(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 108 250**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **83109913.0**

(51) Int. Cl.³: **G 03 C 7/26**

(22) Date of filing: **04.10.83**

(30) Priority: **05.10.82 JP 175201/82**

(43) Date of publication of application:
16.05.84 Bulletin 84/20

(84) Designated Contracting States:
DE GB

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(54) **Silver halide multilayer reversal color photographic material.**

(57) A silver halide multilayer reversal color photographic material is disclosed. The material has a blue-sensitive, a green-sensitive and a red-sensitive silver halide emulsion layers at least one of which forms a group consisting of two or three emulsion layers differing in photographic sensitivity. The emulsion layer group contains silver in its high sensitivity constituent layer or in the combination of its high sensitivity constituent layer and its intermediate sensitivity constituent layer in such an amount that it comprises 40 to 80% of the total silver amount in the emulsion layer group. The emulsion layer group containing silver iodide in its high sensitivity constituent layer or the combination of its high sensitivity constituent layer and its intermediate sensitivity layer in such a content that a proportion of the iodide to the all halides in the high sensitivity constituent layer or the combination of the high sensitivity constituent layer and the intermediate sensitivity constituent layer is smaller than that in its low sensitivity constituent layer by 0.3 mole % or more.

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SILVER HALIDE MULTILAYER REVERSAL COLOR PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to color reproduction in a silver halide reversal color photographic material. In greater detail this invention intends to improve upon color reproducibility through exercising an interimage effect in an improved condition.

BACKGROUND OF THE INVENTION

It is impossible in a reversal color photographic material to improve on its color reproducibility using a DIR compound. Therefore, the interimage effect due to iodine acquires importance. In the latest reversal color photographic materials, a high sensibivity emulsion and a low sensitivity emulsion are coated separatedly to form a double (or multiple) layer with the intention of improving granularity. However, a proportion of iodine with respect to total halogen (which is referred to as "iodine content" hereinafter) in the high sensitivity emulsion layer is generally the same as that in the low sensitivity emulsion layer. From the viewpoint of exercisin the interimage effect from the layer in question upon another layer, it becomes necessary to increase the iodine content in the layer in question. However, desirable reproduction of green, red and skin colors with high saturations cannot be

attained only be equally increasing both iodine contents in the high sensitivity and the low sensitivity layers.

The higher the iodine content is in the layer in question, the greater the interimage effect which the layer in question exercises on another layer becomes, but the harder it becomes for the interimage effect from another layer to be received by the layer in question. Accordingly, if heightening an interimage effect from a certain layer; e.g., a red-sensitive layer, upon another layer; e.g., a green-sensitive layer, is intended and for this purpose, iodine contents in emulsions of the whole constituent layers of the red-sensitive layer are increased, and the interimage effect fromt the green-sensitive layer upon the red-sensitive layer is reduced to result in lowering of the saturation of green color.

When a photographic material is exposed to green monochromatic light, its red-sensitive layer also responds to the light because of imperfections in the spectral sensitivity distribution. Such a phenomenon lowers the green color saturation. However, response of the red-sensitive layer to green monochromatic light to such an extent that perceivable gradation is produced takes place only in its high sensitivity constituent layer or in both its high sensitivity constituent layer and its intermediate sensitivity constituent layer because the respon-

sivity of the red-sensitive layer to green monochromatic light is considerably lower. Accordingly, it will suffice for suppressing color formation in the red-sensitive layer to enhance the interimage effect upon the high sensitivity constituent layer or upon both the high sensitivity and the intermediate sensitivity constituent layers of the red-sensitive layer and thereby, to inhibit the development from taking place in the red-sensitive layer. Namely, decreasing an iodine content in the high sensitivity constituent layer or those in the high sensitivity and the intermediate sensitivity constituent layers will answer the above-described purpose. Even if iodine contents are decreased in the above-described manner, reduction of the reverse interimage effect, from the red-sensitive layer upon the green-sensitive layer, which is ascribed to such a decrease in the iodine content, is attended only by negligible small, adverse effects. This is because although a matter to be put in question in the above-described case consists in a lowering of red color saturation to be ascribed to a decrease in magenta dye formation which is caused by response of the green-sensitive layer to red monochromatic light, such a phenomenon attracts much attention only when the exposure is carried out with such intensity that even the low sensitivity constituent layer of the red-sensitive layer can respond, and

the interimage effect from the red-sensitive layer upon the green-sensitive layer can be produced in full by increasing an iodine content in the emulsion for the low sensitivity constituent layer of the red-sensitive layer.

