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(54) Multilayer silver halide reversal color photographic material.

(57) A multilayer silver halide reversal color photographic material is disclosed. The material has on a support three or more silver halide emulsion layers having the same color sensitivity but different photographic sensitivities. The highest sensitivity emulsion layer and the second highest sensitivity emulsion layer among the above-described silver halide emulsion layers have silver halide emulsions of an iodide content of 4.5 mole % or less and such a grain size distribution that 85% or more, by number or by weight, of whole silver halide grains in the emulsion have sizes which are within ± 40% of its mean grain size. The material provides good granularity of the resulting dye image.

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This invention relates to a color photographic light-sensitive material of a multilayer construction.

The present invention achieves an improvement in granularity of dye image grains which are produced by processing a sensitive material, which contains silver halides and nondiffusible couplers as main components, with a first developing solution containing a black-and-white developing agent of pyrazolidone type and subsequent processing of the resulting material with a reversal color developing solution containing a color developing agent of paraphenylenediamine type.

A coupler incorporated color photographic light-sensitive material comprises a support coated generally with a nondiffusible cyan-forming coupler incorporated red-sensitive silver halide emulsion layer, a nondiffusible magenta-forming coupler incorporated green-sensitive emulsion layer and a nondiffusible yellow-forming coupler incorporated blue-sensitive emulsion layer.

In general, most color photographic light-sensitive materials for taking photographs are constructed of a support,

e.g., a cellulose triacetate film, a polyethylene terephthalate film or the like which is provided with a subbing layer in advance and has provided thereon, a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer in that order. Further a yellow filter layer is put in between the green-sensitive layer and the blue-sensitive layer and further, a gelatin protective layer is provided as the topmost layer of the sensitive material. In each of the sensitive layers differing in color sensitivity, the so-called mixed emulsion, e.g., the combination of a high sensitivity emulsion containing relatively coarse grains and a low sensitivity emulsion containing fine grains, is employed as the silver halide emulsion for the purpose of attaining desired gradation.

Hitherto, it has been the common understanding that the granularity of a dye image is almost decisively influenced by a grain size of silver halide used and further, somewhat changed by what kind of coupler is used therein. However, the grain size of silver halide and its sensitivity bear a nearly proportional relationship to each other. Therefore, an attempt at maintaining sensitivity and improving the granularity of the resulting dye image by decreasing the grain size has an inherent limitation.

On the other hand, using some specific couplers is also a means of effecting the granularity of a dye image. However, it is frequently difficult to balance improvement

in the granularity with attainment of desired hue and other properties.

Moreover, German Patent 1,121,470 and British Patent 923,045 disclose another method of improving granularity of a dye image in which - as described in their respective examples - an emulsion which has been conventionally coated in a single layer is separated into two layers, a high sensitivity emulsion layer and a low sensitivity emulsion layer, which have their sensitivities in the same visible region and which contain their respective nondiffusible couplers which form colors of substantially the same hue, and which are coated in a double layer. Such a method makes it possible to increase the sensitivity of a multilayer color photographic light-sensitive material without deteriorating the granularity in a practically important density range of the gradation curve, and in proportion to this gain in the sensitivity the grain size of the silver halide emulsion can be decreased resulting in the improvement of the granularity. However, though such a method can exhibit its effect on improvement of the granularity in a negative-type film which contains a small amount of coupler in its high sensitivity emulsion layer, it is not effective for reversal-type films, because it is necessary for reversal type film to contain a large amount of coupler in its high sensitivity emulsion layer in order to render the gradation hard in a high density range. Therefore,

the influence of the high sensitivity emulsion tends to appear in the density range which has the greatest influence on the image quality, and in such a density range that any improvement in granularity is not observed. In order to remedy such a condition with reversal type films, there has been proposed a method in which rendering gradation contrasty is carried out by reducing the iodide content in the emulsion of a high sensitivity emulsion layer and thereby, the contribution of the high sensitivity emulsion to the density in the exposure range which the low sensitivity emulsion is to cover is lessened. However, an emulsion contains grains among which there exists a distribution of sizes, and deterioration of granularity due to coarse grains present in a specific proportion is unavoidable. Accordingly, the improvement in granularity attained by the above-described method is far from being sufficient.

