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(54) Silver salt diffusion transfer method and film unit using the same

(57) A silver salt diffusion transfer method comprising imagewise exposing a light-sensitive material comprising a support having provided thereon at least (a) an image receiving layer containing a silver precipitant, (b) a peeling layer, (c) an antihalation layer having a light blocking function, and (d) a light-sensitive silver halide emulsion layer, overlaying the light-sensitive material with a processing sheet comprising a support having provided thereon a hydrophilic colloid layer containing a solvent for silver halide, developing the material by a silver salt diffusion transfer in the presence of a small amount of water, a developing agent, at least one of a base and a base precursor, and peeling off the peeling layer and the layers over the peeling layer from the image receiving layer to obtain a positive image on the image receiving layer. Furthermore, a film unit using the above-described silver salt diffusion transfer method is described.

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Description

FIELD OF THE INVENTION

The present invention relates to an image formation method by a silver salt diffusion transfer method, which is suitable for a monotone color image, e.g., as a film for printing plate, and a film for medical use. Also, the present invention relates to a film unit using the same.

BACKGROUND OF THE INVENTION

An image formation method by a diffusion transfer method using a silver salt such as a silver halide has been known. Specifically, for example, the method comprises processing an imagewise exposed light-sensitive silver halide emulsion with an aqueous alkaline solution containing a developing agent, a solvent for silver halide, and a film-forming agent (a thickener) to reduce the exposed silver halide grains to silver with the developing agent and, on the other hand, to convert the remaining unexposed silver halide grains to a transferring silver complex with the solvent for silver halide, diffusing and transferring the silver complex to a silver precipitant-containing layer (image receiving layer) through impregnation, where the silver salt is reduced with the developing agent by the aid of the silver precipitant to obtain development.

In the method, for example, a film unit used comprises a combination of a light-sensitive element comprising a support having provided thereon a silver halide emulsion layer, an image receiving element comprising a support having provided thereon an image receiving layer containing a silver precipitant, and a processing element comprising an aqueous active alkali solution containing a solvent for silver halide and a film forming agent.

In this film unit, the emulsion layer of the light-sensitive element is imagewise exposed, and then, while the light-sensitive element is laminated with the image receiving layer so that the emulsion layer is opposite to the image receiving layer of the image receiving element, the system is passed through a pair of rollers so that the viscose aqueous alkali solution in the processing element is expanded. After left standing the system for a prescribed period, a print where a given image has been formed can be obtained by peeling off the image receiving element from the light-sensitive element.

Furthermore, as a light-sensitive material using the silver salt diffusion transfer method JP-A-2-205845 (the term "JP-A" used herein means "unexamined published Japanese patent application") discloses a film unit having a construction where a peeling layer is provided between an image receiving layer and an emulsion layer for peeling off and removing the emulsion layer containing a processing composition.

However, the film unit described in JP-A-2-205845 is of highly danger in terms of handling because of using a viscose and highly alkaline liquid.

The film units having a similar peeling layer include a film unit having a peeling layer between an image receiving layer and a light-sensitive layer, the peeling layer having hydrophilic layers on the both sides thereof, and one of the hydrophilic layers containing a granular substance (described in U.S. Patent 4,499,174), a film unit having a light non-permeating layer between an image-receiving layer and a light-sensitive layer (described in U.S. Patent 3,730,718), and a film unit having two peeling layers (layer containing gelatine and layer containing a hydrophilic polymer and no gelatine) provided between an image receiving layer and a light-sensitive layer, and at least one layer of these two layers in adjacent to the peeling layer containing no pigment (described in JP-A-60-42755). However, all of them have the problem in operation because they use a viscose and highly alkaline processing liquid.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a novel film unit which can give a high density image in a safety manner within a short period of time using no developing solution and using substantially only water.

This and other objects of the present invention have been attained by a silver salt diffusion transfer method comprising

imagewise exposing a light-sensitive material comprising a support having provided thereon at least (a) an image receiving layer containing a silver precipitant, (b) a peeling layer, (c) an antihalation layer having a light blocking function, and (d) a light-sensitive silver halide emulsion layer,

overlaying the light-sensitive material with a processing sheet comprising a support having provided thereon a hydrophilic colloid layer containing a solvent for silver halide,

developing the material by a silver salt diffusion transfer in the presence of a small amount of water, a developing agent, at least one of a base and a base precursor, and

peeling off the peeling layer and the layers over the peeling layer from the image receiving layer to obtain a positive image on the image receiving layer.

DETAILED DESCRIPTION OF THE INVENTION

Preferred embodiments of the film unit will be described.

