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(54) Light-sensitive silver halide photographic material.

(57) Disclosed is a light-sensitive silver halide photographic material comprising a support, at least one silver halide emulsion layer provided on at least one side of the support, and a protective layer provided on the silver halide emulsion layer, wherein the silver halide emulsion layer is formed of two kinds of emulsions each having different average grain size of the grains contained therein, the average grain size in the emulsion containing grains of a smaller average grain size comprises from 40 to 70 % of the average grain size in the emulsion containing grains of a larger average grain size, and the silver halide emulsion layer has a silver amount of 4.5 g/m^2 or less, and further at least one layer of the silver halide emulsion layer and the protective layer contains 300 mg/m^2 or more of at least one kind of matting agent.

Disclosed is also a light-sensitive silver halide photographic material comprising a support and provided by coating thereon at least one hydrophilic colloid layer containing a matting agent, wherein the center-line average roughness of the light-sensitive material ranges from 0.15 to 0.8 μm, and the weight percentage of a matting agent having a particle diameter more than 6 μm is 5 % or less based on the whole matting agent.

Further disclosed is a light-sensitive silver halide photographic material for direct positives, comprising a support and provided thereon a direct positive silver halide emulsion layer containing silver halide grains applied with fog in the presence of a reduction fogging agent and a water-soluble gold compound, wherein at least 250 mg/m^2 of at least one kind of matting agent is contained and at least one of any compounds represented by Formulas (I), (II), (III), (IV) and (V) defined in the specification is contained, in a photographic layer of the side on which the direct positive silver halide emulsion layer is provided.

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Light-sensitive silver halide photographic material

BACKGROUND OF THE INVENTION

This invention relates to a light-sensitive silver halide photographic material. More particularly, it relates to a light-sensitive silver halide photographic material having superior inscribability and erasability. Still more particularly, it is concerned with a light-sensitive silver halide photographic material that can be effectively used as a photographing matt film for use in the photocopying of drawings, maps, etc. From another point of view, it is further concerned with a light-sensitive silver halide photographic material for direct positives, and more particularly to a light-sensitive silver halide photographic material for direct positives that has inscribability, a high speed, and an improved whiteness.

As hitherto well known, matt films are used in the photocopying of drawings for machines and constructions, maps, etc.; the macro-photographying or montage-photographying of aerial photographs dot-formed with use of a screen; and so forth. Matt films are meant by films made opaque by adding matting agents in a large quantity in a film. The reasons why the films are matted by adding matting agents in a large quantity are such that matting makes it possible to inscribe something, or make correction thereof, in pencil or ink after exposure and processing, and makes it possible to erase with erasers something inscribed in pencil or ink, and thus it becomes possible to make correction of drawings or writing-in. Accordingly, the matt films are used for the purpose of making correction or writing-in something by inscribing or erasing something as mentioned above after exposure and processing, or used for the purpose of making diazo-printing, taking copies, or the like purposes.

The photographying matt films are used in usual cameras, and usual rapid-access processing is employed for development. Then, what are desired for the photographying of aerial photographs are those approximate to a continuous tone, and, for the photographying, those having a good sharpness. However, hitherto available matt films have had the problems that they have so a soft tone that the line photographying can not be made, or so a high contrast that the continuous tone can not be obtained or the clearing is inferior.

Referring to the inscribing, inks used for inscribing are mostly water-based inks, and, in many instances, operators manually make writing-in with use of a needle pen (Rotring pen: trade name of Rotring-Werke Riepe KG) or the like generally used in the field of drafting. Because of the background that the films are mainly used for drafting, there are demands for inscription performances of a high level, as exemplified by denseness in density of lines, uniformity in density of lines, reproducibility of line width, constancy in line width, etc. Also important is smoothness in writing touch, and not preferred are rugged feeling and overly strong writing resistance as operators may suffer increasing fatigue.

In addition, also important performance is the erasability of the lines inscribed. For erasing, erasers for exclusive use in ink are sometimes used, but it is also widely practiced to make erasing by applying a small quantity of water to usual erasors. When erasing is made with use of erasers applied with water like this, a problem may arise such that the water-base ink dissolved in water spreads to leave blots in surroundings. The blots thus left tend to conflict with the inscribability, and what has been disadvantageous in the conventional matt films is that the blots increase with improvement in ink-fixing performance.

Discussed below are problems arising in direct positive light-sensitive silver halide photographic materials in which the matting agents are used.

Recent years, the direct positive light-sensitive silver halide photographic materials applied with fog are trending achievement of higher speed. For achieving higher speed, it is necessary to obtain sufficient development activities with fog as less as possible. For that reason, advantageously used is a method in which fog is applied in the presence of a reduction fogging agent and a water-soluble gold compound. Examples of such fog-applying method are the methods described in U.S. Patents No. 3,501,305, No. 3,501,306, No. 3,501,307, etc.

On the other hand, widely used as other techniques for increasing the speed of the direct positive light-sensitive silver halide photographic material applied with fog is a method in which an organic desensitizer adsorbed on the surfaces of silver halide grains is used as an electron acceptor. Examples of the above organic desensitizer include the compounds described in U.S. Patents No. 2,930,694, No. 3,431,111, No. 3,492,123, No. 3,501,310, No. 3,501,312, No. 3,567,456, No. 3,582,343, etc.

Incidentally, when a direct positive silver halide emulsion containing the silver halide grains fogged in the presence of the reduction fogging agent and the water-soluble gold compound and the organic

desensitizer is applied in matt films, a problem may arise such that the organic desensitizer elutes with insufficiency to cause coloring at non-image areas. This coloring occurs in a higher degree as compared with direct positive light-sensitive silver halide photographic materials using the matting agent in a less amount, and causes an extreme lowering of the commercial value.

In general, the matt films are handled under red illumination in many instances, and therefore the matt films are usually color-sensitized so as to have color sensitivities to the blue region and green region. Known as sensitizing dyes used for sensitization to the green region are all sorts of cyanine dyes and merocyanine dyes, and those capable of applying sensitivities to blue light and green light may include, for example, cyanine dyes and merocyanine dyes described in Japanese Patent Publications No. 7828/1963, No. 392/1965, No. 10251/1968 and No. 22884/1968, British Patents No. 815,172, No. 955,961, No. 955,912 and No. 142,228, U.S. Patents No. 1,942;854, No. 1,950,876, No. 1,957,869, No. 2,238,231, No. 2,521,705 and No. 2,647,059, Japanese Patent Publications No. 2606/1968, No. 3644/1969, No. 18106/1971, No. 18101/1971, No. 15032/1973, No. 33782/1974, No. 34252/1979 and No. 52574/1983, U.S. Patents No. 2,839,403, No. 3,567,458 and No. 3,625,698, etc.

In general, the higher sensitizing ability the dyes have, the more strongly color remains after development processing, and thus the dyes that can satisfy both the high speed and the color remain are very limitedly available.

In addition, in the case of the matt films containing matting agents, an increase in the color remain is observed which is presumed to occur because of any mutual action between sensitizing dyes and matting agents, resulting in difficulty in selection of sensitizing dyes.

SUMMARY OF THE INVENTION

A first object of this invention is to provide a light-sensitive silver halide photographic material that can produce a continuous tone and make the line photographying on the same film and show very good clearing from fixing, even when the usual rapid-access processing is carried out.

A second object of this invention is to provide a light-sensitive silver halide photographic material having very good inscribability and erasability.

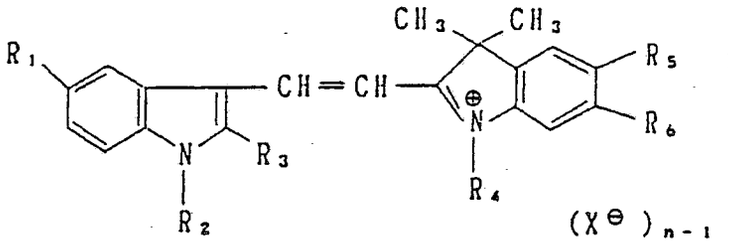
A third object of this invention is to provide a light-sensitive silver halide photographic material for direct positives that has inscribability, a high speed, and an improved whiteness.

A first invention that can achieve the first and second objects is a light-sensitive silver halide photographic material comprising a support, at least one silver halide emulsion layer provided on at least one side of said support, and a protective layer provided on said silver halide emulsion layer, wherein said silver halide emulsion layer is formed of two kinds of emulsions each having different average grain size of the grains contained therein, the average grain size in said emulsion containing grains of a smaller average grain size comprises from 40 to 70 % of the average grain size in said emulsion containing grains of a larger average grain size, and said silver halide emulsion layer has a silver amount of 4.5 g/m^2 or less, and further at least one layer of said silver halide emulsion layer and said protective layer contains 300 mg/m^2 or more of at least one kind of matting agent.

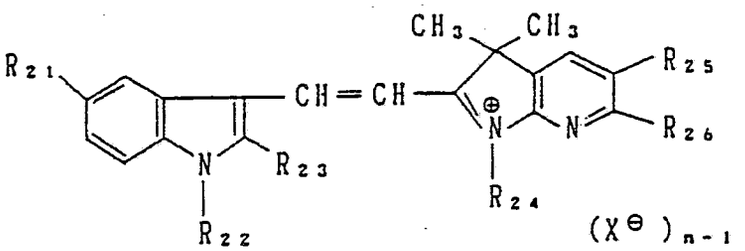
A second invention that can achieve the second object is a light-sensitive silver halide photographic material comprising a support and provided by coating thereon at least one hydrophilic colloid layer containing a matting agent, wherein the center-line average roughness of said light-sensitive material ranges from 0.15 to 0.8 μm, and the weight percentage of a matting agent having a particle diameter more than 6 μm is 5 % or less based on the whole matting agent.

A third invention that can achieve the third object is a light-sensitive silver halide photographic material for direct positives, comprising a support and provided thereon a direct positive silver halide emulsion layer containing silver halide grains applied with fog in the presence of a reduction fogging agent and a water-soluble gold compound, wherein at least 250 mg/m^2 of at least one kind of matting agent is contained and at least one of any compounds represented by Formulas (I), (II), (III), (IV) and (V) shown below is contained, in a photographic layer of the side on which said direct positive silver halide emulsion layer is provided;

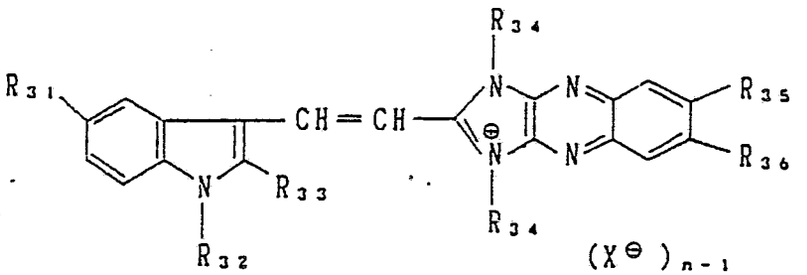
Formula (I)



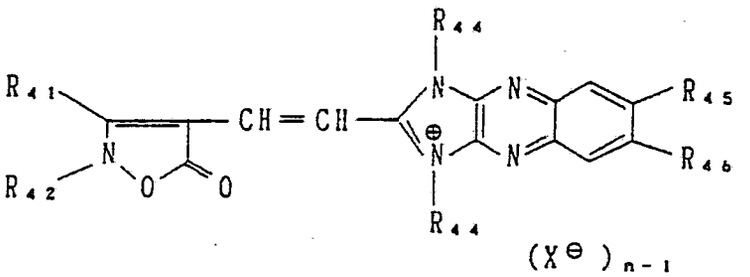
Formula (II)



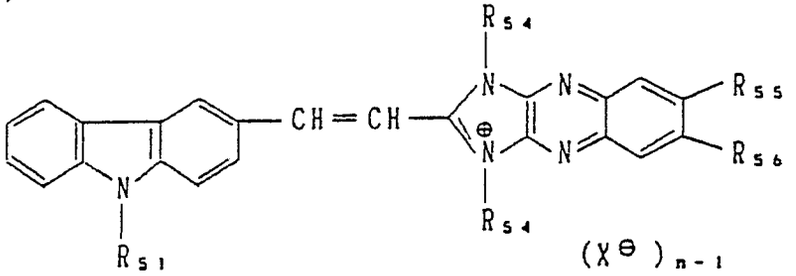
Formula (III)



Formula (IV)



Formula (V)



wherein, in Formulas (I), (II), (III), (IV) and (V), R_1, R_{21} and R_{31} each represent a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryloxy group or a nitro group; R_2, R_3, R_4, R_{22}, R_{23}, R_{24}, R_{32}, R_{33}, R_{34}, R_{44} and R_{54} each represent an alkyl group, alkenyl group, aryl group or aralkyl group which is unsubstituted or has a substituent; R_5, R_6, R_{25}, R_{26}, R_{35}, R_{36}, R_{45}, R_{46}, R_{55} and R_{56} each represent a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a thienyl group, an alkoxy group, a hydroxy group, a cyano group, an alkylsulfonyl group, an alkoxycarbonyl group, a phenylsulfonyl group, a trifluoromethyl group, a trifluoromethylsulfonyl group or a nitro group; R_{41} represents an aryl group; R_{42} represents an alkyl group; R_{51} an alkyl group which is unsubstituted or has a subsituent; $X^{\ominus}$ represents an anion; and n represents 1 or 2, provided that n is 1 when the compound forms an intramolecular salt.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention will be described below in greater detail.

Described first is the emulsion layer in the first invention.

Used as the silver halide emulsion for the silver halide emulsion layer used in this invention are emulsions comprising two kinds of emulsions. These may preferably be monodisperse emulsions. The monodisperse emulsions herein referred to are meant by emulsions in which the grain size of the grains comprising 90 % of the whole in the number of silver halide grains has a distribution within ± 40 % of average grain size. Each average grain size of the two kinds of emulsions (preferably monodisperse emulsions) may preferably range from 0.2 to 0.6 μm, more preferably from 0.3 to 0.5 μm, in respect of larger grains (which is meant by grains in the emulsion containing grains having a larger average grain size; the same applies hereinafter), and may preferably range from 0.1 to 0.4 μm, more preferably from 0.15 to 0.35 μm, in respect of smaller grains (which is meant by grains in the emulsion containing grains having a smaller average grain size; the same applies hereinafter).

In said emulsions, the average grain size of the smaller grains ranges from 40 to 70 % based on the average grain size of the larger grains. This may be arbitrarily selected if it is in the range of from 40 to 70 %, and this range may vary depending on the purpose of use. The range otherwise more than 70 % may result in a high contrast to obtain no gradation, and the same otherwise less than 40 % may result in discontinuous gradation to be of no practical use.

The above two kinds of emulsions used in this invention may be coated to form respectively independent layers, but may preferably be coated to form a layer using an emulsion in which the two kinds of emulsions having different grain size are mixed. The two kinds of emulsions may preferably be mixed in the ratio such that the mixing ratio of the emulsion using the silver halide grains of smaller grain size ranges from 30 to 70 %, and particularly preferable results are obtained when it ranges from 40 to 60 %.

The amount of silver applied in the light-sensitive silver halide photographic material of this invention comprising the two kinds of emulsions should be 4.5 g/m^2 or less. Though variable depending on the purpose, the amount otherwise more than 4.5 g/m^2 may result in danger of undesirably causing poor fixing in the rapid development processing having been practiced in the present industrial field.

In this invention, the silver halide emulsion layer used for constituting the emulsion layer can be prepared by use of the methods described in P. Glafkides, "Chimie et Physique Photographique", published by Paul Montel Co., 1967; G.F. Duffin, "Photographic Emulsion Chemistry", published by The Focal Press Co., 1966; V.L. Zelikman et al, "Making and Coating Photographic Emulsion", published by The Focal Press Co., 1964. More specifically, there may be used any methods such as an acidic method, a neutral method and an ammoniacal method, and, as a form of reacting soluble silver salts with soluble

halogen salts, any of a one-side synthesizing method, a simultaneous mixing method, a combination of these, etc.

It is also possible to use a method in which grains are formed in the presence of excess silver ions (the so-called reverse-mixing method). As a form of the simultaneous mixing method, there can be used a method in which the pAg in the liquid phase wherein silver halides are produced is kept constant, i.e., the so-called controlled double jet method. This method makes it possible to obtain silver halide emulsions comprising grains having regular crystal form and substantially uniform grain size.

The light-sensitive silver halide photographic material of this invention comprises a minimum constituent unit comprising one silver halide emulsion layer provided on one side of a support. A light-sensitive layer typified by the silver halide emulsion layer may be provided in plural layers on at least one side of the support. In the instance of the plural layers, it is usual to provide an intermediate layer between the layers. There may be further provided a subbing layer, a backing layer, an intermediate layer, an anti-halation layer, a protective layer, etc.

The light-sensitive silver halide photographic material of this invention contains at least 300 mg,/m^2 of at least one kind of matting agent in at least one layer of the silver halide emulsion layer and protective layer. The content of the matting agent otherwise less than 300 mg/m^2 may make it difficult to achieve sufficient inscribability. It may also contain a same kind or different kind of matting agent, and in such an instance the layer to which the matting agent is added may be any of emulsion layers and protective layers, or subbing layers, intermediate layers and so forth that are optionally provided. The matting agent may be of any kinds, and various kinds of agents can be appropriately used. Specifically, it is possible to use finely divided particles of water-insoluble organic or inorganic compounds having any particle diameter. Preferably used are those having a particle diameter of from 0.3 μm to 5 μm. Examples of the organic compound are water-dispersible vinyl polymers as exemplified by polymethyl acrylate, polymethyl methacrylate, polyacrylonitrile, an acrylonitrile/α-methylstyrene copolymer, polystyrene, a styrene/divinylbenzene copolymer, polyvinyl acetate, polyethylene carbonate, polytetrafluoroethylene, etc.; cellulose derivatives as exemplified by methyl cellulose, ethyl cellulose, cellulose acetate, cellulose acetate propionate, etc.; starch derivatives as exemplified by carboxy starch, carboxynitrophenyl starch, a urea-formaldehyde-starch reaction product, etc.; gelatin cured with various curing agents and cured gelatin formed into microcapsule hollow particles by coacervation curing; etc., which can be preferably used. Examples of the inorganic compound are silicon dioxide, titanium dioxide, magnesium dioxide, aluminum dioxide, barium sulfate, calcium carbonate, silver chloride desensitized by various methods, silver bromide similarly desensitized, glass, diatomaceous earth, etc., which can be preferably used. The above matting agent can be used by optionally mixing with it materials of different kind.

The light-sensitive silver halide photographic material of this invention may preferably be processed with use of a fixing agent containing no hardening agent.

A step for the fixing is meant by a step of effecting fixing by desilvering using a fixing solution containing a silver halide fixing agent. The silver halide fixing agent used in the fixing solution includes compounds capable of forming water-soluble complex salts by reacting with silver halides as those used in usual fixing, as typically exemplified by thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate, thiocyanates such as potassium thiocyante, sodium thiocyanate and ammonium thiocyanate, thioureas, thioethers, etc. These fixing agents are used generally in an amount of 5 g/lit. or more and an amount with which they can be dissolved, but may preferably be used in an amount of from 70 g to 250 g/lit. The fixing solution may contain solely or in combination, a variety of buffering agents 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 may further contain all sorts of brightening agents and anti-foaming agents or surface active agents. It may also appropriately contain preservatives such as hydroxylamine, hydrazine and bisulfite addition products of aldehyde compounds, organic chelating agents such as aminopolycarboxylic acids, stabilizers such as nitroalcohol and nitrates, organic solvents such as methanol, dimethylsulfonamide and dimethylsulfoxide, etc.

The fixing solution is used generally with pH of 3.0 or more, but may desirably be used with pH 4.0 or more and 9.5 or less. It is used with a processing temperature desirably of 55°C or less while suppressing evaporation or the like.

