⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 573 066 A1**

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **93109036.9**

㉒ Date of filing: **04.06.93**

(51) Int. Cl.^{5}: **G03C 1/485**, G03C 8/08

㉚ Priority: **05.06.92 JP 145664/92**
20.08.92 JP 221537/92

(43) Date of publication of application:
08.12.93 Bulletin 93/49

(84) Designated Contracting States:
DE FR GB

(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma
Minami-Ashigara-shi
Kanagawa(JP)

(72) Inventor: **Matsunaga, Atsushi, c/o Fuji Photo Film Co.,Ltd.**
210, Nakanuma
Minami Ashigara-shi, Kanagawa(JP)
Inventor: **Akiyama, Seiji, c/o Fuji Photo Film Co.,Ltd.**
210, Nakanuma
Minami Ashigara-shi, Kanagawa(JP)

(74) Representative: **Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner**
Maximilianstrasse 58
D-80538 München (DE)

(54) Internal latent image type direct positive silver halide emulsion and color diffusion transfer photographic film unit using the same.

(57) Disclosed is an internal latent image type direct positive silver halide emulsion, which is high in sensitivity and contrasty in low-density portions, comprising a dispersion medium containing at least one metal complex represented by the following general formula (I) and silver halide grains formed therein; and a color diffusion transfer photographic film unit containing the internal latent image type direct positive silver halide emulsion:

$[M(CN)_6]^{n-}$ (I)

wherein M represents Cr, Mn, Co, Ir, Ru, Rh, Re or Os; and n is 3 or 4.

Rank Xerox (UK) Business Services
(3.10/3.6/3.3.1)

FIELD OF THE INVENTION

The present invention relates to an internal latent image type direct positive silver halide emulsion and a color diffusion transfer photographic film unit using the same.

BACKGROUND OF THE INVENTION

Photographic methods using silver halides are excellent in sensitivity and gradation characteristics, as compared with other photographic methods such as electrophotographic methods and diazo photographic methods, and have previously been widely used. Of these methods, methods of forming direct positive images are well known, which are methods for obtaining positive images by giving uniform exposure or using nucleating agents, when internal latent image type direct positive silver halide photographic emulsions are used and silver halide grains in which internal latent images are formed are developed with surface developing solutions (developing solutions which leave image forming sites in the silver halide grains without substantial development), as disclosed, for example, in U.S. Patent 3,761,276 and JP-B-60-55821 (the term "JP-B" as used herein means an "examined Japanese patent publication").

U.S. Patent 2,448,060 discloses that silver halide emulsions can be sensitized by addition of transition metal compounds in some manufacturing stages of the silver halide emulsions. The differences in photographic effects of the transition metal compounds in the silver halide emulsions between the case of adding the transition metal compounds during formation of silver halide grains and the case of adding the compounds after precipitation of the silver halide grains are known to be significant. The transition metal compounds in the former case are called metal dopants. These are described in Research Disclosure, vol. 176, No. 17643 (December, 1978).

For the internal latent image type direct positive silver halide photographic emulsions, low density portions on reversal characteristic curves are known to be enhanced by doping metal ions. This is described, for example, in U.S. Patents 3,271,157, 3,367,778, 3,447,927, 3,531,291, 3,761,267, 3,761,276, 3,850,637, 3,923,513, 4,035,185, 4,444,874, 4,444,865, 4,433,047 and 4,395,478, and British Patents 1,151,782 and 1,529,011. However, the disadvantages have been known that the low density portions on the reversal characteristic curves are not enhanced to a sufficiently satisfactory level by doping with metal ions, and that the maximum density is lowered. In these patents, no ligands of the metal ions are specified and no effects thereof are described.

On the other hand, silver halide emulsions excellent in stability with time of sensitivity and gradation and improved in low intensity of illumination failure in the presence of six-coordinate rhenium, ruthenium, osmium and iridium metal complexes each having at least 4 cyan ligands are described in European Patents 0336425 and 0336426, JP-A-2-20853 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and JP-A-2-20854. Here, the six-coordinate transition metal complex is recognized to be contained in a space of a vacant lattice point of a single halide ion in a crystalline structure, which is different from the conventional known view that the transition metal is surrounded as a single ion or atom by silver halide grains. In these patents, however, the kinds of transition metals are restricted to rhenium, ruthenium, osmium and iridium, and chromium, manganese, cobalt and rhodium are not described. Also, no internal latent image type direct positive silver halide emulsion is described.

In addition, JP-A-2-259749 discloses that direct positive silver halide photographic materials high in maximum density, low in minimum density and reduced in development of re-reversal negative images on high illuminance exposure are obtained by use of internal latent image type direct positive silver halide emulsions particularly containing hexacyano iron complexes of iron complexes, but the central metal is restricted to iron. It does not disclose the use of chromium, manganese, cobalt, iridium, ruthenium, rhodium, rhenium and osmium.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an internal latent image type direct positive silver halide emulsion which is high in sensitivity and contrasty in a low-density portion on a reversal characteristic curve.

Another object of the present invention is to provide a color diffusion transfer photographic film unit using such a silver halide emulsion.

These and other objects of the present invention are attained by an internal latent image type direct positive silver halide emulsion comprising a dispersion medium containing at least one metal complex represented by the following formula (I) and silver halide grains formed in the dispresion medium:

$[M(CN)_6]^{n-}$ (I)

wherein M represents Cr, Mn, Co, Ir, Ru, Rh, Re or Os; and n is 3 or 4.

The internal latent image type direct positive silver halide emulsion preferably includes tabular silver halide grains having a mean grain diameter of 0.3 μm or more and a mean grain diameter/mean grain thickness ratio of 2 or more in an amount of 50% or more of the total silver halide grains.

In another aspect of the present invention, this is provided a color diffusion transfer photographic film unit comprising (a) a light-sensitive sheet having an image receiving layer, a white reflective layer, a light shielding layer and at least one silver halide emulsion layer combined with at least one dye image forming substance, which are formed on a transparent support, (b) a transparent cover sheet having at least a neutralization layer and a neutralization timing layer, which are formed on a transparent support, and (c) a light shielding alkali processing composition spread between the above-described light-sensitive sheet and the above-described transparent cover sheet, and wherein at least one silver halide emulsion layer in the light-sensitive sheet contains the internal latent image type direct positive silver halide emulsion of the present invention described above.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be illustrated in greater detail below.

In formula (I), preferred are Ir and Ru as M.

As pair ions of metal hexacyanide complexes used in the present invention, ions of alkali metals such as potassium and sodium are preferably employed.

The amount of the metal hexacyanide complexes used in the present invention is preferably from 1.0×10^{-10} to 1.0×10^{-4} mol per mol of silver halide, and more preferably form 1.0×10^{-8} to 1.0×10^{-6} mol per mol of silver halide.

The metal hexacyanide complexes used in the present invention may be added to the dispersion medium during preparation of the silver halide grains, namely, at any stage before and after nucleation, growth, physical ripening and chemical sensitization. They are added preferably during growth of grains. When these metal hexacyanide complexes are added during preparation of the silver halide grains, the pAg is preferably 6 or more, more preferably 7 to 10, and most preferably 7 to 8.

It is preferred that the metal hexacyanide complexes used in the present invention are dissolved in water or appropriate solvents in advance, and are added to the dispersion medium. Aqueous solutions of hydrogen halides (for example, HCl and HBr) or alkali halides (for example, KCl, NaCl, KBr and NaBr) may be added to stabilize the solutions. Further, acids or alkalis may be added if necessary.

The metal hexacyanide complexes used in the present invention are preferably directly added to reaction solutions during formation of the silver halide grains, or added to aqueous solutions of halides for forming the silver halide grains, aqueous solution of silver salts or other solutions to form the grains. Furthermore, various addition processes are preferably combined.

When the metal hexacyanide complexes used in the present invention are added, the hydrogen ion concentration (pH) of the reaction solutions is preferably 1 or more, and more preferably 3 or more.

The metal hexacyanide complexes used in the present invention can be used in combination with other metals. Examples of the other metals which can be used include Mg, Ca, Sr, Ba, Al, Sc, Y, La, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ru, Rh, Pd, Re, Os, Pt, Au, Cd, Hg, Tl, In, Sn, Pb and Bi.

These metals can be added as long as they are in salt forms which can be dissolved during formation of the grains, such as ammonium salts, acetates, nitrates, sulfates, phosphates, hydroxides, six-coordinate complexes and four-coordinate complexes.

The present invention is applied to internal latent image type direct positive silver halide emulsions.

The internal latent image type direct positive silver halide emulsion (hereinafter occasionally briefly referred to as an internal latent image type silver halide emulsion) is a silver halide emulsion which forms a latent image mainly in the interior of the silver halide grain, when subjected to image exposure. Specifically, the internal latent image type silver halide emulsion is defined as an emulsion in which the maximum density obtained when a definite amount of the silver halide emulsion is applied to a transparent support, exposed for a fixed time of 0.01 to 1 second, and developed in the following developing solution A ("internal type" developing solution) at 20°C for 5 minutes is at least 5 times as high as the maximum density obtained when a second sample exposed in a similar manner to that described above is developed in the following developing solution B ("surface type" developing solution) at 20°C for 5 minutes.

The maximum density is measured according to a conventional method for measuring photographic density.

Developing Solution A	
N-Methyl-p-aminophenol Sulfite	2 g
Sodium Sulfite (Anhydrous)	90 g
Hydroquinone	8 g
Sodium Carbonate (Monohydrate)	52.5 g
Potassium Bromide	5 g
Potassium Iodide	0.5 g
Water to make	1 liter

Developing Solution B	
N-Methyl-p-aminophenol Sulfite	2.5 g
1-Ascorbic Acid	10 g
Potassium Metanitrate	35 g
Potassium Bromide	1 g
Water to make	1 liter

Examples of the internal latent image type silver halide emulsions include conversion type silver halide emulsions as described in U.S. Patents 2,456,953 and 2,592,250, laminated structure type silver halide emulsions in which first phases are different from second phases in silver halide composition as described in U.S. Patent 3,935,014, and core/shell type silver halide emulsions in which core grains doped with metal ions or subjected to chemical sensitization are covered with shells. Of these emulsions, the core/shell type silver halide emulsions are preferably used as the internal latent image type silver halide emulsions in the present invention. Examples thereof include emulsions described in U.S. Patents 3,206,313, 3,317,322, 3,761,266, 3,761,276, 3,850,637, 3,923,513, 4,035,185, 4,184,878, 4,395,478 and 4,504,570, JP-A-57-136641, JP-A-61-3137, JP-A-61-299155 and JP-A-62-208241.

In order to obtain direct positive images, after the above-described internal latent image type silver halide emulsion is subjected to image exposure, second uniform image exposure is given to the whole surface of the exposed layer before or during development processing ("light fogging process", for example, British Patent 1151363), or development processing is carried out in the presence of a nucleating agent ("chemical fogging process", for example, Research Disclosure, vol. 151, No. 15162, pages 76 to 78 (November, 1976)). In the present invention, the "chemical fogging process" is preferably used to obtain the direct positive images. Nucleating agents which can be used in the present invention will be described later.

As described above, in order to obtain the direct positive images using the internal latent image type silver halide emulsion, a second uniform image exposure is given to the whole surface of the exposed layer before or during development processing, or development processing is carried out in the presence of the nucleating agent, after image exposure.

Nucleating agents which can be used in the present invention include hydrazines described in U.S. Patents 2,563,785 and 2,588,982; hydrazides and hydrazones described in U.S. Patent 3,227,552; heterocyclic quaternary salt compounds described in British Patent 1283835, JP-A-52-69613, JP-A-55-138742, JP-A-60-11837, JP-A-62-210451, JP-A-62-291637, U.S. Patents 3,615,515, 3,719,494, 3,734,738, 4,094,683, 4,115,122, 4,306,016 and 4,471,044; sensitizing dyes having substituents with nucleating action in dye molecules described in U.S. Patent 3,718,470; thiourea bond type acylhydrazine compounds described in U.S. Patents 4,030,925, 4,031,127, 4,245,037, 4,255,511, 4,266,013 and 4,276,364, and British Patent 2012443; and acylhydrazine compounds having thioamide rings or heterocyclic groups such as triazole and tetrazole as adsorbing groups described in U.S. Patents 4,080,270 and 4,278,748, and British Patent 2011391.

It is desirable that the nucleating agent is used in such an amount that a sufficient maximum density is given when the internal latent image type emulsion is developed with a surface developing solution. In practice, the appropriate amount of the nucleating agents contained can vary over a wide range, depending on the characteristics of the silver halide emulsions used, the chemical structure of the nucleating agents and developing conditions. However, the actually useful amount is generally 0.1 mg to 5 g per mol of silver contained in the internal latent image type silver halide emulsion, and the preferred amount is 0.5 mg to 2 g per mol of silver. When the nucleating agent is added to a hydrophilic colloidal layer adjacent to the emulsion layer, it may be added in an amount as described above, based on the amount of silver contained in the internal latent image type emulsion having the same area as the adjacent layer.

In the present invention, various forms of silver halide grains can be used. Examples thereof include regular crystal forms such as cubic, octahedral, tetradecahedral and rhombic dodecahedral forms; irregular crystal forms such as spherical and tabular forms; forms having high-dimensional faces ((hkl) faces); and mixtures of these forms. The grains having the high-dimensional faces can be referred to Journal of Imaging Science, vol. 30, pages 247 to 254 (1986).

The silver halide grains used in the present invention may be either normal crystals free from twin planes or crystals such as explained in The Basis of Photographic Industry, Silver Salt Photography, page 163, edited by Nippon Shashin Gakkai (published by Corona, Co.) such as a single twin containing one twin plane, parallel multiple twins containing two or more parallel twin planes and non-parallel multiple twins containing two or more non-parallel twin planes. These crystals can be selected for use according to their purpose.