Light-sensitive Material:

(1) Protective layer:
    containing at least gelatine;
(2) Silver halide emulsion layer:
    containing at least one silver halide emulsion;
(3) Antihalation layer:
    containing at least one pigment having absorption toward the wavelength of exposure light source;
(4) Peeling layer:
    containing at least one peeling agent;
(5) Image receiving layer:
    containing at least one silver precipitant; and
(6) Support:
    a film or paper.

Processing Sheet:

(1) Sheet containing processing agent:
    containing at least one solvent for silver halide, a base precursor, and a developing agent, and containing at least gelatine as a binder; and
(2) Support:
    a film or paper.

Processing Liquid:

This is substantially water which contains no developing processing component, provided that a small amount of antibacterial agent may be contained for preventing water stain.

As the layer structure, the image receiving layer is provided on the support. The peeling layer is provided on the image receiving layer in adjacent thereto, and the protective layer may also be provided between the image receiving layer and the peeling layer for improving a scratch resistance of images after processing.

On the peeling layer are provided the antihalation layer, the silver halide emulsion layer, and an optionally protective layer in this order.

Examples of the silver precipitant (physical developing cores) contained in the image receiving layer include heavy metals, such as iron, lead, zinc, nickel, cadmium, tin, chromium, copper, and cobalt, and noble metals, such as gold, silver, platinum, and palladium. Other available silver precipitant include sulfides and selenides of heavy metals and noble metals, such as sulfides of mercury, copper, aluminum, zinc, cadmium, cobalt, nickel, silver, lead, antimony, bismuth, cerium, magnesium, gold, platinum, and palladium, and selenides of lead, zinc, antimony, and nickel. In particular, gold, platinum, palladium and sulfides thereof are preferred.

The amount of the silver precipitant cannot be limited because it greatly depends upon the kind and size of the core, but it is preferably 1 g/m^2 or less, and more preferably 0.1 g/m^2 or less. The lower limit thereof is preferably 0.0001 g/m^2.

For improving a color tone of the transfer silver image, a mercapto compound may be used. The mercapto compound may be added to the image receiving layer or may be diffused from any other layer or the processing sheet.

Preferred examples of mercapto compounds are compounds described in JP-A-49-120634, JP-B-56-44418 (the term "JP-B" used herein means an "examined Japanese patent publication"), British Patent 1276961, JP-B-56-21140, JP-A-59-231537, and JP-A-60-122939.

The peeling layer must keep contact between the image receiving element and the light-sensitive element before processing, and peel off clearly after processing. For example, preferred peeling agents therein are described in JP-A-47-8237, JP-A-56-65133, JP-A-59-220727, JP-A-59-229555, JP-B-49-4334, JP-B-49-4653, JP-B-45-24075, U.S. Patents 3,220,835, 4,359,518, 3,227,550, 2,759,825, 4,401,746, and 4,366,227. Typical examples thereof include water-soluble (or alkali-soluble) cellulose derivatives such as hydroxycellulose, cellulose acetate phthalate, plasticized cellulose, and carboxymethylcellulose. Various naturally originating macromolecule such as alginic acid, pectin, and gum arabic can also be mentioned. Various modified gelatine such as acetylated gelatine and phthalated gelatine can also be used. Moreover, water-soluble synthetic polymers such as polyvinyl alcohol, polyacrylate, polymethacrylate, butyl methacrylate and copolymers thereof can be used.

The peeling layer can be composed of a single layer or multi-layer. Examples thereof are described in JP-A-59-220727 and JP-A-60-60642.

The antihalation layer may be formed using known dyes and pigments. It is available for providing an antihalation layer against an infrared sensitivity layer to use an infrared absorber or carbon black. The use of carbon black for preventing halation is particularly available. As for typical embodiments, those described in JP-A-62-177542 can be used.

In the present invention, it is preferred that a basic metal compound sparingly soluble in water and a compound capable of reacting with the metal ion constructing the basic metal compound for forming a complex in the presence of water (hereinafter referred to as "complex-forming compound") as the base precursors are contained in the image-forming system, and the pH value of the system is increased by the reaction between these two compounds in the presence of water.

The term "image-forming system" as used herein means the region where the image forming reaction takes place. For example, it indicates the layer belonging to both the light-sensitive material and the processing sheet.

In the present invention, the water to be used as the medium can be supplied by a method of externally supplying water, a method in which a capsule containing water is previously incorporated and the capsule is ruptured by heating and any other method.

Preferably, in the method of the present invention, the developing agent and at least one of the base and the base precursor are incorporated in at least one of the light-sensitive material and the processing sheet at developing the material, and substantially only water is supplied to at least one of the light-sensitive material and the processing sheet before overlaying the material with the sheet.