Advantageously used as binders or protective colloids in photographic emulsions for constituting the protective layers and emulsion layers used in the light-sensitive silver halide photographic material of this invention, as well as hydrophilic colloids in the backing layer optionally provided, is gelatin. However, there can be used hydrophilic colloids other than it.

Used as this gelatin may be lime-treated gelatin, as well as oxygen-treated gelatin as described in

Bulletin of Society of Science of Photography of Japan (Bull. Soc. Sci. Phot. Japn) No. 16, page 30 (1966), and hydrolysates or enzymolysates of gelatin can be also used.

Used as gelatin derivatives are those obtained by reacting gelatin with various compounds as exemplified by acid halides, acid anhydrides, isocyanates, bromoacetic acid, alkanesultones, vinylsulfonamides, maleinimide compounds, polyalkylene oxides, epoxy compounds, etc..

The silver halide photographic emulsion used in this invention and the backing layer optionally provided may contain various compounds for the purpose of preventing fogging during preparation process, storage or photographic processing of light-sensitive materials, or achieving stabilized photographic performances. More specifically, there can be added a variety of compounds known as antifoggants or stabilizers including azoles as exemplified by benzothiazolium salts, nitroindazoles, triazoles, benzotriazoles and benzimidazoles (particularly nitro-or halogen-substituted compounds); heterocyclic mercapto compounds as exemplified by mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, mercaptotetrazoles (particularly 1-phenyl-5-mercaptotetrazole) and mercaptopyrimidines; the above heterocyclic mercapto compounds having a water-soluble group such as a carboxyl group and a sulfone group; thioketo compounds as exemplified by oxazolinethione; azaindenes as exemplified by tetrazaindenes (particularly 4-hydroxy-substituted (1,3,3a,7)tetrazaindenes) and benzenethiosulfonic acids; benzenesulfinic acids; etc.

The silver halide emulsion used in this invention and the backing layer optionally provided may further contain all sorts of chemical sensitizers, torning agents, hardening agents, surface active agents, thickening agents, plasticizers, lubricants, development restrainers, ultraviolet absorbents, irradiation-preventive agent dyes, heavy metals, matting agents, etc. which are incorporated according to various methods.

The silver halide emulsion used in this invention and the backing layer optionally provided may also contain polymer latex. Used as the polymer latex are aqueous dispersions of homo-or copolymers as exemplified by methyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, glycidyl acrylate, styrene, vinyl chloride, vinylidene chloride, etc.

As the support that can be used in the light-sensitive silver halide photographic material of this invention, transparent supports can be used, and materials for the usable supports may include, for example, cellulose acetate, cellulose nitrate, polyesters such as polyethylene terephthalate, polyolefin such as polyethylene and polystyrene, glass, etc. These supports are optionally subjected to subbing processing.

The light-sensitive silver halide photographic material of this invention can be color-sensitized with use of a variety of sensitizing dyes.

After exposure to light, the silver halide emulsion layer of this invention can be processed for development according to various methods, for example, usually used methods. For example, solutions for black and white development are alkaline solutions containing developing agents such as hydroxybenzenes, aminophenols and aminobenzenes, and may contain other sulfites, carbonates, bisulfites, bromides and iodides of alkali metal salts.

The second invention will be described below.

As the matting agent used in the second invention, there can be used finely divided particles of known water-insoluble organic or inorganic compounds, which are same as those in the first invention.

The matting agent used in this invention can be added in any hydrophilic colloid layers. Specifically, they include silver halide emulsion layers, surface-protective layers, intermediate layers, subbing layers, backing layers, etc., preferably silver halide emulsion layer and protective layer provided upper than the silver halide emulsion layer.

In this invention, the kind, shape, size, amount for addition of the matting agent used can be freely selected, but it is required to control the center-line average roughness (Ra) of the side on which the hydrophilic colloid layers containing the matting agent are provided, so as to be in the range of from 0.15 to 0.8 μm. The Ra otherwise less than 0.15 μm may result in a poor inscribability, and Ra otherwise more than 0.8 μm may result in a poorness in smoothness of writing touch.

The center-line average roughness referred to in this invention is in accordance with the method described in the Japan Industrial Standard JIS B-0601 (corresponds to ISO/R 468).

In addition, desired as the matting agent used in this invention are matting agents containing no matting agent particles having a particularly large particle diameter, and the weight percentage of a matting agent having a particle diameter more than 6 μm is required to be 5 % or less based on the whole matting agent. The above weight percentage otherwise more than 5 % may result in loss of smoothness of writing touch and also make it liable to give irregularities in the density of lines inscribed, also resulting in a poorness in the line-width constancy. The above weight percentage may more preferably be 2 % or less, still more preferably 1 % or less. To remove the matting agent particles having a large particle diameter, usually available centrifugal separation type powder classifiers can be used.

In this invention, the surface tension of a coating solution for the hydrophilic colloid layer positioned at

an uppermost layer is preferably to be modified in the range of from 28 to 38 dyne/cm. The surface tension otherwise lower than 28 dyne/cm may cause the problems that the lines inscribed in water-base ink have a low density and come to have non-uniformity in the density. The surface tension otherwise more than 38 dyne/cm may bring about the problems that the lines inscribed in water-base ink have a greater line width and also stronger blots are left when erased. More preferably, the surface tension may desirably be in the range of from 30 to 36 dyne/cm.

The surface tension referred to in this invention is meant by static surface tension and distinguished from dynamic surface tension.

The surface tension can be measured by use of the method described, for example, in JIKKEN KAGAKU KOZA (Experimental Chemistry Course) Vol. 7, edited by NIPPON KAGAKUKAI (Japan Chemical Society).

The surface tension can be modified by selecting the kind and amount of surface active agents to be added in the coating solution. In this invention, known surface active agents can be used alone or in combination of two or more kinds, and can be used, for example, nonionic surface active agents such as saponin (steroid type), alkylene oxide derivatives (as exemplified by polyethylene glycol, a polyethylene glycol/polypropylene glycol condensate, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycolesters, polyethylene glycol sorbitan esters, polyethylene glycol alkylamines or amides, and polyethylene oxide addition products of silicone), glycidol derivatives (as exemplified by alkenylsuccinic acid polyglyceride and alkylphenol polyglyceride), fatty acid esters of polyhydric alcohols, and alkyl esters of sugars; anionic surface active agents containing an acidic group such as a carboxylic group, a sulfo group, a phospho group and a sulfuric acid ester group, including alkylcarboxilates, alkylsulfonates, alkylbenzene sulfonates, alkylnaphthalene sulfonates, N-acyl-alkyltauric acids, sulfosuccinic acid esters, sulfoalkylpolyoxyethylene alkylphenyl ethers, polyoxyethylene alkylphosphoric acid esters, etc.; surface active agents such as amino acids, aminoalkylsulfonic acids, aminoalkylphosphoric acid or phosphoric acid esters, alkylbetaines and amine oxides; cationic surface active agents such as alkylamines, aliphatic or aromatic quaternary ammonium salts, heterocyclic quaternary ammonium salts such as pyridinium and imidazolium, and phosphonium or sulfonium salts containing an aliphatic or heterocyclic ring, and fluorine-containing surface active agents.

Examples of these surface active agents include those described in U.S. Patents No. 2,240,472, No. 2,831,766, No. 3,158,484, No. 3,210,191, No. 3,294,540 and No. 3,507,660, British Patents No. 1,012,495, No. 1,022,878, No. 1,179,290 and No. 1,198,450, Japanese Unexamined Patent Publication No. 117414/1975, U.S. Patents No. 2,739,891, No. 2,823,123, No. 3,065,101, No. 3,415,649, No. 3,666,475 and No. 3,756,828, British Patent No. 1,397,218, U.S. Patents No. 3,133,816, No. 3,441,413, No. 3,475,174, No. 3,545,974, No. 3,726,683 and No. 3,843,368, Belgium Patent No. 731,126, British Patents No. 1,138,514, No. 1,159,825 and No. 1,374,780, Japanese Patent Publications No. 378/1965, No. 379/1965 and No. 13822/1968, U.S. Patents No. 2,288,226, No. 2,944,900, No. 3,253,919, No. 3,671,247, No. 3,772,021, No. 3,589,906, No. 3,666,478 and No. 3,754,924, West Germany Patent Application OLS 19 61 638, Japanese Unexamined Patent Publication No. 59025/1975, Japanese Patent Publications No. 9303/1972 and No. 43130/1973, German Published Patents No. 19 50 121 and No. 19 61 638, Japanese Unexamined Patent Publication No. 7781/1971, British Patents No.1,330,356 and No. 1,524,631, U.S. Patents No. 3,666,478 and No. 3,589,906, Japanese Patent Publication No. 26687/1977, Japanese Unexamined Patent Publications No. 46733/1974 and No. 32322/1976, etc.

The hydrophilic colloid constituting the light-sensitive material of this invention include not only gelatin (either lime-treated or acid-treated one may be used) as described for the first invention, but also gelatin derivatives as exemplified by gelatin derivatives prepared by reacting gelatin with aromatic sulfonyl chloride, acid chloride, acid anhydride, isocyanate or 1,4-diketones as described in U.S. Patent No. 2,614,928, gelatin derivatives prepared by reacting gelatin with trimeritic acid anhydride as described in U.S. Patent No. 3,118,766, gelatin derivatives prepared by reacting gelatin with an organic acid having an active halogen as described in Japanese Patent Publication No. 5514/1964, gelatin derivatives prepared by reacting gelatin with an aromatic glycidyl ether as described in Japanese Patent Publication No. 26845/1967, gelatin derivatives prepared by reacting gelatin with maleimide, maleamic acid, unsaturated aliphatic diamide or the like as described in U.S. Patent No. 3,186,846, sulfoalkylated gelatin as described in British Patent No. 1,033,189, polyoxyalkylene derivatives of gelatin for example, U.S. Patent No. 3,312,553, etc.; polymeric grafted products of gelatin as exemplified by those obtained by grafting on gelatin any of acrylic acid, methacrylic acid, a monohydric or polyhydric alcohol ester of these, similarly amide, acrylo-or methacrylonitrile, styrene, and other vinyl monomers, which are used alone or in combination; synthetic hydrophilic polymeric substances as exemplified by homopolymers comprised of a monomer such as vinyl alcohol, N-vinylpyrrolidone, hydroxyalkyl acrylate or methacrylate, acryl-or methacrylamide and N-substi-

tuted acryl-or methacrylamide, or copolymers comprised of any mutual combination of these, copolymers of any of these with acrylate or methacrylate, vinyl acetate, styrene or the like, copolymers of any of the above with maleic anhydride, maleamino acid or the like, etc.; naturally occurring hydrophilic polymeric substances other than gelatin, as exemplified by casein, agar, alginic acid polysuccharides, etc.; which can be used alone or as a mixture.

In the light-sensitive material of this invention, the emulsion layers and other component layers may contain plasticizers as exemplified by glycerol, diols as described in U.S. Patent No. 2,960,404, trihydric aliphatic alcohols as described in U.S. Patent No. 3,520,694.

In the light-sensitive material of this invention, the emulsion layers and other component layers may contain dispersions of water-insoluble or slightly soluble synthetic polymers for the purpose of increasing the dimension stability or the like purposes. For example, there can be used alkyl acrylate or methacrylate, alkoxy acrylate or methacrylate, glycidyl acrylate or methacrylate, acryl-or methacrylamide, vinyl acetate, acrylonitrile, olefin, styrene, etc. which are used alone or in combination, or polymers comprised of monomers comprising a combination of any of these with acrylic acid, α,β-unsaturated dicarboxylic acid, sulfoalkyl acrylate, styrene sulfonic acid or the like. Specific examples thereof may include polymers described in U.S. Patents No. 2,376,005, No. 3,607,290 and No.3,645,740, British Patents No. 1,186,699 and No. 1,307,373, U.S. Patents No. 3,062,674, No. 2,739,137, No. 3,411,911, No. 3,488,708, No. 3,635,715 and No. 2,853,457.

In the light-sensitive material of this invention, the emulsion layers and other component layers can be hardened by adding hardening agents usually used. The hardening agents include, for example, aldehydes as exemplified by glyoxal described in U.S. Patent No. 1,870,354, glutaraldehyde described in British Patent No. 825,544; N-methylol compounds as exemplified by N,N′-dimethylol urea, dimethylolhydantoin described in British Patent No. 676,628; dioxane derivatives as exemplified by dihydroxydioxane described in U.S. Patent No. 3,380,829 or similar derivatives described in Japanese Patent Publication No. 38713/1971; compounds having an epoxy group as exemplified by the compounds described in U.S. Patents No. 3,047,394 and No. 3,091,573 and Japanese Patent Publication No. 7133/1959; compounds having a reactive halogen, as exemplified by 2,4-dichloro-6-hydroxy-1,3,5-triazine described in U.S. Patent No.3,325,287; mucohalogen acids as exemplified by mucochloric acid and mucobromic acid described in U.S. Patent No. 2,080,019 or derivatives thereof described in Japanese Patent Publication No. 1872/1971; bis-(methanesulfonic acid ester) described in U.S. Patent No. 2,726,162; sulfonyl compounds as exemplified by bis(benzenesulfonyl chloride) described in U.S. Patent No. 2,725,295; aziridine compounds as exemplified by the compounds described in Japanese Patent Publications No. 4212/1958 and No. 8790/1962; divinyl sulfones as exemplified by compounds described in U.S. Patent No. 2,579,871 or the like compounds; compounds having a reactive olefin bond, as exemplified by divinyl ketones of the compounds described in German Patent No. 872,153, compounds having an acryloyl group as described in U.S. Patents No. 3,255,000 and No. 3,635,718, British Patent No. 994,869 and West German Patent No. 10 90 472; alkylene bismaleimides described in U.S. Patent No. 2,992,109, etc.; isocyanates described in U.S. Patent No. 3,103,437, etc.; carboimides described in U.S. Patent No. 3,100,704; isoxazole derivatives as exemplified by the compounds described in U.S. Patents No. 3,321,313 and No. 3,543,292; carbamoyl chloride derivatives described in Japanese Patent Publication No. 6899/1966; polymeric hardening agents as exemplified by dialdehyde starch described in U.S. Patent No. 3,057,723 or the compounds described in Japanese Patent Publication No. 12550/1967; inorganic hardening agents as exemplified by chrome alum, chromium acetate, zirconium sulfate, etc.; and these many kinds of compounds can be used alone or in combination.

In this invention, the hydrophilic colloid layer containing the matting agent may preferably be hardened with use of active halogen type hardening agents. Of course, it is also possible to use in combination any hardening agents other than the active halogen type hardening agents. Employment of the active halogen type hardening agents makes it possible to decrease the blots at the time of the erasing of water-base ink inscriptions to comtribute enhancement of removability, without damaging the inscribability. The active halogen type hardening agent, the manner of use thereof, etc. are described, for example, in Japanese Patent Publications No. 16928/1964, No. 2602/1968, No. 6151/1972, No. 33380/1972, No. 13709/1973, No. 3527/1973, No. 31937/1973, No. 9434/1976, No. 78788/1976, No. 60612/1977, No. 127229/1977, No. 15958/1979, No. 27135/1981, etc.

Preferred active halogen hardening agents are dichloro-S-triazines, and may typically include, for example, 2,4-dichloro-6-hydroxy-1,3,5-triazine (alkali metal salts), 2,4-dichloro-6-methoxy-1,3,5-triazine, 2,4-dichloro-6-ethylamino-1,3,5-triazine, 2,4-dichloro-6-hydroxyethylamino-1,3,5-triazine, etc.

With the hardening agent of this invention, compounds capable of accelerating the hardening of gelatin can be used in combination. Such hardening accelerators may include non-protonic solvents described in West German Patent (Laid-Open Publication) No. 24 17 586, betaine type surface active agents described

in Japanese Unexamined Patent Publication No. 62045/1982, tertiary amines or salts thereof (as exemplified by those described in Japanese Unexamined Patent Publications No. 1043/1981 and No. 9434/1976, West German Patent (Laid-Open Publication) No. 21 38 305, British Patents No. 1,284,305 and No. 1,269,983, etc.), all sorts of inorganic salts or polyhydric alcohols, etc.

In the silver halide emulsion of this invention, any of silver halides can be used, including silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide, silver chloroiodobromide, silver chloride, etc. which are used in usual silver halide emulsions.

In the light-sensitive material of this invention, various additives can be used depending on the purpose.

These additives are more specifically described in Research Disclosure Vol. 176, Item 17643 (December, 1978) and the ditto Vol. 187, Item 18716 (November, 1979), relevant passages of which are summarized in the table shown below.

Also, there is no particular limitation in regard to the exposure and development processing conditions for the light-sensitive material of this invention, and reference can be made to the above Research Disclosure Vol. 176, pp.28-30.

Kind of additives	RD17643	RD18716
1. Chemical sensitizers	p.23	p.648, right col.
2. Sensitizers		ditto
3. Spectral sensitizers	pp.23-24	p.648, right col.
Supersensitizers		-p.649, right col.
4. Brightening agents	p.24	
5. Antifoggants and stabilizers	pp.24-25	p.649, right col.
6. Light-absorbents, filters	pp.25-26	p.649, right col,
Filter dye and ultraviolet absorbents		-p.650, left col.
7. Anti-stain agents	p.25, right col.	p.650, left to right col.
8. Dye image stabilizer	p.25	
9. Plasticizers, lubricants	p.27	p.650, right col.
10. Antistatic agents	p.27	ditto

The support used in the light-sensitive material of this invention may preferably be transparent. This is because the light-sensitive material of this invention is often used as an original for diazo print copying after development processing. Examples of the support may include cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate, polyamide, etc.

Any known processing can be used for the development processing of the light-sensitive material of this invention. This development processing may be either the processing to form silver images (black and white development processing) or the development processing to form color images, depending on the purpose.

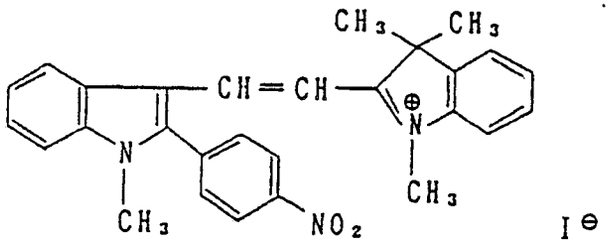
The black and white development processing comprises a developing step, a fixing step and a washing step. The washing step may sometimes be omitted when a stopping step is carried out after the developing step or a stabilizing step is applied after the fixing step. Developing agents or precursors thereof may be incorporated into light-sensitive materials to carry out the developing step with use of an alkali solution only. There may be also carried out a developing step using lith developers as developing solutions.

Terms and materials used in the third invention will be described below.

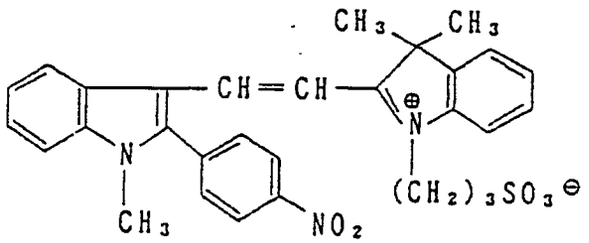
In this invention, at least one of the compounds represented by Formulas (I), (II), (III), (IV) and (V) is contained, and these are advantageously used as organic desensitizers. These compounds are superior in that they can bring about a high speed and a low color remain. In the light-sensitive material of this invention, at least one kind arbitrarily selected from the group consisting of the compounds represented by Formulas (I), (II), (III), (IV) and (V) may be contained, and there may be available either i) one, two or more kinds of the compound represented by any one of the formulas or ii) two or more kinds of the compounds represented by two or more formulas. When two or more kinds of the compounds are used, they may be in any combination.

