4-1633/1992. The typical examples of the compounds include IIIc-1 through IIIc-17 given in JP OPI Publication No. 1-250944/1989, III-1 through III-24 given in JP OPI Publication No. 64-66646/1989, UV-1L through UV-22L given in JP OPI Publication No. 63-187240/1988, UV-1S through UV-19S given in JP OPI Publication No. 63-187240/1999988, and compounds I-1 through I-23 given in JP OPI Publication No. 4-1633/1992. Among them, the particularly preferable compounds include, for example, IIIc-7 and IIIc-12 given in JP OPI Publication No. 1-250944/1989, in the upper left column of p. 15. and a liquid phase UV absorbent UV-23L given in JP OPI Publication No. 63-187240/1988. It is preferable to add the above-given UV absorbents in the foregoing dispersion method. In the invention, however, a high boiling organic solvent applicable to a UV absorbent-containing layer is to be added in a proportion by weight within the range of 0.3 to 0, preferably, 0.1 to 0 and, most preferably, 0 to an amount of a UV absorbent added. A high boiling organic solvent preferably applicable thereto include, for example, a compound to be used for dispersing the foregoing couplers. In the invention, a UV absorbent is preferable to be contained in a light-insensitive layer. Further, it is preferable that the light-insensitive layer is a light-insensitive intermediate layer positioned farther apart from a silver halide emulsion layer positioned farthest from a support, and a light-insensitive layer interposed between an emulsion layer farthest positioned from the support and another emulsion layer second farthest positioned from the support.

In the invention, it is preferable to add fine powder (that is so-called a matting agent) to the layer farthest from a support, that is, the surface layer. The matting agents include, preferably, a compound given in JP OPI Publication No. 2-73250/1990, p. 2, in the upper right column, the 9th line to the 20th line and, most preferably, crystallized or non-crystallized silica. The matting agents may be used independently or in combination. The average particle size of the above-mentioned matting agent is to be within the range of, preferably, 1 to 10 μ m and, more preferably, 2 to 7 μ m. The matting agents may be coated in an amount within the range of, preferably, 0.021 to 0.1 g/m² and, more preferably, 0.025 to 0.08 g/m².

It is preferable to add a high boiling organic solvent to the surface layer. The high boiling organic solvents preferably added to the surface layer include, preferably, a high boiling organic solvent having a vapor pressure of not higher than 0.5 mmHg at 100°C and, more preferably, a compound having a dielectric constant of not higher than 6.0. The typical examples of the compounds include the same as those given in the foregoing description of the coupler dispersion as they are. The amount thereof to be added is within the range of 1 to 100 mg/m² and, preferably, 10 to 50 mg/m².

For the purpose of improving the physical surface characteristics such as surface gloss, stickiness, adhesion resistance, lubricity and scratch resistance, a fluorine-containing surfactant or organopolysiloxane may also be added to a light-sensitive material relating to the invention. The preferable fluorine-containing surfactants include, for example, a compound represented by Formulas (I), (II) and (III) each given in JP Application No. 4-270425/1992. Among them, the particularly preferable compounds include, for example, those denoted by FI-55, FI-81, FK-5, FK-13 and FK-23. The preferable organopolysiloxane include, for example, a compound represented by Formulas (S1), (S2), (I), (II) and (III) each given in JP Application No. 4-270425/1992. Among them, the particularly preferable compounds include, for example, those denoted by S-7 and S-19.

In the invention, an oil-soluble dyestuff is preferable to be used. An oil-soluble dyestuff means an organic dyestuff having a water-solubility of not higher than 0.01 at 20°C. It is preferable to be a compound having a molecular absorptivity coefficient of not less than 20000 in the maximum absorption wavelength in a wavelength of not shorter than 400nm. The preferable compounds thereof include, for example, a compound represented by Formula II or III given in JP OPI Publication No. 2-842/1990, p. 7, the lower right column to p. 8, the upper left column. The preferable compounds thereof include, typically, compounds 1 through 27 given in the same JP OPI Publication, p. 8, the lower left column to p. 9, the upper right column. Among them, compounds 4 and 9 are particularly preferable. An oil-soluble dyestuff is preferable to be added in an amount within the range of 0.05 to 5 mg/m², to a light-insensitive layer.

In the invention, it is preferable to add a fluorescent whitening agent to a light-sensitive material. Such a fluorescent whitening agents as mentioned above include, preferably, a compound represented by Formula II given in JP OPI Publication No. 2-232652/1990. The examples of those compounds include, typically, compounds 1 through 6 given in the same JP OPI Publication, p. 6, the lower right column to p. 7, the upper right column. Among them, compound Nos. 3, 1 and 5 are particularly preferable. These fluorescent whitening agents are preferable to be added in an amount within the range of, preferably, 0.001 to 0.3 mg/m² and, more preferably, 0.1 to 0.2 mg/m², to a light-insensitive layer.

In the invention, it is preferable to add a water-soluble polymer compound so as to assist the above-mentioned fluorescent whitening agent to enhance the fluorescent whitening effect. The preferable compounds thereof include, for example, a polymer containing polyvinyl pyrrolidone or vinyl pyrrolidone as a repetition unit. These compounds are preferable to be contained in a UV absorbent-containing layer positioned farthest from

a support and/or a layer further apart from the above-mentioned UV absorbent-containing layer.

For the purpose of preventing an irradiation and a halation, it is preferable to apply a water-soluble dyestuff having a absorptivity in various wavelength regions to a color light-sensitive material relating to the invention. The preferable anti-irradiation dyestuffs include the following compounds, for example. Namely, the compounds represented by Formulas II given in JP OPI Publication No. 62-253146/1987 (including, typically, compounds II-1 through II-19 given in the same JP OPI Publication, pp. 12-13), the compounds represented by Formula I given in JP OPI Publication No. 64-26850/1989 (including, typically, compounds 1 through 85 given in the same JP OPI Publication, p. 7, the upper left column to p. 11, the lower right column), the compounds represented by Formula I given in JP OPI Publication No. 2-97940/1990 (including, typically, compounds 1 through 103 given in the same JP OPI Publication, p. 5, the upper column to p. 9, the upper column), and the compounds given in JP Application No. 4-182885/1992, p. 3, the 22nd line to p. 5, the 2nd line. Among them, the preferable compounds include, for example, compound No. 47 represented by Formula I given in JP OPI Publication No. 64-26850/1989, compound No. 54 represented by Formula I given in JP OPI Publication No. 2-97940/1990, and compounds 1, 4, 6, 7 and 9 each given in JP Application No. 4-182885/1992.

It is preferable to make combination use of an anti-irradiation dyestuff and a dyestuff having a different maximum absorption wavelength. It is also preferable to make combination use of a dyestuff having the maximum absorption within the range of 600 to 700nm, a dyestuff having the maximum absorption within the range of 500 to 600nm, and a dyestuff having the maximum absorption within the range of 400 to 500nm. These dyestuffs may be added to any layers, however, they are preferred to be added to a light-insensitive layer. Each of the compounds may be added in an amount preferably within the range of 1 to 100 mg/m².

Various apparatuses and processes having been well known in the art may be used respectively for the apparatuses and processes for preparing a silver halide emulsion.

A silver halide emulsion relating to the invention may be those prepared in any one of an acidic process, a neutral process and an ammoniacal process. The grains thereof may be those grown up at the same time or may also be grown up after seed grains are prepared. The process for preparing the seed grains and the process for growing them up may be the same with or may also be different from each other.

As for the systems for making a soluble silver salt and a soluble halide reacted together, any one of a normal precipitation process, a reverse precipitation process, a simultaneous precipitation process, and the combination thereof may be used. However, a reactant thereof is preferable to be obtained in a simultaneous precipitation process. It is also allowed that a pAg-controlled-double-jet process detailed in JP OPI Publication No. 54-48521/1979 and so forth may be used as one of the systems of the simultaneous precipitation process.

It is allowed to use the following apparatuses. Namely, an apparatus for supplying an aqueous solution of a water-soluble silver salt and a water-soluble halide from an adding device arranged inside a mother liquid for making reaction, as detailed in JP OPI Publication Nos. 57-92523/1982 and 57-92524/1982; an apparatus for adding an aqueous solution of a water-soluble silver salt and a water-soluble halide with continuously changing the concentration of the solution, as detailed in German Patent (OLS) No. 2921164; an apparatus for forming grains in such a manner that a mother liquid for making reaction is taken out of a reaction vessel and is then condensed in a ultrafiltration process, and thereby a distance between the silver halide grains is being kept constant, so that the grains can be formed, as detailed in JP Examined Publication No. 56-501776/1981.

A silver halide solvent such as thioether may also be used, if required. When forming silver halide grains or after completing the formation of grains, it is further allowed to add such a compound as a compound having a mercapto group, a nitrogen-containing heterocyclic compound or a sensitizing dye.

An unnecessary soluble salt may be removed from an emulsion containing silver halide grains after completing the growth of the silver halide grains, or such a salt as mentioned above may also be contained therein as they are. When removing the salts, it can be performed in the procedures described in Research Disclosure No. 17643.

Any desired configuration of a silver halide grain relating to the invention can be used. One of the preferable examples thereof is a cube having {100} faces as the crystal faces thereof. In the processes described in such a literature as US Patent Nos. 4,183,756 and 4,225,666; JP OPI Publication No. 55-26589/1980; JP Examined Publication No. 55-42737/1980; and Journal of Photographic Science, Vol. 21, p. 39, 1973, grains having such a configuration as an octahedron, a tetradecahedron and a dodecahedron are prepared and are then used for. Further, grains having twinned crystal faces may also be used. The silver halide grains relating to the invention may be those having one and the same configuration or those formed of a mixture of grains having various configuration.

There is no special limitation to the grain size of any silver halide grain. However, taking other photographic characteristics such as rapid processability and photosensitivity into consideration, it is to be within the range of, preferably, 0.1 to 1.6 μ m and, more preferably, 0.2 to 1.2 μ m. The above-mentioned grain can be measured in various procedures having commonly been used in the technical field of the art. A grain size can be obtained

by making use of the projected area or approximate diameter thereof. When grains have a substantially uniform configuration, a fairly accurate grain size distribution thereof can be obtained by making use of the diameters or projected areas thereof. The grain size distribution of silver halide grains may be of the polydisperse type or of the monodisperse type. Among silver halide grains, monodisperse silver halide grains are preferable when a variation coefficient of the silver halide grain distribution is, preferably, not more than 0.22 and, more preferably, not more than 0.15. The term, a variation coefficient, means a coefficient indicating the range of a grain size distribution, that can be defined by the following ratio.

Variation coefficient = S / R (in which S represents the standard deviation of a grain size distribution, and R represents an average grain size)

When a silver halide grain is spherical shaped, the term, a grain size, herein stated means a diameter. When a silver halide grain is cubic shaped or other shaped than the spherical shaped, it means the diameter of a circle having the same area with the projected image area of the grain.

A silver halide grain relating to the invention comprises silver iodobromide, silver chloriodobromide, silver chlorobromide, silver bromide or silver chloride. A preferable grain is a silver chlorobromide grain comprising silver chloride in a proportion of not less than 90 mol% and without substantially containing any silver iodide, or it is a silver chloride grain. The expression, without substantially containing any silver iodide, means that a silver iodide content is not more than 0.5 mol%, preferably, not more than 0.1 mol% and, more preferably, not contained at all.

When a silver halide grain relating to the invention comprises silver chlorobromide containing silver bromide, it is allowed, without limitation, to be a core/shell type grain having the different compositions inside the silver halide grains, or a grain having a silver bromide-localized phase made present on the surface or inside thereof. However, it is preferable to be a silver halide grain having a uniform composition all through from the inside to the surface thereof.

In the course of forming or physically ripening the grains of a silver halide emulsion relating to the invention, a variety of metal salts or metal complex salts can be introduced into the emulsion.