Examples of the basic compounds sparingly soluble in water for use in the present invention include carbonates, phosphates, silicates, borates, aluminates, hydroxides, oxides, and double salts of these compounds such as basic salts having a solubility in water at 20°C of 0.5 or less (g of substance soluble in 100 g of water). The basic compounds are preferably those represented by formula: $T_m X_n$, wherein T represents a transition metal, such as Zn, Ni, Co, Fe, or Mn, or an alkaline earth metal, such as Ca, Mg, or Ba; X represents an ion or atom capable of forming a pair ion together with M described later under the description of the complex-forming compound and indicates an alkaline property, such as carbonate ion, phosphate ion, silicate ion, borate ion, aluminate ion, hydroxy ion, or oxygen atom; and m and n are integers to maintain the balance of atomic numbers of T and X, respectively.

Preferable examples thereof include calcium carbonate, barium carbonate, magnesium carbonate, zinc carbonate, strontium carbonate, magnesium calcium carbonate ($CaMg(CO_3)_2$), magnesium oxide, zinc oxide, lead oxide, cobalt oxide, zinc hydroxide, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, antimony hydroxide, lead hydroxide, iron hydroxide, bismuth hydroxide, manganese hydroxide, calcium phosphate, magnesium phosphate, magnesium borate, calcium silicate, magnesium silicate, zinc aluminate, calcium aluminate, basic zinc carbonate ($2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$), basic magnesium carbonate ($3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), basic nickel carbonate ($NiCO_3 \cdot 2Ni(OH)_2$), basic bismuth carbonate ($Bi_2(CO_3)O_2 \cdot H_2O$), basic cobalt carbonate ($2CoCO_3 \cdot 3Co(OH)_2$), and aluminum magnesium oxide. Of these compounds uncolored compounds are particularly preferred.

The complex-forming compound for use in the present invention forms a complex having a stable constant expressed as logK of 1 or more together with the metal ion of the above-mentioned basic compound sparingly soluble in water.

The complex-forming compounds are described, for example, by A.E. Martell and R.M. Smith, in *Critical Stability Constants,* Vol. 1-5, Plenum Press in detail.

Examples thereof include salts such as alkali metal salts, guanidine salts, amidine salts, or quaternary ammonium salts of aminocarboxylic acids, iminodiacetic acid and derivatives thereof, aniline carboxylic acids, pyridine carboxylic acids, aminophosphoric acids, carboxylic acids (mono-, di-, tri-, and tetra-carboxylic acids, and compounds having a substituent(s) such as phosphono, hydroxy, oxo, ester, amido, alkoxy, mercapto, alkylthio, and phosphono), hydroxamic acids, polyacrylates, or polyphosphoric acids.

Preferred examples include salts such as alkali metal salts, guanidine salts, amidine salts, or quaternary ammonium salts of picolinic acid, 2,6-pyridinedicarboxylic acid, 2,5-pyridinedicarboxylic acid, 4-dimethylaminopyridine-2,6-dicarboxylic acid, quinoline-2-carboxylic acid, 2-pyridylacetic acid, oxalic acid, citric acid, tartaric acid, isocitric acid, malic acid, gluconic acid, EDTA, NTA, CyDTA, hexametaphosphoric acid, tripolyphosphoric acid, tetraphosphoric acid, and polyacrylic acid.

Of these, aromatic heterocyclic compounds having at least $-CO_2M$ and having one nitrogen atom in the ring thereof are preferable. The ring may be monocyclic or condensed ring such as pyridine ring and quinoline ring. The position where $-CO_2M$ is bonded to the ring is particularly the α-position relative to the N-atom. Here, M represents an alkali metal, a guanidine, amidine or quaternary ammonium ion.

These basic metal compounds sparingly soluble in water and the complex-forming compounds are described in JP-A-64-13546.

In the present invention, it is required for the basic metal compound sparingly soluble in water and the complex-forming compound to be added to each layer in order to prevent the reaction before the development.

A more preferable embodiment is that where each of the basic metal compound sparingly soluble in water and the complex-forming compound is incorporated in at least one separate layer in the supports.

For example, the basic metal compound sparingly soluble in water is preferably incorporated in the light-sensitive material and the complex-forming compound is preferably incorporated in the processing sheet. When the basic metal compound sparingly soluble in water is added to the light-sensitive material, the layer to be added may be any of the emulsion layer, the antihalation layer, and the protective layer. Also, the metal compound may be added to each layer in divided from or added to one of the layer. The basic metal compound is preferably contained as the fine grains prepared by the method described in JP-A-59-174830, JP-A-53-102733, and the average grain size thereof is preferably 50 μm or less, and more preferably 5 μm or less.

In the present invention, the amount of the basic metal compound sparingly soluble in water or the complex-forming compound to be added to a layer on the support depends upon the types of the compounds, the grain size of the sparingly soluble metal compounds, the reaction rate of the complex formation, but is preferably 50% by weight or less, more preferably from 0.01 to 40% by weight, in terms of the weight of the applied film in each case. Moreover, the content of the complex-forming compound in the present invention in molar ratio relative to the content of the sparingly soluble metal compound is preferably 1/100 to 100 times, more preferably 1/10 to 20 times.