Synthesis methods for the organic desensitizer of this invention include, for example, the methods described in U.S. Patents No. 3,567,456, No. 3,582,343, No. 3,598,596, etc. in respect of the compounds represented by Formulas (I), (II) and (III), the methods described in U.S. Patents No. 3,539,349, etc. in respect of the compound represented by Formula (IV), and the methods described in U.S. Patents No. 3,431,111, No. 3,492,123, etc. in respect of Formula (V).

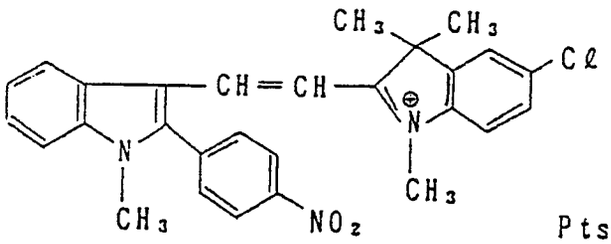
Examples of the compounds represented by Formulas (I), (II), (III), (IV) and (V) are shown below as (I-1) to (I-9), (II-1) to (II-3), (III-1) to (III-6), (IV-1), (IV-2), (V-1) to (V-3), but needless to say this invention is by no means limited to these specific compounds.



(I-2)

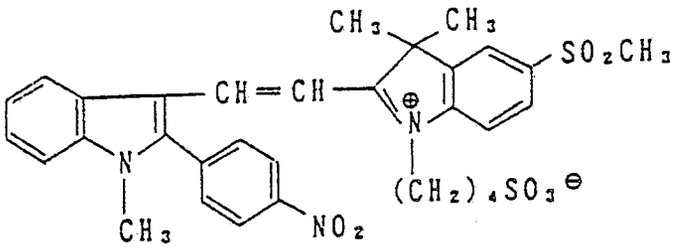


(I-3)



(Pts represents a paratoluenesulfonic acid group. The same applies hereinafter)

〔 I − 4 〕



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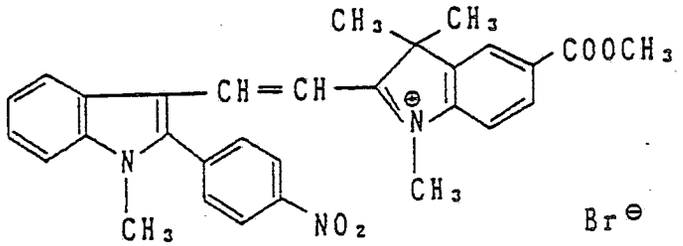
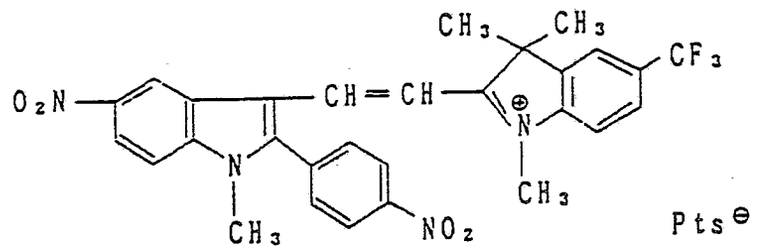
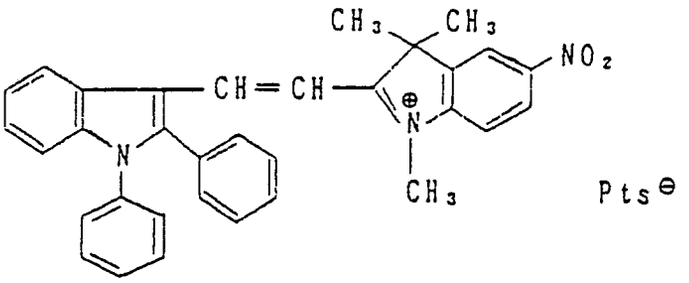


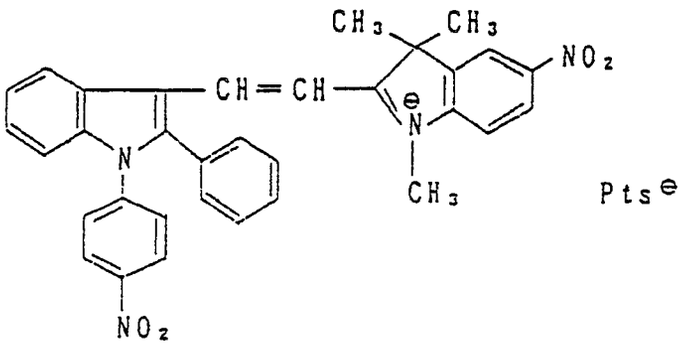
〔 I − 6 〕



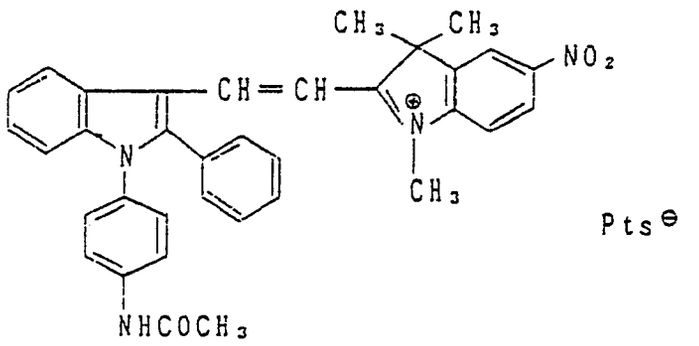
〔 I − 7 〕


CH3
CH3
NO2
CH=CH
N
CH3
Pts⊖

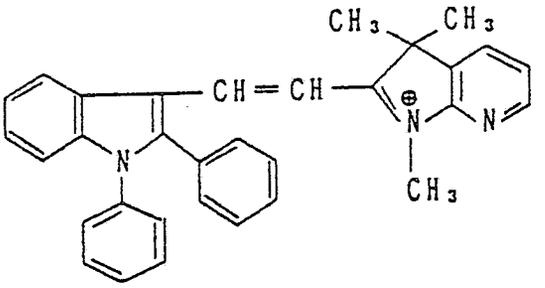
〔 I − 8 〕


CH3
CH3
NO2
CH=CH
N
CH3
Pts⊖
NO2

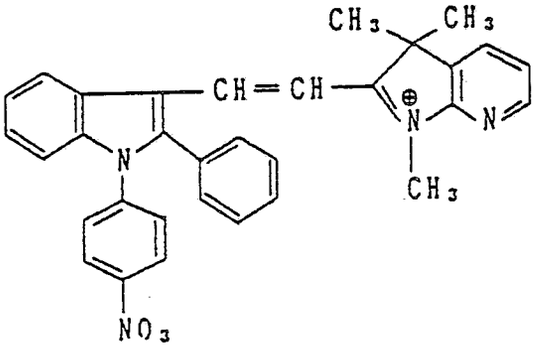
〔 I − 9 〕


CH3
CH3
NO2
CH=CH
N
CH3
Pts⊖
NHCOCH3

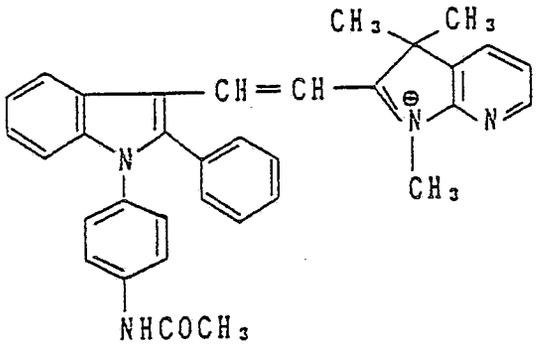
(Ⅱ − 1)


CH3
CH3
CH=CH
N
N
CH3
ClO4⊖

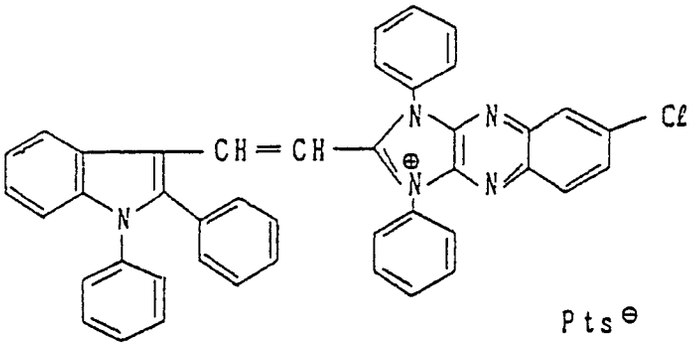
(Ⅱ − 2)


CH3
CH3
CH=CH
N
N
CH3
Pts⊖
NO3

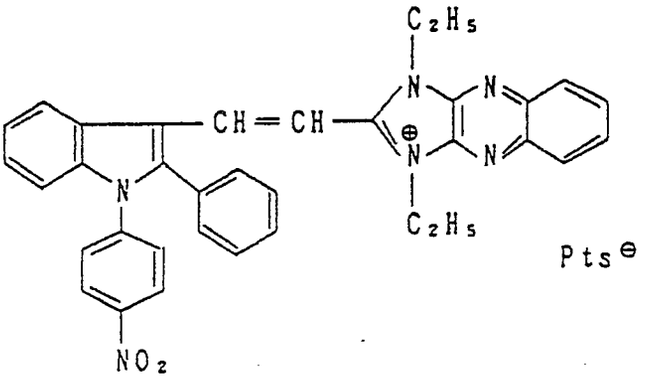
(Ⅱ − 3)


CH3
CH3
CH=CH
N
N
CH3
Pts⊖
NHCOCH3

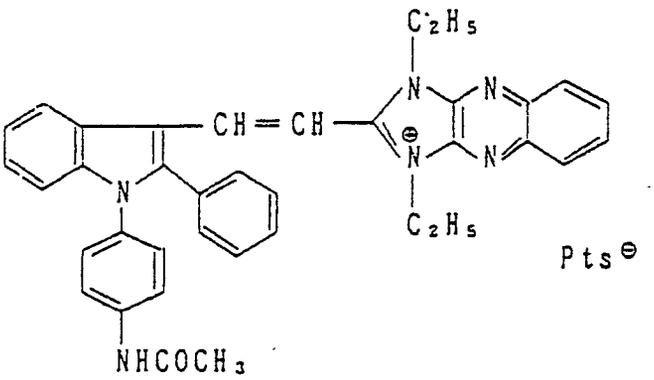
〔Ⅲ－1〕


CH=CH
N
N
N
N
Cℓ
Pts⊖

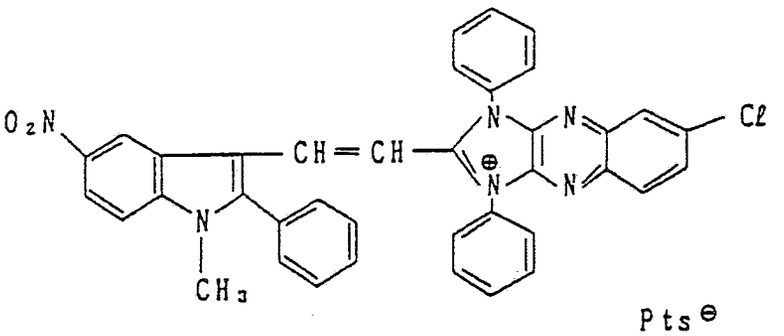
〔Ⅲ－2〕


C2H5
CH=CH
N
N
N
N
C2H5
Pts⊖
NO2

〔Ⅲ－3〕


C2H5
CH=CH
N
N
N
N
C2H5
Pts⊖
NHCOCH3

〔Ⅲ－4〕



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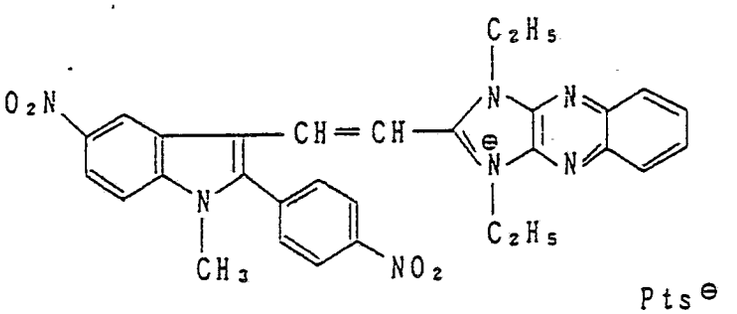

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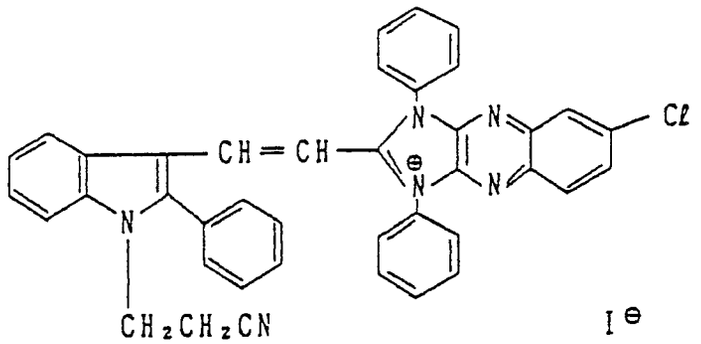

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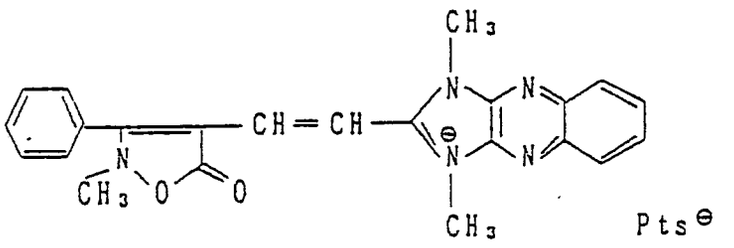

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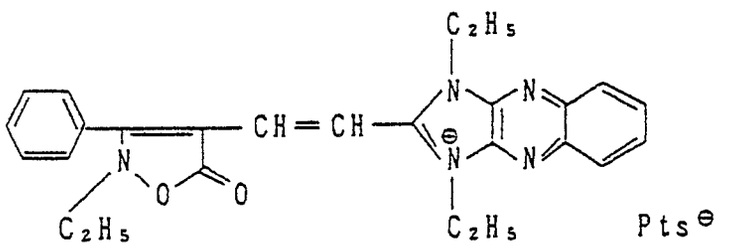
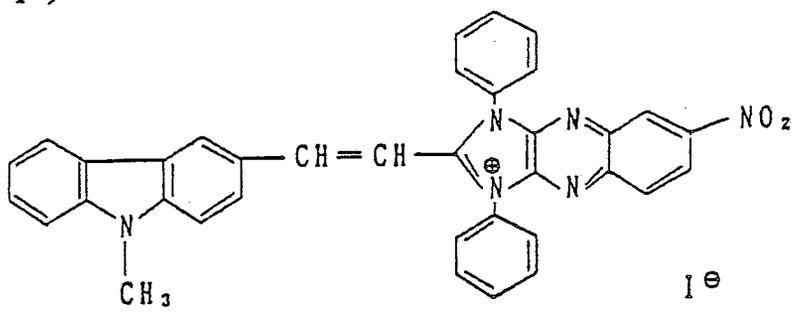
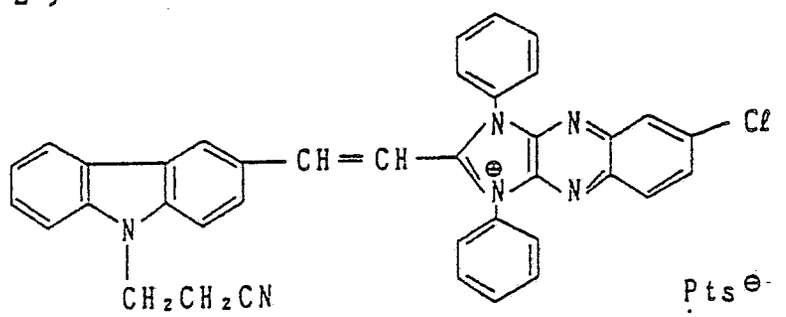


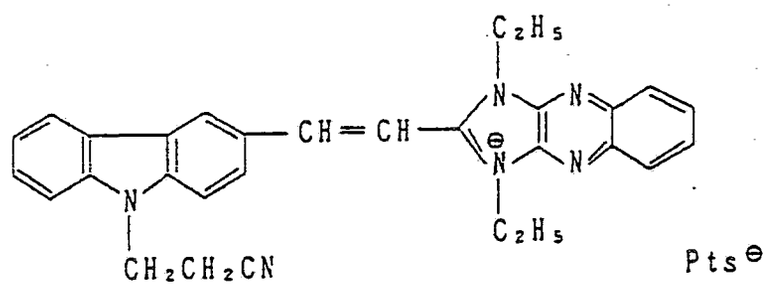
〔V－1〕



〔V－2〕



〔V－3〕



These organic desensitizers may desirably be dissolved in suitable solvents and added in the silver halide having been desalted, in an amount of 10^{-4} to 10^{-2} mol per mole of silver halide. The above organic desensitizers may also be used alone or as a mixture of two or more kinds.

The photographic layer referred to in this invention is a generic term for light-sensitive layers and non-light-sensitive layers. The light-sensitive layers specifically include direct positive silver halide emulsion layers, direct positive silver halide emulsion layers applied with fog in the presence of a reduction fogging agent and a water-soluble gold compound, and the like layers. The non-light-sensitive layers specifically include subbing layers, intermediate layers, protective layers, etc.

In the light-sensitive silver halide photographic material of this invention, at least 250 mg/m^2 of at least one kind of matting agent is contained in at least one layer of the photographic layers. The content of the matting agent otherwise less than 250 mg/m^2 may make it difficult to achieve sufficient inscribability. A matting agent of the same kind or different kind may be also contained in two or more layers. In such an instance, the layer to which the matting agents are added may be any of emulsion layers, protective layers, or subbing layers to be optionally provided, and intermediate layers. The matting agents may be of any kind, and various ones can be used, for example. Specifically, they include particles of water-insoluble organic and inorganic compounds, and there can be used those having any particle diameter. Preferably, those having a particle diameter of from 0.3 to 5 μm should be used. Examples of the organic and

inorganic compounds are the same as those set forth in the first invention.

The reduction fogging agent used in this invention to apply fog includes, for example, formalin, hydrazine, polyamines (as exemplified by triethylenetetramine, tetraethylenepentamine, etc.), thiourea dioxide, tetrahydroxymethylphosphonium chloride, amine borane, boron compound hydrides, stannous chloride, etc. which should be used generally in the range of from 10^{-7} to 10^{-3} mol per mol of silver halide. These reduction fogging agents may also be used alone or as a mixture of two or more kinds.

The water-soluble gold compound also includes, for example, potassium chloroaurate, chloroaurate, potassium gold cyanide, potassium gold thiocyanate, sodium gold thiomaleate, gold thioglucose, etc., which may be used generally in the range of from 10^{-6} to 10^{-4} mol per mol of silver halide.

The silver halide emulsions used in this invention may be those having any grain size, crystal habit, silver halide composition, etc., but useful as light-sensitive materials are those having a grain size of approximately from about 0.1 to about 1 μm as being preferable in view of the graininess and sharpness, and, in silver iodobromide, those comprising preferably not more than 5 mol %, more preferably not more than 3 mol %, of silver iodide as having smaller development restraining properties and being advantageous in practical use. These silver halide emulsions are prepared according to a variety of methods. For example, there can be applied the method in which the group VIII soluble gold complex salts as described in U.S. Patent No. 2,717,833, Japanese Patent Publication No. 4125/1968, British Patent No. 1,186,717, etc., the method of preparing ammoniacal emulsions as described in U.S. Patent No. 2,184,013, the method of preparing monodisperse emulsions as described in U.S. Patent No. 3,501,305, the method of preparing heterodisperse emulsions as described in Japanese Unexamined Patent Publication No. 43627/1974, the method of preparing regular grain emulsions as described in U.S. Patent No. 3,501,306, the method of preparing covered-grain emulsions as described in U.S. Patent No. 3,367,785, British Patent No. 1,229,868, No. 1,186,718, etc., and the method of preparing internal latent image type emulsions as described in U.S. Patent No. 2,592,250.