The metals introducible thereinto include, for example, those belonging to Groups VIB, VIIB, VIII, IIB, IIIA and IVA of the periodic table. Among them, the preferable metals include, for example, the salts or complex salts of Mn, Fe, Co, Ni, Zn, Ga, Ge, Mo, Ru, Pd, Cd, In, Sn, W, Re, Os, Ir, Pt, Tl and Au. They may be used independently or in combination. The preferable metal salts or the complex salts thereof are given in, for example, JP Application Nos. 2-162332/1990, 2-253667/1990, 3-109173/1991, 4-251468/1992 and 4-82250/1992, and JP OPI Publication Nos. 4-125629/1992, 4-251469/1992 and 4-253081/1992.

These compounds may be added in an amount preferably within the range of 10^{-11} to 10^{-3} mols per mol of silver halide used, provided, however, that the amount thereof to be added is so widely varied as to meet the kinds and application purposes of the compounds.

A silver halide grain emulsion can be treated by making combination use of a gold sensitization process using a gold compound and a (sulfur) sensitization process using a chalcogen sensitizing agent.

A gold sensitizer may be added in the form of chloroauric acid, gold chloride, gold thiosulfate or the like and, besides, a variety of gold complex. The oxide compounds applicable thereto include, for example, dimethyl rhodanine, thiocyanic acid, mercaptotetrazole and mercaptotriazole.

A gold sensitizer may usually be used in an amount within the range of, preferably, 1×10^{-9} to 1×10^{-4} mols per mol of silver halide used and, more preferably, 1×10^{-8} to 1×10^{-5} mols.

The chalcogen sensitizers applicable thereto include, for example, a sulfur sensitizer, a selenium sensitizer and a tellurium sensitizer. Among them, a sulfur sensitizer is preferred. The sulfur compounds include, for example, a thiosulfate, allylthiocarbamide, thiourea, allylthiocyanate, cystine, p-toluene sulfonate, rhodanine and inorganic sulfur.

A light-sensitive material of the invention may be treated in a reduction sensitization. There are well-known reduction sensitization processes. For example, it is allowed to use a process of adding various kinds of reducing agents, another process of carrying out a ripening treatment under the conditions of a high silver ion concentration, and a further process of carrying out a ripening treatment under the conditions of a high pH.

The reducing agents applicable to a reduction sensitization treatment include, for example, a stannous salt such as stannous chloride, a borane such as tri-t-butylamine borane, a sulfite such as sodium sulfite and potassium sulfite, a reductone such as ascorbic acid, and thiourea dioxide. Among them, the preferable compounds include, for example, thiourea dioxide, ascorbic acid and the derivatives thereof, and a sulfite. In comparison with the case where a reduction sensitization is carried out by controlling a silver ion concentration or a pH when carrying out a ripening treatment, a process of using such a reducing agent as mentioned above is preferred, because the resulting reduction characteristics can be excellent. These reducing agents may be dissolved in water or a solvent such as alcohol and the resulting solution is then added to a silver halide emulsion, so that a ripening treatment can be carried out, or they may also be added when forming silver halide

grains and then a reduction sensitization is carried out at the same time when forming the grains.

These reducing agents may usually be added preferably in an amount within the range of 10^{-7} to 10^{-2} mols per mol of a silver halide emulsion used.

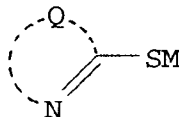
For modifying a reduction sensitization nucleus after completing a reduction sensitization or for deactivating a remaining reducing agent, small amount of an oxidizing agent may be used. The compounds applicable for the above-mentioned purposes include, for example, iron (III) potassium hexacyanate, bromosuccinimide, p-quinone, potassium perchlorate, thiosulfonic acid, and aqueous hydrogen peroxide.

A silver halide emulsion relating to the invention may also be added by a silver halide solvent in the course of carrying out a sensitization treatment. The silver halide solvents preferably applicable thereto include, for example, a thiocyan compound such as potassium thiocyanate, sodium thiocyanate, calcium thiocyanate, magnesium thiocyanate, silver thiocyanate and ammonium thiocyanate,

There is no special limitation to a pH and a pAg in the course of carrying out a sensitization treatment. However, a pH and a pAg are usually kept within the range of 4.0 to 11.0 and 4.5 to 8.5, respectively.

For the purposes of preventing a light-sensitive material from producing any fog in the course of preparing or developing the light-sensitive material, or reducing any characteristic variation in the course of storing the light-sensitive material, an antifoggant and a stabilizer each having been well known may be applied to a silver halide emulsion relating to the invention. The compounds applicable to meet the above-mentioned purposes include, for example, the compounds represented by the following formula [S].

Formula [S]



wherein Q represents a group consisting of non-metal atoms necessary to form a 5- or 6-membered nitrogen-containing heterocyclic ring; and M represents a hydrogen atom or an alkali metal atom.

The 5-membered heterocyclic rings represented by Q include, for example, an imidazole ring, a tetrazole ring, a thiazole ring, an oxazole ring, a selenazole ring, a benzoimidazole ring, a naphthoimidazole ring, a benzothiazole ring, a naphthothiazole ring, a benzoselenazole ring, a naphthoselenazole ring and a benzoxazole ring.

The 6-membered heterocyclic rings represented by Q include, for example, a pyridine ring, a pyrimidine ring and a quinoline ring.

These 5- or 6-membered heterocyclic rings include those having a substituent.

The alkali metal atoms represented by M include, for example, a sodium atom and a potassium atom.

The preferable structures of a mercapto compounds represented by Formula [S] are given in JP Application No. 4-330655/1992, paragraphs 0016 to 0032. The concrete compounds thereof include, for example, S-1-1 through S-4-8 given in *ibid.*, paragraphs 0034 to 0039. The compounds represented by Formula [I] given in JP Application No. 4-80948/1992 are also preferred, and the concrete examples thereof include 1 through 49 given in *ibid.*, paragraphs 0026 to 0028.

The spectrally sensitizing dyes applicable to a silver halide emulsion relating to the invention include any one of well-known compounds. As for the blue light-sensitive sensitizing dyes, those denoted by BS-1 through BS-8 given in JP Application No. 2-51124/1990, pp. 108-109 can preferably be used independently or in combination. As for the green light-sensitive sensitizing dyes, those denoted by GS-1 through GS-5 given in *ibid.*, p. 110, can preferably be used.

When exposing a light-sensitive material relating to the invention to light through a printer equipped with a semiconductive laser unit, it is required to use a sensitizing dye having a light-sensitivity to infrared rays. As for the infrared sensitive sensitizing dyes, the dyes IRS-1 through IRS-11 given in JP Application No. 3-73619/1991, pp. 12-14 can preferably be used. It is also preferable to make combination use of the above-given dyes and supersensitizers SS-1 through SS-9 given in *ibid.*, pp. 14-15.