In the present invention, the light-sensitive silver halide emulsion layer is provided on the peeling layer, and the protective layer may be provided thereon.

As the silver halide, any of silver iodobromide, silver chlorobromoiodide, silver iodide, silver bromide, silver chloroiodide, silver chlorobromide, silver chloride may be used.

In the light-sensitive silver halide emulsion, general additives may be used. For example, chemical sensitizers such as gold compounds and sulfur compounds, reciprocity law failure improving agents such as platinum group compounds, post-age stopping agents such as tetrazaindene, anti-fogging agents such as heavy metal compounds and organic compounds can be mentioned.

Although the average size of the silver halide grain (taking the particle diameter in the case of the sphere grain or the particle resembling the sphere or the edge length in the case of the cube as the grain size, and expressed as the average based on the projected area) is not specifically restricted, but it is preferably 3 μm or less, preferably 2 μm or less, and more preferably from 0.1 to 1.0 μm.

The distribution of the grain size may be either narrow or wide.

The silver halide grain in the silver halide emulsion may be regular system such as cube and octagon or heterogeneous crystal system such as sphere and plate or combination thereof.

The silver halide emulsion may comprise one member or a mixture. The silver halide emulsion layer may be a single layer or a multi-layer comprising two or more layers.

The silver halide grains may be composed of the different phases on the internal layer and surface layer or comprise a uniform phase. It may also comprise grains in which a latent image is formed on the surface or is formed mainly on the interior of grain, or the latent image may not locally exist. Particularly, it is preferable that the latent image is mainly formed on the surface.

The thickness of the silver halide emulsion layer is from 0.5 to 8.0 μm, and preferably from 0.6 to 6.0 μm, and the application amount of the silver particle in terms of silver is from 0.1 to 3 g/m^2, and preferably from 0.2 to 2.0 g/m^2.

It is available to use gelatine as the protective colloid utilized in the preparation of the emulsion of the present invention and as binders for other hydrophilic layers, but other hydrophilic colloids may be used.

Examples thereof include proteins such as gelatine derivatives, graft polymer of gelatine and other polymers, albumin and casein; cellulose derivatives such as hydroxyethylcellulose, carboxymethylcellulose, cellulose sulfates; sodium alginate; saccharide derivatives such as starch derivatives; and various synthetic hydrophilic high molecule substances such as homopolymers or copolymers of polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole, or polyvinyl pyrazole.

As the gelatine, in addition to lime gelatine, acid-processed gelatine, and oxygen-processed gelatine which is described in *Bull Soc. Sci. Photo. Japan,* No. 16, p. 30 (1966) can be used, and a hydrolyzed product of gelatine or enzymatically decomposed gelatine can also be used.

As the photographically processing gelatine, lime-processed bone gelatine is used.

For the general description of the photographically processing gelatine and the contents of impurities are described in *Shashin Kogakuno Kiso* (*Foundation of Photographic Engineering*), p. 116-150, January 30, 1979, Corona Co. in detail.

The photographic emulsion for use in the present invention may be chemically sensitized. For the sensitization, for example, a sulfur sensitization, a reduction sensitization, a selenium sensitization, a noble metal sensitization described by H. Frieser in *Die Grundlagen der Photographishen Prozesse mit Silderhalogeniden*, p. 675-734, 1968, Akademische Verlagsgesellschaft, can be used singly or in combination of two or more thereof.

For example, in the sulfur sensitization, as a sulfur sensitizer, i.e., sulfur-containing compounds which can react with the active gelatine and silver, thiosulfates, allylthiocarbamide, thiourea, allylisocyanate, cystine, p-toluenesulfates, rhodan, mercapto compounds can be used. In addition, those described in U.S. Patents 1,574,944, 2,410,689, 2,278,947, 2,728,668 and 3,656,955 can also be used.

The amount of the sulfur sensitizer to be added can be varied in correspondingly wide range under various conditions, but it is usually preferred to be in the range of from approximately 10^{-7} to 10^{-2} per mol of silver.

In the gold sensitization, the gold sensitizer having an oxidation number of gold may be +1 or +3. Typically, chloroauric acid, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodideaurate, and tetracyanoauric acid can be used.

The amount of the gold sensitizer to be added can be varied in correspondingly wide range under various conditions, but it is usually preferred to be in the range of from approximately 10^{-9} to 10^{-2} per mol of silver. As described in JP-A-62-240951, it is particularly preferred that 80% or more of the gold sensitizer exists in the silver halide grain phase.