SUMMARY OF THE INVENTION

The above-described way of thinking is also valid in both the green-sensitive layer and the blue-sensitive layer. The effects of this invention descrived above is manifested evidently in an emulsion layer group having two or three constituent layers, which have different photographic sensitivities but the same spectral sensitivity characteristics, with the constituent layer, which is made of a silver halide emulsion having a low lodine content, containing silver in such an amount as to comprise 40 to 80%, preferably 45 to 70%, of the total silver amount in the emulsion layer group. Therein, the difference in iodine content between the emulsion having a high iodine content and the emulsion having a low iodine content is controlled to at least 0.3 mole % or more, preferably within the range of 0.5 mole % to 3.0 mole %. In addition, it is desirable that the emulsion which forms a silver halide emulsion layer having a low iodine content has the halide composition of the silver halide being 0.5 to 5.7, preferably 1.5 to 4.5, mole % iodide, while the emulsion which forms a silver halide emulsion layer having a high iodine

content has the halide composition of the silver halide being 0.8 to 6, preferably 2.0 to 5.0, mole % iodide.

Further, the silver halide emulsion layer having a low iodine content may have one constituent layer or two constituent layers. In case of two constitutent layers, emulsions to form them may have the same iodine content or different ones. If the emulsions have different iodine contents, it is desirable to let the emulsion having higher sensitivity have a lower iodine content.

As described above, the present invention is embodied in a silver halide multilayer reversal color photographic material which has three kinds of, that is, a blue-sensitive, a green-sensitive and a red-sensitive, silver halide emulsion layer. Further at least one of the emulsion layess forms a group consisting of two or three emulsion layers differing in photographic sensitivity, with the emulsion layer group containing silver in its high sensitivity constituent layer or in combination of its high sensitivity constituent layer and its intermediate sensitivity constituent layer in such an amount that it comprises 40 to 80% of the total silver amount in the emulsion layer group. The emulsion layer group containing silver iodide in its high sensitivity constituent layer or in combination of its high sensitivity constituent layer and its intermediate sensitivity constituent layer

in such a content that a proportion of the iodide to total halide in the high sensitivity constituent layer or in combination of the high sensitivity constituent layer and the intermediate sensitivity constituent layer is less than that in its low sensitivity constituent layer by 0.3 mole % or more.

This invention makes it possible to obtain simultaneous improvements in blue, red and greeen saturations. It may safely be said that this invention is epochal, taking into account that conventional methods have been attended by, e.g., such a side effect that increase in saturation of, e.g., green color brings about an inevitable decrease in saturation of, e.g., red color. Therefore, using the photographic material of this invention makes it feasible to provide a clear reversal color image of high color purities.

DETAILED DESCRIPTION OF THE INVENTION

The most suitable layer to be employed in this invention as the layer in which its high sensitivity constituent layer and its low sensitivity constituent layer are made to differ in iodine contents is a green-sensitive layer or a red-sensitive layer from the standpoint of the magnitude of the effect attained.

Examples of silver halides which may be present in the silver halide emulsions of this invention include

silver iodobromide and silver iodochlorobromide.

No particular restriction is put on the mean grain size of the silver halide grains in the photographic emulsions (wherein diameters of grains of spherical or nearly spherical grains and edge lengths of grains of cubic grains are employed as a grain size, and they are averaged on the basis of the projection area method). However, a mean grain size of 3 μ or less is preferable.

The grain size distribution may be narrow or broad.

The silver halide grains in the photographic emulsions of this invention may have a regular crystal form such as that of a cube or an octahedron, an irregular crystal form such as that of a sphere, a plate or so on, or a composite form thereof. A mixture of various crystal forms of silver halide grains may be also present.

The interior and the surface of the silver halide grains may differ, or the silver halide grains may be uniform throughout. Further, either silver halide grains of the kind which form latent image predominantly at the surface of the grains, or silver halide grains of the kind which mainly form latent image inside the grains can be used.

Photographic emulsions to be employed in this invention can be made using methods as described in, for

example, P. Glafkides, Chimie et Physique Photographique, Paul Montel, Paris (1967), G.F. Duffin, Photographic Emulsion Chemistry, The Focal Press, London (1966), V.L.Zelikman et al, Making and Coating Photographic Emulsion, The Focal Press, London (1964), and so on. Namely, the acid process, the neutral method, the ammonia process and so on may be employed. As for methods for reacting a water-soluble silver salt with a water-soluble halide, a single jet method, a double jet method, or a combination thereof may be employed.

Also, a method in which silver halide grains are produced in the presence of excess silver ion (the so-called reverse jet method) can be employed in this invention. On the other hand, the so-called controlled double jet method, in which the pAg of the liquid phase in which silver halide grains are to be precipitated is maintained constant, may be also employed in this invention.

According to the above-described method, silver halide emulsions having a regular crystal form and a nearly uniform grain size, that is, the so-called monodisperse emulsions can be obtained.

Two or more of silver halide emulsions made separately may be used in the form of a mixture.