Further, U.S. Patent 4,865,964 discloses an example in which grains having different forms are mixed with each other. This process can be selected if necessary.

In the case of normal crystals, the grains having the cubic form comprising a (100) face, the octahedral form comprising a (111) face, and the dodecahedral form comprising a (110) face disclosed in JP-B-55-42737 and JP-A-60-222842 can be used. Furthermore, as reported in Journal of Imaging Science, vol. 30, page 247 (1986), grains having (hll) faces represented by (211), (hhl) faces represented by (331), (hk0) faces represented by (210) and (hkl) faces represented by (321) can also be selected for use according to their purpose although it is necessary to employ suitable techniques for their preparation.

Grains in which two or more faces coexist, such as a grain having the tetradecahedral form in which the (110) and (111) faces coexist in one grain, a grain in which the (100) and (110) faces coexist and a grain in which the (111) and (110) faces coexist, can also be selected for use according to their purpose.

Examples of the silver halides used for these grains include silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide, silver chloroiodide and silver chloride. Silver bromide and silver iodobromide are preferably used among others. In addition, other silver salts such as silver thiocyanate, silver cyanate, silver sulfide, silver selenide, silver carbonate, silver phosphate and silver salts of organic acids may be present as additional grains or part of the silver halide grains.

The silver halide grain may have different phases or uniform phases in the interior and the exterior layer thereof. The silver halide composition of the grain may be uniform or different in the interior and the exterior thereof, or may have a layered structure (JP-A-57-154232, JP-A-58-108533, JP-A-58-248469, JP-A-59-48755, JP-A-59-52237, U.S. Patents 3,505,068, 4,433,048 and 4,444,877, European Patent 100984 and British Patent 1027146). Further, the grain may have a dislocation line.

When the silver halide grains are used in which two or more silver halides exist as mixed crystals or with a structure, it is important to control the halogen composition distribution between the grains. A method for measuring the halogen composition distribution between the grains is described in JP-A-60-254032. It is a desirable characteristic that the halogen distribution between the grains is uniform. In particular, a highly uniform emulsion having a coefficient of variation of 20% or less is preferred. Another preferred embodiment is an emulsion having a desired correlation between the grain size and the halogen composition.

It is important to control the halogen composition in the vicinity of the surface of the grain. The increased content of silver iodide or silver chloride in the vicinity of the surface changes the adsorption of a dye and the rate of development, so that this can be selected according to its purpose. When the halogen composition is changed in the vicinity of the surface, this can be accomplished either by encapsulating the entirety of the grain structure with a composition which has a halogen composition different from the interior, or by adhering a composition which has a halogen composition different from the interior to only part of the grain structure. For example, with respect to the grain in the tetradecahedral form comprising the (110) and (111) faces, only the halogen composition of one face can be changed, or the halogen composition of one of the side faces of a main plane of the tabular grain can be changed.

The grain size of the emulsions used in the present invention can be evaluated by the diameter of a circle equivalent to a projected area determined by use of an electron microscope, the diameter of a sphere equivalent to a grain volume calculated from the projected area and a grain thickness, or the diameter of a sphere equivalent to a volume determined by the coulter counter method. The grains are selected for use from ultra-fine grains having a grain size of 0.05 μm or less to coarse grains having a grain size of more than 10 μm, calculated as the diameter of an enhanced sphere. Grains having a grain size of 0.1 to 3 μm are preferred.

The grain size distribution of the silver halide grains is arbitrary, but may be monodisperse. The term "monodisperse" is defined as a dispersion system in which 95% of the total weight or the total number of the silver halide grains contained therein fall within the range of ±60% of a number mean grain size, preferably within the range of ±40%, wherein the number mean grain size is a number mean diameter of the diameters of the projected areas of the silver halide grains.

Monodisperse emulsions are described in U.S. Patents 3,574,628 and 3,655,394, and British Patent 1,413,748. These monodisperse emulsions may be mixed to form a mixture of monodisperse emulsions which can be used.

Thus, two or more silver halides different in crystal habit, halogen composition, grain size and grain size distribution can be used in combination, and can be used in each different emulsion layer and/or the same emulsion layer.

In the present invention, a more preferred effect is obtained when tabular silver halide grains are used. Methods for producing the tabular silver halide grains and techniques for using them are already disclosed in Cleve, Photography Theory and Practice, page 131 (1930), Gutoff, Photographic Science and Engineering, vol. 14, pages 248 to 257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048, 4,439,520, 4,414,306 and 4,459,353, British Patent 2,112,157, JP-A-59-99433 and JP-A-62-209445. In particular, the tabular internal latent image type direct positive silver halide emulsions are described in detail in U.S. Patents 4,395,478, 4,504,570 and 4,996,137, JP-B-64-8327 and JP-A-1-131547. These tabular internal latent image type direct positive silver halide emulsions are excellent in that they give direct positive images which are sufficient in sharpness, rapid in development progress and reduced in dependence on development temperature.

As the forms of the tabular grains, triangular, hexagonal and circular forms can be selected. A regular hexagon with six sides approximately equal to one another as described in U.S. Patent 4,996,137 is a preferred form.

In the case of the tabular grains, a dislocation line can be observed with a transmission electron microscope. Grains containing no dislocation line at all, grains each containing several dislocation lines, or grains each containing many dislocation lines can be selected according to their purpose. Further, grains can be selected in each of which a dislocation line is linearly introduced to a specified direction of crystal orientation of the grain or curvedly introduced. Furthermore, grains can be selected in each of which a dislocation line or dislocation lines are introduced over the entire grain or into only a specified site of the grain, for example, a fringe portion of the grain. The dislocation line can be introduced not only in the case of the tabular grains, but also in the case of normal crystal grains or indeterminate grains represented by pubble-like grains.

For example, JP-A-63-220238 and JP-A-1-201649 disclose tabular silver halide grains into which dislocation lines are intentionally introduced.

In the tabular grains, the ratio of the mean grain diameter to the mean grain thickness (hereinafter referred to as grain diameter/thickness) is preferably 2 or more, more preferably 3 to 12, and most preferably 5 to 8, wherein the mean grain diameter in the tabular silver halide grains means a mean value of the diameters of circles equivalent to two parallel or approximately parallel main planes opposite to each other (the diameters of circles having the same projected areas as those of the main planes), and the mean grain thickness means a mean value of the distances between the main planes.

The grain diameter/thickness is obtained by averaging the grain diameter/thickness values of the whole tabular grains, but can also be determined by an easier method, namely, by obtaining the ratio of the mean diameter of the whole tabular grains to the mean thickness of the whole tabular grains.

The mean grain diameter of the tabular grains (circle equivalent) is 0.3 μm or more, preferably 0.3 to 10 μm, more preferably 0.5 to 5.0 μm, and most preferably 0.5 to 3.0 μm.

The grain thickness is less than 1.0 μm, and preferably 0.05 to 0.5 μm.

Further, emulsions highly uniform in thickness, in which the grain thickness has a coefficient of variation of 30% or less, are preferably used. Furthermore, grains described in JP-A-63-163451, in which the thickness of the grains and the distance between twin planes are specified, are also preferred.

In the present invention, the above-described tabular grains account for 50% or more of the whole grains in an emulsion containing them, preferably 70% or more, and more preferably 90% or more.

The grain diameter and the grain thickness of the tabular grains can be measured according to an electron micrograph of the grains, as described in U.S. Patent 4,434,226.

Moreover, in the present invention, the tabular grains are preferably monodisperse. The structure of the monodisperse tabular grains and methods for producing them are described, for example, in JP-A-63-151618.

The silver halide emulsions used in the present invention may be subjected to treatment for rounding grains as described in European Patents 96727 and 64412, or to surface modification as disclosed in West German Patent 2306447 and JP-A-60-221320.

The surface of the grain is generally flat. It is however preferred in some cases that unevenness is intentionally formed on the surface. Examples thereof include methods for perforating a part of a crystal such as a top or a center of a plane which are described in JP-A-58-106532 and JP-A-60-221320, and a ruffle grain described in U.S. Patent 4,643,966.

The silver halide emulsions used in the present invention can be prepared, for example, according to the methods described in Research Disclosure (RD), vol. 176, No. 17643, pages 22 and 23, "I. Emulsion Preparation and Types" (December, 1978), ibid., vol. 187, No. 18716, page 648 (November, 1979), ibid., vol. 307, No. 307105, pages 863 to 865 (November, 1989), P. Glafkides, Chimie et Physique Photographique (Paul Montel, 1967), G.F. Duffin, Photographic Emulsion Chemistry (Focal Press, 1966) and V.L. Zelikman et al., Making and Coating Photographic Emulsion (Focal Press, 1964). Namely, any of an acid process, a neutral process and an ammonia process may be used. A soluble silver salt and a soluble halogen salt may be reacted with each other by using any of a single jet process, a double jet process and a combination thereof. A so-called reverse mixing process in which grains are formed in the presence of excess silver ions can also be used. As a type of double jet process, there can also be used a process for maintaining the pAg in a liquid phase constant, in which a silver halide is formed, namely a so-called controlled double jet process. According to this process, a silver halide emulsion having a regular crystal form and an approximately uniform grain size can be obtained.

Further, the tabular grains can be easily prepared by methods described in Gutoff, Photographic Science and Engineering, vol. 14, pages 248 to 257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520 and British Patent 2,112,157.

The silver halide emulsions comprising the above-described regular grains are obtained by controlling the pAg and the pH during formation of the grains. Details thereof are described, for example, in Photographic Science and Engineering, vol. 6, pages 159 to 165 (1962), Journal of Photographic Science, vol. 12, pages 242 to 251 (1964), U.S. Patent 3,655,394 and British Patent 1413748.

The monodisperse emulsions are described in JP-A-48-8600, JP-A-51-39027, JP-A-51-83097, JP-A-53-137133, JP-A-54-48521, JP-A-54-99419, JP-A-58-37635, JP-A-58-49938, JP-B-47-11386, U.S. Patent 3,655,394 and British Patent 1413748.

In some cases, the methods of adding silver halide grains previously precipitated to a reaction vessel for preparation of emulsions (U.S. Patents 4,334,012, 4,301,241 and 4,150,994) are preferred. These grains are used as seed crystals, and also are effectively provided as silver halides for growth. In the latter case, an emulsion having a small grain size is preferably added. A method for addition can be selected for use from addition of the total amount at once, addition of several divided portions and continuous addition. Further, in order to modify the surface, it is also effective to add grains of various silver halides in some cases.

Methods for converting most or just a part of the halogen composition of silver halide grains by the halogen conversion process are disclosed in U.S. Patents 3,477,852 and 4,142,900, European Patents 273429 and 273430, and West German Patent Publication (OLS) No. 3819241, and are effective grain forming methods. A solution of soluble halogen or silver halide grains can be added to convert to a more insoluble silver salt. These methods can be selected from conversion at once, several divided conversion and continuous conversion.

In addition to methods for allowing grains to grow by adding a soluble silver salt and a halogen salt at a constant concentration at a constant flow rate, methods for forming grains at varied concentrations or at varied flow rates as described in British Patent 1469480, U.S. Patents 3,650,757 and 4,242,455 are preferred. The amount of the silver halide to be supplied can be varied as a linear function, a secondary function or a more complicated function of addition time by increasing the concentration or the flow rate. In some cases, it is also preferred that the amount of the silver halide is decreased if necessary. Furthermore, when a plurality of soluble silver salts or a plurality of soluble halogen salts different in solution composition are added, it is effective that they are added so that one is increased and the other is decreased.

A mixer used when solutions of a soluble halogen salt and a soluble silver salt are reacted with each other can be selected for use from ones described in U.S. Patents 2,996,287, 3,342,605, 3,415,650 and 3,785,777, West German Patent Publication (OLS) Nos. 2556885 and 2555364.

For the purpose of promoting ripening, solvents for silver halides are useful. For example, the presence of an excess amount of halogen ions in a reaction vessel is known to promote ripening. Further, other ripening agents can also be used. The ripening agent can be added in the whole amount to a dispersion medium in a reaction vessel before addition of a silver salt(s) and a halide(s), or can also be introduced into the reaction vessel together with addition of the silver salt(s), the halide(s) and a deflocculant. As another modified embodiment, the ripening agent can also be independently introduced in the stage of addison of the halide(s) and the silver salt(s).

In addition to the halogen ions, ripening agents which can be used include ammonia; amine compounds; and thiocyanates such as alkaline metal thiocyanates, particularly sodium and potassium thiocyanates, and ammonium thiocyanate. The use of the thiocyanate ripening agents is taught in U.S. Patents 2,222,264, 2,448,534 and 3,320,069. Examples of the other ripening agents include organic thioether compounds (such as compounds described in U.S. Patents 3,271,157, 3,574,628, 3,737,313, 3,021,215, 3,057,724, 3,038,805, 4,276,374, 4,297,439, 3,704,130 and 4,782,013, and JP-A-57-104926), thione compounds (such as four-substituted thiourea described in JP-A-53-82408, JP-A-55-77737 and U.S. Patent 4,221,863, and compounds described in JP-A-53-144319), mercapto compounds which can promote growth of silver halide grains (such as compounds described in JP-A-57-202531), and amine compounds (such as compounds described in JP-A-54-100717).

In manufacturing the emulsions containing the tabular grains, the methods of increasing the rates, the amounts and the concentrations of silver salt solutions (for example, an aqueous solution of $AgNO_3$) and halide solutions (for example, an aqueous solution of KBr) are preferably used to speed growth of the grains. For these methods, reference can be made to the descriptions of British Patent 1335925, U.S. Patents 3,672,900, 3,650,757 and 4,242,445, JP-A-55-142329 and JP-A-55-158124. In order to promote the above-described ripening, the above-described solvents for silver halides are effective.