In the present invention, a selenium sensitizer can also be used such as aliphatic isoselenocyanates e.g., allylselenoisocyanate, selenoureas, selenoketones, selenoamides, and selenocarboxylic acids and esters thereof, selenophosphates, selenides such as diethylselenide and diethyldiselenide. Typical examples are described in U.S. Patents 1,574,944, 1,602,592, and 1,623,499.

The amount of the selenium sensitizer to be added can be varied in correspondingly wide range, but it is usually preferred to be in the range of from approximately $10^{-7}$to 10^{-2} per mol of silver.

In addition to the above-mentioned sulfur sensitizer, gold sensitizer, and selenium sensitizer, a reduction sensitization method using a reducing substance (for example, stannous salts, amines, hydrazine derivatives, formamidinesulfinic acid, silane coupling compounds), a noble metal sensitization using (e.g., in addition to gold complexes, complexes of the metals belonging to the Group VIII in the Periodic Table) can be used in combination.

The reduction sensitization is described in U.S. Patents 2,983,609, 2,419,974, and 4,054,458, and the noble sensitization is described in U.S. Patents 2,399,083 and 2,448,060, and British Patent 618,061.

Examples of the combination of the sensitizers include the gold sensitization with the sulfur sensitization and the gold sensitization with the selenium sensitization, but any other combination can be possible. In the case of the combination of the gold sensitization with the sulfur sensitization, although the ratio of these sensitizers to be used is varied by aging conditions, it is usual that the sulfur sensitizer is used in an amount of 1 to 1000 mol per mol of the gold sensitizer.

The period of adding the gold sensitizer in the combination of the gold sensitization with sulfur sensitization or the combination of the gold sensitization with selenium sensitization may be at the same time as the sulfur sensitizer or the selenium sensitizer or during or after the sulfur or selenium sensitization.

Particularly preferable sensitization for use in the present invention is the sulfur sensitization or the combination of the gold sensitization with selenium sensitization.

In the present invention, these chemical sensitizers are added to the silver halide photographic emulsion by the usual method. To be specific, in the case of water-soluble compounds, they are added as aqueous solutions, and in the case of organic solvent-soluble compounds, they are added as solutions in an organic solvent which is easily mixed with water such as methanol or ethanol.

Although the conditions during the chemical sensitization such as pH, pAg, and temperature are not specifically restricted, the pH is preferably kept at from 4 to 9, and more preferably from 5 to 8; and the pAg is preferably kept at 5 to 11, and more preferably from 7 to 10. The temperature is preferably from 40 to 90°C, and more preferably from 45 to 75°C.

In the light-sensitive emulsion layer, various compounds can be incorporated for preventing fogging at the stage for producing the photographic materials, during the storage of these materials or during the photographic processing or stabilizing the photographic performance. Examples thereof include azoles such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidalzoles, bromobenzimidalazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, nitrobenzotriazoles, and benzotriazoles. For example, 1-phenyl-5-mercaptotetrazole is a representative compound. Also, mercaptopyrimidines, mercaptotriazines, thioketo compounds such as oxazolinethione, and azaindenes such as triazaindenes, tetrazaindenes and pentazaindenes are preferred. Also, well-known anti-fogging agents and stabilizers such as benzosulfonic acids, benzosulfinic acids, benzosulfonic amides and the combination of α-lipoic acid or tetrazaindene compounds with imidazole compounds are used.

For the more detail specific examples and method for using them, for example, those described in U.S. Patents 3,954,474 and 3,982,947, and JP-B-52-28660 are applicable.

The light-sensitive element may contain developing agents such as hydrophobic compounds, e.g., pyrizolidone compounds and hydroxylamine compounds, and solvents for silver halide such as uracil compounds and thiosulfuric acid compounds.

The light-sensitive element used in the present invention can be spectrally sensitized. The sensitizing dye which can be preferably used are cyanine dyes, merocyanine dyes, composite cyanine dyes, composite merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxanol dyes. Particularly useful dyes are dyes belonging to cyanine dyes, merocyanine dyes, and composite merocyanine dyes. As described in JP-A-59-114533 and JP-A-61-163334, the combination of two or more sensitizing dyes can be used.

The light-sensitive element and processing sheet of the present invention may contain an inorganic or organic hardener. For example, chromium salts (e.g., chromium alum, chromium acetate), aldehydes (e.g., formaldehyde, glyoxal, glutaraldehyde), N-methylol compounds (e.g., dimethylol urea, methylol dimethylhydantoin), dioxane derivatives (e.g., 2,3-dihydroxydioxane), active vinyl compounds (e.g., 1,3,5-triacryloylhexahydro-s-triazine), mucohalogenic acids (e.g., mucochloric acid, mucophenoxychloric acid) can be used singly or in combination of two or thereof.