In the direct positive light-sensitive silver halide photographic material in this invention, additives for other photography can be also used. There may be contained stabilizers as exemplified by triazoles, azaindenes, quaternary benzothiazolium compounds, mercapto compounds, or water-soluble inorganic salts of cadmium, cobalt, nickel, manganese, gold, thallium, zinc, etc. There may be also contained hardening agents as exemplified by formaldehydes such as formalin, glycoxal and mucochloric acid, s-triazines, epoxys, aziridines, vinylsulfonic acid, etc; coating aids as exemplified by saponin, sodium polyalkylenesulfonate, lauryl or oleyl monoether of polyethylene glycol, amylated alkyltaurines, fluorine-containing compounds, etc.; and sentizers as exemplified by polyalkylene oxide and derivatives thereof. It is also possible for it to further contain couplers. Besides, there can also be optionally contained antiseptic agents, antistatic agents, developing agents, etc.

The support used in this invention includes supports made of paper, glass, cellulose acetate, cellulose nitrate, polyester, polyamide, polystyrene, polypropylene, etc., or laminated materials comprising two or more kinds of substrates, as exemplified by a laminated material comprising paper and a polyolefin (as exemplified by polyethylene, polypropylene, etc.).

As developing solutions according to this invention, those having the composition generally used can be used. Developing agents include hydroquinone, alklylhydroquinones (as exemplified by methylhydroquinone, dimethylhydroquinone and t-butylhydroquinone), catechol, pyrazole, chlorohydroquinone, dichlorohydroquinone, methoxyhydroquinone, ethoxyhydroquinone, aminophenol developing agents (as exemplified by N-methyl-p-aminophenol and 2,4-diaminophenol), ascorbic acid developing agents, N-methyl-p-aminophenolsulfate, pyrazolones (as exemplified by 4-aminopyrazolone), 3-pyrazolidone developing agents (as exemplified by 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone, 1,5-diphenyl-3-pyrazolidone, 1-p-tolyl-3-pyrazolidone and 1-p-hydroxyphenyl-4,4-dimethyl-3-pyrazolidone), etc. which are used alone or in combination. Particularly suited for the rapid processing of this invention is the combination of hydroquinone with 3-pyrazolidones, or hydroquinone with aminophenols.

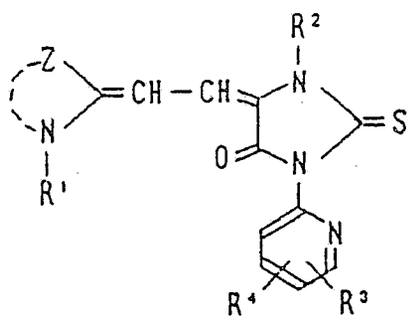
Besides, the developing solution of this invention may optionally contain all sorts of additives including preservatives such as sulfites, bisulfites and hydroxylamines; alkali agents such as hydroxides, carbonates and phosphates; pH adjusters such as acetic acid; dissolution aids such as polyethylene glycols; sensitizers such as quaternary ammonium salts; organic solvents such as methanol, diethylene glycol, diethanolamine, dimethylformamide and dimethylsulfoxide; development accelerators; surface active agents; anti-foaming agents; toning agents; viscosity-imparting agents such as carboxymethyl cellulose and hydroxyethyl cellulose; hardening agents such as glutaraldehyde; silver sludge preventive agents; silver halide solvents such as thioethers, thioamides, thiocyanates and thiosulfates; antifoggants such as potassium bromide and benzotriazole; chelating agents such as aminopolycarboxylic acids, aminopolyphosphonic acids and

phosphonocarboxylic acids; etc.

As fixing solutions used in this invention, those having the composition generally used can be used. There can be contained fixing agents including sodium thiosulfate, ammonium thiosulfate, sodium thiocyanate and ammonium thiocyanate, silver halide solvents including thioureas and amine derivatives, as well as sulfites such as sodium sulfite, ammonium sulfite, sodium bisulfite and potassium metabisulfite; borates such as borax and sodium metaborate; organic carboxylic acids such as acetic acid, citric acid, tartaric acid and malic acid; inorganic acids such as sulfuric acid, boric acid and hydrochloric acid; amines such as ethylenediamine, diethanolamine and triethanolamine; water-soluble aluminum salts such as potash alum, ammonium alum, aluminum sulfate and aluminum chloride; organic compounds such as methanol, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polyoxyethylene glycol and acetone; further optionally iodides such as potassium iodide and sodium iodide; and any other additives.

As a preferred embodiment of the above-described first to third invention, in order to provide a light-sensitive silver halide photographic material having a better inscribability, a higher speed and less color remain, the silver halide grains contained in the emulsion layers may preferably comprise silver chloride or silver chloroiodide containing 10 to 80 mol % of silver chloride, and be subjected to spectral sensitization by use of a compound represented by Formula (VI).

Formula (VI)



In the formula, Z represents a group of atoms necessary for completing an oxazole nucleus, a benzoxazole nucleus or a naphtoxazole nucleus, and these nuclei may have a substituent on a carbon atom. Examples of the substituent may include halogen atoms (as exemplified by a fluorine atom, a chlorine atom and a bromine atom), unsubstituted alkyl groups having 1 to 6 carbon atoms (as exemplified by a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, etc.), alkoxy groups having 1 to 4 carbon atoms (as exemplified by a methoxy group, an ethoxy group, a propoxy group and a butoxy group), a hydroxyl group, alkoxycarbonyl groups having 1 to 6 carbon atoms (as exemplified by a methoxycarbonyl group, an ethoxycarbonyl group, etc.), alkylcarbonyloxy groups having 2 to 5 carbon atoms (as exemplified by an acetyloxy group, a propionyloxy group, etc.), a phenyl group, a hydroxyphenyl group, etc.

Examples of these nuclei may include nuclei of, as the oxazole nucleus, oxazole, 4-methyloxazole, 5-methyloxazole, 4,5-dimethyloxazole, 4-phenyloxazole, etc.; as the benzoxazole nucleus, benzoxazole, 5-chlorobenzoxazole, 5-bromobenzoxazole, 5-methylbenzoxazole, 5-ethylbenzoxazole, 5-methoxybenzoxazole, 5-hydroxybenzoxazole, 5-ethoxycarbonylbenzoxazole, 5-acetyloxybenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 6-methoxybenzoxazole, 5,6-dimethylbenzoxazole, 6-chloro-5-methylbenzoxazole, etc.; as the naphthoxazole nucleus, naphtho[1,2-d]oxazole, naphtho[2,1-d]oxazole, naphtho[2,3-d]oxazole, etc.

R^1 represents a substituted or unsubstituted alkyl group. Examples of the substituent may include a hydroxyl group, a sulfo group, a sulfonate group, a carboxyl group, halogen atoms (as exemplified by a fluorine atom and a chlorine atom), substituted or unsubstituted alkoxy groups having 1 to 4 carbon atoms (the alkoxy group may be further substituted with a sulfo group or a hydroxyl group), alkoxycarbonyl groups having 2 to 5 carbon atoms, alkylsulfonyl groups having 1 to 4 carbon atoms, a sulfamoyl group, substituted or unsubstituted carbamoyl groups (including substituted carbamoyl groups substituted with an alkyl group having 1 to 4 carbon atoms), substituted phenyl groups (examples of the substituent are a sulfo group, a carboxyl group, a hydroxyl group, etc.), a vinyl group, etc.

Examples of the unsubstituted alkyl group may include a methyl group, an ethyl group, a propyl group and a butyl group. Examples of the substituted alkyl group may include as hydroxyalkyl groups, a 2-hydroxyethyl group, a 3-hydroxypropyl group, etc., as sulfoalkyl groups, a 2-sulfoethyl group, a 3-sulfopropyl group, a 3-sulfobutyl group, a 4-sulfobutyl group, a 2-hydroxy-3-sulfopropyl group, a 2-chloro-3-

sulfopropyl group, etc., as carboxyalkyl groups, a carboxymethyl group, a carboxyethyl group, a carboxypropyl group, etc., a 2,2,2-trifluoroethyl group, a 2-(3-sulfopropyloxy)ethyl group, a 2-(2-hydroxyethoxy)-ethyl group, an ethoxycarbonylethyl group, a methylsulfonylethyl group, as sulfamoylalkyl groups, a 2-sulfamoylethyl group, a 2-sulfamoylethylgroup, a 2-N,N-dimethylsulfamoylethyl group, etc., a phenethyl group, a p-carboxyphenethyl group, as sulfoaralkyl groups, a p-sulfophenethyl group, an o-sulfophenethyl group, etc., a p-hydroxyphenethyl group, a phenoxyethyl group, etc.

R^2 represents an alkoxycarbonylalkyl group, a hydroxyalkyl group, a hydroxyalkoxyalkyl group, a carbamoylalkyl group, a hydroxyalkylthioalkyl group, a hydroxyphenyl group, a morpholinoalkyl group, a hydroxyalkylphenyl group, a phenyl group, an alkoxyalkyl group, or a substituent $-\left(CH_2\right)_n A$ or $-\left(CH_2\right)_n O-\left(CH_2\right)_n A$. Herein A represents a nitrile group, an alkylsulfonyl group, a sulfonamide group, an alkylsulfonylamino group or an alkoxy group having 1 to 8 carbon atoms, and n represents an integer of 1 to 4.

The above groups represented by R^2 include those having a substituent. For example, those wherein the alkyl moiety in the above groups has been substituted with a halogen atom can also be preferably used.

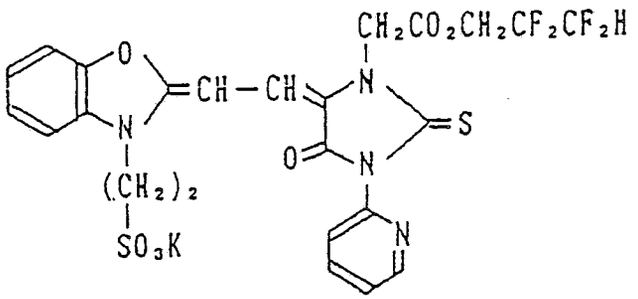
Examples of R^2 include alkoxycarbonylalkyl groups (as exemplified by a methoxycarbonylfluoromethyl group, an ethoxycarbonylfluormethyl group, a fluoroethoxycarbonylethyl group, etc.), hydroxyalkyl groups (as exemplified by a 2-hydroxyfluoroethyl group, 2-hydroxyfluoropropyl group, 3-hydroxyfluoropropyl group, 2,3-dihydroxyfluoropropyl group, etc.), hydroxyalkoxyalkyl groups (as exemplified by a hydroxymethoxyfluoromethyl group, a 2-(2-hydroxyfluoroethoxy)ethyl group, a hydroxyfluoroethoxymethyl group, etc.), carbamoylalkyl groups (including N-alkyl-substituted, N,N-dialkyl-substituted, N-hydroxyalkyl-substituted, N-alkyl-N-hydroxyalkyl-substituted or N,N-di(hydroxylalkyl)-substituted carbamoylalkyl groups and carbamoylalkyl groups of 5-or 6-membered cyclic amines) (as exemplified by a 2-carbamoylchloroethyl group, a 2-N-(2-hydroxyethyl) carbamoylchloroethyl group, a N-hydroxyfluoroethylcarbamoylmethyl group, an N,N-di(2-hydroxyfluoroethyl)carbamoylmethyl group, a 2-N,N-di(2-hydroxyethyl)carbamoylchloroethyl group, an N,N-dimethyl)carbamoylchloromethyl group, a morpholinocarbamoylchloromethyl group, a piperidinocarbamoylmethyl group, etc.), a hydroxyphenyl group, hydroxyalkylphenyl groups having 7 to 9 carbon atoms (as exemplified by a p-(2-hydroxyfluoroethyl)phenyl group, a m-(1-hydroxyfluoroethyl)phenyl group, etc., and a substituent $-\left(CH_2\right)_n A$ or $-\left(CH_2\right)_n O-\left(CH_2\right)_n A$. Herein A represents a nitrile group, an alkylsulfonyl group, a sulfonamide group, an alkylsulfonylamino group or a lower alkoxy group, of which the alkylsulfonyl group may preferably include alkylsulfonyl groups having 1 to 4 carbon atoms (as exemplified by a methylsulfonyl group, an ethylsulfonyl group, etc.), the sulfonamide group may preferably include sulfonamide groups having 1 to 4 carbon atoms (as exemplified by an N-methylsulfonamide group, an N,N-dimethylsulfonamide group, etc.), the alkylsulfonylamino group may preferably include alkylsulfonylamino groups having 1 to 4 carbon atoms (as exemplified by a methylsulfonylamino group, etc.), and the lower alkoxy group may preferably include alkoxy groups having 1 to 4 carbon atoms (as exemplified by a methoxy group, an ethoxy group, etc.). n represents an integer of 1 to 4.

R^3 and R^4 may be the same or different, and each represent a hydrogen atom, an alkyl group (preferably one having 1 to 4 carbon atoms, as exemplified by a methyl group, an ethyl group, etc.), an alkoxy group (preferably one having 1 to 4 carbon atoms, as exemplified by a methoxy group, an ethoxy group, etc.), an alkylsulfonyl group, a sulfo group, a chlorine atom, a fluorine atom or a carboxyl group.

In the compound represented by the above Formula (VI), particularly preferred is an instance where R^1 represents a straight or branched alkyl group having 1 to 4 carbon atoms and substituted with a sulfo group or a carboxyl group and/or a hydroxyl group, specifically including a sulfoethyl group, a sulfopropyl group, a 3-sulfobutyl group, a 4-sulfobutyl group, a carboxymethyl group, a carboxyethyl group, a hydroxyethyl group, a 3-sulfo-2-hydroxypropyl group, etc.

Typical examples of the compound represented by the above Formula (VI) used in this invention are shown below, but of course the compounds used in this invention are by no means limited to these.

VI - 1



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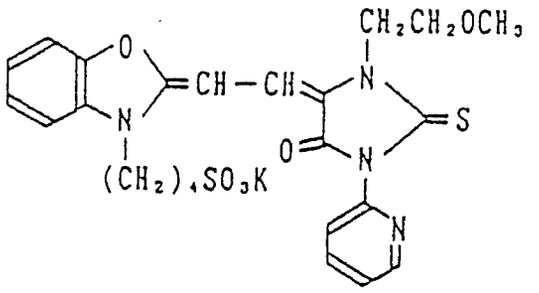

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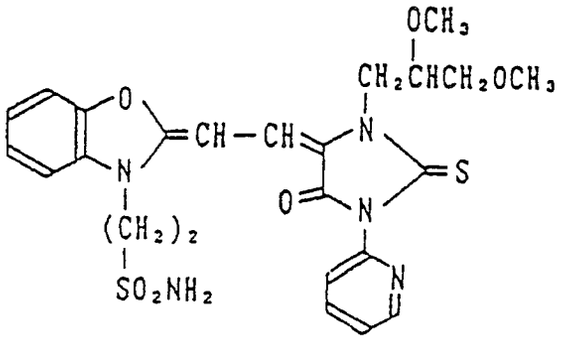

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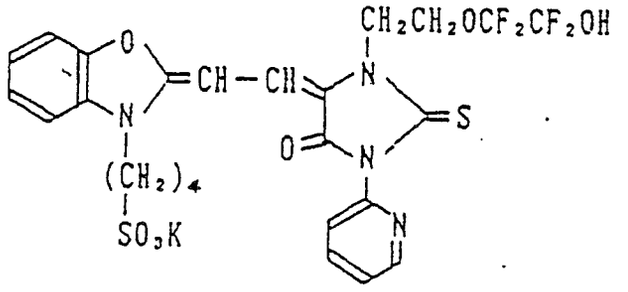

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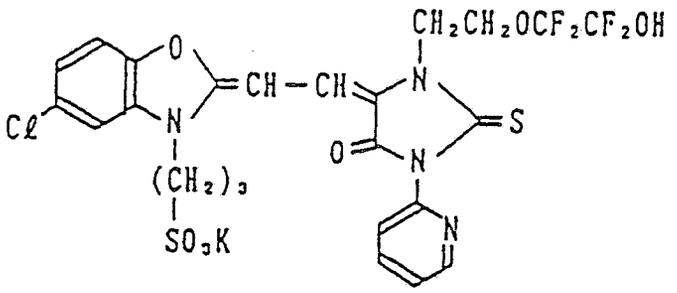

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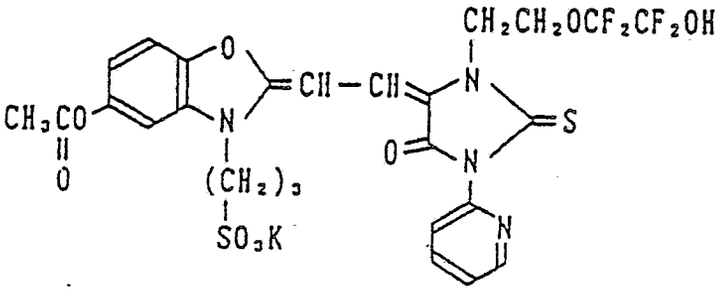

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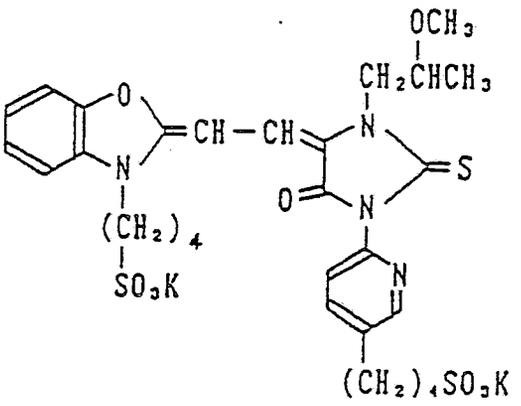

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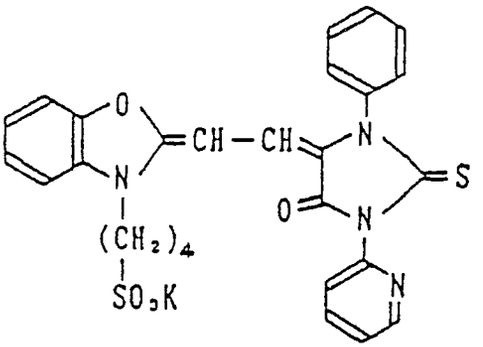

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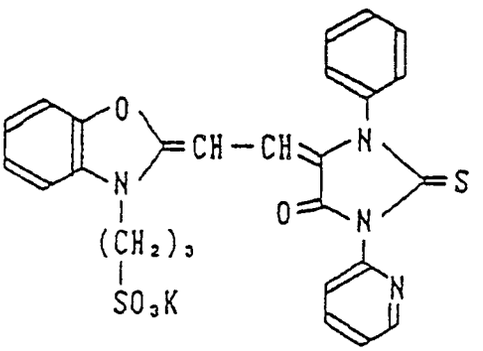