In order to further improve the granularity, it becomes necessary to narrow the width of the grain size distribution of the emulsion of a high sensitivity emulsion layer. Such a means is exceedingly effective in improving the granularity. However, it cannot be applied to the system in which a conventionally single emulsion layer is separated into a high sensitivity emulsion layer and a low sensitivity emulsion layer, because an emulsion having a narrowed distribution of grain sizes comes to have a very

hard gradation, that is, a greatly increased γ value. Thus, when a conventional single layer is separated into two layers (a high sensitivity emulsion layer and a low sensitivity emulsion layer) both having a narrowed distribution of grain sizes, it becomes impossible to prepare gradation capable of reproducing an image.

If one intends to achieve an improvement of the granularity by narrowing a distribution of grain sizes of an emulsion, one must separate the emulsion into at least three layers, that is, a high sensitivity emulsion layer, an intermediate sensitivity emulsion layer and a low sensitivity emulsion layer.

An object of this invention is to improve the granularity of a multilayer reversal color photographic material.

The above-described object is attained by a multilayer silver halide reversal color photographic material having on a support at least three or more of silver halide emulsion layers which have the same color sensitivity but different photographic sensitivities from one another, among which emulsion layers at least both the emulsion layer having the highest photographic sensitivity and the emulsion layer having the second highest photographic sensitivity contain silver halide emulsions in which iodide contents in

their respective halides are 4.5 mole % or less and that their respective distributions of grain sizes are such that 85% or more, by number or by weight, of the whole silver halide grains in the emulsion have sizes which are within ±40% of its mean grain size.

A grain size and a grain size distribution can be determined according to methods described in T.H. James, The Theory of Photographic Process, the 4th Ed.,.pp. 100 - 102 (1977).

Reducing iodide contents in the highest sensitivity emulsion layer and the second highest sensitivity emulsion layer to 4.5 mole % or less results in accelerating the progress of development and consequently, such layers become contrasty and an influence of their granularities upon emulsions having lower sensitivities can be diminished.

This invention makes it possible to improve the granularity without making the gradation contrasty. Namely, in the density range near 1.0 based on the reversal density which has the greatest influence on qualities of reversal image, the highest sensitivity emulsion layer and the second highest sensitivity emulsion layer both exert a slight influence on the granularity and therefore, this invention can provide reversal images excellent in the granularity.

It is desirable in this invention to adjust a developed color density of the highest sensitivity emulsion layer to the range of 0.2 to 2.0, preferably 0.3 to 1.5, and a reversal density of the second highest sensitivity emulsion layer to the range of 0.2 to 2.0, preferably 0.3 to 1.5.

The preferable iodide content in the highest sensitivity emulsion layer and/or the second sensitivity emulsion layer is within the range of 0.5 mole % to 3.0 mole %.

A particularly preferable emulsion is one which has such a grain size distribution that 90% or more, by number or by weight, of the whole silver halide grains in the emulsion have sizes which are within ±40% of its mean grain size.

This invention can produce satisfactory results in any of the sensitive emulsion layers, such as a red-sensitive emulsion layer, a green-sensitive emulsion layer and a blue-sensitive emulsion layer. In particular, it has a great effect in a red-sensitive emulsion layer and a green-sensitive emulsion layer in which difference in granularity is more liable to be perceived.

In addition, it is more preferable in this invention that an emulsion layer having one kind of color sensitivity has three or four constituent layers differing in photographic sensitivity, and the constituent layers

are arranged nearer to the support in order of decreasing sensitivity.

A difference in photographic sensitivity between the highest sensitivity emulsion layer and the second highest sensitivity emulsion layer ranges from 0.2 to 1.0, preferably from 0.3 to 0.8, expressed in terms of logarithm. On the other hand, the preferable difference in photographic sensitivity between the second highest sensitivity emulsion layer and another emulsion layer whose sensitivity ranks next and a preferable difference in photographic sensitivity between the low sensitivity emulsion layers are from 0.3 to 1.5, expressed in terms of logarithm.

Moreover, it is desirable in this invention from the standpoint of improving upon granularity that a mole ratio of silver to coupler in the highest sensitivity emulsion layer is smaller than that in the second highest emulsion layer. It is especially preferable to control the ratio of silver to coupler in the higher sensitivity emulsion layer to a lower value than that in the lower sensitivity emulsion layer.

In a photographic emulsion to be employed in this invention, both silver iodobromide and silver iodochlorobromide can be incorporated.