In the light-sensitive element and the colloid layer of the processing sheet of the present invention, application aids can be used. As the application aids, compounds described in the column of "coating aids" in *Research Disclosure,* Vol. 176, 17643, p. 26, December, 1978 and compounds described in JP-A-61-20035 can be used.

In the silver halide emulsion layer and other hydrophilic colloid layer of the light-sensitive element of the present invention, compounds such as polyalkylene oxides, or ether, ester, amine and other derivatives thereof, thioether compounds, thiomorpholines, quaternary ammonium compounds, urethane derivatives, urea derivatives, imidazole derivatives, 3-pyrazolidones may be incorporated for the purpose of increasing the sensitivity, enhancing the contrast, or accelerating the developing processing. Examples of such compounds which can be used are described in U.S. Patents 2,400,532, 2,423,549, 2,716,062, 3,617,280, 3,772,021, and 3,808,003.

In the silver halide emulsion layer and other hydrophilic colloid layers of the light-sensitive element and the processing sheet of the present invention, dispersion of water-insoluble or sparingly soluble synthetic polymers may be incorporated for improving dimensional salability. For example, polymers comprising one member or combination of alkyl (meth)acrylates, alkoxyalkyl (meth)acrylates, glycidyl (meth)acrylamides, (meth)acrylamides, vinyl esters (e.g., vinyl acetate), acrylonitrile, olefins, styrene, or combination thereof with acrylic acid, methacrylic acid, α,β-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylate, styrenesulfonic acid can be used.

On the silver halide emulsion layer used in the light-sensitive element of the present invention, a protective layer can be provided. The protective layer comprises a hydrophilic polymer such as gelatine, and can contain a matting agent or anti-slipping agent such as polymethyl methacrylate latex and silica as described in JP-A-61-47946 and JP-A-61-75338.

In the light-sensitive element of the present invention, dyes and UV-absorbers may be incorporated in the light-sensitive silver halide emulsion layer and other layers as filter dyes or for preventing irradiation.

In addition, antistatic agents, plasticizers and agents for preventing air fogging can be incorporated in the light-sensitive element of the present invention.

The developing agent (developer) may exist in the light-sensitive material and/or the processing sheet.

The developing agents which can be used are, for example, hydroquinone, tertiary butylhydroquinone, and benzene or naphthalene organic compounds having a hydroxyl group in its para- or ortho-position.

Moreover, reductinic acid as described in U.S. Patent 3,615,440 and α,β-endiol are preferably used. Hydroxylamine developing agents as described in U.S. Patents 3,287,125 and 3,293,034 are also preferably used.

As the developing agent a 1-aryl-3-pyrazolidinone compound or an alkyl-substituted p-aminophenol as described in JP-B-49-13580 may be used in combination with the above-mentioned hydroxylamine developing agent.

The amount of the developing agent used is from 0.5 to 3.0 mol, preferably from 0.6 to 2.0 mol, per mol of the silver application amount. More preferably, the developing agent is added to the processing sheet. The combination of two or more developing agents can be used. In particular, the combination of a hydroquinone developing agent with other developing agent is preferred.

The solvent for silver halide may exist in the light-sensitive material and/or the processing sheet. Of these, the processing sheet is preferred. Ring compounds described in U.S. Patents 2,857,274, 2,857,275, and 2,857,276 are suitable for the solvent. Of these, uracil and 6-methyluracil are preferred.

Moreover, alkali metal thiosulfates, particularly sodium and potassium salts, are preferred. The solvent can also be selected from disulfonylmethane compounds described in U.S. Patents 3,958,992, 3,976,647, 4,009,167, 4,032,538, 4,046,568, 4,047,954, 4,047,955, and 4,107,176 and JP-A-47-330, dihydroxy pyrimidine compounds having a thioether group described in U.S. Patents 4,126,459, 4,150,228, 4,211,559, and 4,211,562, and aminothioethers described in U.S. Patents 4,251,617 4,267,254, and 4,267,256.

The method for applying water which is the solvent to the photographic material include various methods such as a roller application method or wire-bar application method as described in JP-A-59-181353, a method for applying water to the photographic material using an absorbing part as described in JP-A-59-181354, a method for applying water by forming a bead between water-repellent rollers and the photographic material as described in JP-A-59-181348, as well as a dipping method, an extrusion method, a method in which water is injected as jet water from minute pores, and a method in which a water is applied in a manner of pressing a pod.

The term "water" as the solvent described above means to encompass not only so-called "purified water", but also water which has a meaning of conventionally used water in wide scale.