In some cases, the method of adding chalcogenide compounds as described in U.S. Patent 3,772,031 during growth of the emulsions is also effective. Besides S, Se and Te, cyanides, thiocyanides, selenocyanides, carbonates, phosphates and acetates may be allowed to be present. These are described in U.S. Patents 2,448,060, 2,628,167, 3,737,313 and 3,772,031, and Research Disclosure, vol. 134, No. 13452 (June, 1975).

It is preferred that the internal latent image type silver halide grains used in the present invention have the core/shell structure as described above. For shell producing methods, reference can be made to the examples of JP-A-63-151618, U.S. Patents 3,206,316, 3,317,322, 3,761,726, 4,269,927 and 3,367,778. The core/shell molar ratio (by weight) in this case is preferably 1/30 to 5/1, more preferably 1/20 to 2/1, and most preferably 1/20 to 1/1.

In the silver halide emulsions of the present invention, it is preferred that core grains subjected to chemical sensitization are coated with shells, followed by further chemical sensitization to the surface of the grains, but in some embodiments of the present invention no chemical sensitization is conducted to the surface of the grains. In general, chemical sensitization to the surface of the grains increases the maximum density and exhibits good reversal characteristics. When the chemical sensitization is conducted to the surface of the grains, polymers as described in JP-A-57-13641 may be allowed to coexist. The above-described chemical sensitization can be conducted using active gelatin as described in T.H. James, The Theory of the Photographic Process, 4th ed., pages 67 to 76, (published by Macmillan Co., 1977), and further, can be conducted using sulfur, selenium, tellurium, gold, platinum, palladium, iridium, rhodium, osmium, rhenium or a combination thereof at a pAg of 5 to 10 at a pH of 4 to 8 at a temperature of 30 to 80 °C as described in Research Disclosure, vol. 120, No. 12008 (April, 1974), Research Disclosure, vol. 134, No. 13452 (June, 1975), U.S. Patents 2,642,361, 3,297,446, 3,772,031, 3,857,711, 3,901,714, 4,266,018 and 3,904,415, and British Patent 1315755.

The chemical sensitization can also be carried out in the presence of a chemical sensitizing aiding agent. As the chemical sensitizing aiding agents, compounds are used which are known to depress fogging and to enhance the sensitivity in the course of the chemical sensitization, such as azaindene, azapyridazine and azapyrimidine. Examples of the chemical sensitizing assistants are described in U.S. Patents 2,131,038, 3,411,914 and 3,554,757, JP-A-58-126536, JP-A-62-253159 and G.F. Duffin, Photographic Emulsion Chemistry, pages 138 to 143 (Focal Press, 1966).

In the silver halide emulsions, the interior of the grains can be subjected to reduction sensitization in the course of formation of precipitates as described in JP-B-58-1410 and Moisar et al., Journal of Photographic Science, vol. 25, pages 19 to 27 (1977).

The following reduction sensitization can also be utilized as the chemical sensitization. The reduction sensitization can be carried out, for example, using hydrogen as described in U.S. Patents 3,891,446 and 3,984,249, using reducing agents as described in U.S. Patents 2,518,698, 2,743,182 and 2,743,183, or by treatment at a low pAg (for example, lower than 5) or a high pH (for example, higher than 8).

Typical examples of the known reduction sensitizers include stannous salts, ascorbic acid and derivatives thereof, amines and polyamines, hydrazine derivatives, formaminedisulfinic acids, silane compounds and borane compounds. These reduction sensitizers can be selectively used for the reduction sensitization in the present invention, and two or more compounds can also be used in combination. Stannous chloride, thiourea dioxide, dimethylamine borane, ascorbic acid and derivatives thereof are compounds which are preferred as the reduction sensitizers.

Chemical sensitization methods described in U.S. Patents 3,917,485 and 3,966,476 can also be applied.

Further, sensitization methods in which oxidizing agents are used, as described in JP-A-61-3134 and JP-A-61-3136, can also be applied.

Oxidizing agents to silver mean compounds having the function of reacting with metallic silver to convert it to a silver ion. In particular, compounds are effective which convert extremely fine silver grains produced as a by-product in the course of formation of the silver halide grains and chemical sensitization to silver ions. The silver ions produced here may form either silver salts slightly soluble in water such as silver halides, silver sulfide and silver selenide, or silver salts easily soluble in water such as silver nitrate. The oxidizing agents to silver may be inorganic compounds or organic compounds. Examples of the inorganic oxidizing agents include ozone; hydrogen peroxide and adducts thereof (for example, $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, $2NaCO_3 \cdot 3H_2O_2$, $Na_4P_2O_7 \cdot 2H_2O_2$ and $2Na_2SO_4 \cdot H_2O_2 \cdot 2H_2O$); oxygen acid salts such as peroxy acid salts (for example, $K_2S_2O_8$, $K_2S_2O_6$ and $K_2P_2O_8$), peroxy complex compounds (for example, $K_2[Ti(O_2)C_2O_4]\text{-}\cdot 3H_2O$ and $4K_2SO_4 \cdot Ti(O_2)OH \cdot SO_4 \cdot 2H_2O$), permanganates (for example, $KMnO_4$) and chromates (for example, $K_2Cr_2O_7$); halogen elements such as iodine and bromine; perhalogenates (for example, potassium periodate); salts of high valent metals (for example, potassium hexacyanoferrate (II)); and thiosulfonates.

Further, examples of organic oxidizing agents include quinones such as p-quinone; organic peroxides such as peracetic acid and perbenzoic acid; and compounds releasing active halogen (for example, N-bromsuccinimide, chloramine T and chloramine B).

In the present invention, ozone, hydrogen peroxide and the adducts thereof, the halogen elements and the thiosulfonates are preferably used as inorganic oxidizing agents, and the quinones as organic oxidizing agents. It is preferred that the above-described reduction sensitization is used in combination with the oxidizing agent to silver, which is selected for use from the method of subjecting to the reduction sensitization after use of the oxidizing agent, the method of using the oxidizing agent after the reduction sensitization and the method of using both concurrently. These methods can be selectively used either in the grain forming stage or in the chemical sensitization stage.

As protective colloids used in the preparation of the emulsions in the present invention, gelatin is advantageously used, but other hydrophilic colloids can also be used.

Examples Of such protective colloids include proteins such as gelatin derivatives, graft polymers of gelatin with other polymers, albumin and casein; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfates; saccharide derivatives such as sodium alginate and starch derivatives; and various kinds of synthetic hydrophilic polymers such as homopolymers and copolymers of polyvinyl alcohol, partially acetalized polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinylpyrazole.

As gelatin, gelatin treated with an acid or gelatin treated with an enzyme as described in Bull. Soc. Sci. Photo. Japan, vol. 16, page 30 (1966) may be used, besides gelatin treated with lime, and a hydrolyzed or enzymatically decomposed product of gelatin can also be used.

Many impurity ions are contained in gelatin, so that gelatin reduced in the amount of inorganic impurity ions by ion exchange treatment is preferably used.

It is preferred that the emulsions used in the present invention are washed with water for desalination and dispersed with freshly prepared protective colloids. The temperature during washing can be selected according to the purpose, but preferably selected to be 5 to 50°C. The pH during washing can also be selected depending on the purpose, but preferably is selected to be 2 to 10, more preferably 3 to 8. The pAg during washing can also be selected according to the purpose, but preferably is selected to be 5 to 10. A method for washing can be selected for use from the water washing methods with noodle, the dialysis methods using semipermeable membranes, the centrifugal methods, the coagulation precipitation methods and the ion exchange methods. The coagulation precipitation methods which can be selected include methods using nitrates, methods using organic solvents, methods using polymers of washing methods and methods using gelatin derivatives.

In the present invention, color sensitization can be conducted using sensitizing dyes. Preferred examples of the sensitizing dyes used include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolarcyanine dyes, hemicyanine dyes, styryl dyes and hemioxanol dyes. Specifically, they include sensitizing dyes described in U.S. Patent 4,617,257, JP-A-59-180550, JP-A-60-140335, JP-A-61-160739, Research Disclosure, vol. 170, No. 17029, pages 12 and 13 (June, 1978) and Research Disclosure, vol. 176, No. 17643, page 23 (December, 1978).

These sensitizing dyes may be used alone or in combination. Combinations of the sensitizing dyes are often used, particularly for supersensitization. Typical examples thereof are described in U.S. Patents 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862 and 4,026,707, British Patents 1344281 and 1507803, JP-B-43-4936, JP-B-53-12375, JP-A-52-110618 and JP-A-52-109925.

The emulsions may contain dyes having no color sensitization themselves or substances which do not substantially absorb visible light and exhibit supersensitization, in combination with the sensitizing dyes (as described, for example, in U.S. Patents 3,615,613, 3,615,641, 3,617,295, 3,635,721, 2,933,390 and 3,743,510 and JP-A-63-23145).

The sensitizing dyes may be added to the emulsions in any stage of emulsion preparation which has hitherto been known to be useful. Although the sensitizing dyes are usually added between the time when the chemical sensitization is completed and the time when the emulsion is coated, the sensitizing dyes may be added concurrently with addition of the chemical sensitizers to carry out the color sensitization and the chemical sensitization at the same time, as described in U.S. Patents 3,628,969 and 4,225,666. Further, the sensitizing dyes can also be added before the chemical sensitization as described in JP-A-58-113928, or can also be added before completion of precipitation formation of the silver halide grains to initiate the color sensitization. Furthermore, it is also possible to divide each of these sensitizing dye compounds described above into portions to add each of the portions, namely to add a portion of the compound before the chemical sensitization and the remainder after the chemical sensitization, as described in U.S. Patent 4,225,666. As well as a method disclosed in U.S. Patent 4,183,756, these compounds may be added at any time during formation of the silver halide grains.

The sensitizing dyes can be added in an amount of 10^{-8} to 10^{-2} mol per mol of silver halide. When the size of the silver halide grains is 0.2 to 1.2 μm which is more preferred, the sensitizing dyes are more effectively added in an amount of 5×10^{-5} to 2×10^{-3} mol.

The amount of the light-sensitive silver halides in the photographic material of the present invention preferably is from 1 mg/m^2 to 10 g/m^2, caluculated as silver.

In the present invention, various antifogging agents and photographic stabilizers can be used to prevent a reduction in sensitivity and occurrence of fogging. Examples thereof include azoles and azaindenes described in Research Disclosure, vol. 176, No. 17643, pages 24 and 25 (December, 1978) and U.S. Patent 4,629,678; nitrogen-containing carboxylic acid and phosphoric acid compounds described in JP-A-59-168442; mercapto compounds and metal salts thereof described in JP-A-59-111636; and acetylene compounds described in JP-A-62-87957.

These additives are described in Research Disclosure, vol. 176, No. 17643 (December, 1978), ibid., vol. 187, No. 18716 (November, 1979) and ibid., vol. 307, No. 307105 (November, 1989), and corresponding portions thereof are summarized in the following table.

Type of Additives	RD17643 (Dec., 1978)	RD18716 (Nov., 1979)	RD307105 (Nov., 1989)
1. Chemical Sensitizers	p. 23	p. 648, right column	p. 866
2. Sensitivity Increasing Agents	---	ditto	---
3. Spectral Sensitizers, Supersensitizers	pp. 23-24	p. 648, right column to p. 649, right column	pp. 866-868
4. Brightening Agents	pp. 24	p. 647	p. 868
5. Antifoggants, Stabilizers	pp. 24-25	p. 649, right column	pp. 868-870
6. Light Absorbers, Filter dyes, UV Absorbers	pp. 25-26	p. 649, right column to p. 650, left column	p. 873
7. Stain Inhibitors	p. 25, right column	p. 650, left to right columns	p. 872
8. Dye Image Stabilizers	p. 25	p. 650, left column	p. 872
9. Hardeners	p. 26	p. 651, left column	pp. 874-875
10. Binders	p. 26	ditto	pp. 873-874
11. Plasticizers, Lubricants	p. 27	p. 650, right column	p. 876
12. Coating Aids, Surfactants	pp. 26-27	ditto	pp. 875-876
13. Antistatic Agents	p. 27	ditto	pp. 876-877
14. Matte Agents	---	---	pp. 878-879

Respective constitution elements contained in the present invention will hereinafter be described.

I. Light-Sensitive Sheet

A) Support

For a support of a light-sensitive sheet used in the present invention, any support may be used as long as it is a smooth transparent support usually used in a photographic material. The support can be formed of cellulose acetate, polystyrene, polyethylene terephthalate or polycarbonate, and preferably is provided with an undercoating layer. It is preferred that the support usually contain a dye or a pigment such as titanium oxide in small amounts to prevent light piping.

The thickness of the support is generally 50 to 350 µm, preferably 70 to 210 µm, and more preferably 80 to 150 µm.

A curl balancing layer or an oxygen shielding layer described in JP-A-56-78833 may be formed on the back side of the support as so desired.

B) Image Receiving Layer

An image receiving layer which can be used in the present invention generally contains a mordant in a hydrophilic colloid, and may have either a monolayer structure or a multilayer structure in which mordants different from one another in mordant ability are overcoated. This is described in JP-A-61-252551.

As the mordants, polymer mordants are preferably used. Examples of suitable polymer mordants include polymers containing secondary and tertiary amino groups, polymers having nitrogen-containing heterocyclic moieties or polymers containing quaternary cations. Their molecular weight is preferably 5,000 or more, and more preferably 10,000 or more.