10



25



35



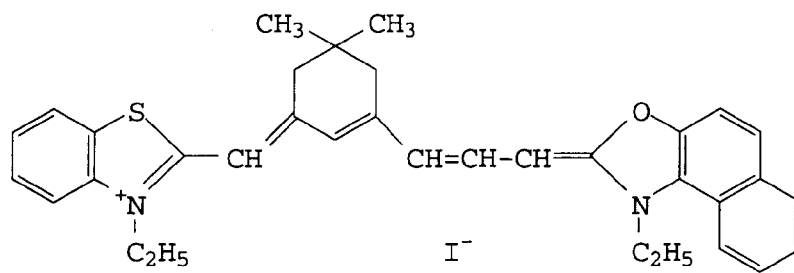
45



IRS-6

5

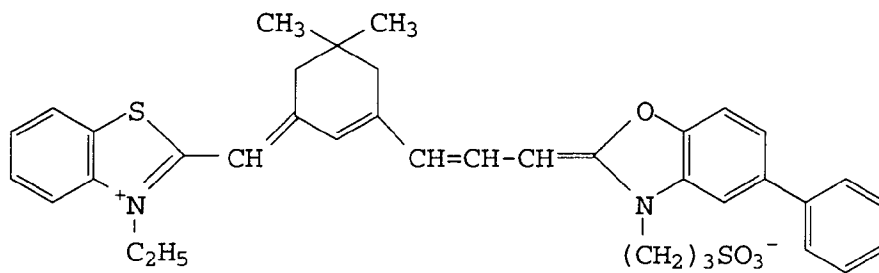
10



IRS-7

15

20

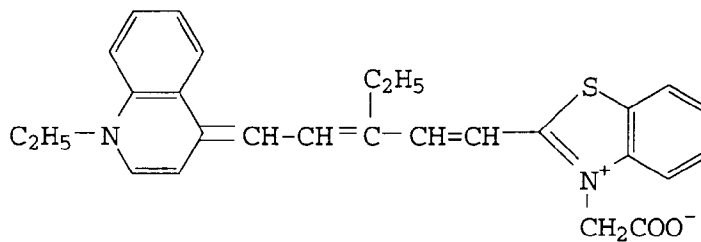


25

IRS-8

30

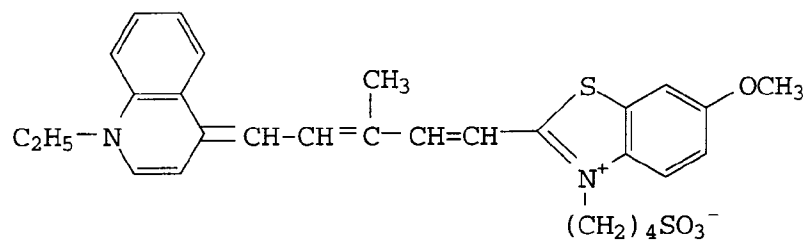
35



IRS-9

40

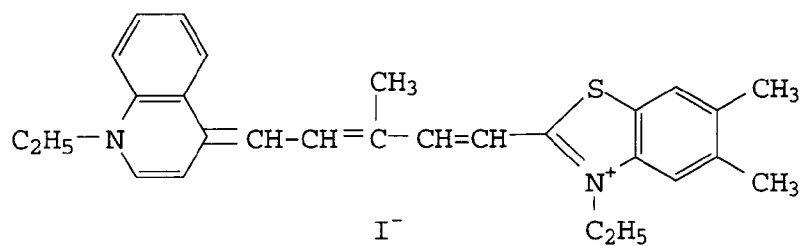
45



IRS-10

50

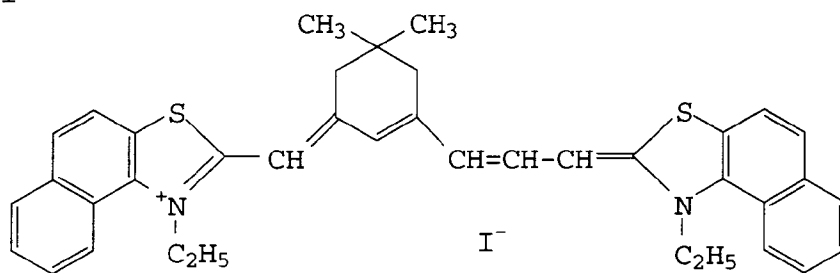
55



IRS-11

5

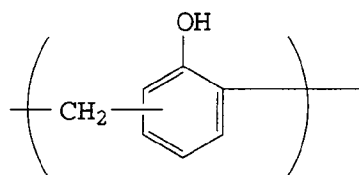
10



SS-1

15

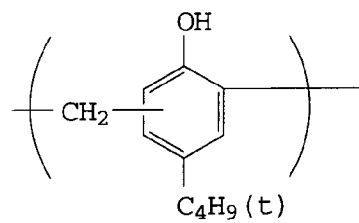
20



SS-2

25

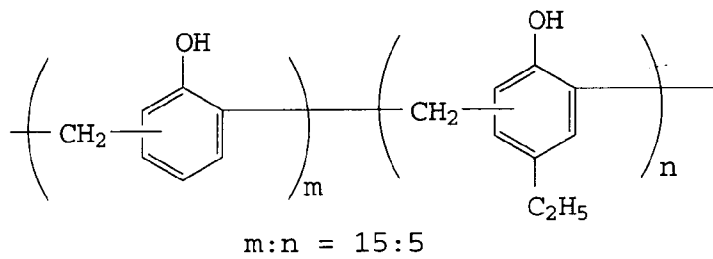
30



SS-3

35

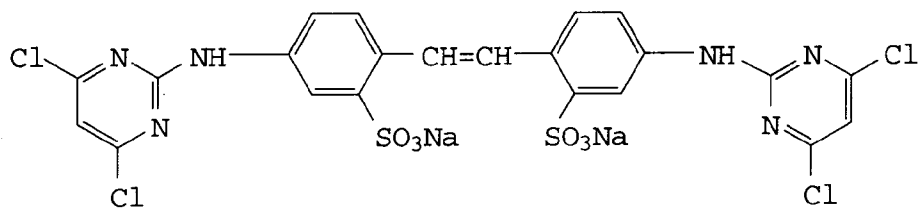
40



SS-4

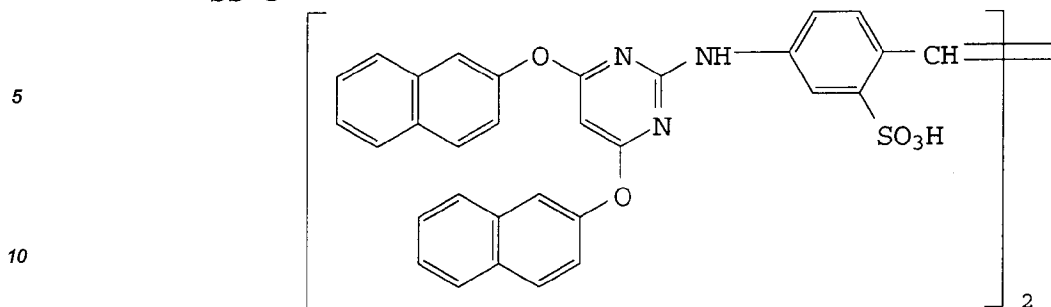
45

50

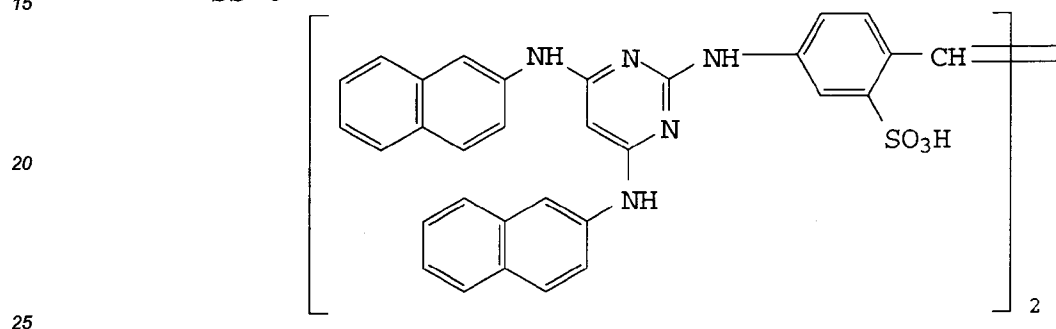


55

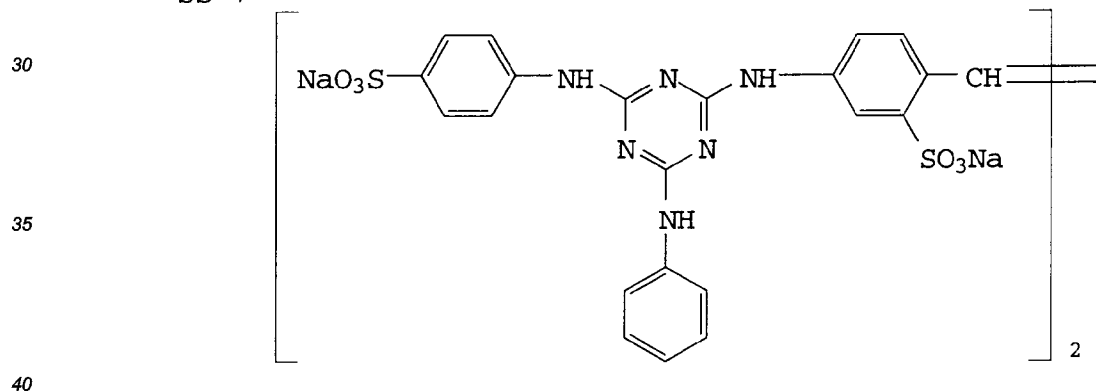
SS-5



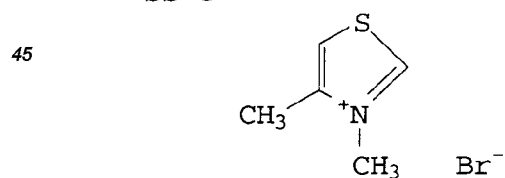
SS-6



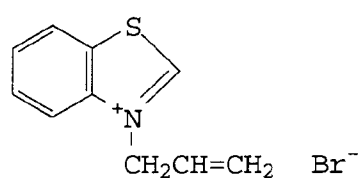
SS-7



SS-8



SS-9



When exposing a light-sensitive material relating to the invention to laser beam, it is advantageous to use an exposure means equipped with a semiconductive laser, because the exposure means can be made smaller in size. When making a scanning exposure, an exposure time per pixel corresponds to an exposure time for actually exposing a silver halide emulsion to light. When a scanning exposure is made to laser beam, an exposure time per pixel may be considered as

(A luminous flux diameter) / (a scanning speed),
provided that, in a spatial variation of a luminous flux intensity, a point where the laser beam intensity becomes one half of the maximum intensity thereof is regarded as the outer edge of the laser luminous flux, and that

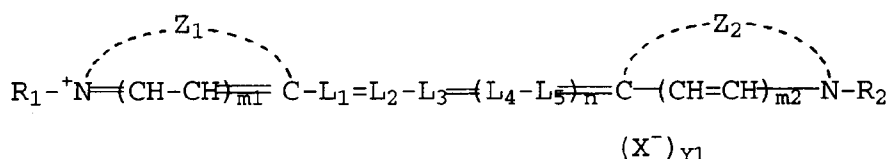
the luminous flux diameter is regarded as a distance between two points at one of which intersecting a line parallel to the scanning line and at the same time passing through a point maximizing the light intensity and at the other of which intersecting the outer edge line of the luminous flux.

However, there is such a tendency that the relation between an exposure time and a developed color density becomes complicated as an exposure time per pixel is made shorter. Therefore, the invention is particularly advantageous when making use of a means having a shorter exposure time per pixel.

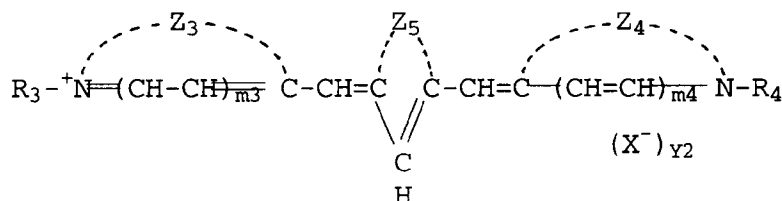
Judging from the applicability to such a system as mentioned above, the laser printers include, for example, those described in JP OPI Publication Nos. 55-4071/1980, 59-11062/1984, 63-197947/1988, 2-74942/1990 and 2-236538/1990, JP Examined Publication Nos. 56-14963/1981 and 56-40822/1981, European Regional Patent No. 77410, "The Institute of Electronics & Communication Engineers' Study Reports", Vol. 80, No. 244, "The Magazine of Cinematography and Television", 1984/6 (382), pp. 34-36, and so forth.

The red-sensitive sensitizing dyes applicable thereto include, for example, a cyan dye represented by the following Formulas [2] and [3].

Formula [2]



Formula [3]



Wherein R₁, R₂, R₃ and R₄ represent each an alkyl group, an alkenyl group or an aryl group; L₁, L₂, L₃, L₄ and L₅ represent each a methyl group; Z₁, Z₂, Z₃ and Z₄ represent each an atom necessary to form a 5- or 6-membered heterocyclic ring or the group consisting of the same atoms; m₁, m₂, m₃ and m₄ are each an integer of 0 or 1; n is an integer of 0 or 1; X⁻ represents an acid anion; and Y₁ and Y₂ are each an integer of 0 or 1, provided that Y₁ and Y₂ are each an integer of 0 when the subject compound produces an intramolecular salt.

A supersensitizers applicable to a silver halide emulsion relating to the invention include, for example, a compound such as stilbene, azaindene, a mercapto-heterocyclic compound, and a condensate of thiourea or a phenol and hexamethylene tetramine. Among them, a heterocyclic ring-containing cyclic compound having a 9-membered or more membered ring is preferred.

The cyclic compounds include, preferably, those having an aliphatic ring and/or an aromatic ring and an ether bond, more preferably, those having not more than four aliphatic rings capable of producing a cyclic compound and, further preferably, a macrocyclic compound having an aromatic ring.

The typical compounds thereof include, for example, a crown ether. The concrete examples of these cyclic compounds include S-1 through S-39 given in JP Application No. 4-330655/1992, paragraphs 0049-0055.

It is advantageous for a light-sensitive material relating to the invention to apply gelatin as a binder for making a dispersion and a coating solution.

Gelatin is prepared in, for example, the process described in T.H. James, The Theory of The Photographic Process, 4th ed., (1977), p. 55, and The Fundamentals of Photographic Engineering · A volume on Silver Salts, pp. 119-124. As for the raw materials thereof, ossein, cowhide, and pig skin are used for. The raw materials made of ossein are preferred, and two or more kinds of the above-mentioned raw materials may be mixed up.

For the treatments of gelatin, an alkali treatment, an acid treatment, an oxygen treatment and so forth may be applied. As for a treatment gelatin, an alkali-treated gelatin is preferred. The isoelectric point of an alkali-treated gelatin is preferably not lower than 4.5 and, more preferably, not lower than 5. Gelatin may usually be ionexchange treated. In the invention, however, amphoteric ionexchange-treated gelatin is preferred, provided that, among cation ion-exchange-treated gelatin, anion-exchange-treated gelatin, and amphoteric ion-

exchange-treated gelatin, any of the gelatin can suitably be so selected as to meet an application purpose. Besides the above, hydrogen peroxide-treated gelatin may also preferably be used.

The hydrogen peroxide treatment may be applied in any steps of a gelatin preparation process. For example, it can be applied directly to ossein, or may also applied in the midst of or after carrying out an alkali treatment, or after extracting a gelatin solution. In the invention, it is preferable to use gelatin prepared by adding aqueous oxygen peroxide in the course of carrying out an alkali treatment. Hydrogen peroxide may be added in an amount within the range of 1 to 100 g in terms of pure H_2O_2 per kg of ossein used. And, it is also preferable to make an ossein reaction with hydrogen peroxide at a pH of not lower than 9.0.

In a gelatin composition, the low molecular weight component thereof is the less, the better, that is, the high molecular weight component thereof is the more, the better. Such a high and low molecular weight thereof can be measured in the procedures described in JP OPI Publication No. 1-265247/1989, p. 2, the 15th line in the lower left column to p. 3, the 8th line in the upper left column. The high and low molecular weight components thereof are preferable to be not lower than 30% for the former and/or not higher than 40% for the latter, according to the expressions given in the procedures. Gelatin is suitable to have a molecular weight within the range of 10,000 to 200,000.

Gelatin is preferable to have a higher jelly strength that is, preferably, not lower than 250 and, more preferably, not lower than 270.

An ion content of gelatin, that is an impurity, is preferable to be lower. For example, the calcium content thereof is to be not more than 5000 ppm and, preferably, not more than 2000 ppm. However, in some emulsion, it may sometimes be preferable that calcium may be made present in a proportion within the range of 4000 to 5000 ppm. It is also preferable that the content of a heavy metal ion such as iron ion and copper ion is to be not more than 500 ppm in total and not more than 10 ppm in each component. In particular, an iron content of gelatin is to be not more than 5 ppm and, preferably, not more than 3 ppm. A specific optical rotation angle of gelatin is preferable to be higher and, particularly, not narrower than 150. When gelatin is used in the uppermost layer, the specific optical rotation angle thereof is preferably not narrower than 210.