In a process of producing silver halide grains or allowing the produced silver halide grains to ripen

physically, cadimium salts, zinc salts, thallium salts, iridium salts or complexes, rhodium salts or complexes, iron salts or complexes and/or the like may be present.

Removal of the soluble salts from the silver halide emulsion is, in general, carried out after the formation of the silver halide or after physical ripening. The removal can be effected using the noodle washing method which comprises gelling the gelatin or using a sedimentation process (thereby causing flocculation in the emulsion) taking advantage of a sedimenting agent such as a polyvalent anion-containing inorganic salt (e.g., sodoum sulfate), an anionic surface active agent or an anionic polymer (e.g., polystyrene sulfonic acid), or a gelatin derivative (e.g., an aliphatic acylated gelatin, an aromatic acylated gelatin, an aromatic carbamoylated gelation or the like). The removal of soluble salts from the silver halide emulsion may be omitted.

The silver halide emulsion of this invention can be a so-called un-after-ripened emulsion (e.g., a primitive emulsion), that is to say, a chemically unsensitized emulsion. However, it is usual and preferred for the emulsion of this invention to also be chemically sensitized. Chemical sensitization can be carried out using processes described in P. Glafkides, supra, V.L.Zelikman et al, supra or H. Frieser, Die Gründlagen der Photographischen

Prozesse mit Silverhalogeniden, Akademische Verlagsfesellschaft (1968).

More specifically, sulfur sensitization using compounds containing surfur capable of reacting with silver ion or active gelatin, reduction sensitization using reducing materials, sensitization with gold or other noble metal compounds and so on can be employed individually or as a combination thereof. Examples of suitable sulfur sensitizers which can be used include thiosulfates, thioureas, thiazoles, rhodanines and other sulfur-containing compounds. Specific examples of sulfur sensitizers are descrived in U.S. Patents 1,574, 944; 2,410,689; 2,278,947; 2,728,668; 3,656,955; 4,032,928 and 4,067,740. Examples of reducing sensitizers include stannous salts, amines, hydrazine derivatives, formamidine sulfinic acid, silane compounds and the like, and specific examples of these sensitizers are described in U.S. Patents 2, 487,850; 2,419,974; 2,518,698; 2,983,609; 2,983,610; 2,694, 637; 3,930,867 and 4,054,458. Group VIII metal complexes such as those of platinum, iridium, palladium, etc., other than gold metal complexes, can be employed for the purpose of sensitization with a noble metal. Specific examples of these metal complexes are disclosed in U.S. Patents 2,399, 083 and 2,448,060; British Patent 618,061; and so on.

The photographic emulsions to be employed in this

invention can contain a wide variety of compounds for purposes of preventing fogging or stabilizing photographic functions during production, storage or processing. Namely, azoles such as benzothiazolium salts, nitroindazoles, triazoles, benzotriazoles, benzimidazoles (especially nitro or halogen substituted ones), etc.; heterocyclic mercapto compounds such as mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, mercaptotetrazoles (especially 1-phenyl-5-mercaptotetrazole), mercaptopyrimidines, etc.; the above-described heterocyclic mercapto compounds containing water soluble groups such as carboxylic group, sulfonyl group and the like; thioketo compounds such as oxazoline thione, etc.; azaindenes such as tetraazaindenes (especially 4-hydroxy substituted (1,3,3a,7)-tetraazaindnes) etc.; benzenethiosulfonic acids; benzenesulfinic acids, and many other compounds known as an antifoggant or a stabilizer can be added to the photographic emulsion of this invention.

The photographic emulsion layers or other hydrophilic colloidal layers of the photographic material prepared in accordance with an embodiment of this invention can contain dispersions of water insoluble or slightly soluble synthetic polymers for the purposes of improvement in dimentional stability and so on. For example, polymers

having as monomer components alkyl (meth) acrylate, alkoxyalkyl (meth) acrylate, glycidyl (meth) acrylate, (meth) acrylamide, vinyl ester (e.g., vinyl acetate), acrylonitrile, olefin, styrene and so on individually or in combination of two or more thereof, or combinations of the above-described monomers with acrylic acid, methacrylic acid, α, β-unsaturated dicarboxylic acid, hydroxy-alkyl (meth) acrylate, sulfoalkyl (meth) acrylate, styrenesulfonic acid or so on can be used. Specific examples of these polymers are described in U.S. Patents 2,376,005; 2,739,137; 2,853,457; 3062,674; 3,411,911; 3,488,708, 3,525,620; 3,607.290; 3,635,715 and 3,645,740: British Patents 1,186,699 and 1,307,373: and so on.