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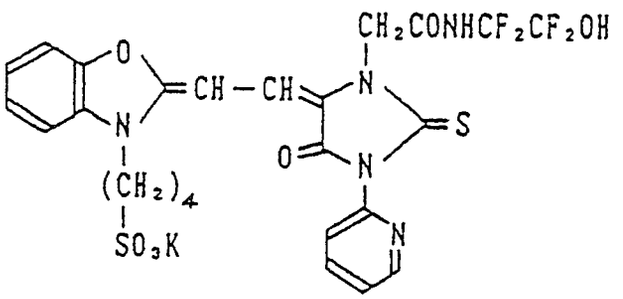

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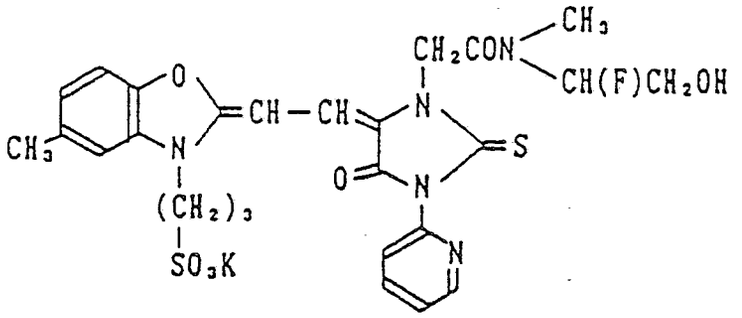

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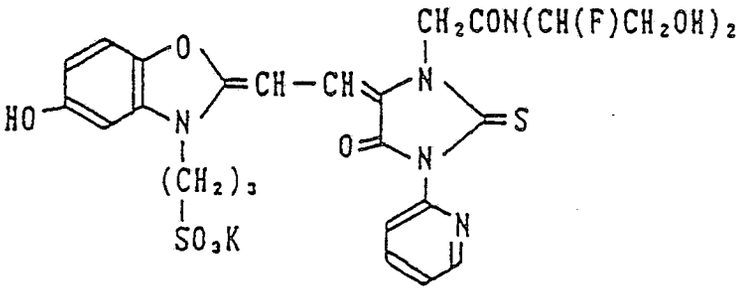

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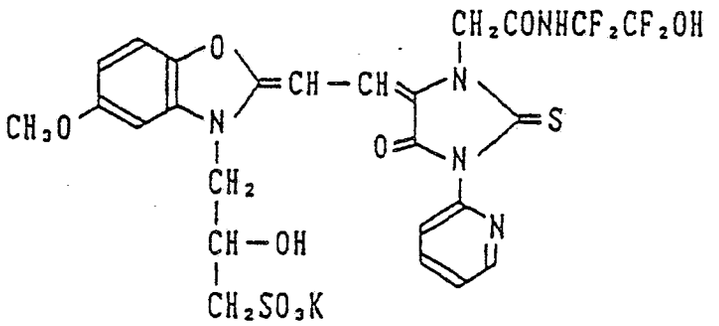

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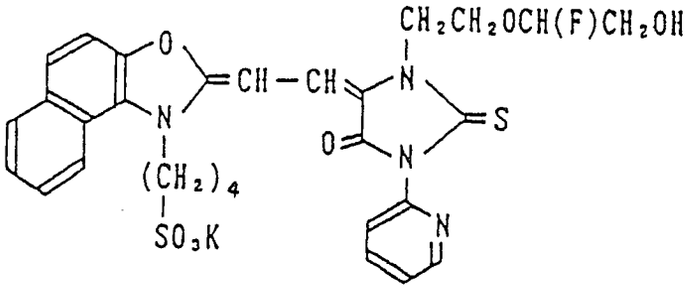

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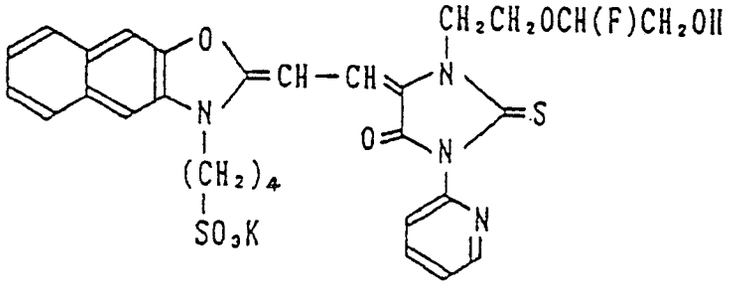

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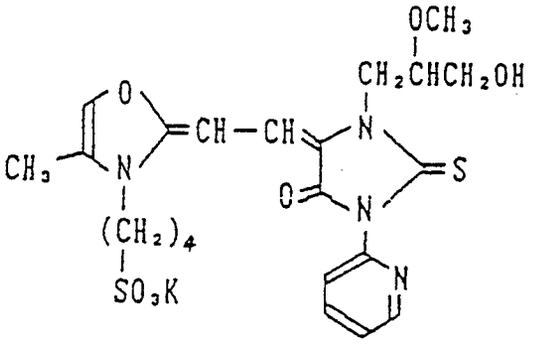

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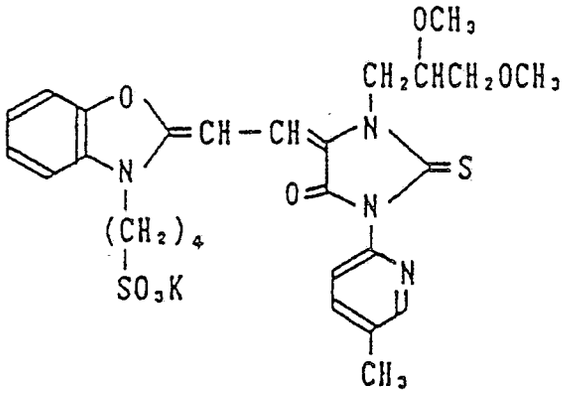

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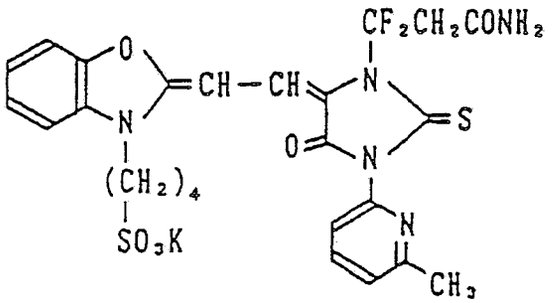

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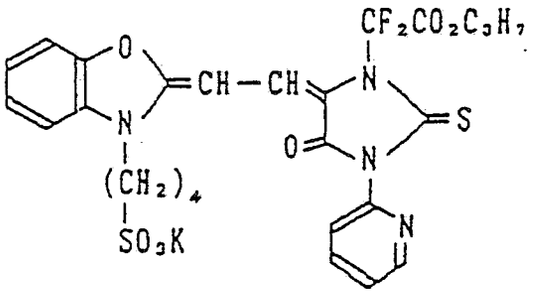

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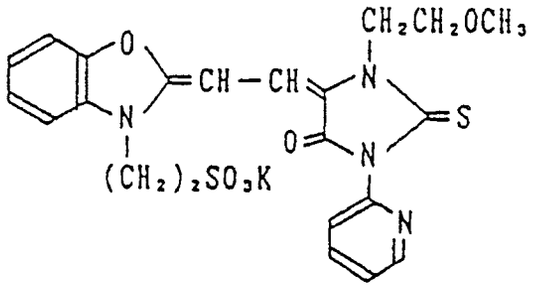

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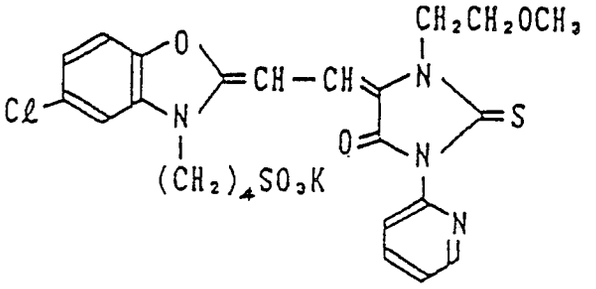

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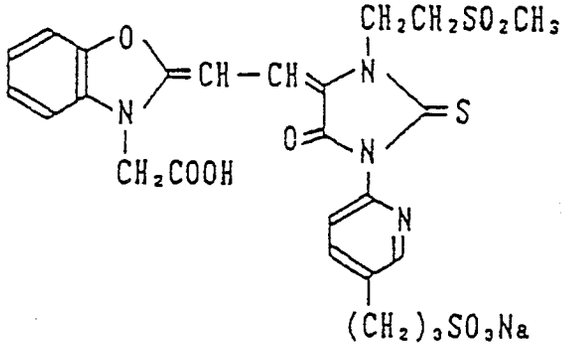

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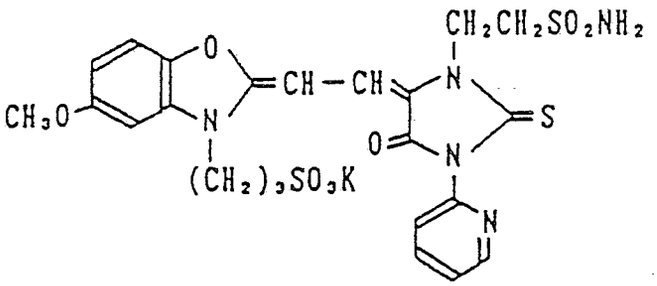

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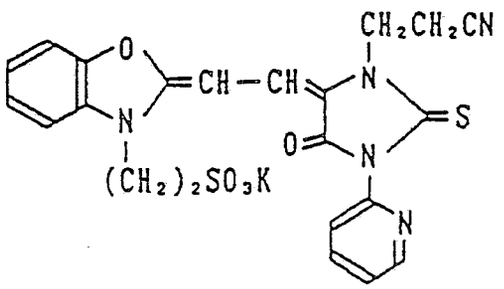

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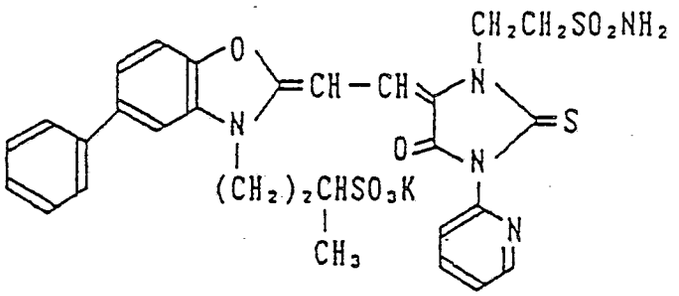

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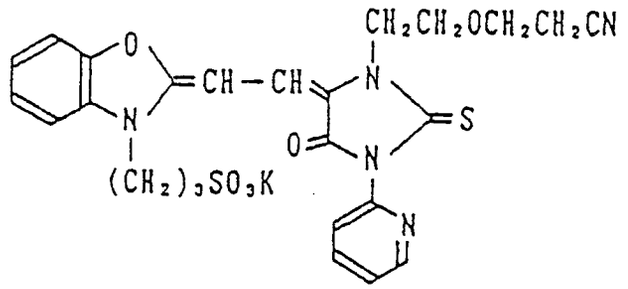

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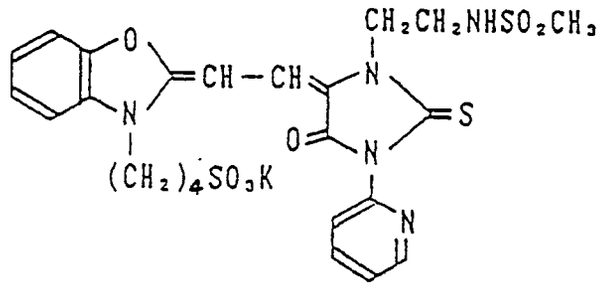

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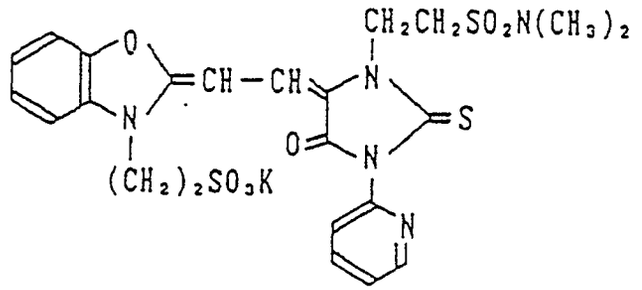

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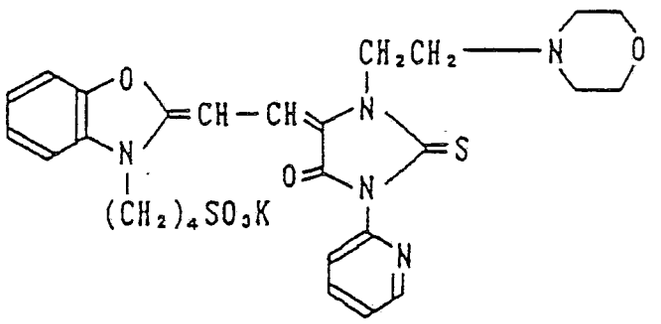

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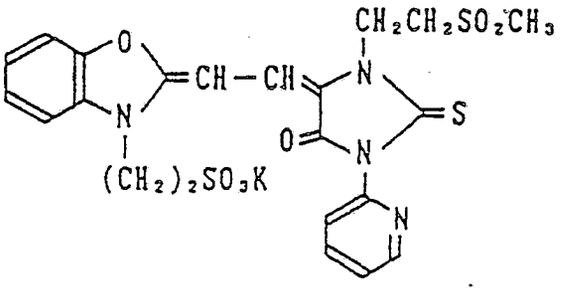

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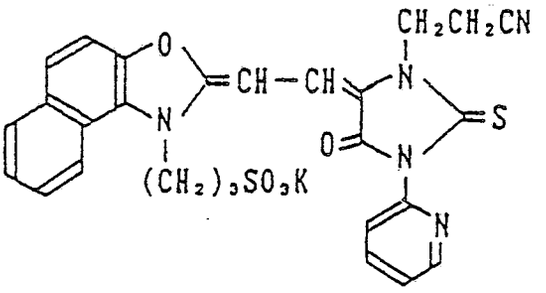

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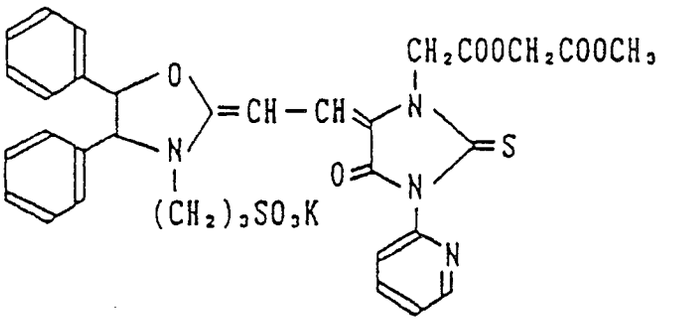
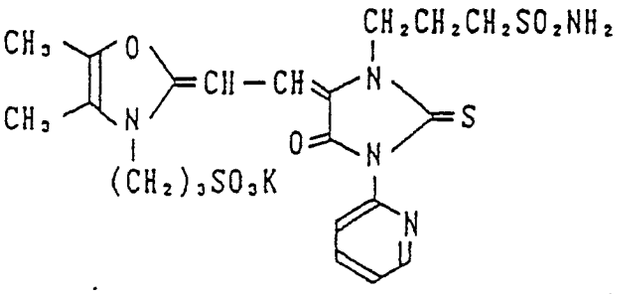
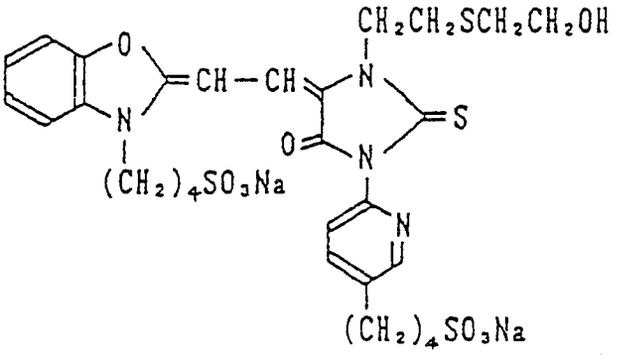


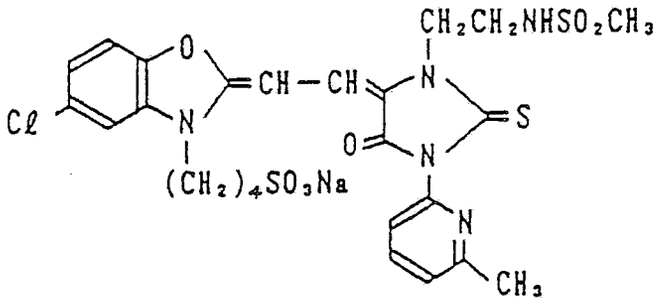
VI — 33



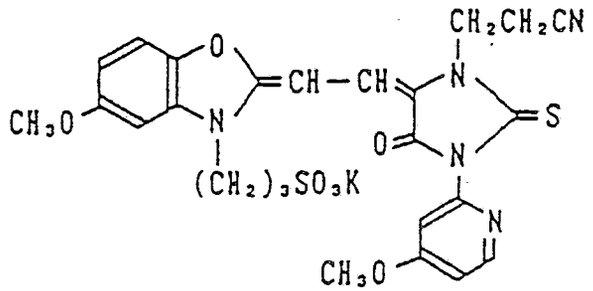
VI — 34



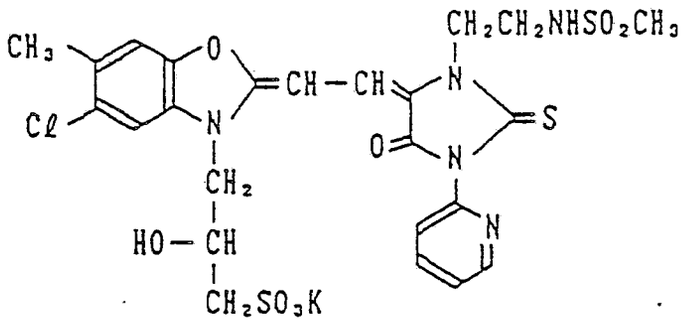
VI— 35



VI— 36



VI— 37



The compound represented by the above Formula (VI) used in this invention can be synthesized by the method of synthesizing dimethinemerocyanines as described in Japanese Patent Publications No. 549/1971, No. 18105/1971, No. 18106/1971, No. 18108/1971, No. 4085/1972 and No. 52574/1983, U.S. Patents No. 2,839,403, No. 3,384,486, No. 3,625,698, No. 3,480,439 and No. 3,567,458, etc.

Addition and dispersion of the merocyanine dye represented by the above Formula (VI) used in this invention in the silver halide emulsion can be carried out, for example, by conventionally known methods. For example, the methods may include a method in which it is added by dispersing it together with a surface active agent as described in Japanese Patent Publication No. 44895/1974 and Japanese Unexamined Patent Publication No. 11419/1975, a method in which it is added as a dispersion with a hydrophilic substrate as described in Japanese Unexamined Patent Publications No. 16624/1978, No. 102732/1978 and No. 102733/1978, U.S. Patents No. 3,469,987 and No. 3,676,147, and a method in which it is added as a solid solution as described in East German Patent No. 143,324. Besides, the merocyanine dye may be

dissolved in a water-soluble solvent as exemplified by a solvent solely comprising water, ethanol, methanol, acetone, propanol, alcohol fluoride, pyridine, or the like or a mixed solvent of any of these, and then added in emulsions. It may be added at any time in the course of preparing emulsions, but may preferably be added during chemical ripening or after chemical ripening. The dye of the above Formula (VI) used in this invention may be added in the amount for carrying out the spectral sensitization of silver halide emulsions, as exemplified by 10^{-5} to 2×10^{-2}, preferably 10^{-4} to 2×10^{-3} mol per mol of silver halide.