The amount of the mordants applied is generally 0.5 to 10 g/m^2, preferably 1.0 to 5.0 g/m^2, and more preferably 2.0 to 4.0 g/m^2.

Examples of the hydrophilic colloids used in the image receiving layer include gelatin, polyvinyl alcohol, polyacrylamide and polyvinylpyrrolidone. Gelatin is particularly preferred among these.

Antifading agents described in JP-B-62-30620, JP-B-62-30621 and JP-A-62-215272 may be incorporated in the image receiving layers.

C) White Reflective Layer

A white reflective layer which forms a white background of a color image usually comprises a white pigment and a hydrophilic binder. The white pigments used for the white reflective layer include barium sulfate, zinc oxide, barium stearate, silver flakes, silicates, alumina, zirconium oxide, sodium zirconium sulfate, kaolin, mica and titanium dioxide. In addition, non-film forming polymer particles which are formed of styrene or the like may also be used. These can also be used alone or in combination within a range which gives a desired reflectance.

A particularly useful white pigment is titanium dioxide.

The whiteness of the white reflective layer varies depending on the kind of pigment, the pigment-binder mixture ratio and the amount of the pigment coated. It is, however, desirable that the light reflectance is 70% or more. In general, the whiteness increases with an increase in the amount of the pigment coated. However, when the image forming dye diffuses through this layer, the diffusion of the dye is resisted by the pigment. It is therefore desirable to coat the pigment in suitable amounts.

It is preferred that titanium dioxide is present in an amount of 5 to 40 g/m^2, preferably 10 to 25 g/m^2, to give a white reflective layer having a light reflectance of 78 to 85% at a wavelength of 540 nm.

Titanium dioxide can be selected for use from various commercial products.

In particular, rutile type titanium dioxide is preferably used among these. Many of the commercial products are surface treated with alumina, silica, zinc oxide or the like. In order to obtain a high reflectance, it is desirable that the titanium dioxide has at least 5% of the surface treating material. Commercially available titanium dioxide includes, for example, products described in Research Disclosure, No. 15162, as well as Ti-Pure R931 (Du Pont Co., Ltd.).

The binders usable in the white reflective layer include alkali-permeable high polymer matrixes, for example, gelatin, polyvinyl alcohol and cellulose derivatives such as hydroxyethyl cellulose and carboxymethyl cellulose.

Gelatin is particularly desirable for use in the white reflective layer. The white pigment/gelatin ratio is generally 1/1 to 20/1 (by weight), and preferably 5/1 to 10/1 (by weight).

It is preferred that antifading agents as described in JP-B-62-30620 and JP-B-62-30621 are incorporated in the white reflective layer.

D) Light Shielding Layer

A light shielding layer containing a light shielding agent and a hydrophilic binder is provided between the white reflective layer and a light-sensitive layer.

As the light shielding agent, any material may be used as long as it has light shielding function. In particular, carbon black is preferably used. Decomposable dyes described in U.S. Patent 4,615,966 may also be used.

As the binder for applying the light shielding agent, any material may be used as long as it can disperse carbon black. Gelatin is preferably used.

Carbon black materials which can be used include carbon black produced by any method such as the channel method, the thermal method and the furnace method, for example, as described in Donnel Voet, Carbon Black, Marcel Dekker Inc. (1976). There is no particular limitation on the particle size of carbon black, but the particle size is preferably 90 to 1,800 Å.

A black dye can be sued as a light sielding agent, and the amount thereof may be adjusted depending on the sensitivity of the photographic material to be shaded.

The optical density of the light shielding layer is preferably adjusted to about 5 to 10.

E) Light-Sensitive Layer

In the present invention, a light-sensitive layer comprising a silver halide emulsion layer combined with a dye image forming substance is formed on the above-described light shielding layer. The constitution elements thereof are described below.

(1) Dye Image Forming Substance

Dye image forming substances which can be used in the present invention are non-diffusible compounds releasing diffusible dyes (or dye precursors) with respect to silver development or compounds whose diffusibility varies, which are described in The Theory of the Photographic Process, the fourth edition. These compounds can all be represented by the following formula (II):

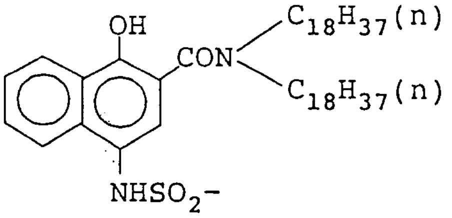
DYE-Y (II)

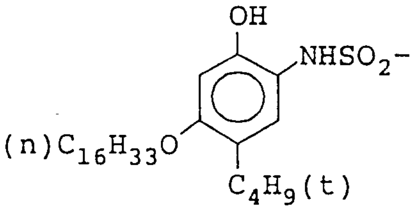
wherein DYE represents a dye or a precursor, and Y represents a component giving a compound different from the compound represented by the above-described geeral formula (II) in diffusibility under alkaline conditions. Based on the function of Y, these compounds are roughly divided into negative type compounds which become diffusible in silver-developed portions and positive type compounds which become diffusible in undeveloped portions.

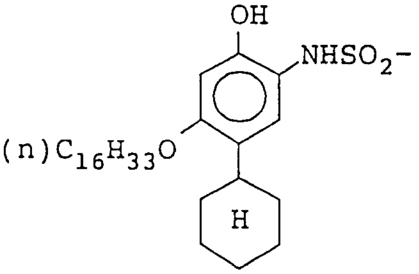
Specific examples of the negative type Y components include components which are oxidized as a result of development and cleaved to release diffusible dyes.

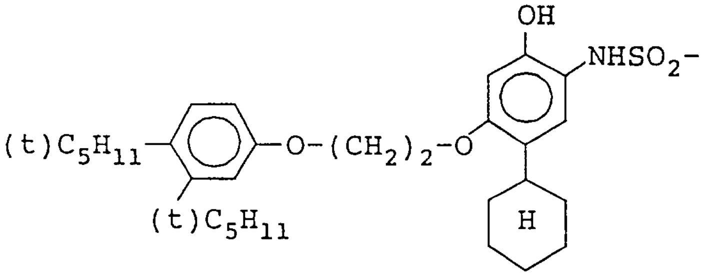
Specific example of the Y components are described in U.S. Patents 3,928,312, 3,993,638, 4,076,529, 4,152,153, 4,055,428, 4,053,312, 4,198,235, 4,179,291, 4,149,892, 3,844,785, 3,443,943, 3,751,406, 3,443,939, 3,443,940, 3,628,952, 3,980,479, 4,183,753, 4,142,891, 4,278,750, 4,139,379, 4,218,368, 3,421,964, 4,199,355, 4,199,354, 4,135,929, 4,336,322 and 4,139,389, JP-A-53-50736, JP-A-51-104343, JP-A-54-130122, JP-A-53-110827, JP-A-56-12642, JP-A-56-16131, JP-A-57-4043, JP-A-57-650, JP-A-57-20735, JP-A-53-69033, JP-A-54-130927, JP-A-56-164342 and JP-A-57-119345.

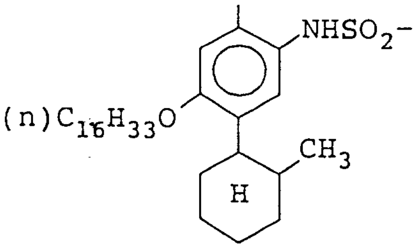
Of the Y components of negative type dye releasing redox compounds, particularly preferred groups include N-substituted sulfamoyl groups (wherein N-substituted groups are groups derived from aromatic hydrocarbon rings or heterocyclic rings). Typical examples of the Y components for negative type compounds are shown below, but are not limited thereto.











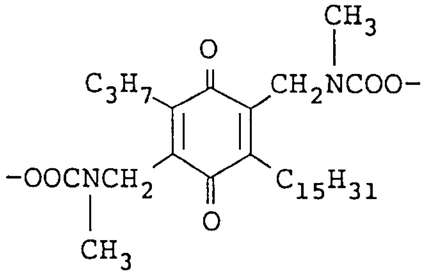
The positive type compounds are described, for example, in Angev. Chem. Inst. Ed. Engl., vol. 22, page 191 (1982).

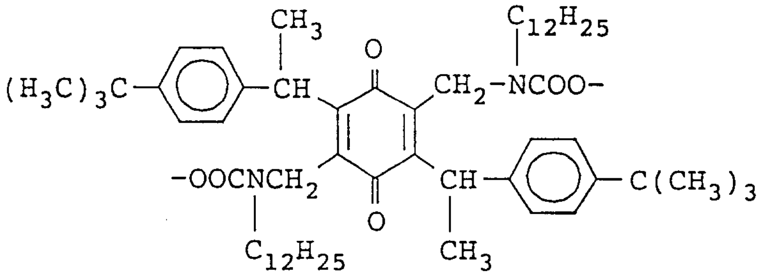
Specific examples thereof include compounds (dye developing agents) which are at first diffusible under alkaline conditions, but oxidized by development to become non-diffusible. Typical Y components effective for the compounds of this type are disclosed in U.S. Patent 2,983,606.

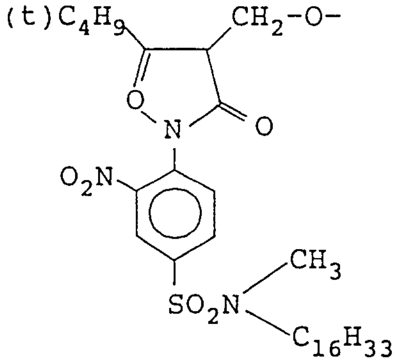
Further, the positive type compounds include compounds of another type which release diffusible dyes by self-cyclization, etc. under alkaline conditions, but substantially cease to release the dyes upon oxidation by development. Specific examples of Y components having such a function are described in U.S. Patent 3,980,479, JP-A-53-69033, JP-A-54-130927, U.S. Patents 3,421,964 and 4,199,355.

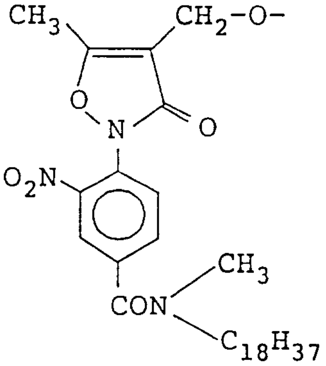
Furthermore, the positive type compounds include compounds of a further type which themselves do not release dyes, but release the dyes upon reduction. The compounds of this type are used in combination with electron donors, and can release the diffusible dyes imagewise by reaction with the remainder of the electron donors oxidized imagewise by silver development. Atomic groups having such a function are described, for example, in U.S. Patents 4,183,753, 4,142,891, 4,278,750, 4,139,379 and 4,218,368, JP-A-53-110827, U.S. Patents 4,278,750, 4,356,249 and 4,358,525, JP-A-53-110827, JP-A-54-130927, JP-A-56-164342, Japanese Disclosure Bulletin 87-6199 and European Patent Publication No. 220746.

Specific examples of the Y components of positive type compounds are enumerated below, but are not limited thereto.



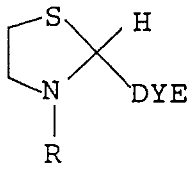


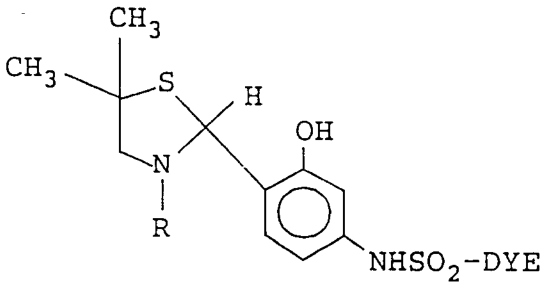




When the compounds of this type are used, they are preferably used in combination with anti-diffusible electron donor compounds (well known as the ED compounds) or precursors thereof. Examples of the ED compounds are described, for example, in U.S. Patents 4,263,393 and 4,278,750 and JP-A-56-138736.

Moreover, as specific examples of dye image forming substances of still another type, the following compounds can also be used.





wherein DYE represents a dye or a precursor thereof having the same meaning as defined above, and R represents an alkyl group.

Details thereof are described in U.S. Patents 3,719,489 and 4,098,783.

On the other hand, specific examples of the dyes represented by DYE of the above-described formula (II) are described in the following literatures:

Examples of yellow dyes:

U.S. Patents 3,597,200, 3,309,199, 4,013,633, 4,245,028, 4,156,609, 4,139,383, 4,195,992, 4,148,641, 4,148,643 and 4,336,322, JP-A-51-114930, JP-A-56-71072, Research Disclosure, vol. 176, No. 17630 (December, 1978) and ibid., vol. 164, No. 16475 (December, 1977);

Examples of magenta dyes:

U.S. Patents 3,453,107, 3,544,545, 3,932,380, 3,931,144, 3,932,308, 3,954,476, 4,233,237, 4,255,509, 4,250,246, 4,142,891, 4,207,104 and 4,287,292, JP-A-52-106727, JP-A-53-23628, JP-A-55-36804, JP-A-56-73057, JP-A-56-71060 and JP-A-55-134;

Examples of cyan dyes:

U.S. Patents 3,482,972, 3,929,760, 4,013,635, 4,268,625, 4,171,220, 4,242,435, 4,142,891, 4,195,994, 4,147,544 and 4,148,642, British Patent 1551138, JP-A-54-99431, JP-A-52-8827, JP-A-53-47823, JP-A-53-143323, JP-A-54-99431, JP-A-56-71061, European Patents (EPC) 53037 and 53040, Research Disclosure, vol. 176, No. 17630 (December, 1978) and ibid., vol. 164, No. 16475 (December, 1977).