The photographic emulsion layers or other hydrophilic colloidal layers of the photographic material prepared in accordance with an embodiment of this invention can contain in organic or organic hardeners. Specific examples of the hardener which can be employed incoude chromium salts (e.g., chrome alum, chromium acetate, etc.), aldehydes (e.g. form-aldehyde, glyoxal, glutaraldehyde, etc.), N-methylol compounds (e.g., dimethylol urea, methylol dimethylhydantoin, etc.), dioxane derivatives (e.g., 2,3-dihydroxydixane, etc.), active vinyl-containing compounds (e.g., 1.3.5-triacryloyl-hexahydro-S-triazine, 1,3-vinylsulfonyl-2-propanol, etc.), active halogen-containing

compounds (e.g., 2,4-dichloro-6-hydroxy-S-triazine, etc.), mucohalogenic acids (e.g., mucochloric acid, mucophenoxychloric acid, etc.). Such hardeners may be added individually or in a combination of two or more thereof.

Specific examples of the above-described hardeners and other hardeners which can be employed are described in U.S. Patents 1,870,354; 2,080,019; 2,726,162; 2,870,013; 2,983,611; 2,992,109; 3,047,394; 3,057,723; 3,103,437; 3,321,313; 3,325,287; 3,362,827 and 3,543,292: British Patents 676,628; 825,544 and 1,270,578: German Patents 872,153 and 1,090,427: published examined Japanese Patent Applications 7133/'57 and 1872/'71: Research Disclosure, vol. 176, p. 26 (Dec. 1978): and so on.

The photographic material prepared in accordance with an embodiment of this invention may contain as a color fog preventing agent a hydroquinone derivative, an aminophenol derivative, a gallic acid derivative, an ascorbic acid derivative and the like.

Specific examples of the color fog preventing agent include those described in U.S. Patents 2,360,290; 2,336,327; 2,403,721; 2,418,613; 2,675,314; 2,701,197; 2,704,713; 2,728,659; 2,732,300 and 2,735,365: published unexamined Japanese Patent Applications 92988/'75, 92989/'75, 93928/'75, 110337/'75 and 146235/'77: published examined Japanese Patent Application 23813/'75: and so on.

Hydrophilic colloidal layers of the photographic material prepared in accordance with an embodiment of this invention may contain an ultraviolet absorbing agent. For example, aryl group-substituted benzotriazole compounds, 4-thiazolidone compounds, benzophenone compounds, cinnamic acid ester compounds, butadiene compounds, benzoxazole compounds and further, ultraviolet absorbing polymers can be employed in the hydrophilic colloidal layers: These ultraviolet absorbing agents may be fixed in the hydrophilic colloidal layer to which they are added.

Specific examples of the ultraviolet absorbing agent are described in U.S. Patents 3,533,794; 3,314,794 and 3,352,681: published unexamined Japanese Patent Application 2784/'71:U.S. Patents 3,705,805; 3,707,375; 4,045,229; 3,700,455 and 3, 499,762: West German Patent Publication 1,547,863: and so on.

The photographic material prepared in accordance with an embodiment of this invention may contain water soluble dyes as a filter dye or for the purposes of preventing irradiation and so on. Examples of such dyes include exonol dyes, hemi-oxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. Amoong these dyes, oxonol dyes, hemioxonol dyes and merocyanine dyes are used to advantage. Specific examples of these dyes which can be used in this invention are described in British

Patents 546,708; 584,609; 1,265,842 and 1,410,488: and U.S. Patents 2,274,782; 2,286,714; 2,526,632; 2,606,833; 2,956,879; 3,148,187; 3,247,127; 3,481,927; 3,575,704; 3,653,905 and 3,718,472.

Preferable couplers which can be added to hydrophilic colloidal layers of the photographic material prepared in accordance with this invention are oil soluble couplers. In addition, polymeric couplers may be incorporated therein.

Magenta couplers which can be used to advantage are those of 5-pyrazolone type, and specific examples thereof are described in U.S. Patents 2,600,788; 2,983,608; 3,062,653; 3,127,269; 3,311,476; 3,419,391; 3,519,429; 3,558,319; 3,582,322; 3,615,506; 3,834,908 and 3,891,445: West German Patent 1,810,464: West German Patent Applications (OLS) 2,408,665; 2,417,945; 2,418,959 and 2,424,467: published examined Japanese Patent Application 6031/'65: published unexamined Japanese Patent Applications 20826/'76, 58922/'77, 129538/'74, 74027/'74, 159336/'75, 42121/'77, 74028/'74, 60233/'75, 26541/'76, 55122/'78, 94752/'82 and 35858/'82: U.S. Patents 3,163,625; 3,211,553; 3,370,952; 3,451,820; 3,926,436; 4,080,211 and 4,128,427: British Patent 1,247,688: Research Disclosure, No. 18815 and No. 19033: Japanese Patent Applications 68978/'81, 60264/'81, 89115/'81, 109056/'81, 140667/'81, 2419/'82 and 29683/'82: and so on.