The merocyanine dye used in this invention can be subjected to supersensitization, for example, by using it in any amount in combination with other dyes as described in Japanese Patent Publications No. 4933/1968, No. 4936/1968, No. 18107/1971, No. 1999/1971, No. 11114/1972, No. 1762/1973, No. 38408/1973, No. 38937/1981 and No. 52574/1983, U.S. Patents No. 2,519,001 and No. 3,745,014, etc.

The silver halide grains contained in the silver halide emulsion layer of this embodiment are required to be comprised of silver chlorobromide or silver chloroiodobromide containing 10 to 80 mol % of silver chloride. This is because the silver chloride otherwise less than 10 mol % may result in a lowering of speed and the silver chloride otherwise more than 80 mol % may cause an increase in fog. In the case of the silver chloroiodobromide, the content of silver iodide may preferably be 5 mol % or less, more preferably 2 mol % or less, for the purpose of achieving a higher speed.

In the course of the formation of silver halide grains or the chemical ripening, a compound containing a metal belonging to Group VIII can be made to coexist for improving developability, making hardened, giving high illumination adaptability, etc.

EXAMPLES

Examples of this invention will be described in detail. As a matter of course, this invention is by no means limited to the following examples.

Example 1

(Preparation of emulsions)

Solution A:

Water	9.7 lit
Sodium chloride	20 g
Gelatin	105 g

Solution B:

Water	3.8 lit
Gelatin	94 g
Sodium chloride	58.5 g
Potassium bromide	1,072 g

Solution C:

water	3.8 lit
Silver nitate	1,700 g

In 9,800 ml of the above Solution A maintained at a temperature of 55°C, the above Solution B and the above Solution C were simultaneously added functionally with the time for addition as shown in Table 1 while keeping pAg 7.2. The function and the time for addition were observed by use of an electron microscope to use a manner for obtaining good monodispersity. The monodispersity was all found to be 10 to 12 %.

Table - 1

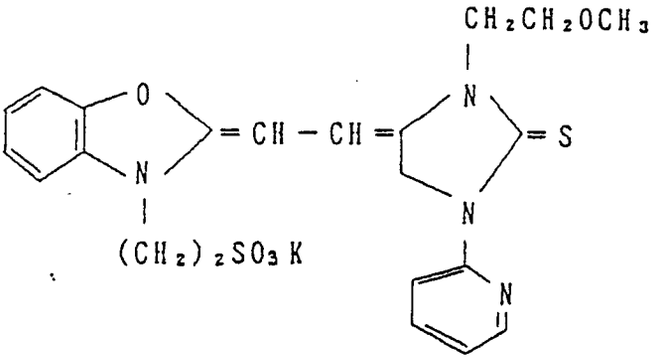
Emulsion No.	Time for addition (sec)	Average grain size
1	30	0.1 µm
2	70	0.2 µm
3	110	0.3 µm
4	130	0.35µm
5	180	0.45µm

Five kinds of solutions thus obtained were respectively continued being stirred for 10 minutes, and thereafter the pH was adjusted to 6.0 with use of sodium carbonate, to which 2 lit. of an aqueous 20 % magnesium sulfate solution and 2.55 lit. of an aqueous 5 % polynaphthalenesulfonic acid solution were added, and then the emulsions were flocculated at 40°C, followed by decantation, and washing with water to remove excess salts in the solutions. Subsequently, 3.7 lit. of water was added to make dispersion, and again 0.9 lit. of an aqueous 20 % magnesium sulfate solution was added to similarly remove excess salts in the solutions. To the resulting solutions, 3.9 lit. of water and 141 g of gelatin were added, and the mixtures were dispersed for 30 minutes at 50°C.

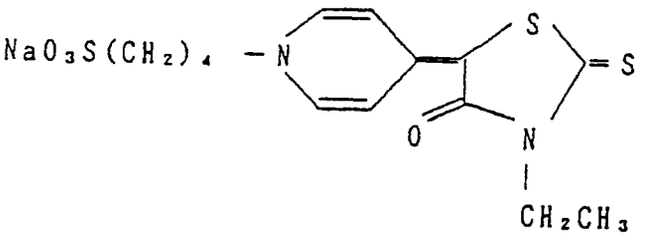
Thereafter 142 ml of a 1 % ammonium thiocyanate solution, 68 ml of a 1 % solution of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, sodium thiosulfate in an amount optimum for the respective grains and 227 ml of a 1 % silver nitrate solution were added, and the mixtures were ripened at 45°C to have a maximum speed.

Five kinds of the solutions prepared in the above manner were mixed as shown in Table 2 in the proportion of 1 : 1 (respectively 5 mols calculated as silver), and thereafter added were 80 ml of an aqueous 0.5 % solution of 1-phenyl-5-mercaptotetrazole as an antifoggant, 350 ml of an aqueous 10 % solution of hydroquinone, 1,600 ml of an aqueous 1 % solution of 4-hydroxy-6-methyl-1,3,3a-7-tetrazaindene as a stabilizer, 1.5 g of Compound (1) represented by the following formula as a sensitizing dye and 600 mg of Compound (2).

Compound (1)



Compound (2)



Further added were 180 ml of an aqueous 20 % saponin solution as a spreading agent, 300 ml of an aqueous 4 % solution of a styrene/maleic acid copolymer as a thickening agent, 250 g of a polymeric latex polymer of ethyl acrylate, 150 ml of 3 % formalin as a hardening agent and 4 g of sodium 2-hydroxy-4,6-dichloro-1,3,5-triazine.

Further as a solution for protective layers, 500 mg of sodium 2-sulfonate succinic acid bis(2-ethylhexyl) ester as a spreading agent was added in 560 g of gelatin, followed by making up to 10 lit. with water.

Table - 2

Emulsion No.	Emulsion mixed	Percentage of larger and smaller grains (%)
E - 1	1 and 2	50
E - 2	2 and 3	67
E - 3	2 and 4	57
E - 4	2 and 5	44
E - 5	3 and 5	67
E - 6	1 and 3	33
E - 7	1 and 4	28
E - 8	1 and 5	22
E - 9	3 and 4	86
E - 10	4 only	100

(Coating)

On one side each of polyethylene terephthalate supports having been subjected to subbing processing, the above emulsions and the above protective layer solution were simultaneously coated to obtain 18 kinds of light-sensitive silver halide photographic materials as shown in Table 3.

Also, the silver amount and the type of the matting agent and coating amount thereof in the emulsion layer of each sample were as shown in Table 3, and the type of the matting agent and coating amount thereof in the protective layer were as shown in Table 3.

Table - 3

Sample No.	1	2	3	4	5	6	7	8	9	10
Em	E - 1	E - 2	E - 3	E - 4	E - 5	E - 6	E - 7	E - 8	E - 9	E - 10
Coated-silver amount (g/m^2)	3.5	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left
Type of matting agent in emulsion	Rice starch; average particle diameter: 3.5 μm	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left
Coating amount of matting agent in emulsion (mg/m^2)	500	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left
Type of matting agent in protective layer	Amorphous silica; average particle diameter: 3.5 μm	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left
Coating amount of matting agent in protective layer (mg/m^2)	500	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left
Remarks	Present invention	Same as left	Same as left	Same as left	Same as left	Comparative	Same as left	Same as left	Same as left	Same as left

(Note) PMMA: Polymethyl methacrylate

Table - 3 (continued)

Sample No.	11	12	13	14	15	16	17	18
Em	E - 3	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left	Same as left
Coated-silver amount (g/m^2)	Same as left	Same as left	Same as left	4.5	4.5	5	6	4.5
Type of matting agent in emulsion	Same as left	Same as left	Same as left	-	-	Rice starch; average particle diameter: 3.5 μm	Same as left	(Note) PMMA
Coating amount of matting agent in emulsion (mg/m^2)	700	Same as left	100	-	-	500	Same as left	Same as left
Type of matting agent in protective layer	Same as left	Diatomaceaous earth; average particle diameter: 3.5 μm	Amorphous silica; average particle diameter: 3.5 μm	Same as left	Same as left	Same as left	Same as left	Same as left
Coating amount of matting agent in protective layer (mg/m^2)	300	100	Same as left	500	100	500	Same as left	Same as left
Remarks	Present invention	Same as left	Comparative	Present invention	Comparative	Same as left	Same as left	Present invention

(Note) PMMA: Polymethyl methacrylate

0 289 023

(Exposure and processing)

Part of each sample prepared in the above manner was imagewise exposed to light and other part thereof was kept unexposed. Developing was carried out over the period of 15 seconds at 43°C using Sakura Automatic Processor GR-26 (manufactured by Konishiroku Photo Industry Co., Ltd.), fixing was carried out over the period of 15 seconds at 35°C, washing was carried out over the period of 15 seconds at room tremperature, and drying was carried out for 20 seconds with warm air of 45°C.

(Developing solution recipe)
Pure water about 800 ml
Potassium sulfite 60 g
Disodium ethylenediaminetetraacetate 2 g
Sodium sulfite 2 g
Potassium hydroxide 10.5 g
5-Methylbenzotriazole 300 mg
Diethylene glycol 25 g
1-Phenyl-4,4-dimethyl-3-pyrazolidinone 300 mg
1-Phenyl-5-mercaptotetrazole 600 mg
Potassium bromide 3.5 g
Hydroquinone 20 g
Potassium carbonate 15 g
Made up to 1,000 ml by adding pure water (ion-exchanged water).

At the time when the developing solution was used, the whole amount of the above developing solution was dissolved in 3 lit. of pure water (ion-exchanged water) and used.

The developing solution had the pH of about 11.4 before dilution with water, and the developing solution had the pH of about 10.8 after dilution with water.

(Fixing solution recipe)
Ammonium thiosulfate (an aqueous 72.5 % W/V solution) 240 ml
Sodium sulfite 17 g
Sodium acetate trihydrate 6.5 g
Boric acid 6 g
Sodium citrate dihydrate 2 g
Acetic acid (an aqueous 90 % W/V solution) 25 ml

At the time when the fixing solution was used, the above composition was dissolved in 500 ml of water, made up to 1 lit. and used. This fixing solution had the pH of about 4.5.

(Evaluation method)

In the table, the sharpness in line photographying was visually evaluated with use of a 100-power magnifier, and evaluateded by a 5 rank system, indicating that 5 is the best. Also, the gamma represents the gradation in a continuous tone, which is a gamma value of the film density of from 0.1 to 2.5, showing that 2 to 2.6 is good for the characteristics of the present films. The larger the value is, the higher the contrast is, so that it becomes impossible to use the films as continuous tone films.

The clearing performance of fixing and the inscribability and erasability with use of a drafting pencil and a needle pen (Rotring pen) were evaluated according to the 3 rank system shown below.

(Measurement results)

Results of the measurement are shown in Table 4. Samples Nos. 1 to 5, 11, 12, 14 and 18 falling under this invention showed the sharpness of line photographying as good as 4 to 4.5 and also the gamma value as good as 2.1 to 2.5, and also showed good results for the inscribability and erasability with use of the pencil and the inscribability and erasability with use of the needle pen (Rotring pen).

In contrast with this, Samples No. 6 to No. 8 falling under the comparative sample show poorness in the sharpness of line photographying, and Samples No. 9 and No. 10 have so a high contrast that it is impossible to use them as continuous tone films. Also, Samples No. 13 and No. 15 show a poorness in the inscribability and erasability with use of the pencil and the needle pen (Rotring pen), and Samples Nos. 1, 6 and 17, a serious poorness in the clearing in fixing.

Table - 4

Sample No.	1	2	3	4	5	6	7	8	9	10
Sharpness in line photographying	4	4.5	4	Same as left	4.5	3	2.5	2	4.5	5
Gamma	2.4	Same as left	2.3	2.1	2.5	1.6	1.5	1.0	3.5	4.0
Fixing clearing	A	A	A	A	A	A	A	A	A	A
Pencil inscri-bability and erasability	A	A	A	A	A	A	A	A	A	A
Ink inscri-bability and erasability	A	A	A	A	A	A	A	A	A	A

Table - 4 (continued)

Sample No.	11	12	13	14	15	16	17	18
Sharpness in line photographying	4.5	Same as left	Same as left	4.0	Same as left	4.5	Same as left	Same as left
Gamma	2.2	Same as left	2.7	2.0	Same as left	2.6	2.7	2.4
Fixing clearing	A	A	A	A	A	B	C	A
Pencil inscribability and erasability	A	A	B	A	C	A	A	A
Ink inscribability and erasability	A	A	B	A	C	A	A	A

(Notes)
A : Good (no problem in practical use)
B : Poor (problematic in practical use)
C : Further poor (can not be put into practical use at all)

As described above, it is possible according to this invention to obtain a light-sensitive silver halide photographic material that can be processed with usual rapid access, can effect a continuous tone and line photographing on the same film, can achieve very good fixing clearing, and can be greatly superior in the inscribability and erasability.

Example 2

Preparation of coating solutions for silver halide emulsion layers

Prepared first were the following Solutions (A), (B), (C) and (D). (A):

Water	980 ml
Gelatin	10 g
Sodium chloride	2 g
Water	380 ml

(B):

Gelatin	10 g
Sodium chloride	30 g
Potassium bromide	60 g

(C):

Water	380 ml
Silver nitrate	170 g

(D):

Water	100 ml
Potassium bromide	35 g

Solution (A) was maintained at 45°C, and Solutions (B) and (C) were functionally added thereto with stirring, taking 41 minutes while keeping pH = 6.0 and pAg = 7.5. After 2 minutes from completion of the addition, Solution (D) was added taking 4 minutes, and subsequently the temperature was dropped to 40°C to carry out desalting and washing according to a conventional method, followed by addition of 15 g of gelatin as a final step to obtain Emulsion I having an average grain size of 0.25 μm.

Prepared next were the following Solutions (E), (F), (G), (H), (I) and (J). (E):

Water	980 ml
Gelatin	10 g
Sodium chloride	2 g

(F):

Water	120 ml
Gelatin	2.5 g
Sodium chloride	0.85 g
Potassium bromide	1.7 g

(G):

Water	370 ml
Gelatin	8.8 g
Sodium chloride	28 g
Potassium bromide	58 g

(H):

Water	120 ml
Silver nitrate	4.8 g

(I):

Water	370 ml
Silver nitrate	165.2 g

(J):

Water	100 ml
Potassium bromide	35 g

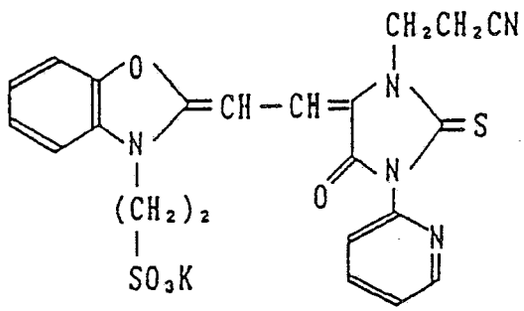
Solution (E) was maintained at 45°C, and Solutions (F) and (H) were functionally added thereto with stirring, taking 10 minutes while keeping pH = 6.0 and pAg = 7.5, and subsequently Solutions (G) and (I) were functionally added taking 70 minutes. Two minutes after completion of the addition, Solution (J) was added taking 4 minutes, and subsequently the temperature was dropped to 40°C to carry out desalting and washing according to a conventional method, followed by addition of 15 g of gelatin as a final step to obtain Emulsion II having an average grain size of 0.40 μm.

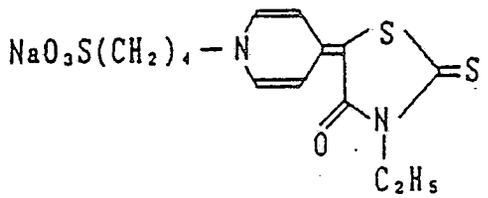
Next, 0.1 g of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 6 mg of sodium thiosulfate were added to

Emulsion I to apply sulfur sensitization with ripening for 60 minutes at 50°C, followed by addition of 70 mg of 1-phenyl-5-mercaptotetrazole, 1 g of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 40 g of gelatin.

Also, 1.5 mg of sodium thiosulfate was added to Emulsion II to apply sulfur sensitization with ripening for 80 minutes at 50°C, followed by addition of 70 mg of 1-phenyl-5-mercaptotetrazole, 1 g of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 40 g of gelatin.

Subsequently, Emulsion I and Emulsion II were mixed. Thereafter 200 mg of Compound (a) shown below and 60 mg of Compound (b), per mol of silver halide, were added to effect spectral sensitization, and further added were 3.7 g of saponin as a coating aid, 2 g of hydroquinone as a stabilizer, rice starch, as a matting agent, having the particle diameter characteristics as shown in Table 5 and in the amount as shown in Table 5, 30 g of polybutyl acrylate as a latex polymer, 1 g of a styrene/maleic anhydride copolymer as a thickening agent and 0.8 g of sodium 2,4-dichloro-6-hydroxy-s-triazine as a hardening agent, followed by adjustment of the pH to 5.5 with use of citric acid as a final step to prepare a coating solution for emulsion layers.

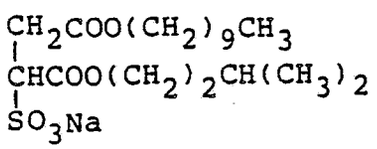




Preparation of coating solutions for protective layers

In 100 g of gelatin, 1,400 ml of water was added to effect dissolution, and thereafter added were silica having the particle diameter characteristics as shown in Table 5 and in the amount as shown in Table 5, 2 g of saponin as a surface active agent, and Compound (c) shown below so that the surface tension of the coating solutions for protective layers comes to 42, 38, 36, 30, 28 and 24 dyne/cm, respectively, with further addition of 3 g of formalin as a hardening agent, to prepare coating solutions for protective layers. Here, the surface tension when no Compound (c) was added was 42 dyne/cm. The coating solutions had the pH of 6.0. The surface tension was measured according to a vertical plate method employing a platinum plate.

(c)



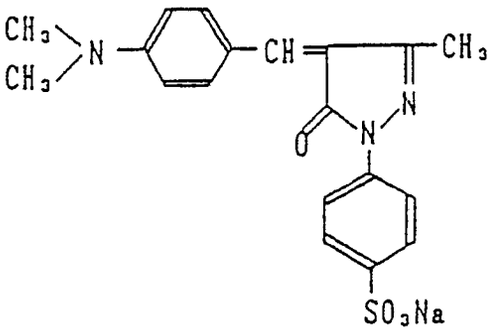
The classification of rice starch and silica was carried out with use of Spedic Classifier manufactured by

Seishin Kigyo, and the average particle diameter and the weight percentage of the matting agent having a particle diameter exceeding 6 μm to the whole matting agent were measured by Laser Micronsizer manufactured by Seishin Kigyo.

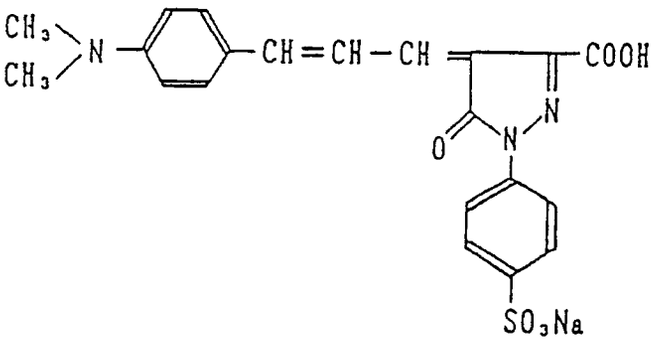
Preparation of coating solution for lower backing layers

In 100 g of gelatin, 1,600 ml of water was added to effect dissolution, and thereafter added were 5 g of Compound (d), 1 g of (e) and 1.5 of (f) shown below, as dyes, 40 g of rice starch as a matting agent, having the average particle size of 3 μm and the weight percentage of the matting agent having a particle diameter exceeding 6 μm to the whole matting agent, of 0.5 %, 5 g of saponin as a surface active agent, 1 g of styrene-maleic anhydride as a thickening agent and 1 g of glyoxal as a hardening agent, followed by adjustment of the pH to 5.5 with use of citric acid as a final step to prepare a coating solution for lower backing layers.