In a photographic emulsion of this invention, no particular regard need be paid to the mean grain size of

silver halide grains to be contained therein (the mean grain size being determined by averaging grain sizes based on the projection area wherein a grain diameter in case of spherical or nearly spherical grains and an edge length in case of cubic grains are taken as the grain sizes). However, a silver halide emulsion having a mean grain size of 3 μm or less is preferred.

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 grains of the kind which mainly form latent image inside the grains can be used.

The photographic emulsion to be employed in this invention can be prepared using various 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), and V.L. Zelikman et al, Making and Coating

Photographic Emulsion, The Focal Press, London (1964). Namely, such methods include the acid process, the neutral process, the ammonia process and so on. Suitable methods for reacting a water-soluble silver salt with a water-soluble halide include a single jet method, a double jet method, a combination thereof and so on.

Also, a method in which silver halide grains are produced in the presence of excess silver ions(the so-called reverse mixing 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 also be employed therein.

According to the above-described method, a silver halide emulsion having a regular crystal form and almost uniform grain size, that is to say, a monodisperse silver halide emulsion can be obtained.

A mixture of two or more silver halide emulsions prepared separately may be employed.

In a process of producing silver halide grains or allowing the produced silver halide grains to ripen physically, cadmium salts, zinc salts, lead 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 well-known 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., sodium 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 gelatin 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 for the emulsion of this invention to 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 Grundlagen der Photographischen Prozesse mit Silberhalogeniden, Akademische Verlagsgesellschaft (1968).

More specifically, sulfur sensitization using compounds containing sulfur capable of reacting with silver 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 disclosed 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 suitable 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. Complex salts of the metals of Group VIII of the Periodic Table (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 emulsion 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 of the sensitive material. 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 carboxyl group, sulfonyl group or the like; thioketo compounds such as oxazolinethiones; azaindenes such as tetraazaindenes (especially 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes); benzenethiosulfonic acids; benzenesulfinic acids; and other many compounds known as an antifoggant or a stabilizer can be added for the above-described purposes.

The photographic emulsion layers and 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 water soluble synthetic polymers for purposes of improvement in dimensional stability and so on. Suitable examples of such polymers include those which contain as monomer components alkyl(metha)acrylate, alkoxyalkyl(metha)acrylate, glycidyl-(metha)acrylate, (metha)acrylamide, vinyl ester (e.g., vinyl acetate, etc.), acrylonitrile, olefins, styrene and so on individually or in combination of two or more thereof, or

in combination with one or two of the above-described monomers with acrylic acid, methacrylic acid, α,β-unsaturated dicarboxylic acid, hydroxyalkyl(metha)acrylate, sulfoalkyl-(metha)acrylate, styrenesulfonic acid or so on. Specific examples thereof are described in U.S. Patents 2,376,005; 2,739,137; 2,853,457; 3,062,674; 3,411,911; 3,488,708; 3,525,620; 3,607,290; 3,635,715 and 3,645,740 and British Patents 1,186,699 and 1,307,373.

The photographic emulsion layers and other hydrophilic colloidal layers of the photographic material prepared in accordance with an embodiment of this invention can contain inorganic or organic hardeners. For example, chromium salts (e.g., chrome alum, chromium acetate, etc.), aldehydes (e.g., formaldehyde, glyoxal, glutaraldehyde, etc.), N-methylol compounds (e.g., dimethylol urea, methylol dimethylhydantoin, etc.), dioxane derivatives (e.g., 2,3-dihydroxydioxane, etc.), active vinyl-containing compounds (e.g., 1,3,5-triacryloyl-hexahydroxy-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, mucophenoxy-chloric acid, etc.) and so on can be used individually or in a combination of two or more thereof.

Specific examples of the above-described hardeners and other hardeners which can be used in this invention 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/'59 and 1872/'71, Research Disclosure, vol. 176, p. 26 (Feb. 1978) and so on.

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

Specific examples of such color fog-preventing agents are 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, 110,337/'75 and 146235/'77, published examined Japanese Patent Application 23813/'75, and so on.

The sensitive material prepared in accordance with an embodiment of this invention may contain an ultraviolet ray-absorbing agent in its hydrophilic colloidal layer. For example, benzotriazole compounds substituted with aryl groups, 4-thiazolidone compounds, benzophenone compounds, cinnamic acid esters, butadiene compounds, benzoxazole

compounds and further, such polymers as to absorb ultraviolet rays can be employed as such an agent. These ultraviolet absorbing agents may be fixed in the hydrophilic colloidal layer to which they are added.