Yellow couplers which can be used to advantage are compounds of benzoyl acetanilide type and those of pivaloyl acetaniliede type, and specific examples thereof are described in U.S. Patents 2,875,057; 3,265,506; 3,408,194; 3,551, 155; 3,582,322; 3,725,072 and 3,891,445: West German Patent 1,547,868: West German Patent Applications (OLS) 2,219,917; 2,261,361 and 2,414,006: British Patent 1,425,020: published examined Japanese Patent Application 10783/'76: published unexamined Japanese Patent Applications 26133/'72, 73147/'73, 102636/'76, 6341/'75 123342/'75, 130442/'75, 21827/'76, 87650/'75, 82424/'77 and 115219/'77: U.S. Patents 3,211,552; 3,370,952; 3,451,820; 3,926,436; 4,080,211 and 4,128,427: Research Disclosure, No.19033 and No. 21728: Japanese Patent Application 140667/'81: and so on.

Cyan couplers which can be used to advantage are compounds of phenol type and those of naphthol type, and specific examples thereof are described in U.S. Patents 2,369,929; 2,434,272; 2,474,293; 2,521,908; 2,895,826; 3,034,892; 3,311,476; 3,458,315; 3,476,563; 3,583,971; 3,591,383; 3,767,411 and 4,004,929: West German Patent Applications (OLS) 2, 414,830 and 2,454,329: published unexamined Japanese Patent Applications 59838/'73, 26034/'76, 5055/'73, 146828/'76, 69624/'77 and 90932/'77: U.S. Patents 3,211,552; 3,370,952; 3,451,820; 3,926,436; 4,080,211 and 4,128,427: Research Disclosure, No. 21728: Japanese Patent

Application 140667/'81 and so on.

Photographic emulsions to be employed in this invention may be spectrally sensitized with methine dyes and others.

Suitable examples of sensitizing dyes which can be used include those described in German Patent 929,080: U.S. Patents 2,493,748; 2,503,776; 2,519,001; 2,912,329; 3,656,959; 3,672,897 and 4,025,349: British Patent 1,242,588: and published examined Japanese Patent Application 14030/'69.

These sensitizing dyes may be employed individually or in combination. Combinations of sensitizing dyes are often employed for the purpose of supersensitization. Typical examples of supersensitizing combinations are described in U.S. Pantents 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; 3,814,609 and 4,026,707: British Patent 1,344,28I: published examined Japanese Patent Applications 4936/'68 and 12375/'78: and published unexamined Japanese Patent Applications 110618/'77 and 109,925/77.

Hydrophilic colloidal layers of the photographic material prepared in accordance with an embodiment of this invention can contain a so-called gas fog preventing agent for the purpose of preventing deterioration of photographic properties, e.g., lowering of developed color density, in-

crease in color stain and fog, and so on, from being caused by harmful gases like formaldehyde. Suitable examples of such an agent include amines (including alkylamines, arylamines and heterocyclic amines), amides, cyclic or acyclic ureas, sulfinic acids. imides, active methylenes, hydroxybensenes, sulfites and so on.

Specific examples of such compounds are described in published examined Japanese Patent Applications 34675/'71, 38418/'73 and 23908/'76: published unexamined Japanese Patent Applications 47335/'73, 43923/'75 and 87028/'75: Japanese Patent Application 177989/'76: U.S. Patent 3,770,431 and 3,811,891: U.S. Defensive Publication T900028: Research Disclosoure, vol. 101, RD-10133: and so on.

Typical examples of the gas fog preventing agents which can be used to advantage include urea, ethylenediurea, ethyleneurea, melamine, hydantoin, allantoin, urazol, parabanic acid, biuret, glycoluril, 1-methylglycoluril, phthalimide, succinimide, benzenesulfinic acid, styrenesulfinic acid polymer, malonic acid, cyanoacetic acid, dimedone barbituric acid, semicarbazide, 5-pyrazolone type magenta couplers, acylacetanilide type yellow couplers, resorcinol, phloroglucinol, 2, 3 dihydroxynaphthalene, sodium sulfite and so on. The present invention will be explained in greater detail with reference to the following examples.

EXAMPLE 1

On a triacetyl cellulose support having a subbing layer, were coated the emulsion layers and assistant layers described below in this order to prepare a sample.

The first layer: Low sensitivity red-sensitive emulsion layer

100 g of 2-(heptafluorobutyramido)-5-{2'-(2",4"-di-t-acylphenoxy)butyramido}-phenol, which functions as a cyan couplers, was dissolved in a mixture consisting of 100 cc of tricresyl phosphate and 100 cc of ethyl acetate, and the resulting solution was mixed 1 Kg of a 10% gelatin aqueous solution with stirring at a high speed to make an emulsion. 500 g portion of the thus made emulsion was mixed with 1 Kg of a red-sensitive, low sensitivity silver iodobromide emulsion (containing 70 g of silver and 60 g of gelatin, and having an iodine content of 3 mole %), and coated in a layer having a dry thickness of 2 μ (corresponding to a dry coverage of 0.5 g silver per square meter).