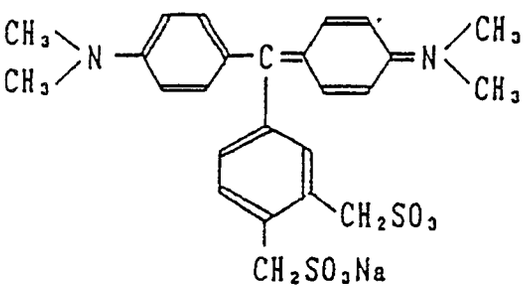
(d)



(e)



(f)



Preparation of coating solution for upper backing layers

In 100 g of gelatin, 1,200 ml of water was added to effect dissolution, and thereafter added were 50 g of silica as a matting agent, having the average particle size of 3 μm and the weight percentage of the matting agent having a particle diameter exceeding 6 μm to the whole matting agent, of 0.5 %, 3 g of saponin as a surface active agent, 0.2 g of the above Compound (c) and 1 g of glyoxal as a hardening agent, to prepare a coating solution for lower backing layers. The coating solution had the pH of 6.0 and surface tension of 36 dyne/cm.

Preparation of samples

On polyethylene terephthalate supports having a thickness of 100 μm and applied with subbing processing on both sides thereof, the above lower backing layer coating solution and upper backing layer coating solution were simultaneously coated with lamination. Subsequently, on the side opposite to the backing layers, the above emulsion layer coating solutions and protective layer coating solutions were simultaneously coated with lamination to make Samples No. 1 to No. 15.

Coated silver amount was 3.5 g/m^2, and gelatin amounts were 2.5 g/m^2 for the lower backing layer, 1 g,/m^2 for the upper backing layer, 1.9 g/m^2 for the emulsion layer, and 1.4 g./m^2 for the protective layer.

[Evaluation of inscribability and erasability]

The above samples were kept unexposed to light, and processed with an automatic processor GR-26 (manufactured by Konishiroku Photo Industry Co., Ltd.) in which the developing solution and fixing solution shown below were introduced, to obtain samples for use in evaluation.

Processing conditions were 40°C, 20 seconds for developing, 35°C, 20 seconds for fixing, and room temperature and 20 seconds for washing.

Next, the center-line average roughness of the surfaces were measured with use of Perthometer manufactured by Perthen AG, West Germany. Subsequently the inscribability was evaluated with water-base ink by use of a drafting needle pen (Rotring pen).

The evaluation was made with use of a 10-power magnifier to visually evaluate the density of lines, the uniformity of density and the constancy of line width, and the line width reproducibility was measured with use of a 25-power magnifier having gradations of length. Target line width is 500 μm. Smoothness in writing touch was evaluated at the same time.

Lines were erased with a plastic eraser for use in pencils, applied with water in a small quantity, to further visually evaluate the degree of blotting.

[Results of evaluation]

Results of evaluation are shown in Table 5.

Comparison of Samples No. 19 to No. 23 demonstrates that Samples No. 20 to No. 23 in which the center-line average roughness of the surfaces is in the range of from 0.15 to 0.80 have superior inscribability.

Comparison of Samples No. 22 and No. 24 to No. 28 demonstrates that Samples No. 22 and No. 24 to No. 26 in which the weight percentage of the matting agent having a particle diameter exceeding 6 μm to the whole matting agent is 5 % or less have superior inscribability.

Comparison of Samples No. 22, and No. 29 to No. 33 demonstrates that Samples No. 22 and No. 30 to 32 in which the surface tension of the protective layers is in the range of from 28 to 38 dyne/cm have superior inscribability and erasability.

<Developing solution recipe>
Pure water (ion-exchanged water) about 800 ml
Potassium sulfite 60 g
Disodium ethylenediaminetetraacetate 2 g
Potassium hydroxide 10.5 g
5-Methylbenzotriazole 300 mg
Diethylene glycol 25 g
1-Phenyl-4,4-dimethyl-3-pyrazolidinone 300 mg
1-Phenyl-5-mercaptotetrazole 600 mg
Potassium bromide 3.5 g
Hydroquinone 20 g
Potassium carbonate 15 g
Made up to 1,000 ml by adding pure water (ion-exchanged water).

The developing solution had the pH of about 10.8.

<Fixing solution recipe>
Ammonium thiosulfate (an aqueous 72.5 % W/V solution) 240 ml
Sodium sulfite 17 g
Sodium acetate trihydrate 6.5 g
Boric acid 6 g
Sodium citrate dihydrate 2 g
Acetic acid (an aqueous 90 % W/V solution) 25 ml

At the time when the fixing solution was used, the above composition was dissolved in 500 ml of water, made up to 1 lit. and used. This fixing solution had the pH of about 4.5.

Table - 5

Sample No.	Starch in emulsion layer			Silica in protective layer			Center-line average roughness (μm)	Surface tension of protective layer (dyne/cm)
	Amount (g/m^2)	Average particle diameter (μm)	Weight percentage exceeding 6μm	Amount (g/m^2)	Average particle diameter (μm)	Weight percentage exceeding 6μm		
19	-	-	-	0.10	3.5	0.5%	0.10	36
20	-	-	-	0.18	3.5	0.5%	0.15	36
21	-	-	-	0.50	3.5	0.5%	0.30	36
22	0.50	3.0	0.5%	0.50	3.5	0.5%	0.50	36
23	1.50	3.0	0.5%	0.50	3.5	0.5%	0.80	36
24	0.50	3.3	1.0%	0.50	3.7	1.0%	0.50	36
25	0.50	3.7	2.0%	0.50	3.9	2.0%	0.55	36
26	0.50	4.0	5.0%	0.50	4.2	5.0%	0.65	36
27	0.50	4.5	8.0%	0.50	3.9	2.0%	0.60	36
28	0.50	4.5	8.0%	0.50	4.5	8.0%	0.70	36
29	0.50	3.0	0.5%	0.50	3.5	0.5%	0.50	42
30	0.50	3.0	0.5%	0.50	3.5	0.5%	0.50	38
31	0.50	3.0	0.5%	0.50	3.5	0.5%	0.50	30
32	0.50	3.0	0.5%	0.50	3.5	0.5%	0.50	28
33	0.50	3.0	0.5%	0.50	3.5	0.5%	0.50	24

Table - 5 (continued)

Sample No.	Inscribability					Erasability	
	Density	Uniformity	Line-width constancy	Line-width (μm)	Smoothness		
19	2	2	2	500	5	4	Comparative
20	3	3	3	500	5	4	Present invention
21	4	4	4	500	5	4	Present invention
22	5	5	5	500	4	4	Present invention
23	5	5	5	500	3	4	Present invention
24	5	5	5	500	4	4	Present invention
25	5	5	5	500	3.5	4	Present invention
26	5	4	4	500	3	4	Present invention
27	4	3	3	500	2.5	4	Comparative
28	4	3	3	500	2	4	Comparative
29	5	5	5	600	4	3	Comparative
30	5	5	5	530	4	4	Present invention
31	5	5	5	500	4	4	Present invention
32	4	4	4	500	4	4	Present invention
33	2	2	2	500	4	4	Comparative

Meaning of ranking:
5: Superior
4: Ordinary
3: Minimum level for commercial use
2: Inferior

1: Can not be used at all

This invention has made it possible to provide a light-sensitive silver halide photographic material having superior inscribability and erasability.

Example 3

Preparation of emulsion coating solution

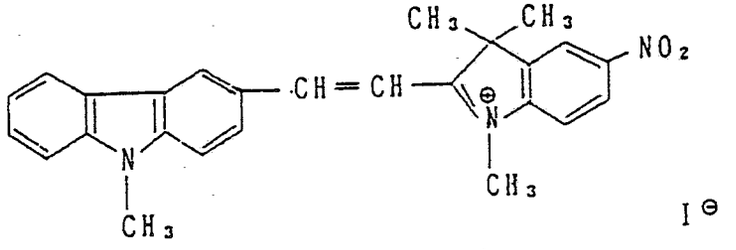
In 1 lit. of an aqueous 1 % gelatin solution of 65°C, 220 ml of an aqueous 3 % silver nitrate solution and 220 ml of an aqueous solution containing 98 mol % of potassium bromide and 2 mol % of potassium iodide based on said silver nitrate were added taking 30 minutes, simultaneously and while controlling the addition rate so that it increases with time. Subsequently 280 ml of an aqueous 40 % silver nitrate solution and 280 ml of an aqueous solution containing 98 mol % of potassium bromide and 2 mol % of potassium iodide based on said silver nitrate were added taking 100 minutes, simultaneously and while controlling the addition rate so that it increases with time. The pH during the above process was kept to about 2 with nitric acid, and the pAg was kept to about 7.5 with potassium bromide. After completion of the above process, the pH was adjusted to about 5.5 with an aqueous sodium carbonate solution, and water soluble salts were removed according to a conventional condensation method, followed by making up with addition of 15 g of gelatin.

As a result of this, there was obtained a silver iodobromide emulsion comprising regular cubic grains having an average grain size of 0.27 μm, containing 2 mol % of silver iodide and having a high monodispersity.

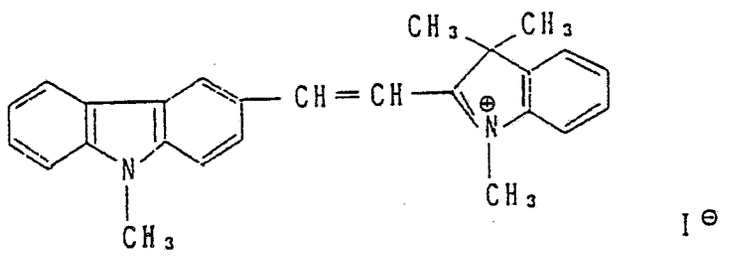
The above emulsion was adjusted to pH = 6.8 with an aqueous sodium carbonate solution, to which 0.12 mg of thiourea dioxide per mol of silver halide was added under pAg = 6.8 to carry out ripening for 60 minutes at 70°C, and then 0.50 mg of chloroaurate per mol of silver halide was added to carry out ripening for 60 minutes at 70°C, thus producing reduction fog and gold fog.

To the emulsion applied with fog, potassium bromide was added to make adjustment to pAg = 9.2, followed by addition of 600 mg per mole of silver halide, of the above compound (1-4), (II-1), (III-3), (IV-1) or (V-1) as an organic desensitizer according to this invention, and also the following compound of Formula [A], [B], [C], [D] or [E] as an organic desensitizer having nothing to do with this invention, and further making adjustment to pH = 5.3 using citric acid.

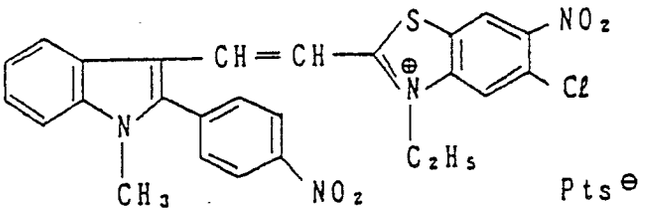
〔A〕



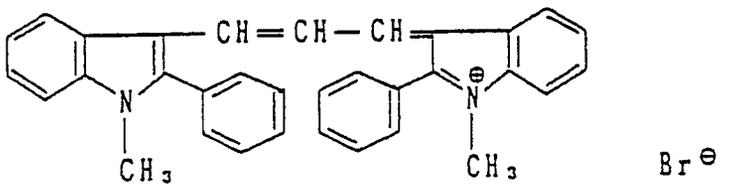
〔B〕



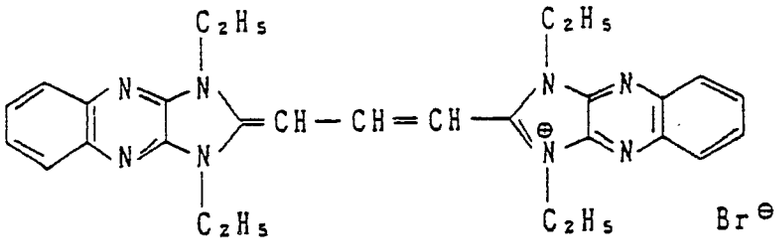
[C]



[D]



[E]

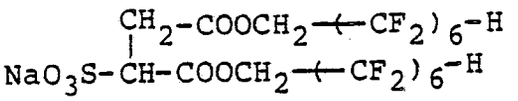


Next, added were 0.2 g/m^2 of diethylene glycol as a wetting agent, 40 mg/m^2 of sodium 1-decyl-2-(3-isopentyl)succinate-2-sulfonate as a coating aid, 60 mg/m^2 of a styrene/maleic anhydride copolymer as a thickening agent and 16 mg of formalin as a hardening agent per 1 g of gelatin, to prepare a coating solution for direct positive silver halide emulsions.

Preparation of coating solution for protective layers

In an aqueous gelatin solution adjusted to pH = 5.3 with an aqueous citric acid solution, 1.2 g of potassium bromide per 100 g of gelatin was added, with further addition of amorphous silica having an average particle diameter of 3.5 μm as a matting agent and by the amount as shown in Table 6, and then added were 30 mg/m^2 of 2-sulfonatosuccinic acid bis(2-ethylhexyl) ester sodium salt as a coating aid, 20 mg/m^2 of the compound of [A] shown below as a fluorine-containing surface active agent, 100 mg/m^2 of a styrene/maleic anhydride copolymer as a thickening agent and 16 mg of formalin as a hardening agent per 1 g of gelatin, to prepare a coating solution for protective layers

[A]



Preparation of coating samples

The above emulsion coating solution and protective layer coating solution were coated with lamination on polyethylene-coated paper of 150 μm thick having a subbing layer to prepare samples. Coated silver amount was 1.4 g/m², and gelatin coating amounts were 2.0 g/m² for the emulsion layer and 1.5 g/m² for the protective layer.

Evaluation of photographic performances, color remain intensity and inscribability.

The coating samples were exposed to light through a wedge, and thereafter development processing was carried out using Sakura Automatic Processor GR-26 (manufactured by Konishiroku Photo Industry Co., Ltd.) as an automatic processing machine and solutions having the following recipes as a developing solution and a fixing solution, and the photographic performances were evaluated. The development processing conditions were 38°C, 20 seconds for developing, 35°C, 20 seconds for fixing, room temperature and 20 seconds for washing, and about 45°C for drying.

Developing solution recipe

Pure water (ion-exchanged water) about 800 ml
Potassium sulfite 60 g
Disodium ethylenediaminetetraacetate 2 g
Potassium hydroxide 10.5 g
5-Methylbenzotriazole 300 mg
Diethylene glycol 25 g
1-Phenyl-4,4-dimethyl-3-pyrazolidinone 300 mg
1-Phenyl-5-mercaptotetrazole 60 mg
Potassium bromide 3.5 g
Hydroquinone 20g
Potassium carbonate 15 g

Made up to 1,000 ml by adding pure water (ion-exchanged water). At the time when the developing solution was used, the whole amount of the above developing solution was dissolved in 3 lit. of pure water (ion-exchanged water) and used.

The developing solution had the pH of about 11.4 before dilution with water, and the developing solution had the pH of about 10.8 after dilution with water.

Fixing solution recipe

(Composition A)
Ammonium thiosulfate (an aqueous 72.5 % W/V solution) 240 ml
Sodium sulfite 17 g
Sodium acetate trihydrate 6.5 g
Boric acid 6 g

Sodium citrate dihydrate 2 g
Acetic acid (an aqueous 90 % W/V solution) 13.6 ml

At the time when the fixing solution was used, the above Composition A was dissolved in 500 ml of water, made up to 1 lit. and used. This fixing solution had the pH of about 4.9.

Evaluation method

The speed is a relative value of a reciprocal of the exposure amount necessary for giving the density of 0.5.

Regarding the color remain intensity, the reflection density of non-image areas of the processed samples was measured under a halogen lamp light source with use of a Type 607 color analyzer manufactured by Hitachi, Ltd., to indicate it as the absorbence at max of the remaining organic desensitizer.

The pencil inscribability was evaluated by examining with a 10-power magnifier the thickness and density of the lines produced when inscribed with use of a pencil having a hardness of 2H.

The ink inscribability was evaluated by examining with a 10-power magnifier the thickness and density of the lines produced when inscribed with use of a drafting needle pen (Rotring pen) having an inner diameter of 0.5 mm.

Evaluation results

Results of measurement are shown in Table 6. It was found from Table 6 that Samples No. 34 to No. 38 all have a high speed as the relative speed is as high as 80 to 120, have less color remain as the color remain density is zero, have also superior inscribability, and thus can be put into practical use.

In contrast with this, it was found that all of Samples No. 39 to No. 43 in Table 6, though having superior inscribability, have much color remain as the color remain intensity is 0.03 to 0.05, have also a poorness in speed as the relative sensitivity is 40 to 80 except for Sample No. 40 showing a speed as high as 100, and thus can not be put into practical use.

It was also found that Samples No. 44 to 47 all have a high speed as the relative speed is as high as 100 to 120 and have less color remain as the color remain intensity is zero, but have so a poor inscribability that they can not be put into practical use.

It was further found that Samples No. 48 to No. 51 all have a high speed as the relative speed is as high as 80 to 100 and have less color remain as the color remain intensity is 0.01 to 0.02, but have also so a poor inscribability that they can not be put into practical use.

Table - 6

Sample No.	Organic desensitizer	Amount of matting agent in protective layer (mg/m^2)	Relative speed	Color remain intensity	Pencil inscribability	Ink inscribability	Remarks
34	I-4	400	100	0	A	A	Present invention
35	II-1	400	100	0	A	A	Present invention
36	III-3	400	120	0	A	A	Present invention
37	IV-1	400	120	0	A	A	Present invention
38	V-1	400	80	0	A	A	Present invention
39	A	400	80	0.03	A	A	Outside present invention
40	B	400	100	0.03	A	A	Outside present invention
41	C	400	50	0.02	A	A	Outside present invention
42	D	400	60	0.04	A	A	Outside present invention
43	E	400	40	0.05	A	A	Outside present invention
44	I-4	200	100	0	B	B	Outside present invention

Table - 6 (continued)

Sample No.	Organic desensitizer	Amount of matting agent in protective layer (mg/m^2)	Relative speed	Color remain intensity	Pencil inscribability	Ink inscribability	Remarks
45	I-4	100	100	0	C	C	Outside present invention
46	III-3	200	120	0	B	B	Outside present invention
47	III-3	100	120	0	C	C	Outside present invention
48	A	200	80	0.02	B	B	Outside present invention
49	A	100	80	0.01	C	C	Outside present invention
50	B	200	100	0.02	B	B	Outside present invention
51	B	100	100	0.01	C	C	Outside present invention

(Notes)

Evaluation of pencil inscribability and ink inscribability
A: Good (no problem in practical use)
B: Poor (problematic in practical use)
C: Further poor (can not be put into practical use at all)

Example 4

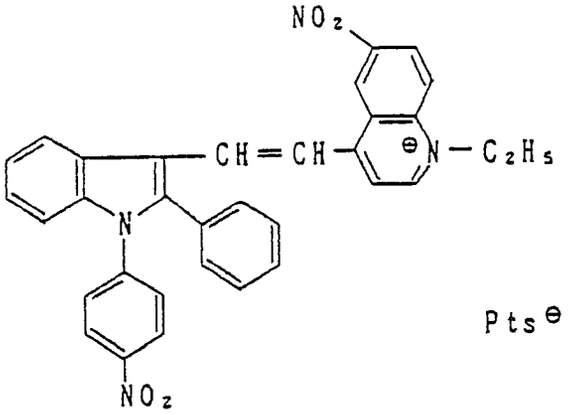
Example 3 was repeated except that the temperature was set to 55°C, to prepare a silver iodobromide solution.