The tinctorial power of gelatin is the less, the better. In an aqueous 10 wt% gelatin solution, it is advantageous for the invention when the transmittance of gelatin at 420nm is to be not less than 50%, preferably not less than 60% and, more preferably not less than 70%. For increasing a gelatin transmittance, a raw material selection, a hydrogen peroxide treatment, an ion-exchange treatment, an adsorption treatment with a chelating resin and so forth are suitably carried out.

A total amount of gelatin to be contained in a light-sensitive material of the invention is to be not more than 10.0 g/m² and, preferably, not more than 7.0 g/m². There is no limitation to the lower limit of a total gelatin content. However, from the viewpoint of physical or photographic characteristics, the lower limit thereof is generally preferable to be not less than 3.0 g/m². A gelatin amount can be obtained in the moisture measurement procedures described in PAGI method in which a gelatin amount is obtained by converting it into an amount by weight of gelatin containing 11.0% of moisture.

In the invention, there uses a layer hardener for a binder. The layer hardeners preferably applicable thereto include, for example, a vinyl sulfone type layer hardener and a chlorotriazine type layer hardener. A vinylsulfone type layer hardener preferably applicable thereto include, for example, the compounds given in JP OPI Publication No. 61-249054/1986, p. 25, the 13th line in the upper right column to p. 27, the 2nd line in the upper right column. Besides the above, compound H-12 given in *ibid.*, p. 26 can more preferably be used. The chlorotriazine type layer hardeners preferably applicable thereto include, for example, the compounds given in JP OPI Publication No. 61-245153/1986, p. 3, the 1st line in the lower left column to p. 3, the 4th line from the bottom in the lower right column and p. 3, the 4th line from the bottom in the lower right column to p. 5, the lower left column. Besides the above, the compound denoted by XII-1 given in *ibid.*, p. 4 is more preferable. These layer hardeners are preferable to be used with other kinds of compounds in combination. They may also be added to any layers. The layer hardeners are preferable to be used in a proportion within the range of 0.1 to 10% by weight to a binder used.

In the invention, it is preferable to add an antimold to any one of layers. The preferable antimolds include, for example, the compounds represented by Formula II given in JP Application No. 1-298092/1989, p. 9. The concrete examples of the compounds include, typically, compound examples No. 9 through No. 22 each given in *ibid.*, pp. 69-70. Among them, the particularly preferable one is compound No. 9.

In the invention, a preservative and an antimold can be used. The preferable examples thereof include the compounds given in JP OPI Publication No. 3-157646/1991, p. 17, the 16th line in the lower right column to p. 19, the lower left column.

The base paper applicable to a support of the invention can be selected out of any materials having been commonly used. To be more concrete, the base paper for a support use include, for example, a natural wood pulp such as a sulfuric acid-bleached needle-leaved wood pulp (or NBKP), a sulfuric acid-bleached broad-

leafed wood pulp (or LBKP), a sulfurous acid-bleached needle-leaved wood pulp (or NBSP) and a sulfurous acid-bleached broad-leaved wood pulp (or LBSP). They may be used independently or in combination. When making combination use thereof, a desired mixing ratio of the broad-leaved pulps to the needle-leaved pulps is to be within the range of 95/5 to 60/40.

In the invention, it is advisable to add the following various additives to a base paper so that the paper strength such as moisture resistance can be enhanced. For example, sizing agents applicable thereto include, for example, an alkylketene dimer fatty acid salt, rosin, maleic rosin, an alkenyl succinic acid salt, an alkyl succinic acid salt and a polysaccharide. Among them, an alkylketene dimer fatty acid salt can preferably be used. They are preferably used in a proportion within the range of 0.2 to 2% per an amount of pulp used. Dry paper strength reinforcing agents applicable thereto include, for example, a cationic polyacrylamide, an anionic polyacrylamide and a carboxy-denatured polyvinyl alcohol. Among them, a cationic starch and an anionic polyacrylamide are preferred. Wet paper strength reinforcing agents applicable thereto include, for example, a melamine resin, a urea resin and an epoxidated polyamido resin. Among them, an epoxidated polyamido resin is preferred. Generally, the surface of pulp is tub-sized or size-pressed with a solution containing a water-soluble macromolecular additive. The macromolecular additives applicable thereto include, for example, cationic starch, polyvinyl alcohol, carboxy-denatured polyvinyl alcohol, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, polyacrylamide and gelatin. Among them, cationic starch and polyvinyl alcohol are preferred.

The antifoggants applicable thereto include, for example, the water-soluble iodine compounds given in JP OPI Publication No. 55-103549/1980, the weak acid salts or oxides of magnesium, calcium or zinc each given in JP OPI Publication No. 56-43637/1981, the urea compounds having a molecular weight of not more than 150 such as described in JP OPI Publication No. 56-97343/1981 and the magnesium compounds given in JP OPI Publication No. 5-19405/1993. Among them, magnesium hydroxide, magnesium oxide, calcium oxide and zinc oxide are preferred, and they are used in a proportion within the range of 0.1 to 10% by weight of the weight of a pulp used. The inorganic electrolytes applicable thereto include, for example, edible salt and Glauber's salt and, among them, edible salt is preferred. The hygroscopic substances applicable thereto include, for example, glycerol and polyethylene glycol. The pH controllers applicable thereto include, for example, hydrochloric acid, sodium hydroxide and sodium carbonate. Besides the above, the additives such as a dyestuff (including, preferably, a blue dyestuff and an ultramarine blue dye), a fluorescent whitening agent, an antistatic agent and a defoamer may be used in combination. A pulp is processed in the following treatments. After it is suitably pulverized to prepare a pulp slurry containing the above-given additives if required. The resulting slurry is formed into paper by a paper-making machine such as a Fourdrinier paper making machine, and the resulting paper is dried up and then super-calendered. Before or after drying the paper, it is surface-sized.

It is preferable that a support is coated with a polyolefin resin on both sides of the resulting base paper of the support. The polyolefin resins include, for example, a single polymer of α -polyolefin such as polyethylene and polypropylene and the mixtures of each of the polymers. The particularly preferable polyolefins include, for example, a high-density polyethylene, a low-density polyethylene, or the mixtures thereof. There is no special limitation to the molecular weights of the above-mentioned polyolefins. However, a polyolefin having a molecular weight within the range of 20,000 to 200,000 is commonly used. There is also no special limitation to the thickness of a polyolefin resin-coated layer, but the layer thickness thereof is usually within the range of about 15 to 50 μm . When a support is made of paper, Any supports having various types can be used. For example, it is also allowed to use a thin type base paper having a thickness within the range of 80 to 180 μm , a delaminable and adhesive type support described in Japanese Utility Model Application No. 64-29550/1989, and a thick type base paper. When making use of a support made of polypropylene or polyethylene terephthalate, it is also allowed to prepare them in such a manner that a white pigment is coated in a controlled amount over each of transparent, translucent or opaque type base paper. The oxygen permeability of a support is preferable to be not more than 2.0 cc/m²·hr·atm.

After a light-sensitive material relating to the invention is, if required, corona-discharged, UV-irradiated, flame-treated and so forth, it is also allowed to be coated directly or through a sublayer (that is one or not less than two under-coat layers for improving the adhesiveness, antistatic property, dimensional stability, frictional resistance, hardness, antihalation property, frictional property and/or other characteristics each of the surface of a support).

For improving a coatability, a thickening agent may be used when coating a light-sensitive material applied with a silver halide emulsion. Among the coating methods thereof, an extrusion coating method capable of coating two or more layers at the same time, or a curtain coating method are particularly useful.

In the invention, it is allowed to take any period of time from an exposure to a development. It is, however, preferable to take shorter from the viewpoint of making the whole processing time shorter. With a light-sensitive material relating to the invention, an image density variation can be reduced and a high image quality can be

stably obtained, even when it takes only 30 seconds or shorter to perform the processing steps from an exposure through a development.

As for the aromatic primary amine developing agents applicable to the invention, any well-known compounds thereof can be used. The typical examples of the compounds will be given below.

- 5 CD-1 : N,N-diethyl-p-phenylenediamine,
- CD-2 : 2-amino-5-diethylaminotoluene,
- CD-3 : 2-amino-5-(N-ethyl-N-laurylamino) toluene,
- CD-4 : 4-(N-ethyl-N- β -hydroxyethylamino) aniline,
- CD-5 : 2-methyl-4-(N-ethyl-N- β -hydroxyethylamino) aniline,
- 10 CD-6 : 4-amino-3-methyl-N-ethyl-N-(β -methanesulfonamidoethyl) aniline,
- CD-7 : N-(2-amino-5-diethylaminophenylethyl) methanesulfonamide,
- CD-8 : N,N-dimethyl-p-phenylenediamine,
- CD-9 : 4-amino-3-methyl-N-ethyl-N-methoxyethyl aniline,
- CD-10: 4-amino-3-methyl-N-ethyl-N-(β -ethoxyethyl) aniline,
- 15 CD-11: 4-amino-3-methyl-N-ethyl-N-(β -butoxyethyl) aniline, and
- CD-12: 4-(N-ethyl-N-(β -hydroxypropylamino) aniline

The above-given color developing agents may be used independently or in combination with any well-known p-phenylenediamine derivatives.

The color developing agents are each used commonly in an amount within the range of 1×10^{-2} to 2×10^{-1} mols per liter of a developer used. From the viewpoint of a rapid process, they are preferably used in an amount within the range of 1.5×10^{-2} to 2×10^{-1} mols per liter of a color developer used. In the invention, color developing agents CD-5, CD-6 and CD-9 are preferred. Among them CD-5 is particularly preferred so as to make it closer to a printing ink tone.

The above-mentioned p-phenylenediamine derivatives are commonly used in the salt forms such as a sulfate, a hydrochloride, a sulfite, a nitrate and a p-toluene sulfonate.

In a developer preferably applicable to the invention, it is preferable that any benzyl alcohol is not substantially contained therein. The expression, "--- be not substantially contained ---", herein means that benzyl alcohol is contained in an amount of 2cc per liter of the subject developer. In the invention, it is most preferable when none of benzyl alcohol is contained at all.

In a color developer, the following developer components, besides the above-mentioned components, may be contained. As for an alkalizer, for example, sodium hydroxide, potassium hydroxide, sodium metaborate, potassium metaborate, trisodium phosphate, tripotassium phosphate, borax and a silicate may be used independently or in combination, provided that they are used without producing any precipitation and a pH stabilizing effect can be maintained. From the viewpoint of the necessity for preparation, or for the purposes of enhancing an ionic strength and so forth, it is possible to use various kinds of salts such as disodium hydrogen phosphate, dipotassium hydrogen phosphate, sodium bicarbonate, potassium bicarbonate and a borate.

In the invention, it is preferable that a color developer contains chloride ions in an amount within the range of 2.5×10^{-2} to 5×10^{-1} mols per liter of the color developer.

In this case, chloride ions and bromide ions may be added directly to a developer, or it may be dissolved out of a light-sensitive material into the developer in the course of carrying out the development. When adding the ions directly to a color developer, the substances for supplying chloride ions include, for example, sodium chloride, potassium chloride, ammonium chloride, lithium chloride, nickel chloride, magnesium chloride, manganese chloride, calcium chloride and cadmium chloride. Among them, sodium chloride and potassium chloride are preferred. They may also be supplied from a fluorescent whitening agent contained in a developer.

The substances for supplying bromide ions include, for example, sodium bromide, potassium bromide, ammonium bromide, lithium bromide, nickel bromide, magnesium bromide, manganese bromide, calcium bromide, cadmium bromide, cerium bromide and thallium bromide. Among them, the preferable substances include, for example, sodium bromide and potassium bromide. When they are dissolved out of a light-sensitive material in the course of carrying out a development, chlorine ions and bromine ions may also be supplied respectively from an emulsion or the others than the emulsion.