The second layer: High sensitivity red-sensitive emulsion layer

100 g of 2-(heptafluorobutyramido)-5-{2'-(2",4"-di-t-acylphenoxy)butyramido}-phenol, which functions as a cyan coupler, was dissolved in a mixture consisting of 100 cc of tricresyl phosphate and 100 cc of ethyl acetate, and the resulting solution was mixed with 1 Kg of a 10% gelatin aqueous solution with stirring at a high speed to

make an emulsion. A 1,000 g portion of the thus made emulsion was mixed with 1 Kg of a red-sensitive, high sensitivity silver iodobromide emulsion (containing 70 g of silver and 60 g of gelatin, and having an iodine content of 3 mole %), and coated in a layer having a dry thickness of 2 μ (which corresponds to a dry coverage of 0.8 g silver per square meter).

The third layer: Interlayer

2,5-Di-t-octylhydroquinone was dissolved in a mixture consisting of 100 cc of dibutyl phthalate and 100 cc of ethyl acetate, and the resulting solution was mixed with 1 Kg of a 10% gelatin aqueous solution with stirring at a high speed to make an emulsion. A 1 Kg portion of the thus made emulsion was mixed with 1 Kg of a 10% gelatin aqueous solution, and coated in a layer having a dry thickness of 1 μ.

The fourth layer: Low sensitivity green-sensitive emulsion layer

A 500 g portion of an emulsion prepared in the same manner as the emulsion used in the first layer except that 1-(2,4,6-trichlorophenyl)-3-{3-(2,4-di-t-amylphenoxy-acetamido)benzamido}-5-pyrazolone was employed as a magenta coupler in place of the cyan coupler was mixed with 1 Kg of a green-sensitive, low sensitivity silver iodobromide emulsion (containing 70 g of silver and 60 g of gelatin,

and having an iodine content of 2.5 mole %), and coated in a layer having a dry thickness of 2.0 μ (which corresponds to a dry coverage of 0.7 g silver per square meter).

The fifth layer: High sensitivity green-sensitive emulsion layer

A 1,000 g portion of an emulsion prepared in the same manner as the emulsion used in the first layer except that 1-(2,4,6-trichlorophenyl)-3-{3-(2,4-di-t-amylphenoxyacetamido)benzamido}-5-pyrazolone was employed as a magenta coupler in place of the cyan coupler was mixed with 1 Kg of a green-sensitive, high sensitivity silver iodobromide emulsion (containing 70 g of silver and 60 g of gelatin, and having an iodine content of 2.5 mole %), and coated in a layer having a dry thickness of 2.0 μ (which corresponds to a dry coverage of 0.7 g silver per square meter).

The sixth layer: Interlayer

A 1 Kg portion of the emulsion used in the third layer was mixed with 1 Kg of a 10% gelatin aqueous solution, and coated in a layer having a dry thickness of 1 μ.

The seventh layer: Yellow filter layer

An emulsion containing yellow colloidal silver was coated in a layer having a dry thickness of 1 μ.

The eighth layer: Low sensitivity blue-sensitive emulsion layer

A 1,000 g portion of an emulsion prepared in the same manner as the emulsion used in the first layer except

that α-(pivaloyl)-α-(1-benzyl-5-ethoxy-3-hydantoinyl)-2-chloro-5-dodecyloxycarbonylacetanilide was employed as a yellow coupler in place of the cyan coupler was mixed with 1 Kg of a blue-sensitive low sensitivity silver iodobromide emulsion (containing 70 g of silver and 60 g of gelatin, and having an iodine content of 2.5 mole %), and coated in a layer having a dry thickness of 2.0 μ (which corresponds to a dry coverage of 0.6 g silver per square meter).

The nineth layer: High sensitivity blue-sensitive emulsion layer

A 1,000 g portion of an emulsion prepared in the same manner as the emulsion used in the first layer except that α-(pivaloyl)-α-(1-benzyl-5-ethoxy-3-hydantoinyl)-2-chloro-5-dodecyloxycarbonylacetanilide was employed as a yellow coupler in place of the cyan coupler was mixed with 1 Kg of a blue-sensitive, high sensitivity silver iodobromide emulsion (containing 70 g of silver and 60 g of gelatin, and having an iodine content of 2.5 mole %), and coated in a layer having a dry thickness of 2.0 μ (which corresponds to a dry coverage of 1.0 g silver per square meter).