The amount of the water used is at least 0.1 time of the total weight of the applied films of the light-sensitive material and the processing sheet, and is preferably at least 0.1 time described above and equal to or less than the weight of the solvent corresponding to the maximum swelling volume of the total applied films (in particular, equal to or less than the amount of the weight of the solvent corresponding to the maximum swelling volume of the total applied films excluding the weight of the total applied films). The state of the film at the swelling is unstable, and depending upon the conditions, there is a fear that water is locally immersed. In order to avoid this, preferably the amount of water is equal to or less than the volume corresponding to the total weight of the applied films of the light-sensitive material and the processing sheet at the maximum swelling. Typically, the amount thereof is usually from 1 to 50 g, preferably from 2 to 35 g, and more preferably from 3 to 25 g, per m^2 of total area of the light-sensitive material and the processing sheet.

The light-sensitive material and the processing sheet are overlaid and contacted with each other. In the contact, the pressure conditions and pressure applying methods are described in, for example, JP-A-61-147244.

The present invention will now be described in greater detail by the following Examples and Comparative Examples, but it should be noted that the present invention is never restricted to these Examples. All weights, percents, ratios and the like are by weight unless otherwise indicated.

EXAMPLE

1. Production of Light-sensitive Material

A light-sensitive material was produced by providing the following layers on a PET (polyethylene terephthalate) support in this order.

(1) Image Receiving Layer

Preparation of Silver Precipitant Used in Image Receiving Layer (Palladium sulfide):

Liquid A:	Palladium chloride	3.3 g
	Concentrated Hydrochloric acid	20 mℓ

After they are dissolved, 500 mℓ of water was added.

Liquid B:	$Na_2S \cdot 9H_2O$	4.5 g
	Gelatine	140 g
	H_2O	2400 mℓ

After heating Liquid B at 70°C, Liquid A was added with stirring.

After the addition of Liquid A, the temperature was lowered to 40°C, and then the pH value was adjusted to 5.0 with NaOH.

An application solution to which 0.4 g of a vinylsulfonic hardener, $CH_2{=}CHSO_2CH_2CONH(CH_2)_2$-$NHCOCH_2SO_2CH{=}CH_2$, was added per 100 g of the above-mentioned silver precipitant, and was applied so that the amount of the silver precipitant was 2 g/m^2.

(2) Image Protective Layer

For protecting the image after the processing, gelatine was applied on the image receiving layer so that the application amount was 0.3 g/m^2.

(3) Peeling Layer

Hydroxyethylcellulose (HEC SP-500, produced by Daicel Chemical Industries, Ltd.) was applied so that the application amount was 0.15 g/m^2.

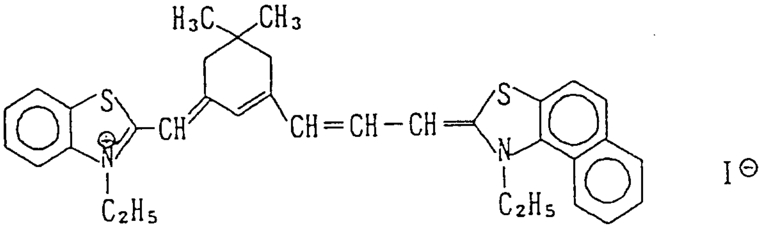
(4) Antihalation Layer

A dispersion of carbon black CB 10B (produced by Mitsubishi Chemical Corp.) in gelatine was prepared and was applied so that the amount of carbon black as solid content was 0.15 g/m^2 and that of gelatine was 0.3 g/m^2.

(5) Silver Halide Emulsion Layer

An aqueous 1.0 M silver nitrate solution and an aqueous silver halide solution containing 3×10^{-7} mol of $(NH_4)_3RhC\ell_6$ per mol of silver and 0.3 M of potassium bromide and 0.74 M of sodium chloride were added to an aqueous gelatine solution containing sodium chloride and 1,3-dimethyl-2-imidazolinethione with stirring by a double jet method at 45°C for 30 minutes to obtain silver chlorobromide grains having an average grain size of 0.28 μm and a silver chloride content of 70 mol%. Thereafter, they were washed with water according to the conventional method by a flocculation method, 40 g of gelatine was added thereto, pH value and pAg value were adjusted to 6.5 and 7.5, respectively, 5 mg of sodium thiosulfate and 8 mg of chloroauric acid were added per mol of silver, the mixture was heated at 60°C for 60 minutes and subjected to chemical sensitization, and 150 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added thereto. The resulting grains were silver chlorobromide cubic grains having an average grain size of 0.28 μm and a silver chloride content of 70 mol% (variation coefficient: 10%).

To this emulsion, 80 mg of the following sensitizing dye per mol of Ag, and 300 mg of disodium 4,4'-bis(4,6-dinaphthoxypyrimidin-2-ylamino)stilbenedisulfonic acid as a strong color sensitizer and 450 mg of 2,5-dimethyl-3-allylbenzothiazole iodide as a stabilizer were added per mol of Ag, and then the emulsion was subjected to red sensitization. Sensitizing Dye:



The emulsion described above was applied so that the amount of silver applied was 1.0 g/m^2, and that of gelatine was 0.8 g/m^2.