In a color developer, the following organic preservatives can preferably be used in place of hydroxyl amine having so far been used as a preservative; namely, organic preservatives including, for example, a hydroxyl amine derivative such as those given in JP OPI Publication Nos. 63-146043/1988, 63-146042/1988, 63-146041/1988, 63-146040/1988, 63-135938/1988, 63-118748/1988 and 63-179351/1988, a hydroxamic acid, a hydrazine, a phenol, an α -hydroxyketone, α -aminoketone, a sugar, a monoamine, a diamine, a quaternary ammonium salt, a nitroxy radical, an alcohol, an oxime, a diamido compound, and a condensed-ring type amine.

It is also allowed to make combination use of the above-given compounds, a hydroxyl amine and the fore-

going organic preservatives. It is, however, preferable that no hydroxyl amine is not rather used, from the viewpoint of a development characteristics.

Further, a development accelerator may also be used, if required. The development accelerators include, for example, various kinds of pyridinium compounds typified by those given in, for example, US Patent Nos. 2,648,604 and 3,671,247 and JP Examined Publication No. 44-9503/1969, cationic dyes such as other cationic compounds and phenosafranine, neutral salts such as thallium nitrate, a polyethylene glycol and the derivatives thereof such as those given in, for example, US Patent Nos. 2,533,990, 2,531,832, 2,950,970 and 2,577,127 and JP Examined Publication No. 44-9504/1969, nonionic compounds such as a polythioether, organic solvents given in, for example, JP Examined Publication No. 44-9509/1969, an organic amine, ethanolamine, ethylenediamine, diethanolamine and triethanolamine. In addition to the above, phenethyl alcohol given in, for example, US Patent No. 2,304,925 and, besides, acetylene glycol, methylethyl ketone, cyclohexanone, pyridine, ammonia, hydrazine, a thioether, an amine, and so forth may also be included.

For improving the solubility of a developing agent, it is allowed, if required, to use a dissolving aid such as ethylene glycol, methyl cellosolve, methanol, acetone, dimethyl formamide, β -cyclodextrin, p-toluene sulfonic acid and, besides, the compounds given in, for example, JP Examined Publication Nos. 47-33378/1972 and 44-9509/0969.

Further, an auxiliary developer can also be used together with a developing agent. The auxiliary developers having been known include, for example, a N-methyl-p-aminophenol sulfate, phenidone, an N,N-diethyl-p-aminophenol chloride and an N,N,N',N'-tetramethyl-p-phenylene diamine chloride. They may be added usually in an amount within the range of 0.01 to 1.0 g per liter of a developer used. Besides the above-mentioned auxiliary developers, a competing coupler, a foggant, a development-inhibitor-releasing type coupler (or a DIR coupler), a development-inhibitor-releasing type compound and so forth may also be added. Further, a variety of additives such as other antistaining agent, an antisludging agent, an interlayer effect accelerator and so forth may be added.

Each component of the above-mentioned color developers can be prepared by adding and stirring it in a specific amount of water. In this case, a component having a relatively lower solubility to water may be added upon mixing it with the foregoing organic solvents such as triethanol amine. To be more usual, a color developer can also be prepared in the following manner. A plurality of components thereof which can stably coexist together are prepared in the form of an aqueous concentrated solution or in the solid state. The resulting conc.-solution is put into a small vessel in advance and is added to and then stirred in water, so that the color developer can be prepared.

The sulfite concentration of a color developer is preferably not more than 1×10^{-2} mols per liter of the developer. It becomes excellent when the concentration thereof is not more than 7×10^{-3} mols per liter, including 0 and, particularly, it is preferable when the concentration thereof is not more than 5×10^{-3} mols per liter, including 0.

In the invention, a color developer can be used in any pH regions. However, it is preferably within the range of pH9.5 to 13.0 and, more preferably, 9.8 to 12.0, from the viewpoint of a rapid processing.

In a color development, a processing temperature is preferably within the range of 25 to 70°C. It is preferable when a processing temperature is higher, because a processing time can be shortened. However, the processing temperature is preferable to be rather lower, from the viewpoint of the stability of a processing solution, and it is, therefore, preferable to process with a color developer at a temperature within the range of 25 to 50°C. A color development time is to be within the range of 70 to 240 seconds. When it is shorter than 70 seconds, the maximum density will come out instable when carrying out a continuous processing. When it is longer than 240 seconds, there will come out such a defect that a sludge is liable to produce in a color developer. It is, therefore, preferably within the range of 90 to 220 seconds.

An amount of a color developer to be replenished is preferably not more than 700cc per liter, more preferably, not more than 500cc and, further preferably, within the range of 20 to 280cc.

The processing steps comprise substantially a color developing step, a bleach-fixing step and a washing step (including a stabilizing step in place of the washing step). It is allowed to add the other processing steps or to replace the above-mentioned steps by any steps having the functions equivalent to those of the above-mentioned steps. For example, the above-mentioned bleach-fixing step may be separated into a bleaching step and a fixing step and, further, another bleaching step may be added before the bleach-fixing step. In the processing steps for a color light-sensitive material of the invention, it is preferable to carry out a bleach-fixing step immediately after carrying out the color developing step.

There is no limitation to a bleaching agent applicable to a bleach-fixer. However, the metal complex salts of an organic acid are preferred. The complex salts thereof include, for example, polycarboxylic acid, aminopolycarboxylic acid or an organic acid such as oxalic acid and citric acid is coordinated with a metal ion such as that of iron, cobalt or copper. As for the most preferable organic acids applicable to form the metal complex

salts of such an organic acid as mentioned above, polycarboxylic acid and aminopolycarboxylic acid may be given. The above-mentioned polycarboxylic acid or aminopolycarboxylic acid is allowed to be an alkali-metal salt, an ammonium salt or a water-soluble amine salt. The concrete compounds thereof include, for example, compounds 2 through 20 given in JP OPI Publication No. 1-205262/1989, pp. 58-59.

5 The above-mentioned bleachers are each used in an amount within the range of 5 to 450 g per liter of a bleach-fixer used and, more preferably, 20 to 250 g.

A bleach-fixer contains a silver halide fixing agent, as well as the above-mentioned bleaching agent. If required, a solution having a composition containing a sulfite is also applied as a preservative. It is also allowed to use a bleach-fixer comprising a composition added with a relatively large amount of a halide such as ammonium bromide, and a specialty bleach-fixer having a composition comprising a combination of an iron(III) ethylenediamine tetraacetate bleaching agent and a relatively large amount of a halide such as ammonium bromide, besides an iron(III) ethylenediamine tetraacetate bleaching agent and a silver halide fixing agent.

10 The above-mentioned halides also applicable thereto include, for example, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, potassium bromide, sodium iodide, potassium iodide and ammonium iodide, besides ammonium bromide.

The above-mentioned halide fixing agents contained in a bleach-fixer include, for example, a compound capable of producing a water-soluble complex salt upon making a reaction with such a silver halide as is commonly applicable to a fixing treatment. They include, typically, a thiosulfate such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate, a thiocyanate such as potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate, thiourea and thioether.

20 These fixing agents may be used in an amount of not less than 5g per liter of a bleach-fixer used, provided that it can be dissolved. It is commonly used in an amount within the range of 70 to 250g.

A bleach-fixer is allowed to contain a variety of pH buffer, independently or in combination, such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide. It can also contain a variety of fluorescent whitening agents, defoamers and surfactants. It can further suitably contain a preservative such as hydroxyl amine, hydrazine and the bisulfurous acid adducts of an aldehyde compound, an organic chelating agent such as aminopolycarboxylic acid, a stabilizer such as nitroalcohol and a nitrate, and an organic solvent such as methanol, dimethyl formamide and dimethyl sulfoxide.

30 The bleach-fixers are allowed to be added by a variety of such a bleaching accelerator as given in JP OPI Publication No. 46-280/1971, JP Examined Publication Nos. 45-8506/1970 and 46-556/1971, Belgian Patent No. 770,910, JP Examined Publication Nos. 45-8836/1970 and 53-9854/1978, JP OPI Publication Nos. 54-71634/1979 and 49-42349/1974, and so forth.

A bleach-fixer is used at a pH of not lower than 4.0, commonly, within the range of 4.0 to 9.5, preferably, 4.5 to 8.5 and, most preferably, 5.0 to 8.5. It is also used at a temperature of not higher than 80°C and, preferably, not higher than 55°C so as to inhibit it from producing an evaporation. A bleach-fixing time thereof is preferably not longer than 240 seconds.

In a development process relating to the invention, a washing treatment is carried out after a color development and then a bleach-fixing process. A preferable embodiment of the washing treatment will now be detailed.

40 The compounds preferably applicable to a washing liquid include, for example, a chelating agent having a chelation-stabilization constant to an iron ion of not less than 8. The term, a chelation-stabilization constant, herein means a constant having generally been known in L.G. Sillen & A.E. Martell, "Stability Constant of Metal Ion Complexes", The Chemical Society, London, (1964); S. Chaberek & A.E. Martell, "Organic Sequestering Agents", Wiley, (1959); and so forth.

The chelating agents each having a chelation-stabilization constant to iron ion of not less than 8 include, for example, an organic carboxylic acid chelating agent, an organic phosphoric acid chelating agent, an inorganic phosphoric acid chelating agent and a polyhydroxy compound. The above-mentioned iron ion means ferric ion. The concrete compounds for a chelating agent having a chelation-stabilization constant to ferric ion of not less than 8 include, for example, the compounds given in JP OPI Publication No. 1-205162/1989, p. 63, the 15th line to p. 64, the 17th line. The above-mentioned chelating agent may be used in an amount within the range of, preferably, 0.01 to 50g and, more preferably, 0.05 to 20g per liter of a washing liquid used.

50 As for the compounds to be added to a washing liquid, an ammonium compound is particularly preferred. They are supplied from an ammonium salt of various kinds of inorganic compounds. They include, concretely, the compounds given in JP OPI Publication No. 1-205162/1989, p. 65, the 5th line to p. 66, the 11th line. Such an ammonium compounds as mentioned above may be added in an amount of, preferably, not less than 1.0×10^{-5} mols per liter of a washing liquid used, more preferably, within the range of 0.001 to 5.0 mols and, particularly, within the range of 0.002 to 1.0 mols.

It is preferable that an aqueous solution contains a sulfite in such an amount that no bacteria can be produced. The sulfites to be contained in an aqueous solution may be any one of organic or inorganic matters, provided that the sulfites can release sulfite ions. However, the preferable sulfites are of the inorganic salts. The concrete compounds thereof include, for example, sodium sulfite, potassium sulfite, ammonium sulfite, ammonium bisulfite, potassium bisulfite, sodium bisulfite, sodium metabisulfite, potassium metabisulfite, ammonium metabisulfite, sodium hydrosulfite, sodium glutaraldehyde bisulfite and sodium succinaldehyde bisulfite.

EXAMPLES

Now, the invention will be detailed by citing the following examples. However, the embodiments of the invention shall not be limited thereto.

Example 1

Support A was prepared by laminating a high density polyethylene on the both sides of a pulp paper having a balance weight of 130 g/m², wherein a surface-treated anatase type titanium dioxide is contained in an amount of 15 % by weight in a polyethylene laminated layer of emulsion layer side.

Support B was prepared in the same manner as in Support A, except that 90 parts by weight of polyethylene terephthalate and 10 parts by weight of anatase type titanium dioxide white pigment were each added and kneaded together, and then, a water-proof resin layer containing 30 g/m² was coated on the surface of emulsion side of a pulp paper.

On the other hand, an electron beam-hardenable coating solution having the following composition was prepared.

Epoxyacrylate oligomer (with the trade name of FS-3118, produced by Mitsubishi Rayon Co.)	70 wt%
Titanium oxide (with the trade name of A-220, produced by Ishihara Sangyo Co.)	30 wt%

The above-mentioned compositions were well mixedly dispersed for 20 minutes by making use of a cowl-less dissolver. The resulting coating solution was coated at a line-speed of 30 m/min. on the circumferential surface of a rotary drum being rotated having a high-glossy, mirror-finished circumferential surface, by making use of a slit-orifice coater so that the amount coated (of the solid parts) could be 6 g/m². A base paper for photographic print paper support having a balance weight of 180 g/m² and being run by coupling to the drum rotation speed was pressed down and laminated on the resulting coating solution layer, and an electron beam was irradiated from the back side of the base paper so that the beam absorption could be 1 Mrad at an acceleration voltage. The coating solution layer was hardened thereby and the resulting multilayered member was peeled off, so that a support (Support C) could be obtained.