The tenth layer: The second protective layer

1 Kg of the emulsion employed in the third layer was mixed with 1 Kg of a 10% gelatin aqueous solution, and coated in a layer having a dry thickness of 2 μ.

The eleventh layer: The first protective layer

A 10% gelatin aqueous solution containing a chemically unsensitized fine grain emulsion (grain size: 0.15 μ, 1 mole % silver iodobromide emulsion) was coated in a layer having a dry thickness of 1 μ at a dry coverage of 0.3 g/m^2.

The thus obtained multilayer coated film was named Sample A.

On the other hand, Sample B was produced in the same manner as Sample A except that the iodine content in the emulsion employed in the first layer was changed to 4.0 mole % and further, the iodine content in the emulsion employed in the second layer was changed to 2.5 mole %. Similarly, Sample C, Sample D and Sample E were produced in the same manner as Sample A except that the iodine content in the emulsion employed in the first layer was changed to 3.5 mole %, 4.5 mole % and 4.0 mole % respectively and further, the iodine content in the emulsion employed in the second layer was changed to 1.5 mole %, 2.5 mole % and 3.5 mole % respectively.

Each of these films was exposed to green light through a wedge for sensitometry, and subjected to the reversal processings described below.

Cyan densities of each sample at the points where magenta densities (D_M) were 2.00 and 1.00 respec-

tively were measured. Under the condition employed for such measurements, the maximum of magenta densities (D_M^{Max}) was 3.20, and that of cyan densities (D_C^{Max}) was 3.14. Results obtained are shown in Table 1.

Table 1

Sample	Cyan Density D_M=2.00	Cyan Density D_M=1.00
A (Comparison)	2.96	2.70
B (This Invention)	3.12	2.98
C (This Invention)	3.08	2.95
D (This Invention)	3.10	2.97
E (This Invention)	3.05	2.87

Processing Step:

Step	Time	Temp.
First Development	6'	38°C (± 0.3)
Washing	2'	"
Reversal	2'	"
Color Development	6'	"
Adjustment	2'	"
Bleaching	6'	"
Fixation	4'	"
Washing	4'	"
Stabilization	1'	Ordinary Temp.
Drying		

Composition of First Developing Solution:

Water	700 ml
Sodium Tetrapolyphosphate	2 g
Sodium sulfite	20 g
Hydroquinone Monosulfonate	30 g
Sodium Carbonate (Monohydrate)	30 g
1-Phenyl 4-methyl 4-hydroxymethyl-3-pyrazolidone	2 g
Potassium Bromide	2.5 g
Potassium Thiocyanate	1.2 g
Potassium Iodide (0.1% solution)	2 ml
Water to make	1,000 ml

Composition of Reversal Solution:

Water	700 ml
Hexasodium Nitrilo-N,N,N-trimethylene-phosphonate	3 g
Stannous Chloride (Dihydrate)	1 g
p-Aminophenol	0.1 g
Sodium Hydroxide	8 g
Glacial Acetic Acid	15 ml
Water to make	1,000 ml

Composition of Color Developing Solution:

Water	700 ml
Sodium Tetrapolyphosphate	2 g
Sodium Sulfite	7 g
Sodium Tertiary Phosphate (Dodecahydrate)	36 g

Potassium Bromide	1 g
Potassium Iodide (0.1% solution)	90 ml
Sodium Hydroxide	3 g
Citrazinic Acid	1.5 g
N-ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate	11 g
Ethylenediamine	3 g
Water to make	1,000 ml

Composition of Adjusting Solution:

Water	700 ml
Sodium Sulfite	12 g
Sodium Ethylenediaminetetraacetate (Dihydrate)	8 g
Thioglycerine	0.4 ml
Glacial Acetic Acid	3 ml
Water to make	1,000 ml

Composition of Bleaching Solution:

Water	800 ml
Sodium Ethylenediaminetetraacetate (Dihydrate)	2 g
Ammonium Ethylenediaminetetraacetato-ferrate (II) (Dihydrate)	120 g
Potassium Bromide	100 g
Water to make	1 ℓ

Composition of Fixing Solution:

Water	800 ml
Ammonium Thiosulfate	80 g

Sodium Sulfite	5 g
Sodium Hydrogensulfite	5 g
Water to make	1 ℓ

Composition of Stabilizing Solution:

Water	800 ml
Formalin (37 wt%)	5 ml
Fuji Driwell	5 ml
Water to make	1 ℓ

Next, each of the above-described films was exposed to red light through a wedge for sensitometry and then, subjected to the above-described reversal processings. Magenta densities of each of the resulting films were measured at the points of cyan densities (D_C) 2.00 and 1.00, respectively. Results obtained are shown in Table 2.

Table 2

Sample	Magenta Density	
	D_C=2.00	D_C=1.00
A	3.09	3.02
B	3.07	3.01
C	3.05	2.98
D	3.08	3.00
E	3.09	3.02

Therein, D_C^{Max} was 3.11, and D_M^{Max} was 3.18.