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

Hydrophilic colloidal layers of the sensitive material prepared in accordance with an embodiment of this invention may contain water soluble dyes as a filter dye, or for other various purposes, e.g., antiirradiation and so on. Useful examples of such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. Among those dyes, oxonol dyes, hemioxonol dyes and merocyanine dyes are used to greater advantage.

Specific examples of such dyes are described in British Patents 546,708; 584,609; 1,265,842 and 1,410,488, 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, and so on.

Suitable couplers to be incorporated in hydrophilic colloidal layers of the sensitive material prepared

in accordance with an embodiment of this invention are oil soluble couplers. Such couplers may be polymeric ones.

Preferred magenta couplers include 5-pyrazolone type couplers. Specific examples of magenta couplers which can be used in this invention are those 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; 3,834,980 and 3,891,445, German Patent 1,810,464, West Germany 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; 3,211,552; 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.

Preferred yellow couplers include benzoylacetoanilide type and pivaloylacetoanilide type compounds. Specific examples of yellow couplers which can be used in this invention are those which 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, and so on.

Useful cyan couplers include phenolic compounds and naphtholic compounds. Specific examples of such compounds include those which 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, 25034/'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 and Research Disclosure, No. 21728.

The photographic emulsions to be used in this invention may be spectrally sensitized using methine dyes or other dyes. Useful sensitizing dyes 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. 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; 3,814,609 and 4,026,707, British Patent 1,344,281, published examined Japanese Patent Applications 4936/'68 and 12375/'78; and published unexamined Japanese Patent Applications 110618/'77 and 109925/'77.

The sensitive material prepared in accordance with an embodiment of this invention can contain in its hydrophilic colloidal layers a so-called gas fog preventing agent which can prevent deterioration of photographic properties, e.g., decrease in developed color density, increase in color stain and fog, etc., from occurring upon contact with harmful gases such as formaldehyde and the like. For example, amines (including alkylamine, arylamines and heterocyclic amines), amides, cyclic or acyclic ureas, sulfinic acids, imides, active methylenes, hydroxybenzenes, sulfites and so on can be used for the above-described purpose.

Specific examples of gas fog preventing agents 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, U.S. Patents 3,770,431 and 3,811,891, U.S. (Def. Pub) T900028; Research Disclosure, vol. 101, RD-10133, and so on.

Suitable examples of gas fog preventing agents which can be used in this invention include urea, ethylene diurea, ethylene urea, melamine, hydantoin, allantoin, urazol, parabanic acid, biuret, glycoluril, 1-methylglycoluril, phthalimide, succinimide, benzenesulfunic acid, styrene-sulfinic acid polymer, malonic acid, cyanoacetic acid, dimedone barbituric acid, semicarbazie, 5-pyrazolone type magenta couplers, acylacetoanilide type yellow couplers, resorcinol, phloroglucinol, 2,3-dihydroxynaphthalene, sodium sulfite and so on.

The invention will now be described with respect to the following examples. However, the scope of the invention is not limited to the examples.

EXAMPLE 1

On a triacetylcellulose support having a subbing layer, were coated the emulsion layers and the assistant layers described below in order of the following description to prepare Sample A.

The first layer: Low sensitivity red-sensitive emulsion layer

100 g of a cyan coupler, 2-(heptafluorobutylamido)-5-{2'-(2",4"-di-t-amylphenoxy)butylamido}-phenol, was dissolved in a mixture of 100 ml of tricresyl phosphate and 100 ml of

ethyl acetate, and the resulting solution was stirred at a high speed together with 1 kg of a 10% gelatin water solution to prepare an emulsion. A 500 g portion of the thus obtained emulsion was mixed with 1 kg of a red-sensitive low sensitivity silver iodobromide emulsion (containing silver iodobromide grains having such a grain size distribution that 81% by number of the whole grains have sizes which are within ±40% of its mean grain size, 70 g of silver, 60 g of gelatin and 6 mole % of silver iodide), and coated in a layer having a dry thickness of 2 μm(containing 0.5 g/m^2 of silver).