These compounds can be dispersed by a method described in JP-A-62-215272, pages 144 to 146. These dispersions may contain compounds described in JP-A-62-215272, pages 137 to 144.

(2) Silver Halide Emulsion

In the present invention, the silver halide emulsions of the present invetnion described above are used.

(3) Constitution of Light-Sensitive Layer

For reproduction of natural colors by the subtractive color process, the light-sensitive layer is used which comprises the combination of at least two components of an emulsion optically sensitized with the above-described color sensitizing dye and the above-described dye image forming materials for providing a dye having selective spectral absorption within the same wavelength range. The emulsion and the dye image forming materials may be either formed one over the other as different layers, or formed as one layer by mixing them. When the dye image forming substance has absorption in the optical sensitivity region of the emulsion combined therewith in its coated state, it is preferred that they are formed as different layers. The emulsion layer may comprise a plurality of emulsion layers different in sensitivity, and any type of auxiliary layer may be provided between the emulsion layer and the dye image forming substance. For example, the dye image density can be raised by providing a layer containing a nucleating development accelerator described in JP-A-60-173541 or a barrier layer described in JP-B-60-15267, or the sensitivity of the light-sensitive elements can be enhanced by providing a reflective layer.

The reflective layer is a layer containing a white pigment and a hydrophilic binder. The white pigment is preferably titanium oxide and the hydrophilic binder is preferably gelatin. The amount of titanium oxide applied is 0.1 to 8 g/m^2, and preferably 0.2 to 4 g/m^2. Examples of the reflective layers which are preferred embodiments of the present invention are described in JP-A-60-91354.

In the preferred multilayer structure, a combined unit of blue-sensitive emulsions, a combined unit of green-sensitive emulsions and a combined unit of red-sensitive emulsions are arranged in turn from the exposure side.

Any type of auxiliary layer can be provided between the respective emulsion layer units as so desired. In particular, an intermediate layer is preferably provided in order to prevent other emulsion layer units from being unfavorably affected by the development effect of a certain emulsion layer.

When the developing agent is used in combination with the non-diffusible dye image forming substance, it is preferred that the intermediate layer contains a non-diffusible reducing agent to prevent development oxidant from diffusing. Specific examples of the reducing agents include non-diffusible hydroquinone, sulfonamidophenol and sulfonamidonaphthol. More specifically, they are described in JP-B-50-21249, JP-B-50-23813, JP-A-49-106329, JP-A-49-129535, U.S. Patents 2,336,327, 2,360,290, 2,403,721, 2,544,640, 2,732,300, 2,782,659, 2,937,086, 3,637,393 and 3,700,453, British Patent 557750, JP-A-57-24941, JP-A-58-21249. Dispersing methods thereof are described, for example, in JP-A-60-238831 and JP-B-60-18978.

When a compound releasing a diffusible dye with silver ions as described in JP-B-55-7576 is used, it is preferred that the intermediate layer contains a compound for supplementing the silver ions.

The light-sensitive layers used in the present invention are provided with irradiation-preventing layers, ultraviolet light absorber layers, protective layers, etc. as so desired.

F) Separation Layer

In the present invention, a separation layer can be provide to perform stripping off at any place of the sensitive-sheet in the unit after processing, as so desired.

This separation layer must therefore be easily separated after processing. Examples of materials which can be used for this purpose include ones described in JP-A-47-8237, JP-A-59-220727, JP-A-59-229555, JP-A-49-4653, U.S. Patents 3,220,835 and 4,359,518, JP-A-49-4334, JP-A-56-65133, JP-A-45-24075, U.S. Patents 3,227,550, 2,759,825, 4,401,746 and 4,366,227. Specific examples thereof include water-soluble (or alkali-soluble) cellulose derivatives such as hydroxyethyl cellulose, cellulose acetate-phthalate, plasticized methyl cellulose, ethyl cellulose, cellulose nitrate and carboxymethyl cellulose; various natural polymers such as alginic acid, pectin and gum arabic; various modified gelatins such as acetylated gelatin and phthalated gelatin; water-soluble synthetic polymers such as polyvinyl alcohol, polyacrylate, polymethyl methacrylate and polybutyl methacrylate.

The separation layer may be a single layer, or may be composed of a plurality of layers as described, for example, in JP-A-59-220727 and JP-A-60-60642.

II. Cover Sheet

In the present invention, a transparent cover sheet comprising layers having a neutralization function (a neutralization layer and a neutralization timing layer) is used to spread a processing solution uniformly on the light sensitive elements, and neutralize an alkali after processing to stabilize images.

G) Support

For a support for the cover sheet used in the present invention, any support may be used as long as it is a smooth transparent support usually used as a photographic material. The support is formed of cellulose acetate, polystyrene, polyethylene terephthalate or polycarbonate, and preferably provided with an undercoating layer.

It is preferred that the support contains a dye in slight amounts to prevent light piping.

H) Layer Having Neutralization Function

The layer having neutralization function used in the present invention is a layer containing an acidic material in an amount which is enough to neutralize an alkali incorporated from processing compositions, and may have a multilayer structure comprising layers such as a neutralization speed control layer (a timing layer) and an adhesion-enhancing layer as so desired. Preferred examples of such acidic materials include materials containing an acidic group having a pKa of 9 or less (or a precursor group giving such an acidic group by hydrolysis). More preferably, the acidic materials include higher fatty acids such as oleic acid described in U.S. Patent 2,983,606; polymers of acrylic acid, methacrylic acid or maleic acid, partial esters thereof or acid anhydrides thereof as disclosed in U.S. Patent 3,362,819, copolymers of acrylic acid and acrylates as disclosed in French Patent 2290699; and latex type acidic polymers as disclosed in U.S. Patent 4,139,383 and Research Disclosure, vol. 161, No. 16102 (September, 1977).

In addition, they also include acidic materials disclosed in U.S. Patent 4,088,493, JP-A-52-153739, JP-A-53-1023, JP-A-53-4540, JP-A-53-4541 and JP-A-53-4542.

Specific examples of the acidic polymers include copolymers of maleic anhydride and vinyl monomers such as ethylene, vinyl acetate and methyl vinyl ether; copolymers of n-butyl ester thereof, butyl acrylate and acrylic acid; and cellulose acetate hydrogen phthalate.

The above-described acidic polymers can be mixed with hydrophilic polymers. Such polymers include polyacrylamide, polymethylpyrrolidone, polyvinyl alcohol (including partially saponified polyvinyl alcohol), carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose and polymethyl vinyl ether. Polyvinyl alcohol is preferred among these.

The above-described acidic polymers may be mixed with polymers other than the hydrophilic polymers, for example, cellulose acetate.

The amount of the acidic polymer coated is adjusted according to the amount of the alkali spread in the light sensitive elements. The equivalent ratio of the acidic polymer per unit area to the alkali is preferably 0.9 to 2.0. If the amount of the acidic polymer is too small, the hue of a transfer dye changes or stains are generated on a white ground portion. If the amount is too large, troubles such as a change in hue and a decrease in light fastness are produced. More preferably, the equivalent ratio is 1.0 to 1.3. Too large or too small an amount of the hydrophilic polymer to be mixed deteriorates the quality of a photograph. The weight ratio of the hydrophilic polymer to the acidic polymer is generally 0.1 to 10, and preferably 0.3 to 3.0.

For various purposes, additives may be incorporated in the layer having the neutralization function used in the present invention. For example, a hardening agent known in the art can be added to this layer to harden it, and a multivalent hydroxyl compound such as polyethylene glycol, polypropylene glycol or glycerol can be added to this layer to improve brittleness thereof. In addition, an antioxidant, a fluorescent brightening agent, a development inhibitor or a precursor thereof can also be added as so desired.

Useful polymers for the timing layers used in combination with the neutralization layers include polymers reducing alkali permeability such as gelatin, polyvinyl alcohol, partially acetalized products of polyvinyl alcohol, cellulose acetate and partially hydrolyzed polyvinyl acetate; latex polymers elevating the activation energy of alkali permeance which are produced by copolymerizing a small amount of hydrophilic comonomers such as acrylic acid monomers; and polymers having lactone rings.

Particularly useful polymers used for the timing layers include cellulose acetate disclosed in JP-A-54-136328, U.S. Patents 4,267,262, 4,009,030 and 4,029,849; latex polymers produced by copolymerizing a small amount of hydrophilic comonomers such as acrylic acid which are disclosed in JP-A-54-128335, JP-A-56-69629, JP-A-57-6843, U.S. Patents 4,056,394, 4,061,496, 4,199,362, 4,250,243, 4,256,827 and 4,268,604; polymers having lactone rings disclosed in U.S. Patent 4,229,516; and other polymers disclosed in JP-A-56-25735, JP-A-56-97346, JP-A-57-6842, European Patent (EPC) Publication Nos. 31957, 37724 and 48412, among these.

Besides, polymers can also be used which are described in U.S. Patents 3,421,893, 3,455,686, 3,575,701, 3,778,265, 3,785,815, 3,847,615, 4,088,493, 4,123,275, 4,148,653, 4,201,587, 4,288,523 and 4,297,431, West German Patent Publication (OLS) Nos. 1622936 and 2162277 and Research Disclosure, vol. 151, No. 15162, (November, 1976).

The timing layers using these polymers can be used alone or in combination of at least two layers.

Further, it is also possible to incorporate, for example, development inhibitors disclosed in U.S. Patent 4,009,029, West German Patent Publication (OLS) Nos. 2913164 and 3014672, JP-A-54-155837 and JP-A-55-138745 and/or their precursors, or hydroquinone precursors disclosed in U.S. Patent 4,201,578, or other useful photographic additives or their precursors in the timing layers formed of these polymers.

Furthermore, a supplementary neutralization layer may be provided as a layer having neutralization function as described in JP-A-63-168648 and JP-A-63-168649, whereby a change in transfer density with time after processing is decreased.

I) Others

In addition to the layer having a neutralization function, the cover sheet may have a backing layer, a protective layer, a capturing mordant layer, a filter dye layer, etc.

The backing layer is provided to control curl or to impart sliding property. A filter dye may be added to this layer.

The protective layer is used mainly to prevent adhesion to a cover sheet back surface and adhesion to the protective layer of the photographic material when the cover sheet is overlapped on the photographic material.

The capturing mordant layer can prevent the delay of image completing time and deterioration of sharpness by capturing a dye diffused on the alkali processing composition side. Usually, a dye capturing layer is formed as the outermost layer of the cover sheet. The dye capturing layer contains a polymer mordant in a hydrophilic colloid as is the case with the dye image receiving layer previously described, and is described in JP-A-1-198747 and JP-A-2-282253.

The cover sheet can contain a dye to adjust the sensitivity of the light sensitive layer. The filter dye may be directly added to the support of the cover sheet, the layer having neutralization function, the backing layer, the protective layer, the capturing mordant layer or the like, or a separate layer containing the filter dye may be formed.

The light-sensitive sheets, the cover sheets or the alkali processing compositions may contain development accelerators described on pages 72 to 91, hardening agents described on pages 146 to 155, surface active agents described on pages 201 to 210, fluorine-containing compounds described on pages 210 to 222, thickeners described on pages 225 to 227, antistatic agents described on pages 227 to 230, polymer latices described on pages 230 to 239 and matte agents described on page 240 in JP-A-62-215272.

III. Alkali Processing Composition

The alkali processing composition used in the present invention is uniformly spread in the light sensitive elements after exposure thereof, is provided on the back surface of the supports of the light-sensitive sheet and cover sheet or on the side opposite to a processing solution for the light sensitive layer to make a pair with the light shielding layer, thereby completely shielding the light sensitive layer from external light, and concurrently develops the light-sensitive layer with components contained therein. For this purpose, the alkali processing composition contains an alkali, a thickener, a light shielding agent and a developing agent, and further contains a development accelerator for controlling development, a development inhibitor and an antioxidant for preventing the developing agent from deteriorating. A light shielding agent is necessarily contained in the alkali processing composition.

The alkali is a compound which can adjust the pH of 12 to 14. Examples thereof include hydroxides of alkaline metals (for example, sodium hydroxide, potassium hydroxide and lithium hydroxide), phosphates of alkaline metals (for example, potassium phosphate), guanidine derivatives and hydroxides of quaternary amines (for example, tetramethyl-ammonium hydroxide). Potassium hydroxide and sodium hydroxide are preferred among these.

The thickener is necessary to spread the processing solution uniformly and to maintain adhesion between the light-sensitive layer and the cover sheet. For example, polyvinyl alcohol, hydroxyethyl cellulose and alkaline metal salts of carboxymethyl cellulose are used, and preferably, hydroxyethyl cellulose and sodium carboxymethyl cellulose are used.

As the light shielding agent, either a dye or a pigment, or a combination thereof can be used as long as it does not produce stains by diffusing to the dye image receiving layer. Typical examples thereof include carbon black.

As the developing agent, any can be used as long as it cross oxidizes the dye image forming materials and does not substantially produce stains when oxidized. Such developing agents may be used alone or in combination, and may be used in the form of precursors. These developing agents may be added to appropriate layers of the light-sensitive elements, or to alkali processing solutions. Specific examples thereof include aminophenols and pyrazolidinone compounds. Of these, the pyrazolidinone compounds are particularly preferred because stains are less produced.

Examples of such compounds include 1-phenyl-3-pyrazolidinone, 1-p-tolyl-4,4-dihydroxymethyl-3-pyrazolidinone, 1-(3'-methyl-phenyl)-4-methyl-4-hydroxymethyl-3-pyrazolidinone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidinone and 1-p-tolyl-4-methyl-4-hydroxymethyl-3-pyrazolidinone.