Similar to Support C, Supports D and D were prepared each by making use of the following compositions, respectively.

Composition of the coating solution for Support D	
Polyester acrylate (having four double-bonds per about 1000 molecules)	25 wt%
Trimethylolpropane triacrylate	25 wt%
Titanium dioxide (of the rutile type)	50 wt%

Composition of the coating solution for Support E	
Urethane acrylate	25 wt%
Epoxy acrylate	25 wt%
Titanium dioxide (anatase type)	50 wt%

A color photographic light-sensitive material was prepared by coating the following Layer 1 through Layer 7 on Support A and then by coating a backing layer on the back side of Support A.

EP 0 675 404 A1

The amounts added are indicated in terms of g/m², provided that the silver halide emulsions are indicated by the silver contents of the silver halides of the emulsions, respectively.

5	Layer	Composition	Amount coated (in g/m ²)
	Layer 7 (A protective layer)		
10		Gelatin	1.00
		Antistaining agent (HQ-1)	0.002
15			
20			
25			
30			
35			
40			
45			
50			
55			

	Antistaining agent (HQ-2)	0.002
5	Antistaining agent (HQ-3)	0.004
	Antistaining agent (HQ-4)	0.02
	Compound B, C, D and E	2×10^{-5} each
10	DIDP	0.005
	Silicon dioxide	0.003
15	Antimold (F-1)	0.002
	Layer 6 (A UV absorption layer)	
	Gelatin	1.50
20	AI-2	0.02
	AI-4	0.01
25	UV absorbent (UV-1)	0.38
	UV absorbent (UV-2)	0.32
	UV absorbent (UV-3)	0.54
30	Antistaining agent (HQ-4)	0.04
	Compound E	4×10^{-4}
35	DNP	0.20
	Compounds F and G	2×10^{-4} each
	PVP	0.03
40	Layer 5 (A red-sensitive layer)	
	Gelatin	1.3
45	Red-sensitive silver chloro- bromide emulsion (Em-R)	0.36
	Cyan coupler (C-1)	0.30
50	Antistaining agent (HQ-5)	0.01
	HBS-1	0.20

55

Layer 4 (An intermediate layer)

5	Gelatin	1.00
	Antistaining agent (HQ-1)	0.01
	Antistaining agent (HQ-2)	0.01
10	Antistaining agent (HQ-3)	0.02
	Antistaining agent (HQ-4)	0.10
15	Compounds B, C, D and E	2×10^{-5} each
	DIDP	0.03
	Antimold (F-1)	0.02

20 Layer 3 (A green-sensitive layer)

	Gelatin	1.20
25	Green-sensitive silver chloro- bromide emulsion (Em-G)	0.30
	Magenta coupler (M-1)	0.40
	Dye-image stabilizer	0.20
30	HBS-1	0.40

Layer 2 (An intermediate layer)

35	Gelatin	1.00
	AI-1	0.01
	AI-3	0.01
40	Antistaining agent (HQ-1)	0.03
	Antistaining agent (HQ-2)	0.03
45	Antistaining agent (HQ-3)	0.05
	Antistaining agent (HQ-4)	0.23
	Compounds B, C, D and E	3×10^{-4} each
50	DIDP	0.06

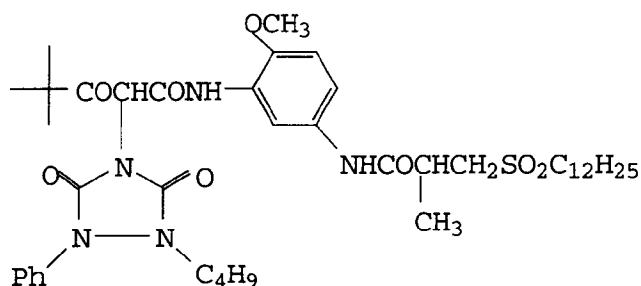
55

	Fluorescent whitening agent (W-1)	0.10
	Layer 1 (A blue-sensitive layer)	
5	Gelatin	1.20
	Blue-sensitive silver chloro- bromide emulsion (Em-B)	0.28
10	Yellow coupler (Y-1)	0.80
	Antistaining agent (HQ-4)	0.02
15	Compound A	2×10^{-4}
	HBS-1	0.50
20	Support	Polyethylene-laminated paper containing a very small amount of colorant

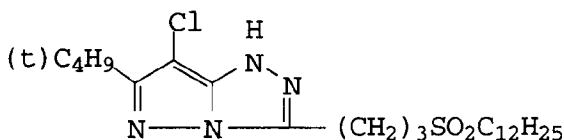
The amounts of the silver halide emulsions added are indicated in terms of the silver contents of the emulsions, respectively.

- SU-1 : Sodium tri-*i*-propylnaphthalene sulfonate,
 SU-2 : Sodium di(2-ethylhexyl)-sulfosuccinate,
 SU-3 : Sodium (2,2,3,3,4,4,5,5-octafluoropentyl) sulfosuccinate,
 DNP : Dinonyl phthalate,
 DIDP : Di-*i*-decyl phthalate,
 PVP : Polyvinyl pyrrolidone,
 H-1 : Tetrakis(vinylsulfonyl methyl) methane, and
 H-2 : Sodium 2,4-dichloro-6-hydroxy-*S*-triazine

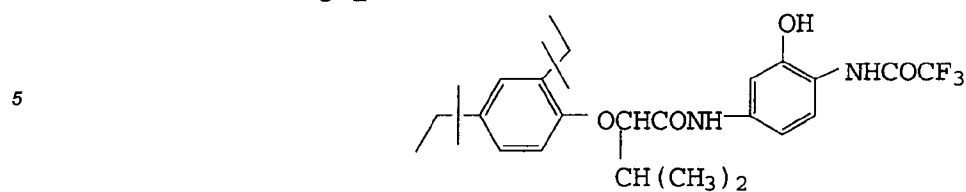
Y-1



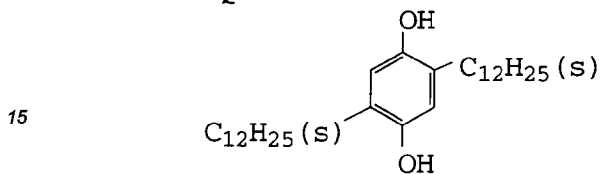
M-1



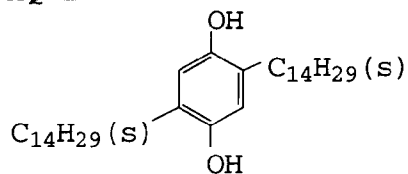
C-1



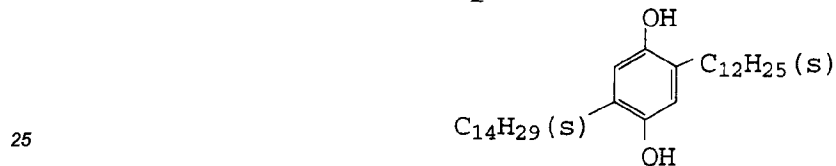
HQ-1



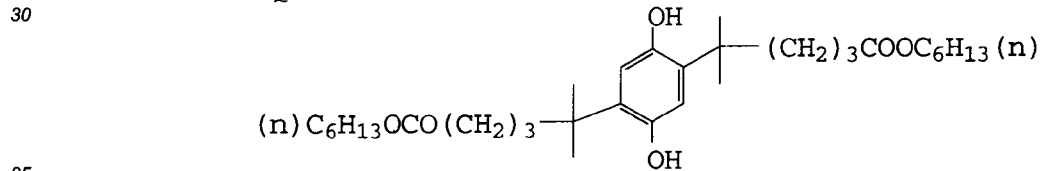
HQ-2



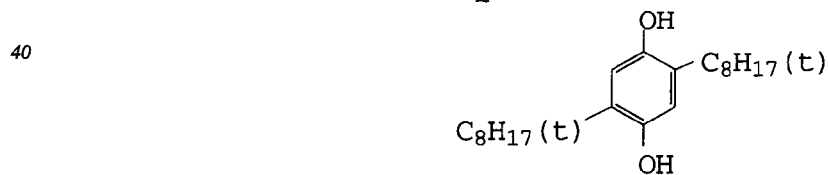
HQ-3



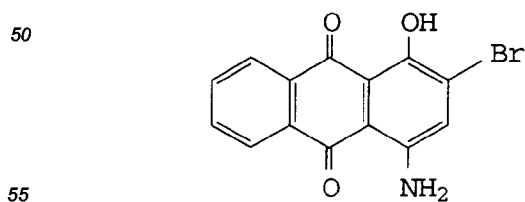
HQ-4



HQ-5

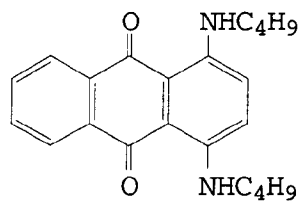


Compounds A,B,C,D and E (each was a quinone member of HQ-5,1,2,3 and 4, respectively.)
Compound F



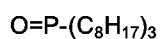
(Compound 4 given in JP OPI
Publication No. 2-842/1990)

Compound G

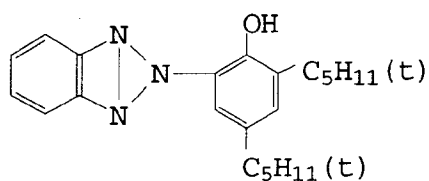


(Compound 9 given i JP OPI
Publication No. 2-842/1990)

HBS-1

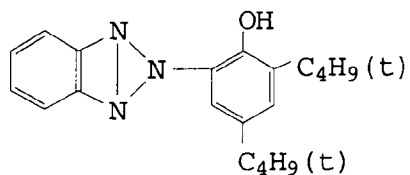


UV-1



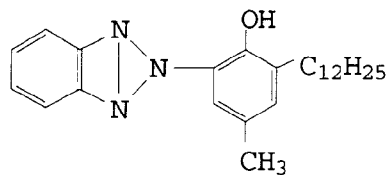
(IIIc-1 given in JP OPI Publication
No. 1-2590944/1989)

UV-2



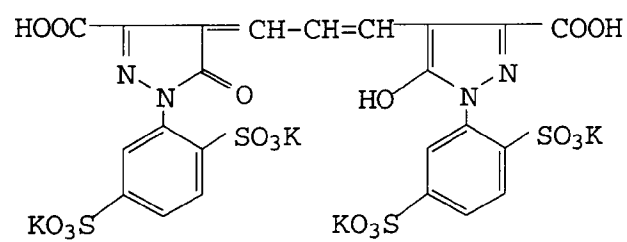
(IIIc-7 given in JP OPI Publication
No. 1-2590944/1989)

UV-3

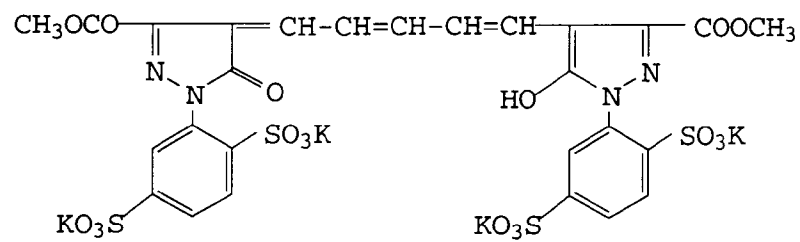


(UV-23L given in JP OPI Publication
No. 63-187240/1988)