The second layer: Intermediate sensitivity red-sensitive emulsion layer

100 g of a cyan coupler, 2-(heptafluorobutylamino)-5-{2'-(2",4" -di-t-amylphenoxy)butylamido}-phenol, was dissolved in a mixture of 100 ml of tricresyl phosphate and 100 ml of ethyl acetate, and the resulting solution was stirred at high speed together with 1 kg of a 10% gelatin water solution to prepare an emulsion. A 1,000 g portion of the thus obtained emulsion was mixed with 1 kg of a red-sensitive intermediate sensitivity silver iodobromide emulsion (having such a grain size distribution that the percentage of grains as described in the first layer was 76% and containing 70 g of silver, 60 g of gelatin and 6 mole % of silver iodide), and coated in a layer having a dry thickness of 1 μm(containing 0.4 g/m^2

of silver).

The third layer: High sensitivity red-sensitive emulsion layer

100 g of a cyan coupler, 2-(heptafluorobutylamido)-5-{2'-(2",4"-di-t-amylphenoxy)butylamido}-phenyl, was dissolved in a mixture of 100 ml of tricresyl phosphate and 100 ml of ethyl acetate, and the resulting solution was stirred at a high speed together with 1 kg of a 10% gelatin water solution to prepare an emulsion. A 1,000 g portion of the thus obtained emulsion was mixed with 1 kg of a red-sensitive high sensitivity silver iodobromide emulsion (having such a grain size distribution that the percentage of grains as described in the first layer was 78%, and containing 70 g of silver, 60 g of gelatin and 6 mole % of silver iodide), and coated in a layer having a dry thickness of 1 μm(containing 0.4 g/m^2 of silver).

The fourth layer: Interlayer

2,5-di-t-octylhydroquinone was dissolved in a mixture of 100 ml of dibutyl phthalate and 100 ml of ethyl acetate, and the resulting solution was stirred at a high speed together with 1 kg of 10% gelatin water solution. A 1 kg portion of the thus obtained emulsion was mixed with 1 kg of a 10% aqueous gelating solution, and coated in a layer having a dry thickness of 1 μm.

The fifth layer: Low sensitivity green-sensitive emulsion layer

A 500 g portion of the emulsion prepared in the same

manner as in the first layer except that 1-(2,4,6-trichlorophenyl)-3-{3-(2,4-di-t-amylphenoxyacetamido)benzamido}-5-pyrazolone was used as a magenta coupler in place of the cyan coupler was mixed with 1 kg of a green-sensitive low sensitivity silver iodobromide emulsion (having such a grain size distribution that the percentage of grains as described in the first layer was 81%, and containing 70% of silver, 60 g of gelatin and 5.2 mole % of silver iodide), and coated in a layer having a dry thickness of 2.0 μm (containing 0.7 g/m^2 of silver).

The sixth layer: Intermediate sensitivity green-sensitive emulsion layer

A 1,000 g portion of the emulsion prepared in the same manner as in the first layer except that 1-(2,4,6-trichlorophenny)-3-{3-(2,4-di-t-amylphenoxyacetamido)benzamido}-5-pyrazolone was used as a magenta coupler in place of the cyan coupler was mixed with 1 kg of a green-sensitive intermediate sensitivity silver iodobromide emulsion (having such a grain size distribution that the percentage of grains as described in the first layer was 75%, and containing 70 g of silver, 60 g of gelatin and 5.2 mole % of silver iodide), and coated in a layer having a dry thickness of 1 μm (containing 0.35 g/m^2 of silver).

The seventh layer: High sensitivity green-sensitive emulsion layer

A 1,000 g portion of the emulsion prepared in the

same manner as in the first layer except that 1-(2,4,6-trichlorophenyl)-3-{3-(2,4-di-t-amylphenoxyacetamido)-benzamido}-5-pyrazolone was used as a magenta coupler in place of the cyan coupler was mixed with 1 kg of a green-sensitive high sensitivity silver iodobromide emulsion (having such a grain size distribution that the percentage of grains as described in the first layer was 75%, and containing 70 g of silver, 60 g of gelatin and 5.2 mole % of silver iodide), and coated in a layer having a dry thickness of 1 μm(containing 0.35 g/m^2 of silver).

The eighth layer: Interlayer

A 1 kg portion of the same emulsion as employed in the fourth layer was mixed with 1 kg of a 10% aqueous gelatin solution, and coated in a layer having a dry thickness of 1 μm.