As a result of this, there was obtained a silver iodobromide emulsion comprising regular cubic grains having an average grain size of 0.2 μm, containing 2 mol % of silver iodide and having a high monodispersity.

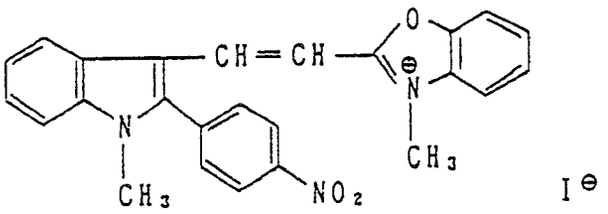
The above emulsion was adjusted to pH = 6.8 with an aqueous sodium carbonate solution, to which 0.3 mg of thiourea dioxide per mol of silver halide was added under pAg = 6.8 to carry out ripening for 60 minutes at 70°C, and then 1.0 mg of chloroaurate per mol of silver halide was added to carry out ripening for 60 minutes at 70°C, thus producing reduction fog and gold fog.

To the emulsion applied with fog, potassium bromide was added to make adjustment to pAg = 9.2, followed by addition of 600 mg per mole of silver halide, of the above compound (1-7), (II-3), (III-6), (IV-2) or (V-3) as an organic desensitizer according to this invention, and also the following compound of Formula [J], [K], [L], [M] or [N] as an organic desensitizer having nothing to do with this invention, and further making adjustment to pH = 5.8 using citric acid.

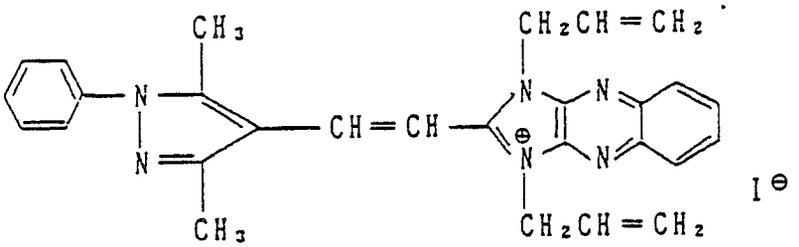
〔 J 〕



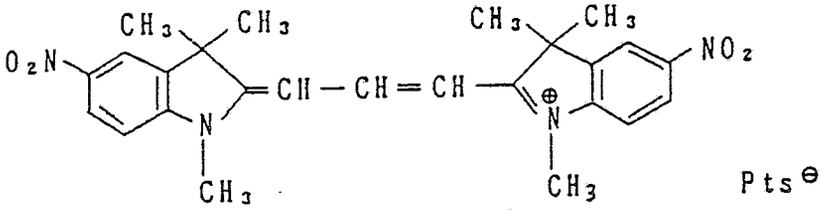
〔 K 〕



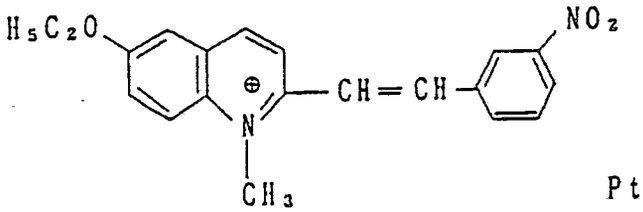
〔 L 〕



〔M〕



〔N〕



Next, added were rice starch having an average particle diameter of 4.0 μm as a matting agent and by the amount as shown in Table 7, 20 mg/m² of sodium 1-decyl-2-(3-isopentyl)succinate-2-sulfonate as a coating aid, 0.8 mg/m² of polyethyl acrylate as a polymer latex and 16 mg of formalin as a hardening agent per 1 g of gelatin, to prepare a coating solution for direct positive silver halide emulsions.

Preparation of coating solution for protective layers

In an aqueous gelatin solution adjusted to pH = 5.3 with an aqueous citric acid solution, 1.2 g of potassium bromide per 100 g of gelatin was added, with further addition of amorphous silica having an average particle diameter of 3.5 μm as a matting agent and by the amount as shown in Table 7, and then added were 20 mg/m² of 2-sulfonatosuccinic acid bis(2-ethylhexyl) ester sodium salt as a coating aid, 100 mg/m² of a styrene/maleic anhydride copolymer as a thickening agent, 50 mg/m² of colloidal silica for the purpose of improving the ink inscribability and 16 mg of formalin as a hardening agent per 1 g of gelatin, to prepare a coating solution for protective layers.

Preparation of coating samples

The above emulsion coating solution and protective layer coating solution were coated with lamination on polyethylene terephthalate films of 100 μm thick having a subbing layer to prepare samples. Coated silver amount was 3.5 g/m², and gelatin coating amounts were 2.0 g/m² for the emulsion layer and 1.5 g/m² for the protective layer. Also, on the surfaces opposite to the emulsion layers of the film supports, previously coated was a back coat layer containing 3.6 g/m² of gelatin containing 1.0 g/m² of rice starch and 400 mg/m² of amorphous silica having an average particle diameter of 3.5 μm.

Evaluation method

Evaluation was made in the same manner as in Example 3. In measuring the color remain intensity, measurement was made by applying to the back surfaces of the processed samples the polyethylene-coated paper of 150 μm thick used in Example 3.

Evaluation results

Results of measurement are shown in Table 7. It was found from Table 7 that Samples No. 54 to No. 58 all have a high speed as the relative speed is as high as 90 to 120, have less color remain as the color remain density is 0.01 to 0.02, have also superior inscribability, and thus can be put into practical use.

In contrast with this, it was found that all of Samples No. 59 to No. 63 in Table 7, though having superior inscribability, have much color remain as the color remain intensity is 0.03 to 0.04, have also a poorness in speed as the relative sentivity is 40 to 60 except for Sample No. 61 showing a speed as high as 120, and thus can not be put into practical use.

It was also found that Samples No. 64 to No. 69 all have a high speed as the relative speed is as high as 100 to 120 and have less color remain as the color remain intensity is 0 to 0.01, but have so a poor inscribability that they can not be put into practical use.

It was further found that Samples No. 70 to No. 75 have a poorness in speed except for Samples No. 73 to 75 showing a speed as high as 120, have much color remain as the color density is 0.02 and 0.03 in respect of Samples No. 70 and No. 73, though having less color remain in respect of Samples Nos. 71, 72, 74 and 75 as the density is 0.01, and have so a poor inscribability in respect of all of Samples Nos. 70 to 75 that they can not be put into practical use.

Table - 7

Sample No.	Organic desensitizer	Amount of matting agent in emulsion layer (mg/m^2)	Amount of matting agent in protective layer (mg/m^2)	Relative speed	Color remain intensity	Pencil inscribability	Ink inscribability	Remarks
54	I-7	500	400	100	0.01	A	A	Present invention
55	II-3	500	400	100	0.01	A	A	Present invention
56	III-6	500	400	120	0.02	A	A	Present invention
57	IV-2	500	400	120	0.01	A	A	Present invention
58	V-3	500	400	90	0.02	A	A	Present invention
59	J	500	400	60	0.03	A	A	Outside Present invention
60	K	500	400	40	0.03	A	A	Outside present invention
61	L	500	400	120	0.04	A	A	Outside present invention
62	M	500	400	50	0.03	A	A	Outside Present invention
63	N	500	400	40	0.04	A	A	Outside present invention

Table - 7 (continued)

Sample No.	Organic desensi-tizer	Amount of matting agent in emulsion layer (mg/m^2)	Amount of matting agent in protec-tive layer (mg/m^2)	Relative speed	Color remain intensity	Pencil inscri-bability	Ink inscri-bability	Remarks
64	II-3	100	100	100	0.01	B	B	Outside present invention
65	II-3	100	---	100	0	C	C	Outside present invention
66	II-3	---	100	100	0	C	C	Outside present invention
67	IV-2	100	100	120	0.01	B	B	Outside present invention
68	IV-2	100	---	120	0	C	C	Outside present invention
69	IV-2	---	100	120	0	C	C	Outside present invention
70	J	100	100	60	0.02	B	B	Outside present invention
71	J	100	---	60	0.01	C	C	Outside present invention

Table - 7 (continued)

Sample No.	Organic desensi-tizer	Amount of matting agent in emulsion layer (mg/m^2)	Amount of matting agent in protec-tive layer (mg/m^2)	Relative speed	Color remain intensity	Pencil inscri-bability	Ink inscri-bability	Remarks
72	J	---	100	60	0.01	C	C	Outside present invention
73	L	100	100	120	0.03	B	B	Outside present invention
74	L	100	---	120	0.01	C	C	Outside present invention
73	L	---	100	120	0.01	C	C	Outside present invention

As described above, this invention can obtain a direct positive light-sensitive silver halide photographic material having superior inscribability and high whiteness.

Claims

1. A light-sensitive silver halide photographic material comprising a support, at least one silver halide emulsion layer provided on at least one side of said support, and a protective layer provided on said silver halide emulsion layer, wherein said silver halide emulsion layer is formed of two kinds of emulsions each having different average grain size of the grains contained therein, the average grain size in said emulsion containing grains of a smaller average grain size comprises from 40 to 70 % of the average grain size in said emulsion containing grains of a larger average grain size, and said silver halide emulsion layer has a silver amount of 4.5 g/m^2 or less, and further at least one layer of said silver halide emulsion layer and said protective layer contains 300 mg/m^2 or more of at least one kind of matting agent.

2. The light-sensitive silver halide photographic material according to Claim 1, wherein the two kinds of emulsions are monodispersed emulsions in which the grain size of the grains comprising 90 % of the whole in the number of silver halide grains has a distribution within ± 40 % of average grain size.

3. The light-sensitive silver halide photographic material according to Claim 1, wherein the average grain size of the grains of the larger average grain size is 0.3 to 0.5 μm.

4. The light-sensitive silver halide photographic material according to Claim 1, wherein the average grain size of the grains of the smaller average grain size is 0.15 to 0.35 μm.

5. The light-sensitive silver halide photographic material according to Claim 1, wherein the two kinds of emulsions are mixed in the ratio such that the mixing ratio of the emulsion using the silver halide grains of smaller grain size ranges from 40 to 60 %.

6. The light-sensitive silver halide photographic material according to Claim 1, wherein the matting agent is contained in both of the silver halide emulsion layer and the protective layer.

7. The light-sensitive silver halide photographic material according to Claim 6, wherein the silver halide emulsion layer contains rice starch and the protective layer contains silica.

8. The light-sensitive silver halide photographic material according to Claim 1, wherein the center-line average roughness of said light-sensitive material ranges from 0.15 to 0.8 μm, and the weight percentage of a matting agent having a particle diameter more than 6 μm is 5 % or less based on the whole matting agent.

9. A light-sensitive silver halide photographic material comprising a support and provided by coating thereon at least one hydrophilic colloid layer containing a matting agent, wherein the center-line average roughness of said light-sensitive material ranges from 0.15 to 0.8 μm, and the weight percentage of a matting agent having a particle diameter more than 6 μm is 5 % or less based on the whole matting agent.

10. The light-sensitive silver halide photographic material according to Claim 9, wherein the hydrophilic colloid layer containing the matting agent is a silver halide emulsion layer and a protective layer provided upper than the silver halide emulsion layer.

11. The light-sensitive silver halide photographic material according to Claim 9, wherein the surface tension of a coating solution for the hydrophilic colloid layer positioned at an uppermost layer is modified in the range of from 28 to 38 dyne/cm.

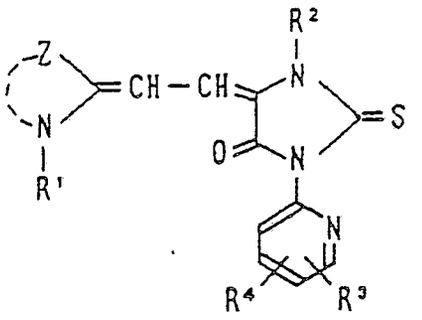
12. The light-sensitive silver halide photographic material according to Claim 9, wherein the center-line average roughness of the light-sensitive material ranges form 0.3 to 0.5 μm.

13. The light-sensitive silver halide photographic material according to Claim 9, wherein the weight percentage of a matting agent having a particle diameter more than 6 μm is 2 % or less based on the whole matting agent.

14. The light-sensitive silver halide photographic material according to Claim 9, wherein the hydrophilic colloid layer containing the matting agent is hardened with use of active halogen type hardening agents.

15. The light-sensitive silver halide photographic material according to Claim 9, wherein the light-sensitive silver halide photographic material further comprises a silver halide emulsion layer containing silver halide grains which comprise silver chlorobromide or silver chloroiodobromide containing 10 to 80 mol % of silver chloride, be subjected to spectral sensitization by use of a compound represented by Formula (VI) and the matting agent is contained in the hydrophilic colloid layer in an amount of 150 mg/m^2 or more.

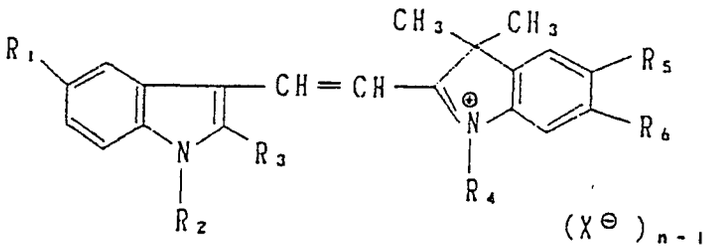
Formula (VI)



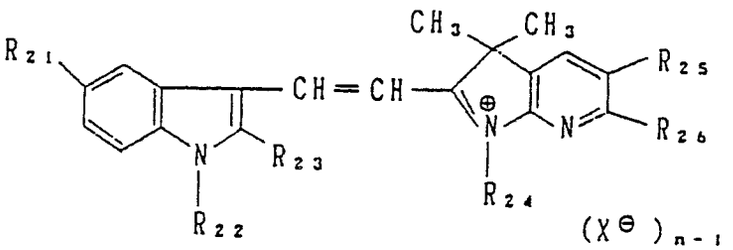
wherein Z represents a group of non-metal atoms necessary for completing an oxazole nucleus, a benzoxazole nucleus or a naphtoxazole nucleus; R^1 represents a substituted or unsubstituted alkyl group; R^2 represents an alkoxycarbonylalkyl group, a hydroxyalkyl group, a hydroxyalkoxyalkyl group, a carbamoylalkyl group, a hydroxyalkylthioalkyl group, a hydroxyphenyl group, a morpholinoalkyl group, a hydroxyalkylphenyl group, a phenyl group, an alkoxyalkyl group, or a substituent $-\langle CH_2 \rangle_n A$ or $-\langle CH_2 \rangle_n O-\langle CH_2 \rangle_n A$, where A represents a nitrile group, an alkylsulfonyl group, a sulfonamide group, an alkylsulfonylamino group or an alkoxy group having 1 to 8 carbon atoms, and n represents an integer of 1 to 4; and R^3 and R^4 may be the same or different, and each represent a hydrogen atom, an alkyl group, an alkoxy group, an alkylsulfonyl group, a sulfo group, a chlorine atom, a fluorine atom or a carboxyl group.

16. A light-sensitive silver halide photographic material for direct positives, comprising a support and provided thereon a direct positive silver halide emulsion layer containing silver halide grains applied with fog in the presence of a reduction fogging agent and a water-soluble gold compound, wherein at least 250 mg/m^2 of at least one kind of matting agent is contained and at least one of any compounds represented by Formulas (I), (II), (III), (IV) and (V) shown below is contained, in a photographic layer of the side on which said direct positive silver halide emulsion layer is provided;

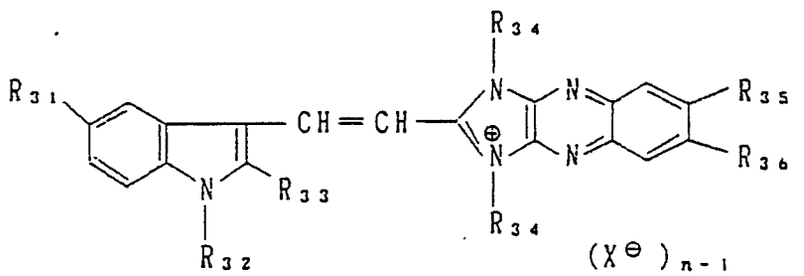
Formula (I)



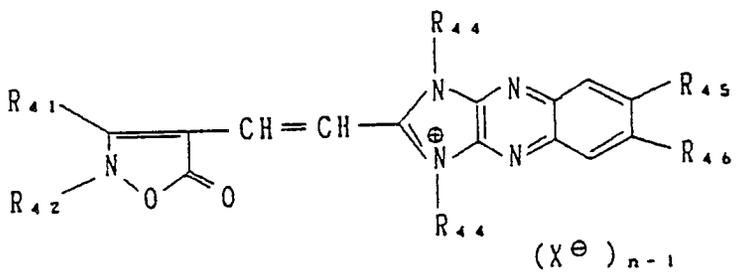
Formula (II)



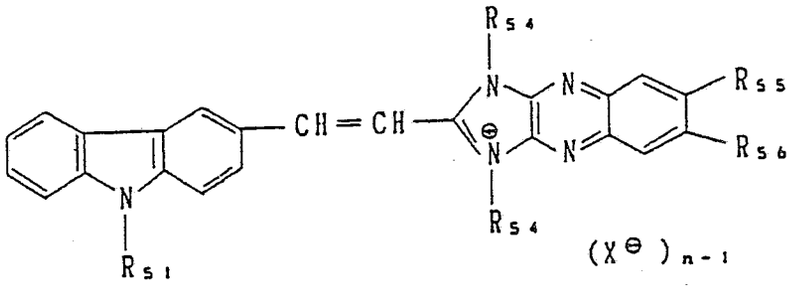
Formula (III)



Formula (IV)



Formula (V)



wherein, in Formulas (I), (II), (III), (IV) and (V), R_1, R_{21} and R_{31} each represent a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryloxy group or a nitro group; R_2, R_3, R_4, R_{22}, R_{23}, R_{24}, R_{32}, R_{33}, R_{34}, R_{44} and R_{54} each represent an alkyl group, alkenyl group, aryl group or aralkyl group which is unsubstituted or has a substituent; R_5, R_6, R_{25}, R_{26}, R_{35}, R_{36}, R_{45}, R_{46}, R_{55} and R_{56} each represent a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a thienyl group, an alkoxy group, a hydroxy group, a cyano group, an alkylsulfonyl group, an alkoxycarbonyl group, a phenylsulfonyl group, a trifluoromethyl group, a trifluoromethylsulfonyl group or a nitro group; R_{41} represents an aryl group; R_{42} represents an alkyl group; R_{51} an alkyl group which is unsubstituted or has a subsituent; $X^{\ominus}$ represents an anion; and n represents 1 or 2, provided that n is 1 when the compound forms an intramolecular salt.

17. The light-sensitive silver halide photographic material according to Claim 16, wherein the matting agent is contained in an amount of 400 mg/m^2 or more.

18. The light-sensitive silver halide photographic material according to Claim 16, wherein at least one of the compounds represented by Formulas (I), (II), (III), (IV) and (V) is the compound represented by Formula (IV).

19. The light-sensitive silver halide photographic material according to Claim 16, wherein the particle size of the matting agent is from 0.3 to 5 μm.

20. The light-sensitive silver halide photographic material according to Claim 16, wherein the silver halide grains comprise silver iodobromide comprising not more than 3 mol % of silver iodide.