(6) Protective Layer

Gelatine was applied onto the uppermost layer of the light-sensitive material so that the amount was 1.4 g/m^2. In the protective layer, 1.3 g/m^2 of $Zn(OH)_2$ as a base precursor and 0.1 g/m^2 of polymethyl methacrylate grains as a matting agent were incorporated.

2. Production of Processing Sheet

Onto a PET film support were applied the following substances to produce a processing sheet.

Gelatine	7.6 g/m^2
Guanidinum picolinate	2.3 g/m^2
Sodium picolinate	2.1 g/m^2
Hypo	0.5 g/m^2
Hydroquinone	0.4 g/m^2
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.1 g/m^2
Vinylsulfonic hardener	0.15 g/m^2

The vinylsulfonic harder was the same as that used in the light-sensitive material.

3. Sensitometry Processing

The light-sensitive material thus obtained was subjected to scanning exposure (light irradiation amount: 50 erg/cm^2) using a semiconductor laser having luminescence at 780 nm from the side of the emulsion film.

On the processing sheet was applied 30 mℓ/m^2 of water by a wire bar, and immediately thereafter, it was laminated with an exposed light-sensitive material so that the film surface was brought into contact therewith.

Thereafter, the laminate was warmed at 40°C for 30 seconds, the processing sheet was peeled off. At this time, all of the layers such as the antihalation layer and the silver halide emulsion layer were peeled off from the side of the peeling layer to be shifted to the side of the processing sheet. A definite black positive image (D_{max} = 3.0) was produced on the light-sensitive material after the peeling.

As described above, a very excellent system which could produce an image having a good definition and a high density by applying a small amount of water without using any developing solution and any processing solution within a short period, and did not discharge any exhaust liquid was obtained.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver salt diffusion transfer method comprising

imagewise exposing a light-sensitive material comprising a support having provided thereon at least (a) an image receiving layer containing a silver precipitant, (b) a peeling layer, (c) an antihalation layer having a light blocking function, and (d) a light-sensitive silver halide emulsion layer,

overlaying the light-sensitive material with a processing sheet comprising a support having provided thereon a hydrophilic colloid layer containing a solvent for silver halide,

developing the material by a silver salt diffusion transfer in the presence of a small amount of water, a developing agent, at least one of a base and a base precursor, and

peeling off the peeling layer and the layers over the peeling layer from the image receiving layer to obtain a positive image on the image receiving layer.

2. The method as claimed in claim 1, wherein the developing agent and at least one of the base and the base precursor are incorporated in at least one of the light-sensitive material and the processing sheet at developing the material, and substantially only water is supplied to at least one of the light-sensitive material and the processing sheet before overlaying the material with the sheet.

3. The method as claimed in claim 1, wherein the base precursor is a combination of a basic metal compound sparingly soluble in water with a compound capable of reacting with the metal ion constructing the basic metal compound for forming a complex in the presence of water.

4. A film unit comprising a light-sensitive material and a processing sheet for a silver salt diffusion transfer method,

   wherein the method comprises,

   imagewise exposing a light-sensitive material comprising a support having provided thereon at least (a) an image receiving layer containing a silver precipitant, (b) a peeling layer, (c) an antihalation layer having a light blocking function, and (d) a light-sensitive silver halide emulsion layer,

   overlaying the light-sensitive material with a processing sheet comprising a support having provided thereon a hydrophilic colloid layer containing a solvent for silver halide,

   developing the material by a silver salt diffusion transfer in the presence of a small amount of water, a developing agent, at least one of a base and a base precursor, and

   peeling off the peeling layer and the layers over the peeling layer from the image receiving layer to obtain a positive image on the image receiving layer.

5. The film unit as claimed in claim 4, wherein the developing agent and at least one of the base and the base precursor are incorporated in at least one of the light-sensitive material and the processing sheet at developing the material, and substantially only water is supplied to at least one of the light-sensitive material and the processing sheet before overlaying the material with the sheet.

6. The film unit as claimed in claim 4, wherein the base precursor is a combination of a basic metal compound sparingly soluble in water with a compound capable of reacting with the metal ion constructing the basic metal compound for forming a complex in the presence of water.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 0493

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-3 826 653 (JACOBS J ET AL) 30 July 1974 ---		G03C8/06 G03C5/26
D,A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 167 (P-372), 12 July 1985 & JP-A-60 042755 (FUJI SHASHIN FILM KK), 7 March 1985, * abstract * ---		
A	EP-A-0 221 599 (AGFA GEVAERT NV) 13 May 1987 -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	8 May 1996	Philosoph, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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