The ninth layer: Yellow filter layer

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

The tenth layer: Low sensitivity blue-sensitive emulsion layer

A 1,000 g portion of the emulsion prepared in the same manner as in the first layer except that α-(pivaloyl) α-(1-benzyl-5-ethoxy-3-hydantoinyl)-2-chloro-5-dodecyloxy-carbonylacetoanilide was used as a yellow coupler in place of the cyan coupler was mixed with 1 kg of a blue-sensitive low

sensitivity silver iodobromide emulsion (having such a grain size distribution that the percentage of grains as described in the first layer was 77%, and containing 70 g of silver, 60 g of gelatin and 5.5 mole % of silver iodide), and coated in a layer having a dry thickness of 2.0 μm (containing 0.6 g/m^2 of silver).

The eleventh layer: Intermediate sensitivity blue-sensitive emulsion layer

A 1,000 g portion of the emulsion prepared in the same manner as in the first layer except that α-(pivaloyl)-α-(1-benzyl-5-ethoxy-3-hydantoinyl)-2-chloro-5-dodecyloxy-carbonylacetoanilide was used as a yellow coupler in place of the cyan coupler was mixed with 1 kg of a blue-sensitive intermediate sensitivity silver iodobromide emulsion (having such a grain size distribution that the percentage of grains as described in the first layer was 72%, and containing 70 g of silver, 60 g of gelatin and 5.5 mole % of silver iodide), and coated in a layer having a dry thickness of 1.0 μm (containing 0.5 g/m^2 of silver).

The twelfth layer: High sensitivity blue-sensitive emulsion layer

A 1,000 g portion of the emulsion prepared in the same manner as in the first layer except that α-(pivaloyl)-α-(1-benzyl-5-ethoxy-3-hydantoinyl)-2-chloro-5-dodecyloxy-carbonylacetoanilide was used as a yellow coupler in place of the cyan coupler was mixed with 1 kg of a blue-sensitive

high sensitivity silver iodobromide emulsion (having such a grain size distribution that the percentage of grains as described in the first layer was 72%, and containing 70 g of silver, 60 g of gelatin and 5.5 mole % of silver iodide), and coated in a layer having a dry thickness of 1.0 μm(containing 0.5 g/m^2 of silver).

The thirteenth layer: Second protective layer

A 1 kg portion of the same emulsion as used in the third layer was mixed with 1 kg of a 10% aqueous gelatin solution, and coated in a layer having a dry thickness of 2 μm.

The fourteenth layer: First protective layer

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

On the other hand, Sample B was prepared in the same manner as in Sample A except that in the emulsion used in the second layer the silver iodide content and the percentage in the grain size distribution were changed to 2.5 mole % and 87%, respectively, and in the emulsion used in the third layer the silver iodide content and the percentage in the grain size distribution were changed to 2.5 mole % and 87 %, respectively.

Sample C was prepared in the same manner as in Sample A except that in the emulsion used in the second layer the silver iodide content and the percentage in the grain size distribution were changed to 6 mole % and 88%, respectively, and in the emulsion used in the third layer the silver iodide content and the percentage in the grain size distribution were 6 mole % and 88%, respectively.

Sample D was prepared in the same manner as in Sample A except that in the emulsion used in the second layer the silver iodide content and the percentage in the grain size distribution were changed to 2.5 mole % and 80%, respectively, and in the emulsion used in the third layer the silver iodide content and the percentage in the grain size distribution were changed to 2.5 mole % and 80%, respectively.

Sample E was prepared in the same manner as in Sample A except that in the emulsion used in the second layer the silver iodide content and the percentage in the grain size distribution were changed to 3 mol % and 91 %, respectively, and in the emulsion used in the third layer the silver iodide content and the percentage in the grain size distribution were changed to 3 mole % and 91%, respectively.

Each of these sample films was exposed to light through a step wedge for RMS measurement (root mean square

measurement) and then, subjected to the following reversal processings.

RMS granularity (aperture diameter used upon measurement: 10 μm x 10 μm) of each sample was measured in both areas of cyan densities 0.75 and 1.50. Results obtained are shown in Table 1.

Table 1

	RMS Granularity	
Sample	0.75 (Cyan Density)	1.50 (Cyan Density
A (Comparison)	0.062	0.085
B (This Invention)	0.041	0.058
C (Comparison)	0.056	0.076
D (Comparison)	0.058	0.081
E (This Invention)	0.033	0.051

When, as embodied in Sample B and Sample E of this invention, a monodisperse emulsion was employed and a silver iodide content was reduced to 4.5 mole % or less, the granularity was found to be markedly improved.