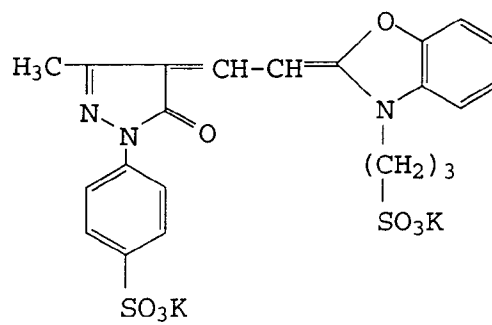
AI-1



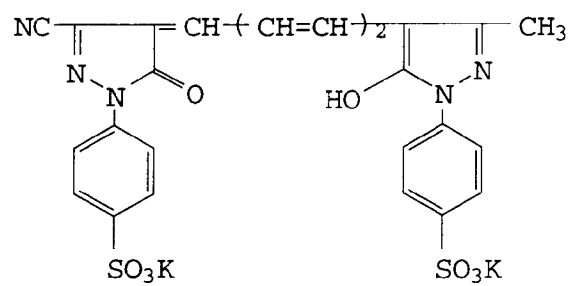
AI-2



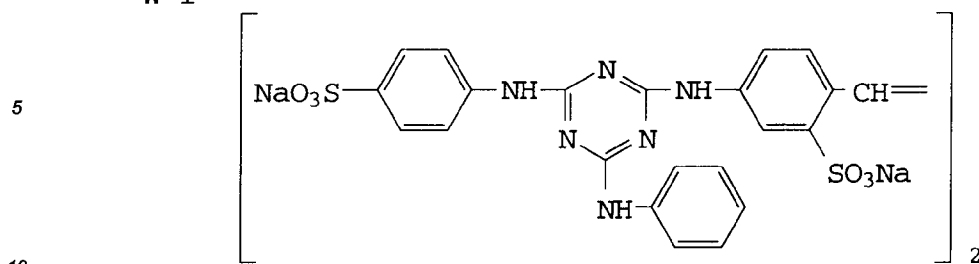
AI-3



AI-4



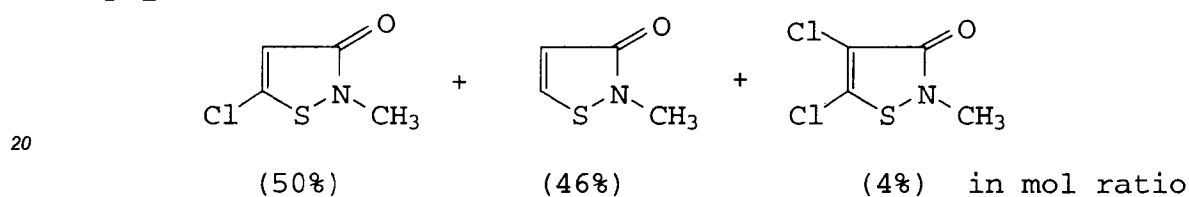
W-1



(No. 3 given in JP OPI Publication
No. 2-232652/1990)

15

F-1



A mixture having a mol ratio of (50:46:4)

25

(No. 9 given in JP OPI Publication No. 3-157646/1991)

Samples 102 through 111 were each prepared in the same manner as in Sample 101, except that the materials were changed as shown in Table 1 and added to the samples.

30

In the dyes shown in Table 1, the amounts thereof added were changed as shown below.

35

	Al-1	Al-2	Al-3	Al-4
Dye a	0.01	0.02	0.01	0.01
Dye b	0.03	0.10	0.04	0.05

In the level of the presence of NBC shown in Table 1, the following layers were interposed between Layer 1 and the support.

40

45

50

55

Layer	Component	Amount added (in g/m ²)
HC-2 (intermediate layer)		
5 10	Gelatin	0.54
	HQ-1	0.01
	HQ-2	0.01
	HQ-3	0.01
	HQ-4	0.01
	DOP	0.072
HC-1 (an HC layer)		
15 20	Gelatin	0.54
	Black colloidal	
	silver	0.08
	PVP	0.03

In the level of the presence of a white pigment shown in Table 1, The following white pigment layers were interposed between Layer 1 and the support.

Layer	Component	Amount added (in g/m ²)
Layer S-2 (an intermediate layer)		
30	Gelatin	0.5
	Layer S-1 (a white pigment layer)	
35	Gelatin	2.0
	Rutile type titanium dioxide	5.0

Further to Layers HC-1, HC-2 and S-2 each, (H-2) was added as a gelatin layer hardener so as to be in a proportion of 5 mg/m²; and to Layer S-2, it was so added as to be in a proportion of 20 mg/m².

Em-B, Em-C and Em-R were each prepared in the following manners.

(Blue color-sensitive silver chlorobromide emulsion)

A silver chlorobromide emulsion having an average grain size of 0.7 μ m and a silver bromide content of 80% was subjected to the optimum sensitization at 57°C by making use of sodium thiosulfate, and sensitizing dye (BS-1) and a stabilizer STB-1 were then added thereto.

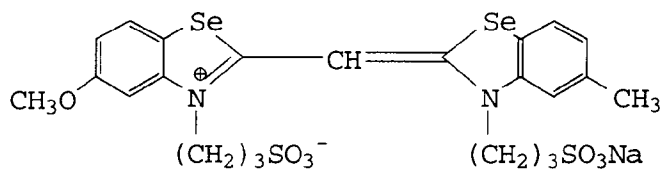
(Green color-sensitive silver chlorobromide emulsion)

A silver chlorobromide emulsion having an average grain size of 0.5 μ m and a silver bromide content of 70% was subjected to the optimum sensitization at 59°C by making use of sodium thiosulfate, and sensitizing dye (GS-1) and a stabilizer STB-1 were then added thereto.

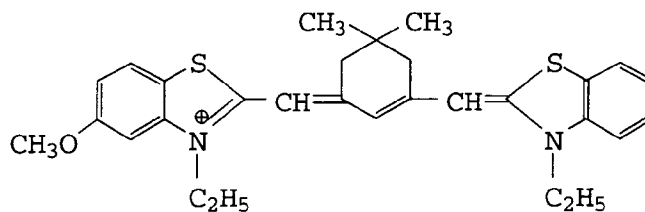
(Red color-sensitive silver chlorobromide emulsion)

A silver chlorobromide emulsion having an average grain size of 0.4 μ m and a silver bromide content of 60% was subjected to the optimum sensitization at 59°C by making use of sodium thiosulfate, sensitizing dye (RS-1) and phenol resin, and a stabilizer STB-1 was then added thereto.

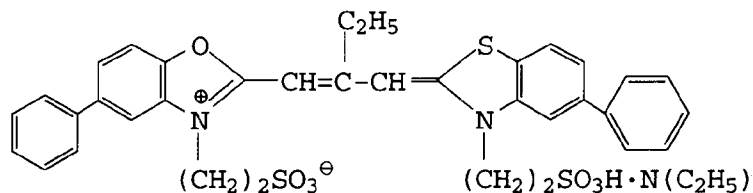
BS-1



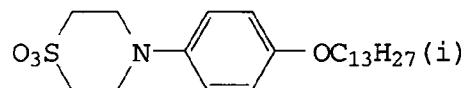
RS-1



GS-1



STB-1



By making a He-Ne gas-laser (having 632.8nm and 543.5nm in wavelength) and a He-Cd gas-laser (having 441.6nm in wavelength) each as the light sources, an apparatus was assembled so as to be capable of exposing scanningwise a luminous flux having a 100 μ m-pitch and a 80 μ m-flux size to samples being moved toward the direction vertical to the scanning direction, at a scanning speed of 1.6m/second.

After making a halftone-dot exposure for a sensitometric gradation-exposure and for a halftone dot-evaluation was applied to every samples 101 through 111, by making use of the above-mentioned apparatus, The exposed samples were each processed in the following processing steps.

(Processing steps I)

	Processing step	Processing temp.	Processing time
5	Color developing	38.0±0.3°C	120 sec.
	Bleach-fixing	35.0±0.5°C	45 sec.
10	Stabilizing	30-34°C	90 sec.
	Drying	60-80°C	30 sec.

(Color developer)

15	Benzyl alcohol	15 ml
	Ce ₂ (SO ₄) ₃	0.015 g
	Ethylene glycol	8.0 ml
20	Potassium sulfite	2.5 g
	Potassium bromide	0.6 g
25	Sodium chloride	0.2 g
	Potassium carbonate	25.0 g
	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	0.1 g
30	Hydroxyl amine sulfate	5.0 g
	Sodium diethylenetriamine pentaacetate	2.0 g
35	4-amino-N-ethyl-N-(β-hydroxyethyl) aniline sulfate	4.5 g
	Fluorescent whitening agent (a 4,4'-diaminostilbene disulfonic acid derivative)	1.0 g
40	Potassium hydroxide	2.0 g
	Diethylene glycol	15.0 ml
45	Add water to make in total	1 liter

50

55

	Adjust pH to be	pH10.15
	(Bleach-fixer)	
5	Ferric ammonium diethylenetriamine pentaacetate	90.0 g
	Diethylenetriamine pentaacetic acid	3.0 g
10	Ammonium thiosulfate (in an aqueous 70% solution)	180 ml
	Ammonium sulfite (in an aqueous 40% solution)	27.5 ml
15	3-mercapto-1,2,4-triazole	0.15 g
	Adjust pH with potassium carbonate or glacial acetic acid to be	pH7.1
20	Add water to make in total	1 liter
	(Stabilizer)	
25	O-phenylphenol	0.3 g
	Potassium sulfite (in an aqueous 50% solution)	12 ml
30	Ethylene glycol	10 g
	1-hydroxyethylidene-1,1-disulfonic acid	2.5 g
35	Bismuth chloride	0.2 g
	Septahydrate of zinc sulfate	0.7 g
40	Ammonium hydroxide (in an aqueous 28% solution)	2.0 g
	Polyvinyl pyrrolidone (K-17)	0.2 g
45	Fluorescent whitening agent, (a 4,4'-diaminostilbene disulfonic acid derivative)	2.0 g
	Add water to make in total	1 liter
50	Adjust pH with ammonium hydroxide or sulfuric acid to be	pH7.5

The stabilizing was carried out in a counter-current system comprising a double-tank structure.

55 The resulting characteristic curve was measured through a PD-84 (produced by Konica Corp.). The resulting white background was measured through X-rite 310 (produced by X-rite Co.) and it was evaluated. The resulting halftone dot quality was evaluated with the eye through a magnifier. The results thereof will be shown in Table 1.

Table 1

Sample No.	Dye	NBC	White pigment	Support	White background*			Halftone-dot quality	
					ΔDB	ΔDG	ΔDR		
101	b	Not used	Not used	A	0.000	0.000	0.000	×	Comp.
102	a	Not used	Not used	A	0.005	0.005	0.008	○	Comp.
103	b	Used	Not used	A	0.009	0.008	0.011	○	Comp.
104	b	Not used	Used	A	0.000	0.000	0.000	○	Inv.
105	b	Not used	Not used	B	0.001	0.000	0.000	×	Comp.
106	a	Not used	Not used	B	0.006	0.005	0.008	○	Comp.
107	b	Used	Not used	B	0.011	0.011	0.012	○	Comp.
108	b	Not used	Used	B	0.001	0.000	0.000	○	Inv.
109	b	Not used	Not used	C	0.001	0.000	0.000	○	Inv.
110	b	Not used	Not used	D	0.002	0.001	0.000	◎	Inv.
111	b	Not used	Not used	E	0.001	0.000	0.000	◎	Inv.

Comp.: Comparison Inv.: Invention

* ΔDB , ΔDG , ΔDR : White background difference from that of Sample 101.

As shown in Table 1, the white background and halftone-dot quality can be compatible in the invention.

Example 2

In the following procedures, Em-B2, Em-G2 and Em-R2 were prepared, respectively.

(Preparation of blue-sensitive silver chloride emulsion)

The following solutions A and B were added at the same time to 1000 ml of an aqueous 2% gelatin solution being kept at 40°C by taking 30 minutes while controlling the pAg and pH to be 6.5 and 3.0, respectively. Further, the following solutions C and D were also added at the same time thereto by taking 180 minutes while controlling the pAg and pH to be 7.3 and 5.5, respectively.

While adding the above-mentioned solutions, the pAg was controlled in the method described in JP OPI Publication No. 59-45437/1984 and the pH was controlled by making use of an aqueous sulfuric acid or sodium sulfate solution.

(Solution A) Water was added to 3.42g of sodium bromide and 0.03g of potassium bromide so as to make 200ml.

(Solution B) Water was added to 10g of silver nitrate so as to make 200ml.