With respect to color reproducibility and color saturation of green color, it can be safely said that the greater the difference between magenta density and cyan density under the condition of exposure to green light, the better the saturation of green color. As for the saturation of red color, it can be evaluated by the difference between magenta density and cyan density under the condition of exposure to red light. In this case also, the greater the difference, the better the saturation. Therefore, the data in Table 1 and Table 2 are re-edited as follows.

Sample	Green Light Exposure		Red Light Exposure	
	D_M=2.00	D_M=1.00	D_C=2.00	D_C=1.00
A (Comparison)	0.96	1.70	1.09	2.02
B (This Invention)	1.12	1.98	1.07	2.01
C (This Invention)	1.08	1.95	1.05	1.98
D (This Invention)	1.10	1.97	1.08	2.00
E (This Invention)	1.05	1.87	1.09	2.02

It can be seen from the above-described table that in the samples of this invention the difference between cyan density and magenta density under green light exposure was greater, and a decrease in the difference between cyan density and magenta density under red light exposure was hardly observed, that is to say, an increase in color saturation was attained.

EXAMPLE 2

Sample F was prepared in the same manner as Sample B in Example 1 except that the iodine content in the emulsion of the third layer was changed to 4.0 mole % and the iodine content in the emulsion of the fourth layer was changed to 2.5 mole %, and exposed to red light or green light through a wedge for sensitometry, followed by the above-described reversal processings.

Color saturation of this sample was measured and thereby, this sample has proved to be excellent in both red color saturation and green color saturation.

While the invention has been described in detail and with reference to specific embodiment 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.

WHAT IS CLAIMED IS:

1. A silver halide multilayer reversal photographic material, comprising:

a support base having thereon;

a blue-sensitive silver halide emulsion layer:

a green-sensitive silver halide emulsion layer; and

a red-sensitive silver halide emulsion layer;

wherein one of the emulsion layers is comprised of a plurality of layers of differing photographic sensitivity including a layer of a highest sensitivity and a layer of a second highest sensitivity, the layer of highest sensitivity and second highest sensitivity containing 40 to 80% of the total silver in the plurality of layers of differing sensitivity;

further wherein the layer of highest sensitivity contains iodide such that the proportion of iodide to all halides in the layer of highest sensitivity is less than the iodide in a low sensitivity layer by 0.3 mole % or more.

2. A silver halide multilayer reversal photographic material as claimed in Claim 1, wherein the layer of highest sensitivity contains 40 to 80% of the total silver in the plurality of layers of different sensitivity and further wherein the combination of the layer of highest

sensitivity and the layer of second highest sensitivity contain iodide such that the portion of iodide to all halides in the combination is less than the iodide in the low sensitivity layer by 0.3 mole % or more.

3. A silver halide multilayer reversal photographic material as claimed in Claim 1, wherein the layer of highest sensitivity and the second highest sensitivity contain 45 to 70% of the total silver in the plurality of layers of different sensitivity.

4. A silver halide multilayer reversal photographic material as claimed in Claim 1, wherein the layer of highest sensitivity contains iodides such that the proportion of iodide to all halides in the layer of highest sensitivity is in the range of 0.5 mole % to 3.0 mole % of the iodide in the low sensitivity layer.

5. A silver halide multilayer reversal photographic material as claimed in Claim 1, wherein the layer of highest sensitivity includes silver halide having a halide composition including 0.5 to 7.5 mole % iodide.

6. A silver halide multilayer reversal photographic material as claimed in Claim 5, wherein the layer of highest sensitivity contains silver halide having a halide composition containing 1.5 to 4.5 mole % iodide.

7. A silver halide multilayer reversal photographic material as claimed in Claim 5, wherein the layer of low

sensitivity includes silver halide having a halide composition containing 0.8 to 6 mole % iodide.

8. A silver halide multilayer reversal photographic material as claimed in Claim 7, wherein the layer of low sensitivity contains silver halide having a halide composition containing 2.0 to 5.0 mole % iodide.

0108250

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 83 10 9913

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. ³)
Y	DE-A-2 744 489 (FUJI PHOTO FILM) * Example 1 *	1-8	G 03 C 7/26
Y	GB-A-1 474 994 (FUJI PHOTO FILM) * Example 2; claims 1,11 *	1-8	
Y	DE-A-2 718 437 (AGFA-GEVAERT) * Page 13, line 1 - page 16; example 2 *	1-8	
A	DE-A-2 453 664 (FUJI PHOTO FILM)		
A	DE-A-2 530 645 (EASTMAN KODAK)		TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			G 03 C 7 G 03 C 1

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01-03-1984	PHILOSOPH L.P.

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
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