Processing Steps:

Step	Time (min.)	Temperature (°C)
First Development	6	38 (±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	1000 ml

Composition of Reversal Processing Solution:

Water	700	ml
Hexasodium Nitrilo-N,N,N-trimethylenephosphonate	3	g
Stannous Chloride (Dihydrate)	1	g
p-Aminophenol	0.1	g
Sodium Hydroxide	8	g
Glacial Acetic Acid	15	ml
Water to make	1000	ml

Composition of Color Developing Solution:

Water	700	ml
Sodium Tetrapolyphosphate	2	g
Sodium Sulfite	7	g
Sodium Tertiary Phosphate (Dihydrate)	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-methanesulfoamidoethyl)-3-methyl-aminoaniline Sulfate	11	g
Ethylenediamine	3	g
Water to make	1000	ml

Composition of Adjustment Processing Solution:

Water	700	ml
Sodium Sulfite	12	g
Sodium Ethylenediaminetetraacetate (Dihydrate)	8	g
Thioglycerine	0.4	g
Glacial Acetic Acid	3	ml
Water to make	1000	ml

Composition of Bleaching Solution:

Water	800	ml
Sodium Ethylenediaminetetraacetate (Dihydrate)	2.0	g
Ammonium Ethylenediaminetetraacetatoferrate (II) (Dihydrate)	120.0	g
Potassium Bromide	100.0	g
Water to make	1.0	ℓ

Composition of Fixing Solution:

Water	800	ml
Ammonium Thiosulfate	80.0	g
Sodium Sulfite	5.0	g
Sodium Hydrogensulfite	5.0	g
Water to make	1.0	ℓ

Composition of Stabilizing Solution:

Water	800	ml
Formaline (37 wt%)	5.0	ml
Fuji Driwel	5.0	ml
Water to make	1.0	ℓ

EXAMPLE 2

Sample F was prepared in the same manner as in Sample A of Example 1 except that in the emulsion used in the sixth layer the silver iodide content and the percentage in the grain size distribution were changed to 5.2 mole % and 88% respectively, and in the emulsion used in the seventh layer the silver iodide content and the percentage in the grain size distribution were changed to 5.2 mole % and 90% respectively.

Further, Sample G was prepared in the same manner as in Sample A of Example 1 except that in the emulsion used in the sixth layer the silver iodide content and the percentag in the grain size distribution were changed to 3.2 mole % and 90% respectively, and in the emulsion used in the seventh layer the silver iodide content and the percentage in the grain size distribution were changed to 3.2 mole % and 90 % respectively.

Furthermore, Sample H was prepared in the same manner as in Sample A of Example 1 except that in the emulsior used in the sixth layer the silver iodide content and the percentage in the grain size distribution were changed to 4.5 mole % and 77% respectively, and in the emulsion used in the seventh layer the silver iodide content and the percentage in the grain size distribution were changed to 4.5 mole % and 80% respectively.

In addition, Sample I was prepared in the same manner as in Sample A of Example 1 except that in the emulsion used in the sixth layer the silver iodide content and the percentage in the grain size distribution were changed to 4.3 mole % and 90% respectively, and in the emulsion used in the seventh layer the silver iodide content and the percentage in the grain size distribution were changed to 4.3 mole % and 92% respectively.

Each of the thus obtained films was subjected to the same exposure processing and the same measurement as in Example 1 and thereby, RMS granularity in each of areas having magenta densities 0.75 and 1.50 was determined. Results obtained are shown in Table 2.

Table 2

Sample	RMS Granularity	
	0.75 (Magenta Density)	1.50 (Magenta Density)
A (Comparison)	0.045	0.061
F (Comparison)	0.038	0.052
G (This Invention)	0.033	0.046
H (Comparison)	0.042	0.058
I (This Invention)	0.031	0.048

The samples of this invention in which emulsions used were monodisperse ones and had silver iodide contents of 4.5 mole% or less are markedly improved in granularity.

EXAMPLE 3

Sample J was prepared in the same manner as in Sample A of Example 1 except that in the emulsion used in the eleventh layer the silver iodide content and the percentage in the grain size distribution were changed to 6 mole % and 92% respectively, and in the emulsion used in the twelfth layer the silver iodide content and the percentage in the grain size distribution were changed to 6 mole % and 90 % respectively.

Further, Sample K was prepared in the same manner as in Sample A except that in the emulsion used in the eleventh layer the silver iodide content and the percentage in the grain size distribution were changed to 4.2 mole % and 88% respectively, and in the emulsion used in the twelfth layer the silver iodide content and the percentage in the grain size distribution were changed to 4.2 mole % and 88 % respectively.