(Solution C) Water was added to 102.7g of sodium chloride and 1.0g of potassium bromide so as to make 600ml.

(Solution D) Water was added to 300g of silver nitrate so as to make 600ml.

After completing the addition thereof, the desalting treatment was carried out by making use of an aqueous solution of 5% Demol N produced by Kao-Atlas Corp. and an aqueous 2% magnesium sulfate solution, and the resulting desalted solution and an aqueous gelatin solution were mixed together, so that a monodisperse type cubic-grained emulsion EMP-1 having an average grain size of 0.85 μ m, the variation coefficient of the grain-size distribution of 0.07 and a silver chloride content of 99.5 mol% could be prepared.

The resulting EMP-1 was subjected to the optimum chemical sensitization at 50°C by making use of the following compounds, so that a blue-sensitive silver halide emulsion (Em-B2) could be prepared.

5

Sodium thiosulfate	0.8 mg/mol of AgX
Chloroauric acid	0.5 mg/mol of AgX
Stabilizer STAB-1	6×10^{-4} mols/mol of AgX
Sensitizing dye BS-1	4×10^{-4} mols/mol of AgX
Sensitizing dye BS-3	1×10^{-4} mols/mol of AgX

10

In the following procedures, Em-G2 and Em-R2 were each prepared. And, the chemical structures of the stabilizer and sensitizing dyes will be given later.

(Preparation of a green-sensitive silver chloride emulsion)

15

A monodisperse type cubic-grained emulsion EMP-2 having an average grain size of $0.43 \mu\text{m}$, a variation coefficient of 0.08 and a silver chloride content of 99.5% could be prepared in the same manner as in EMP-1, except that the time of adding Solutions A and B and the time of adding Solutions C and D were each changed.

20

The resulting EMP-2 was subjected to the optimum chemical sensitization at 55°C by making use of the following compounds, so that a green-sensitive silver chloride emulsion (Em-G2) could be prepared.

25

Sodium thiosulfate	1.5 mg/mol of AgX
Chloroauric acid	1.0 mg/mol of AgX
Stabilizer STAB-1	6×10^{-4} mols/mol of AgX
Sensitizing dye GS-1	4×10^{-4} mols/mol of AgX

30

(Preparation of a red-sensitive silver chloride emulsion)

35

A monodisperse type cubic-grained emulsion EMP-3 having an average grain size of $0.50 \mu\text{m}$, a variation coefficient of 0.08 and a silver chloride content of 99.5% could be prepared in the same manner as in EMP-1, except that the time of adding Solutions A and B and the time of adding Solutions C and D were each changed.

To the above-mentioned Solution C, the following metal compounds were added.

40

K_2IrCl_6	3.8×10^{-8} mols/mol of AgX
$\text{K}_4\text{Fe}(\text{CN})_6$	1.2×10^{-5} mols/mol of AgX

The resulting EMP-3 was subjected to the optimum chemical sensitization at 60°C by making use of the following compounds, so that a green-sensitive silver chloride emulsion (Em-R2) could be prepared.

45

Sodium thiosulfate 1.8 mg/mol of AgX

Chloroauric acid 2.0 mg/mol of AgX

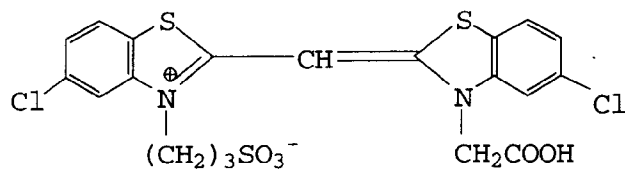
50

Stabilizer STAB-1 6×10^{-4} mols/mol of AgX

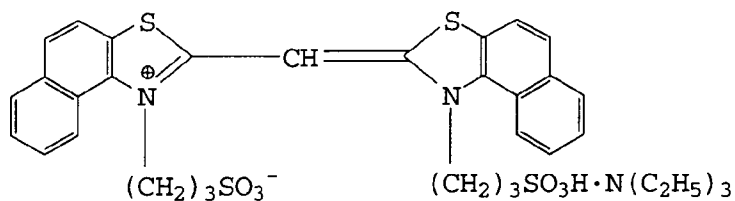
Sensitizing dye RS-1 1×10^{-4} mols/mol of AgX

55

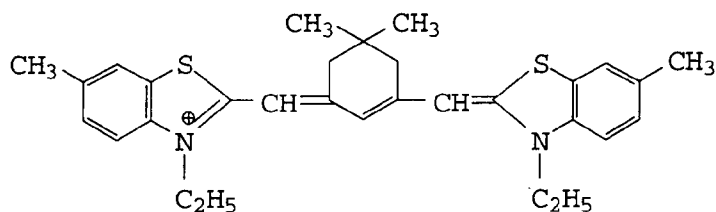
BS-2



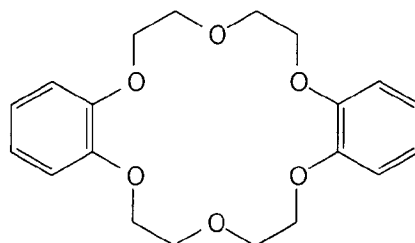
BS-3



RS-2



RSS-1



After the emulsions (Em-B, Em-G and Em-R) of Samples 101 through 111 of Example 1 were replaced by Em-B2, Em-G2 and Em-R2, they were similarly exposed to light and were then processed in the following processing steps, respectively.

Processing step	Processing temperature	Processing time	Amount replenished
Color developing	37.0±0.3°C	120 sec.	300cc
Bleach-fixing	35.0±0.5°C	45 sec.	300cc
Stabilizing	30 to 35°C	90 sec.	600cc
Drying	50 to 80°C	40 sec.	

The compositions of the development processing solutions will be given below.
Color developing tank solution & the replenisher thereof

	Tank solution	Replenisher
	(800cc)	(800cc)
5	Pure water	
	Diethylene glycol	2 g
	Potassium bromide	0.2 g
10	Potassium chloride	3.5 g
	Potassium sulfite	0.25 g
15	N-ethyl-N-(β -hydroxyethyl)-4-aminoaniline sulfate	3.0 g
	N,N-diethyl hydroxyamine	6.8 g
	Triethanol amine	10.0 g
20	Sodium diethylenetriamine pentaacetate	2.0 g
25	Fluorescent whitening agent, (4,4'-diaminostilbene disulfonic acid derivative)	2.0 g

30

35

40

45

50

55

	Potassium carbonate	30 g	30 g
	Add water to make in total	1 liter	
5	Adjust pH to be	pH=10.10	pH=10.42
	Bleach-fixer tank solution & the replenisher thereof		
10	Ferric ammonium diethylenetriamine pentaacetate dihydrate		65 g
	Diethylenetriamine pentaacetic acid		3 g
15	Ammonium thiosulfate (in an aqueous 70% solution)		100cc
	2-amino-5-mercapto-1,3,4-thiadiazole		2.0 g
20	Ammonium sulfite (in an aqueous 40% solution)		27.5cc
	Add water to make in total		1 liter
25	Adjust pH with potassium carbonate or glacial acetic acid to be		pH=6.5
	Stabilizer tank solution & the replenisher thereof		
30	O-phenylphenol		1.0 g
	5-chloro-2-methyl-4-isothiazoline-3-one		0.02 g
	2-methyl-4-isothiazoline-3-one		0.02 g
35	Diethylene glycol		1.0 g
	Fluorescent whitening agent (Cinopar SFP)		2.0 g
40	1-hydroxyethylidene-1,1-diphosphonic acid		1.8 g
	Sodium ethylenediaminetetraacetate		1.5 g
	Potassium sulfite		5.0 g
45	Add water to make in total		1 liter
	Adjust pH with aqueous ammonia to be		pH=8.0

50

55

Table 2

Sample No.	Dye	NBC	White pigment	Support	White background*			Half-tone-dot quality	* Color stain	
					ADB	ADG	ADR			
112	b	Not used	Not used	A	0.000	0.000	0.000	X	0.04	Comp.
113	a	Not used	Not used	A	0.005	0.005	0.008	O	0.26	Comp.
114	b	Used	Not used	A	0.015	0.014	0.015	O	0.05	Comp.
115	b	Not used	Used	A	0.001	0.000	0.000	O	0.04	Inv.
116	b	Not used	Not used	B	0.000	0.000	0.000	X	0.04	Comp.
117	a	Not used	Not used	B	0.006	0.005	0.008	O	0.28	Comp.
118	b	Used	Not used	B	0.011	0.011	0.012	O	0.05	Comp.
119	b	Not used	Used	B	0.000	0.000	0.000	O	0.04	Inv.
120	b	Not used	Not used	C	0.001	0.000	0.000	O	0.04	Inv.
121	b	Not used	Not used	D	0.002	0.000	0.000	⊙	0.03	Inv.
122	b	Not used	Not used	E	0.01	0.000	0.000	⊙	0.03	Inv.

Comp.: Comparison Inv.: Invention

The result of the color-stain was evaluated in the following manner. When a red-color exposure was made by making a red-color-separation exposure with a coating solution obtained by two-cycle-running a fresh solution, D_G obtained in the portion of $D_R=1.5$ was compared to a D_G obtained from the fresh solution, and the resulting color-stain was evaluated by the difference between the both resulting D_G s each obtained after carrying out two-cycle running.

As shown in Table 2, the effects of the invention can be remarkably displayed when a high silver chloride containing emulsion is used.

Claims

1. An image forming method comprising the steps of:
 - (1) exposing a silver halide color photographic light-sensitive material with scanning laser-light; and
 - (2) developing said exposed silver halide color photographic light-sensitive material comprising a support having a resin layer, provided thereon at least one of light-sensitive layers including silver halide grains and at least one of layers other than said light-sensitive layers provided under the lowermost layer of said light-sensitive layers, wherein at least one of said layers other than said light-sensitive layers or said resin layer contains a white pigment in an amount of not less than 20 % by weight.
2. The image forming method of claim 1, wherein at least one of said layers other than said light-sensitive layers or said resin layer contains a white pigment in an amount of from 20 % to 80 % by weight.
3. The image forming method of claim 1, wherein at least one of said layers other than said light-sensitive layers has a percentage of voids within the range of 5 to 35 % by weight.
4. The image forming method of claim 1, wherein a silver chloride content of said silver halide grains is not less than 80 mol %.
5. The image forming method of claim 1, wherein a silver chloride content of said silver halide grains is not

less than 95 mol %.

- 5 **6.** The image forming method of claim 1, wherein said white pigment is selected from the group consisting of a rutile titanium dioxide, an anatase titanium dioxide, a barium sulfate, a barium stearate, a silica, an alumina, a zirconium oxide and a kaolin.
- 7.** The image forming method of claim 1, wherein said white pigment is selected from the group consisting of a rutile titanium dioxide and an anatase titanium dioxide.
- 10 **8.** The image forming method of claim 1, wherein said resin layer comprises a organic compound hardened by applying electron beam, and said organic compound has not less than two carbon-carbon double bonds in one molecule thereof.
- 9.** The image forming method of claim 8, wherein said organic compound is selected from the group consisting of an acrylic oligomer, a methacrylic oligomer, an acrylic monomer, an methacrylic monomer, a multifunctional acrylic monomer, a multifunctional methacrylic monomer.
- 15 **10.** The image forming method of claim 1, wherein said silver halide color photographic light-sensitive material is exposed with scanning laser-light according to a halftone dot image information color-separated into a yellow, magenta, cyan and black image information.
- 20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 2141

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)
X	EP-A-0 578 249 (FUJI)	1, 2, 4-10	G03C1/95
Y	* page 42, line 44 - line 55 *	3	G03C1/79
	* page 43, line 1 - line 5 *		
	* page 43, line 29 - line 44 *		
	* page 45, line 23 - line 39 *		
	* page 57, line 38 - line 41 *		
	* page 60, line 12 - line 14 *		

Y	JP-A-4 306 647 (FUJI)	3	
	* abstract *		
	* column 2, line 35 - line 43 *		

The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		5 July 1995	Magrizos, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>.....</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1503 01.82 (P04C01)