The present invention will be further illustrated in greater detail with reference to the following examples, which are, however, not to be construed as limiting the invention.

EXAMPLE 1

First, methods for preparing silver halide emulsions are described.

Emulsion A-1 (Octahedral Internal Latent Image Type Direct Positive Emulsion for Comparison)

A 0.4 M aqueous solution of silver nitrate (300 mℓ) was added to 1000 mℓ of an 8wt% aqueous solution of gelatin containing 13 g of potassium bromide and 0.05 g of 1,8-dihydroxy-3,6-dithioctane for 40 minutes, the temperature was maintained at 75 °C and the rate of addition of a 0.4 M aqueous solution of potassium bromide was adjusted so as to give a pBr of 1.30 by the controlled double jet process.

When the addition was completed, octahedral silver halide grains (hereinafter referred to as core grains) were formed which were uniform in grain size and had a mean grain size (a sphere corresponding size) of about 0.8 µm.

Then, 0.7 mg of sodium thiosulfate and 0.4 mg of potassium chloroaurate were added to the silver halide grains (both were added as aqueous solutions), and the mixture was heated at 75 °C for 80 minutes, thereby conducting chemical sensitization. A 0.8 M aqueous solution of silver nitrate (740 mℓ) was added during a period of 60 minutes to the core grains which had been thus subjected to chemical sensitization, the temperature was maintained at 75 °C and the rate of addition of a 0.8 M aqueous solution of potassium bromide was adjusted so as to give a pBr of 1.30 by the controlled double jet process, as with the preparation of the core grains, to form shells.

The resulting emulsion was washed with water by the flocculation process, and gelatin was added thereto to obtain octahedral silver bromide crystals uniform in size and having a mean grain size (a sphere corresponding size) of about 1.4 µm (hereinafter referred to as internal latent image type core/shell grains).

Then, 0.4 mg per mol of silver of sodium thiosulfate and 20 mg of poly(N-vinylpyrrolidone) were added to this internal latent image type core/shell emulsion, and the mixture was heated at 60 °C for 60 minutes, thereby subjecting the surface of the grains to chemical sensitization to obtain an octahedral internal latent image type direct positive emulsion.

Emulsion B (Octahedral Internal Latent Image Type Direct Positive Emulsion)

A 0.4 M aqueous solution of silver nitrate (300 mℓ) was added to 1000 mℓ of an 8wt% aqueous solution of gelatin containing 13 g of potassium bromide and 0.05 g of 1,8-dihydroxy-3,6-dithioctane for 23 minutes, the temperature was maintained at 75 °C and the rate of addition of a 0.4 M aqueous solution of potassium bromide was adjusted so as to give a pBr of 1.30 by the controlled double jet process.

When the addition was completed, octahedral silver halide grains (hereinafter referred to as core grains) were formed which were uniform in grain size and had a mean grain size (a sphere corresponding size) of about 0.45 µm.

Then, 0.22 mg of sodium thiosulfate and 0.12 mg of potassium chloroaurate were added to the silver halide grains (both were added as aqueous solutions), and the mixture was heated at 75 °C for 80 minutes, thereby conducting chemical sensitization. A 0.8 M aqueous solution of silver nitrate (740 mℓ) was added for 35 minutes to the core grains which had been thus subjected to chemical sensitization, the temperature was nmaintained at 75 °C and the rate of addition of a 0.8 M aqueous solution of potassium bromide was adjusted so as to give a pBr of 1.30 by the controlled double jet process, as with the preparation of the core grains, to form shells.

The resulting emulsion was washed with water by the flocculation process, and gelatin was added thereto to obtain octahedral silver bromide crystals uniform in size and having a mean grain size (a sphere corresponding size) of about 0.8 µm (hereinafter referred to as internal latent image type core/shell grains).

Then, 0.13 mg per mol of silver of sodium thiosulfate and 6.5 mg of poly(N-vinylpyrrolidone) were added to this internal latent image type core/shell emulsion, and the mixture was heated at 60 °C for 60 minutes, thereby subjecting the surface of the grains to chemical sensitization to obtain an octahedral internal latent image type direct positive emulsion.

Emulsions A-2 to A-8 (Comparison) and A-9 to A-11 (Invention)

Emulsions A-2 to A-11 were prepared in the same manner as with Emulsion A-1, with the exception that the metal complexes shown in Table 1 were added in amounts (per mol of silver nitrate) shown in Table 1 for the respective emulsions during the formation of the shells.

TABLE 1

Emulsion	Metal Complex	Amount Added (mol)
A-1 (Comparison)	---	---
A-2 (Comparison)	$K_3Ir(Cl)_6$	1.4×10^{-4}
A-3 (Comparison)	$K_3Ir(CN)_4Cl_2$	1.4×10^{-4}
A-4 (Comparison)	$K_3Ir(CN)_5Cl$	1.4×10^{-4}
A-5 (Comparison)	$K_3Co(Cl)_6$	1.4×10^{-4}
A-6 (Comparison)	$K_3Co(CN)_4Cl_2$	1.4×10^{-4}
A-7 (Comparison)	$K_3Co(CN)_5Cl$	1.4×10^{-4}
A-8 (Comparison)	$K_3Fe(CN)_6$	1.4×10^{-4}
A-9 (Invention)	$K_3Ir(CN)_6$	1.4×10^{-4}
A-10 (Invention)	$K_3Co(CN)_6$	1.4×10^{-4}
A-11 (Invention)	$K_4Ru(CN)_6$	1.4×10^{-6}

Subsequently, a light-sensitive element for comparison having the structure shown in Table 2 (Sample 101) was prepared using Emulsion A-1.

TABLE 2

Constitution of Light-Sensitive Element 101 for Sample 101 for Comparison

Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
21st	Protective Layer	Gelatin	1.00
		Matte Agent (1)	0.25
20th	Ultraviolet Light Absorbing Layer	Gelatin	0.50
		Ultraviolet Light Absorber (1)	4.0×10^{-4}
		Ultraviolet Light Absorber (2)	4.0×10^{-4}
19th	Yellow-Sensitive Layer (high sensitivity)	Internal Latent Image Type Direct Positive Emulsion A-1 (grain size: 1.4 µm, octahedral)	0.60 (converted to silver)
		Sensitizing Dye (3)	1.4×10^{-3}
		Nucleating Agent (1)	6.8×10^{-8}
		Additive (2)	0.03
		Gelatin	0.70
18th	Yellow-Sensitive Layer (low sensitivity)	Internal Latent Image Type Direct Positive Emulsion B (grain size: 0.8 µm, octahedral)	0.25 (converted to silver)
		Sensitizing Dye (3)	9.0×10^{-4}
		Nucleating Agent (1)	8.0×10^{-8}
		Additive (2)	4.5×10^{-2}
		Gelatin	0.40

TABLE 2 (cont'd)

Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
17th	White Reflective Layer	Titanium Dioxide	0.70
		Gelatin	0.18
16th	Yellow Color Material Layer	Yellow Dye Releasing Compound (1)	0.53
		High Boiling Organic Solvent (1)	0.13
		Additive (1)	1.4×10^{-2}
		Gelatin	0.70
15th	Intermediate Layer	Gelatin	0.30
14th	Color Mixing Preventing Layer	Additive (1)	0.80
		Polymethyl Methacrylate	0.80
		Gelatin	0.45
13th	Green-Sensitive Layer (high sensitivity)	Internal Latent Image Type Direct Positive Emulsion A-1 (grain size: 1.4 μm, octahedral)	0.80 (converted to silver)
		Sensitizing Dye (2)	2.1×10^{-3}
		Nucleating Agent (1)	2.5×10^{-8}
		Additive (2)	0.08
		Gelatin	1.00

TABLE 2 (cont'd)

Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
12th	Green-Sensitive Layer (low sensitivity)	Internal Latent Image Type Direct Positive Emulsion B (grain size: 0.8 μm, octahedral)	0.25 (converted to silver)
		Sensitizing Dye (2)	1.1×10^{-3}
		Nucleating Agent (1)	4.4×10^{-8}
		Additive (2)	0.03
		Gelatin	0.50
11th	White Reflective Layer	Titanium Dioxide	1.00
		Gelatin	0.25
10th	Magenta Color Material Layer	Magenta Dye Releasing Compound (1)	0.50
		High Boiling Organic Solvent (1)	0.10
		Additive (1)	9.0×10^{-3}
		Gelatin	0.90
9th	Intermediate Layer	Gelatin	0.30
8th	Color Mixing Preventing Layer	Additive (1)	1.20
		Polymethyl Methacrylate	1.20
		Gelatin	0.70

TABLE 2 (cont'd)

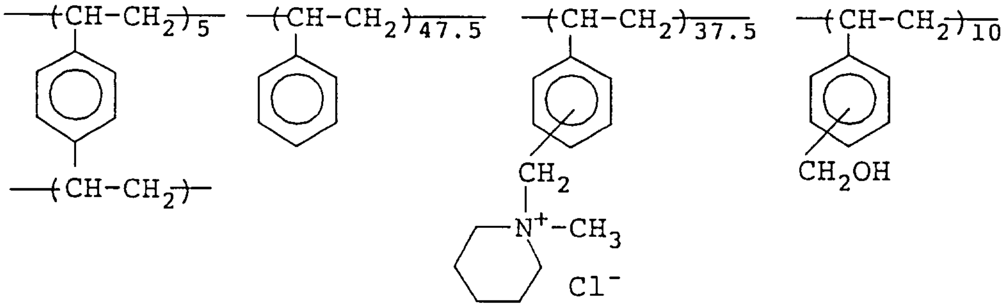
Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
7th	Red-Sensitive Layer (high sensitivity)	Internal Latent Image Type Direct Positive Emulsion A-1 (grain size: 1.4 µm, octahedral)	0.50 (converted to silver)
		Sensitizing Dye (1)	6.2×10^{-4}
		Nucleating Agent (1)	5.0×10^{-8}
		Additive (2)	0.04
		Gelatin	0.80
6th	Red-Sensitive Layer (low sensitivity)	Internal Latent Image Type Direct Positive Emulsion B (grain size: 0.8 µm octahedral)	0.15 (converted to silver)
		Sensitizing Dye (1)	3.0×10^{-4}
		Nucleating Agent (1)	5.0×10^{-8}
		Additive (2)	0.02
		Gelatin	0.40
5th	White Reflective Layer	Titanium Dioxide	3.00
		Gelatin	0.80
4th	Cyan Color Material Layer	Cyan Dye Releasing Compound (1)	0.50
		High Boiling Organic Solvent (1)	0.10
		Additive (1)	0.10
		Gelatin	1.0

TABLE 2 (cont'd)

Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
3rd	Opaque Layer	Carbon Black	1.70
		Gelatin	1.70
2nd	White Reflective Layer	Titanium Dioxide	22.00
		Gelatin	2.75
1st	Image Receiving Layer	Polymer Mordant (1)	3.00
		Gelatin	3.00

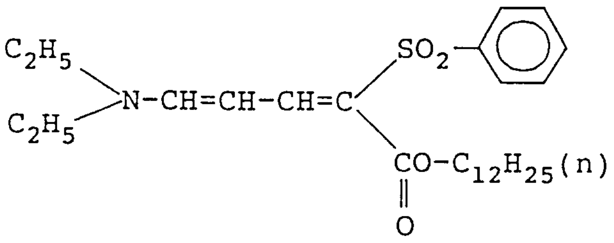
Support (polyethylene terephthalate, 150 µm)

Polymer Mordant:

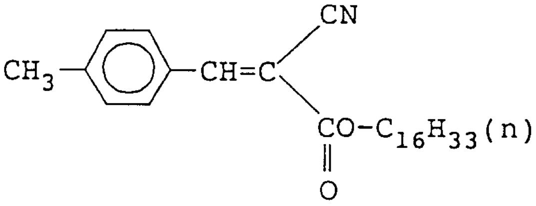


(by mole ratio)

Ultraviolet Light Absorber (1):



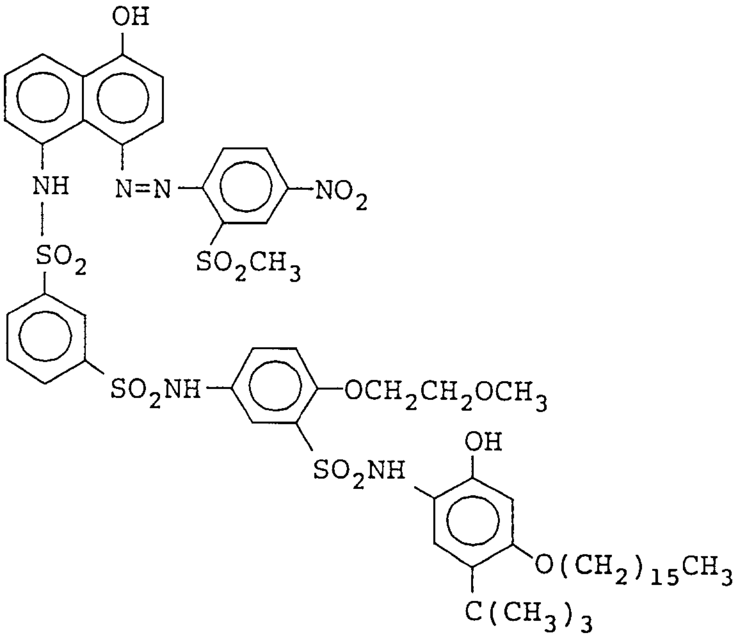
Ultraviolet Light Absorber (2):