Furthermore, Sample L was prepared in the same manner as in Sample A except that in the emulsion used in the eleventh layer the silver iodide content and the percentage in the grain size distribution were changed to 3.5 mole % and 91 % respectively, and in the emulsion used in the twelfth layer the silver iodide content and the percentage in the grain size distribution were changed to 3.5 mole % and 91 % respectively.

In addition, Sample M was prepared in the same manner as in Sample A except that in the emulsion used in the eleventh layer the silver iodide content and the percentage in the grain size distribution were changed to 3.5 mole % and 77 % respectively, and in the emulsion used in the twelfth layer the silver iodide content and the percentage in the grain size distribution were changed to 3.5 mole % and 75% respectively.

Each of the thus obtained films was subjected to the same exposure processing and the same measurement as in Example 1 and thereby, RMS granularity in each of areas having yellow densities 0.75 and 1.50 was determined. Results obtained are shown in Table 3.

Table 3

Sample	RMS Granularity 0.75 (Yellow Density)	RMS Granularity 1.50 (Yellow Density)
A (Comparison)	0.086	0.134
J (Comparison)	0.078	0.128
K (This Invention)	0.069	0.119
L (This Invention)	0.061	0.111
M (Comparison)	0.082	0.131

Graininess is better the smaller a value of RMS granularity is and therefore, as can be seen from Table 1, Table 2 and Table 3, all the samples prepared in accordance

with the embodiments of this invention were improved in graininess in all of their respective red-sensitive, green-sensitive and blue-sensitive emulsion layers.

Claims:

1. A multilayer silver halide reversal color photographic material having on a support at least three or more silver halide emulsion layers which have the same color sensitivity but different photographic sensitivities, among said emulsion layers at least both the emulsion layer having the highest photographic sensitivity and the emulsion layer having the second highest photographic sensitivity, containing silver halide emulsions in which iodide contents in their respective halides are 4.5 mole % or less and their respective grain size distributions being such that 85 % or more, by number or by weight, of the whole silver halide grains in said emulsion have sizes which are within ± 40 % of its mean grain size.

2. A multilayer silver halide reversal color photographic material as claimed in Claim 1, wherein the highest photographic sensitivity emulsion layer has a developed color density in the range of 0.2 to 2.0 and the second highest photographic sensitivity emulsion layer has a reversal densitiy in the range of 0.2 to 2.0.

3. A multilayer silver halide reversal color photographic material as claimed in Claim 2, wherein the highest photographic sensitivity emulsion layer has a developed color density in the range of 0.3 to 1.5 and the second highest photographic sensitivity emulsion layer has a reversal density in the range of 0.3 to 1.5.

4. A multilayer silver halide reversal color photographic material as claimed in one of the preceding Claims, wherein the highest photographic sensitivity emulsion layer and the second highest photographic sensitivity emulsion layer have iodide contents in the range of 0.5 mole % to 3.0 mole %.

5. A multilayer silver halide reversal color photographic material as claimed in one of the preceding Claims, wherein the highest photographic sensitivity emulsion layer and the second highest sensitivity emulsion layer have grain size distributions such that 90 % or more, by number or by weight, of the whole silver halide grains in said emulsions have sizes which are within ± 40 % of its mean grain size.

6. A multilayer silver halide reversal color photographic material as claimed in one of the preceding Claims, wherein the difference in a photographic sensitivity between the highest photographic sensitivity emulsion layer and the second highest photographic sensitivity emulsion layer is in the range of 0.2 to 1.0 as expressed in terms of logarithm.

7. A multilayer silver halide reversal color photographic material as claimed in Claim 6, wherein the difference in a photographic sensitivity between the highest photographic sensitivity emulsion layer and the second highest photographic sensitivity emulsion layer is in the range of 0.3 to 0.8 as expressed in terms of loga-

rithm.

8. A multilayer silver halide reversal color photographic material as claimed in one of the preceding Claims, wherein the difference in a photographic sensitivity between the second highest photographic sensitivity emulsion layer and another or one of other low photographic sensitivity emulsion layers is in the range of 0.3 to 1.5 as expressed in terms of logarithm.

9. A multilayer silver halide reversal color photographic material as claimed in one of the preceding Claims, wherein the difference in a photographic sensitivity between the low photographic sensitivity emulsion layers is in the range of 0.3 to 1.5 as expressed in terms of logarithm.