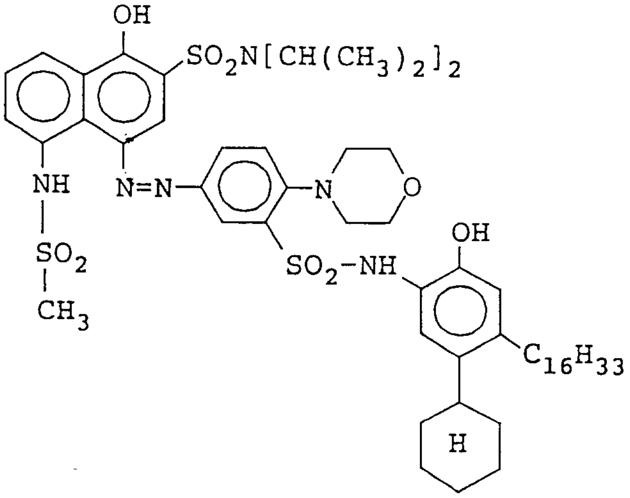
Matte Agent (1):

Spherical Latex of Polymethyl Methacrylate (mean grain size: 4 µm)

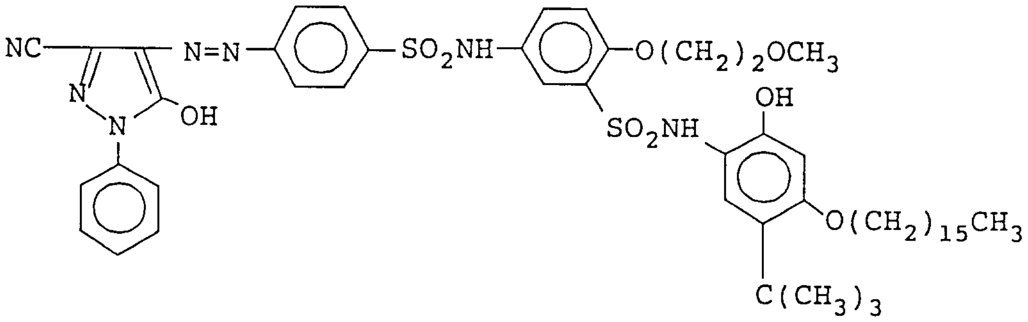
Cyan Dye Releasing Compound (1):



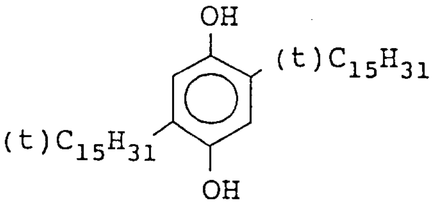
Magenta Dye Releasing Compound (1):



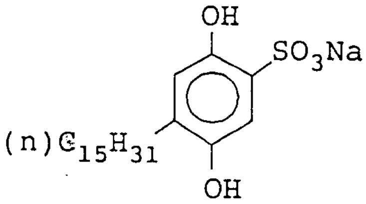
Yellow Dye Releasing Compound (1):



Additive (1):



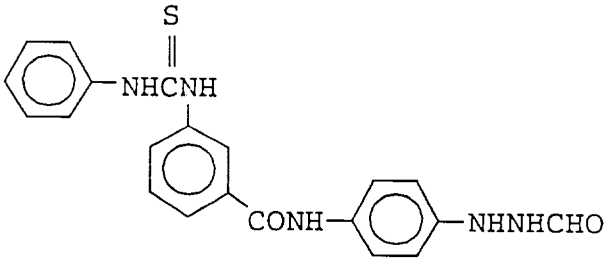
Additive (2):



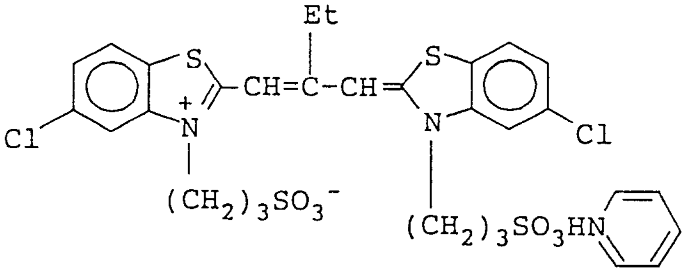
High Boiling Organic Solvent (1):

Tricyclohexyl Phosphate

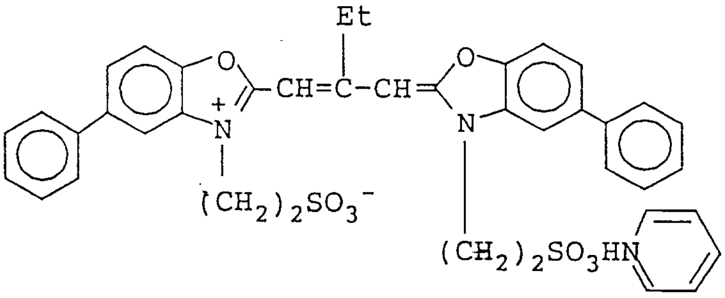
Nucleating Agent (1):



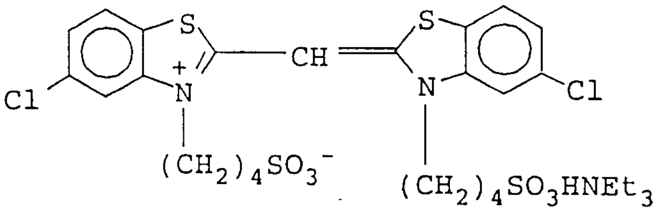
Sensitizing Dye (1):



Sensitizing Dye (2):



Sensitizing Dye (3):



A cover sheet was prepared in the following manner.

A transparent polyethylene terephthalate support having a gelatin undercoat and containing a light piping preventing dye was coated with the following layers:

(1) a neutralization layer containing 10.4 g/m^2 of an acrylic acid-butyl acrylate copolymer (molar ratio 8:2) having an average molecular weight of 50,000 and 0.1 g/m^2 of 1,4-bis(2,3-epoxypropoxy)-butane;
(2) a neutralization timing layer containing 4.3 g/m^2 of acetyl cellulose having an acetylation degree of 51% and 0.2 g/m^2 of poly(methyl vinyl ether-comonomethylmaleate);
(3) a layer containing a mixture of a polymer latex obtained by emulsion polymerization of styrene/ butyl acrylate/acrylic acid/N-methylolacrylamide in a weight ratio of 49.7/42.3/4/4 and a polymer latex obtained by emulsion polymerization of methyl methacrylate/acrylic acid/N-methylolacrylamide in a weight ratio of 93/3/4, which are blended at a solid ratio of 6:4 so as to give a total solid content of 2.5 g/m^2; and
(4) a layer containing 1 g/m^2 of gelatin.

The formulation of an alkali processing composition is shown below:

1-p-Tolyl-4-hydroxymethyl-4-methyl-3-pyrazolidinone	10.0 g
Methylhydroquinone	0.18 g
5-Methylbenzotriazole	3.0 g
Sodium Nitrite (Anhydrous)	0.2 g
Benzyl Alcohol	1.5 mℓ
Carboxymethyl Cellulose Na Salt	58 g
Carbon Black	150 g
Potassium Hydroxide (28% Aqueous Solution)	200 mℓ
Water	680 mℓ

"A pressure-destroyable container" was filled with 0.8 g of a processing solution having the above-described composition.

Then, the emulsions of the 7th, 13th and 19th layers were substituted by Emulsions A-2 to A-11 shown in Table 1 to prepare Samples 102 to 111 shown in Table 3.

TABLE 3

Sample No.	Emulsions		
	7th Layer	13th Layer	19th Layer
101 (Comparison)	A-1	A-1	A-1
102 (Comparison)	A-2	A-2	A-2
103 (Comparison)	A-3	A-3	A-3
104 (Comparison)	A-4	A-4	A-4
105 (Comparison)	A-5	A-5	A-5
106 (Comparison)	A-6	A-6	A-6
107 (Comparison)	A-7	A-7	A-7
108 (Comparison)	A-8	A-8	A-8
109 (Invention)	A-9	A-9	A-9
110 (Invention)	A-10	A-10	A-10
111 (Invention)	A-11	A-11	A-11

After being exposed from the emulsion layer side through a continuous gray filter, the above-described light-sensitive Samples 101 to 111 were overlapped with the above-described cover sheet, and the above-described processing solution was spread between both of the materials to a thickness of 75 µm using a pressure roll at 25°C. After 10 minutes, the transfer density was measured with a color densitometer.

Results thereof are shown in Table 4. The midpoint sensitivity shown here indicates the reciprocal of the exposure giving the intermediate density between the maximum density and the minimum density as a relative value to that of the standard sample. Further, the low-density sensitivity indicates the reciprocal of the exposure giving the density corresponding to (the minimum density + 0.2) as a relative value to that of the standard sample. In Table 4, Y, M, and Cy represent yellow, magenta, and cyan, respectively.

TABLE 4

Sample	Maximum Density			Minimum Density			Midpoint Sensitivity			Low-Density Sensitivity		
	Y	M	Cy	Y	M	Cy	Y	M	C	Y	M	C
101 (Comparison)	2.10	2.25	2.40	0.31	0.33	0.32	100 (standard)	100 (standard)	100 (standard)	100 (standard)	100 (standard)	100 (standard)
102 (Comparison)	1.68	1.75	1.88	0.58	0.59	0.62	72	74	75	52	53	55
103 (Comparison)	2.01	2.08	2.20	0.32	0.34	0.34	82	82	84	81	81	83
104 (Comparison)	2.05	2.23	2.35	0.31	0.33	0.32	90	91	92	88	89	90
105 (Comparison)	1.65	1.73	1.86	0.52	0.55	0.58	76	77	79	56	58	60
106 (Comparison)	2.01	2.19	2.32	0.30	0.32	0.32	83	86	88	84	84	89
107 (Comparison)	2.08	2.22	2.38	0.31	0.33	0.32	95	94	97	92	91	93
108 (Comparison)	2.08	2.19	2.33	0.35	0.36	0.36	94	93	95	96	95	98
109 (Invention)	2.10	2.24	2.40	0.31	0.33	0.32	133	134	137	146	149	155
110 (Invention)	2.11	2.25	2.40	0.31	0.33	0.32	134	133	135	142	142	148
111 (Invention)	2.11	2.25	2.40	0.31	0.33	0.32	136	135	138	147	150	158

Table 4 reveals that the samples of the present invention are high in both midpoint sensitivity and low-density sensitivity and made contrasty in the low-density portions.

EXAMPLE 2

First, methods for preparing silver halide emulsions are described.

Emulsion C-1 (Hexagonal Tabular Internal Latent Image Type Direct Positive Emulsion for Comparison)

With 1 liter of a 0.7wt% aqueous solution of gelatin containing 0.04 M of potassium bromide, 25 mℓ of a 2 M aqueous solution of silver nitrate containing gelatin and 25 mℓ of a 2 M aqueous solution of potassium bromide containing gelatin were concurrently mixed with vigorous stirring for 1 minute by the double jet process. The gelatin solution was maintained at 30 ° C during this period. After addition, the solution was elevated to 75 ° C, and 300 mℓ of a 10et% solution of gelatin was added thereto.

Subsequently, 20 mℓ of a 1 M aqueous solution of silver halide was added allowing 5 minutes, and then a 25wt% aqueous ammonia was added thereto, followed by ripening at 75 ° C.

After termination of ripening, ammonia was neutralized, and then a 1 M aqueous solution of silver nitrate and a 1 M aqueous solution of potassium bromide were added at an accelerated flow rate (the flow rate at the end is 4 times that at the start) while maintaining the pBr to 2.5 by the double jet process. The aqueous solution of silver nitrate was used in an amount of 600 mℓ.

The grains thus formed (hereinafter referred to as core grains) were washed with water by the conventional flocculation process, and gelatin was added thereto to obtain 800 g of hexagonal tabular core grains.

The resulting hexagonal tabular core grains have a mean grain size of 1.0 µm and a mean thickness of 0.21 µm, the mean grain size corresponding to the mean diameter of circles equivalent to projected areas, and occupied 95% of the total projected areas.

Then, 750 mℓ of water and 30 g of gelatin were added to 250 g of the above-described hexagonal tabular core emulsion, and the temperature of the mixture was elevated to 75 ° C. Thereafter, 0.5 g of 1,8-dihydroxy-3,6-dithioctane, 0.8 mg of sodium thiosulfate and 0.4 mg of potassium chloroaurate were added (all were added as aqueous solutions), and the mixture was heated at 75 ° C for 80 minutes, thereby conducting chemical sensitization. A 2 M aqueous solution of silver nitrate and a 2.5 M aqueous solution of potassium bromide were added to the core grains thus subjected to chemical sensitization at an accelerated flow rate (the flow rate at the end is 5 times that at the start) by the double jet process, as with the preparation of the core grains. The amount of the aqueous solution of silver nitrate was used in an amount of 810 mℓ.

This emulsion was washed with water by the conventional flocculation process, and gelatin was added thereto. Thus, a hexagonal tabular internal latent image type core/shell emulsion was obtained. The resulting hexagonal tabular grains have a mean grain size of 2.3 µm, a mean thickness of 0.34 µm and a mean volume size of 1.4 $(\mu m)^3$, the mean grain size corresponding to the mean diameter of circles equivalent to projected areas, and occupied 88% of the total projected areas.

Then, 0.45 mg per mol silver of sodium thiosulfate and 15 mg of poly(N-vinylpyrrolidone) were added to this hexagonal tabular internal latent image type core/shell emulsion, and the mixture was heated at 60 ° C for 60 minutes, thereby subjecting the surface of the grains to chemical sensitization to prepare a hexagonal tabular internal latent image type direct positive emulsion.

Emulsion C-2 to C-8 (Comparison) and C-9 to C-11 (Invention)

Emulsions C-2 to C-11 were prepared in the same manner as Emulsion C-1 with the exception that the metal complexes shown in Table 5 were added in amounts (per mol of silver nitrate) shown in Table 5 for the respective emulsions when the shells were formed.

TABLE 5

Emulsion	Metal Complex	Amount Added (mol)
C-1 (Comparison)	---	---
C-2 (Comparison)	$K_3Ir(Cl)_6$	1.4×10^{-4}
C-3 (Comparison)	$K_3Ir(CN)_4Cl_2$	1.4×10^{-4}
C-4 (Comparison)	$K_3Ir(CN)_5Cl$	1.4×10^{-4}
C-5 (Comparison)	$K_3Co(Cl)_6$	1.4×10^{-4}
C-6 (Comparison)	$K_3Co(CN)_4Cl_2$	1.4×10^{-4}
C-7 (Comparison)	$K_3Co(CN)_5Cl$	1.4×10^{-4}
C-8 (Comparison)	$K_3Fe(CN)_6$	1.4×10^{-4}
C-9 (Invention)	$K_3Ir(CN)_6$	1.4×10^{-4}
C-10 (Invention)	$K_3Co(CN)_6$	1.4×10^{-4}
C-11 (Invention)	$K_4Ru(CN)_6$	1.4×10^{-6}

Subsequently, a light-sensitive element for comparison having the structure shown in Table 6 (sample 201) was prepared using Emulsion C-1.

TABLE 6

Constitution of Light-Sensitive Element 201 for Sample 201 for Comparison

Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
21st	Protective Layer	Gelatin	1.00
		Matte Agent (1)	0.25
20th	Ultraviolet Light Absorbing Layer	Gelatin	0.50
		Ultraviolet Light Absorber (1)	4.0×10^{-4}
		Ultraviolet Light Absorber (2)	4.0×10^{-4}
19th	Yellow-Sensitive Layer (high sensitivity)	Internal Latent Image Type Direct Positive Emulsion C-1 (grain size: 2.3 μm, hexagonal tabular)	0.60 (converted to silver)
		Sensitizing Dye (3)	1.4×10^{-3}
		Nucleating Agent (1)	6.8×10^{-8}
		Additive (2)	0.03
		Gelatin	0.70

TABLE 6 (cont'd)

Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
18th	Yellow-Sensitive Layer (low sensitivity)	Internal Latent Image Type Direct Positive Emulsion B (grain size: 0.8 μm, octahedral)	0.25 (converted to silver)
		Sensitizing Dye (3)	9.0×10^{-4}
		Nucleating Agent (1)	8.0×10^{-8}
		Additive (2)	4.5×10^{-2}
		Gelatin	0.40
17th	White Reflective Layer	Titanium Dioxide	0.70
		Gelatin	0.18
16th	Yellow Color Material Layer	Yellow Dye Releasing Compound (1)	0.53
		High Boiling Organic Solvent (1)	0.13
		Additive (1)	1.4×10^{-2}
		Gelatin	0.70
15th	Intermediate Layer	Gelatin	0.30
14th	Color Mixing Preventing Layer	Additive (1)	0.80
		Polymethyl Methacrylate	0.80
		Gelatin	0.45

TABLE 6 (cont'd)

Layer No.	Layer Name	Additive	Amount Applied (g/m²)
13th	Green-Sensitive Layer (high sensitivity)	Internal Latent Image Type Direct Positive Emulsion C-1 (grain size: 2.3 μm, hexagonal tabular)	0.80 (converted to silver)
		Sensitizing Dye (2)	2.1×10^{-3}
		Nucleating Agent (1)	2.5×10^{-8}
		Additive (2)	0.08
		Gelatin	1.00
12th	Green-Sensitive Layer (low sensitivity)	Internal Latent Image Type Direct Positive Emulsion B, (grain size: 0.8 μm octahedral)	0.25 (converted to silver)
		Sensitizing Dye (2)	1.1×10^{-3}
		Nucleating Agent (1)	4.4×10^{-8}
		Additive (2)	0.03
		Gelatin	0.50
11th	White Reflective Layer	Titanium Dioxide	1.00
		Gelatin	0.25
10th	Magenta Color Material Layer	Magenta Dye Releasing Compound (1)	0.50
		High Boiling Organic Solvent (1)	0.10
		Additive (1)	9.0×10^{-3}
		Gelatin	0.90

TABLE 6 (cont'd)

Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
9th	Intermediate Layer	Gelatin	0.30
8th	Color Mixing Preventing Layer	Additive (1)	1.20
		Polymethyl Methacrylate	1.20
		Gelatin	0.70
7th	Red-Sensitive Layer (high sensitivity)	Internal Latent Image Type Direct Positive Emulsion C-1 (grain size: 2.3 μm, hexagonal tabular)	0.50 (converted to silver)
		Sensitizing Dye (1)	6.2×10^{-4}
		Nucleating Agent (1)	5.0×10^{-8}
		Additive (2)	0.04
		Gelatin	0.80
6th	Red-Sensitive Layer (low sensitivity)	Internal Latent Image Type Direct Positive Emulsion B (grain size: 0.8 μm octahedral)	0.15 (converted to silver)
		Sensitizing Dye (1)	3.0×10^{-4}
		Nucleating Agent (1)	5.0×10^{-8}
		Additive (2)	0.02
		Gelatin	0.40
5th	White Reflective Layer	Titanium Dioxide	3.00
		Gelatin	0.80

TABLE 6 (cont'd)

Layer No.	Layer Name	Additive	Amount Applied (g/m^2)
4th	Cyan Color Material Layer	Cyan Dye Releasing Compound (1)	0.50
		High Boiling Organic Solvent (1)	0.10
		Additive (1)	0.10
		Gelatin	1.0
3rd	Opaque Layer	Carbon Black	1.70
		Gelatin	1.70
2nd	White Reflective Layer	Titanium Dioxide	22.00
		Gelatin	2.75
1st	Image Receiving Layer	Polymer Mordant (1)	3.00
		Gelatin	3.00

Support (polyethylene terephthalate, 150 µm)

The various compounds identified in Table 6 are the same as those described in Example 1.

Then, the emulsions of the 7th, 13th and 19th layers were substituted by Emulsions C-2 to C-11 shown in Table 5 to prepare Samples 202 to 211 shown in Table 7.

TABLE 7

Sample No.	Emulsions		
	7th Layer	13th Layer	19th Layer
201 (Comparison)	C-1	C-1	C-1
202 (Comparison)	C-2	C-2	C-2
203 (Comparison)	C-3	C-3	C-3
204 (Comparison)	C-4	C-4	C-4
205 (Comparison)	C-5	C-5	C-5
206 (Comparison)	C-6	C-6	C-6
207 (Comparison)	C-7	C-7	C-7
208 (Comparison)	C-8	C-8	C-8
209 (Invention)	C-9	C-9	C-9
210 (Invention)	C-10	C-10	C-10
211 (Invention)	C-11	C-11	C-11

After being exposed from the emulsion layer side through a continuous gray filter, the above-described light-sensitive Samples 201 to 211 were overlapped with the above-described cover sheet of Example 1, and the above-described processing solution of Example 1 was spread between both of the materials to a thickness of 75 µm using a pressure roll at 25 ° C. After 10 minutes, the transfer density was measured with a color densitometer.

Results thereof are shown in Table 8. The mid-point sensitivity shown here indicates the reciprocal of the exposure giving the intermediate density between the maximum density and the minimum density as a relative value to that of the standard sample. Further, the low-density sensitivity indicates the reciprocal of the exposure giving the density corresponding to (the minimum density + 0.2) as a relative value to that of the standard sample.

TABLE 8

Sample	Maximum Density			Minimum Density			Midpoint Sensitivity			Low-Density Sensitivity		
	Y	M	Cy	Y	M	Cy	Y	M	C	Y	M	C
201 (Comparison)	2.10	2.25	2.40	0.31	0.33	0.32	100 (standard)	100 (standard)	100 (standard)	100 (standard)	100 (standard)	100 (standard)
202 (Comparison)	1.42	1.55	1.62	0.58	0.59	0.61	72	72	73	51	51	52
203 (Comparison)	2.01	2.18	2.30	0.33	0.34	0.34	80	80	82	81	80	81
204 (Comparison)	2.10	2.24	2.40	0.31	0.33	0.32	89	88	90	87	86	88
205 (Comparison)	1.48	1.59	1.65	0.53	0.55	0.58	77	79	80	57	56	59
206 (Comparison)	2.03	2.21	2.33	0.33	0.33	0.33	85	85	87	82	84	85
207 (Comparison)	2.11	2.25	2.42	0.31	0.33	0.32	95	96	98	93	94	95
208 (Comparison)	2.00	2.19	2.28	0.36	0.38	0.35	93	94	97	93	94	96
209 (Invention)	2.10	2.25	2.40	0.31	0.33	0.32	138	139	141	153	153	155
210 (Invention)	2.10	2.24	2.39	0.30	0.33	0.31	133	135	137	148	149	152
211 (Invention)	2.10	2.25	2.40	0.31	0.33	0.33	140	140	142	155	156	158

Table 8 reveals that the samples of the present invention are high in both midpoint sensitivity and low-density sensitivity and made contrasty in the low-density portions.

According to the present invention, the images can be obtained which are high in sensitivity and contrasty in the low-density portions on the reversal characteristic curve.

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. An internal latent image type direct positive silver halide emulsion comprising a dispersion medium containing at least one metal complex represented by the following formula (I) and silver halide grains formed in the dispersion medium:

   $[M(CN)_6]^{n-}$ (I)

   wherein M represents Cr, Mn, Co, Ir, Ru, Rh, Re or Os; and n is 3 or 4.

2. The internal latent image type direct positive silver halide emulsion as in claim 1, wherein the silver halide grains include tabular silver halide grains having a mean grain diameter of 0.3 μm or more and a mean grain diameter/mean grain thickness ratio of 2 or more in an amount of 50% or more of the total silver halide grains.

3. A color diffusion transfer photographic film unit comprising (a) a light-sensitive sheet having an image receiving layer, a white reflective layer, a light shielding layer and at least one silver halide emulsion layer combined with at least one dye image forming substance, which are formed on a transparent support, (b) a transparent cover sheet having at least a neutralization layer and a neutralization timing layer, which are formed on a transparent support, and (c) a light shielding alkali processing composition spread between the light-sensitive sheet and the transparent cover sheet, and wherein at least one silver halide emulsion layer in the light-sensitive sheet contains the internal latent image type direct positive silver halide emulsion defined in claim 1.

4. A color diffusion transfer photographic film unit comprising (a) a light-sensitive sheet having an image receiving layer, a white reflective layer, a light shielding layer and at least one silver halide emulsion layer combined with at least one dye image forming substance, which are formed on a transparent support, (b) a transparent cover sheet having at least a neutralization layer and a neutralization timing layer, which are formed on a transparent support, and (c) a light shielding alkali processing composition spread between the light-sensitive sheet and the transparent cover sheet, and wherein at least one silver halide emulsion layer in the light-sensitive sheet contains the internal latent image type direct positive silver halide emulsion defined in claim 2.

5. The internal latent image type direct positive silver halide emulsion as in claim 1, wherein an alkali metal ion is employed as a pair ion of the metal complex.

6. The internal latent image type direct positive silver halide emulsion as in claim 1, wherein the amount of the metal complex is from 1.0×10^{-10} to 1.0×10^{-4} mol per mol of silver halide.

7. The internal latent image type direct positive silver halide emulsion as in claim 1, wherein M is Ir or Ru.

8. The internal latent image type direct positive silver halide emulsion as in claim 2, wherein the mean grain diameter of the tabular silver halide grains is from 0.3 to 10 μm.

9. The internal latent image type direct positive silver halide emulsion as in claim 2, wherein the mean grain diameter/mean grain thickness ratio of the tabular silver halide grains is from 3 to 12.

10. The internal latent image type direct positive silver halide emulsion as in claim 1, wherein at least one metal complex represented by $[M(CN)_6]^{n-}$ is added during growth of grains.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 9036
Page 1

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.5)
X,Y	EP-A-0 336 689 (EASTMAN KODAK COMPANY) * page 5, line 38 * * page 6, line 30 - line 32 * * page 8, line 40 - line 46 * ---	1-10	G03C1/485 G03C8/08
X,Y	DATABASE WPI Section Ch, Week 9105, Derwent Publications Ltd., London, GB; Class E35, AN 91032565 & JP-A-2 301 746 (KONICA CORPORATION) 13 December 1990 * abstract * ---	1-10	
Y	EP-A-0 488 737 (KONICA CORPORATION) * table 2 * * page 5, line 58 - page 6, line 2 * * page 15, line 44 - line 45 * ---	1-10	
Y	US-A-5 112 732 (K.HAYASHI ET AL.) * claims *	1-10	
D	& JP-A-2 259 749 (FUJI) ---		**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
Y	JP-A-3 252 649 (FUJI PHOTO FILM K.K.) * table on p.42 * ---	1-10	G03C
Y	JP-A-4 056 846 (FUJI PHOTO FILM K.K.) * compound list on p.4 * ---	1-10	
Y	JOURNAL OF PHOTOGRAPHIC SCIENCE vol. 11, 1963, LONDON GB pages 140 - 144 H.W.WOOD 'Photographic Action of Complex Cyanides' * the whole document * --- -/--	1-10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 SEPTEMBER 1993	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 9036
Page 2

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.5)
Y	CHEMICAL ABSTRACTS, vol. 87, no. 2, 11 July 1977, Columbus, Ohio, US; abstract no. 14218k, 'Production of silver halide photographic emulsions' page 567 ; * abstract * & SU-A-554522(Shapiro et al.) -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 SEPTEMBER 1993	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document