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

(11) Publication number: **0 610 597 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **93121086.8**

(51) Int. Cl.^{5}: **G03C 1/005**

(22) Date of filing: **29.12.93**

(30) Priority: **13.01.93 JP 19473/93**

(43) Date of publication of application:
17.08.94 Bulletin 94/33

(84) Designated Contracting States:
BE DE FR GB NL

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(54) **Method of preparing a tabular grain silver halide emulsion.**

(57) A method of preparing a tabular silver halide emulsion involves growing a silver halide seed emulsion in which tabular silver halide grains having an aspect ratio of 2 to 12 account for 50% to 100% of a total projected area of all silver halide grains of the seed emulsion, to prepare a grown tabular silver halide emulsion in which tabular silver grains having an aspect ratio of 3 to 40 account for 50% to 100% of a total projected area of all silver halide grains of the grown emulsion.

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The present invention relates to a method of preparing a tabular silver halide emulsion, and a silver halide light-sensitive material which uses the tabular silver halide emulsion and is improved in production stability and sensitivity.

Tabular silver halide emulsions exhibit a high sensitivity in spectral sensitization range, and provide a high sharpness. However, it is difficult to prepare only desired grains stably.

A process of grain formation of tabular grains is generally a complicated process of short-time rush addition - Ostwald ripening - ripening using a silver halide solvent - growth. If, therefore, variations exit in the individual steps, the shape and the performance of final grains vary largely. For this reason, a batch difference in the preparation is large in performance of tabular grains, so it is impossible to successively obtain grains with a stable performance in many cases. In the preparation of tabular grains, the shape and the performance of the grains largely depend on particularly nucleation performed by short-time rush addition - Ostwald ripening - ripening using a silver halide solvent. In the formation of tabular grains, since selective formation of tabular grains alone is impossible in nucleation, it is necessary to perform the Ostwald ripening and the step of extinguishing grains except for tabular grains by using a silver halide solvent described above. Batch differences in these steps, however, are particularly large to cause variations in the shape of tabular grains, making it difficult to stably obtain grains with a high aspect ratio and a high monodispersity.

As a method of solving these problems, a seed crystal method is known in which a large amount of grains finished up to grain growth are prepared as seed crystal grains in the same batch, and a portion of the seed crystal grains thus prepared is used to perform the steps after the grain growth. As a method of preparing octahedral emulsion grains according to the seed crystal method, JP-A-1-15234 discloses a method in which octahedral seed crystals are prepared, and a core/shell emulsion is formed by using them. As a method of preparing cubic emulsion grains, JP-A-1-131542 describes a method in which monodisperse cubic seed crystal grains are prepared in advance, and shells are grown by using a portion of these grains. As a method of forming tabular grains according to the seed crystal method, JP-B-3-46811 discloses a method in which spherical seed crystals are formed as seed crystals, which are grown for the purpose of obtaining tabular grains with a high monodispersity. In this method, however, since the spherical seed crystals are grown as nuclei, grains obtained after the growth are large in thickness. The method is therefore unsuitable for formation of grains with a high aspect ratio, which take advantage of the characteristics of tabular grains.

To obtain high-aspect-ratio tabular grains by using the seed crystal method, it is required to obtain small-size tabular grains that are small in thickness as seed crystal grains. Although the method described in JP-A-62-18555 is available as a method of preparing small-size tabular grains, this method is inadequate as a method of obtaining seed crystals because the yield of a silver halide emulsion with respect to a reactor vessel is low. In the method of obtaining small-size tabular grains described in Japanese Patent Application No. 3-280961, the size distribution of grains formed is broad, and so the size distribution further broadens if these grains are used as seed crystals. Since this makes it impossible to perform after-ripening evenly for the grains, no high performance can be expected. As described above, no method of stably preparing tabular grains with a high aspect ratio and a narrow size distribution by using seed crystals has been developed yet, so the development of such a method is currently being demanded.

It is an object of the present invention to provide a method of stably preparing tabular silver halide emulsion in which tabular grains having an aspect ratio of 3 or more is high and which has a narrow grain size distribution.

According to the present invention, there is provided a method of preparing a tabular silver halide emulsion, comprising growing a silver halide seed emulsion in which tabular silver halide grains having an aspect ratio of 2 to 12 account for 50% to 100% of a total projected area of all silver halide grains of the seed emulsion, to prepare a grown tabular silver halide emulsion in which tabular silver grains having an aspect ratio of 3 to 40 account for 50% to 100% of a total projected area of all silver halide grains of the grown emulsion.

In the grown tabular emulsion, a variation coefficient of equivalent-circle diameters of projected areas of all the tabular grains is preferably 8% to 22%.

In the seed emulsion, a variation coefficient of equivalent-circle diameters of projected areas of all the tabular grains is preferably 8% to 22%.

The seed emulsion is prepared by a process including a nucleation step in which a dispersion medium is used which preferably comprises a low molecular weight gelatin having an average molecular weight of 5,000 to 25,000. An aqueous halide salt solution added during the nucleation preferably contains 0.5 to 20 mol% of iodide ions. The nucleation temperature is preferably 20°C to 50°C, and the nucleation time is preferably 5 to 60 seconds.

The grown tabular silver halide emulsion prepared by the method of the present invention is also within a scope of the invention.

The tabular silver halide grains of the present invention will be described in detail.

A tabular grain is a general term for grains having one twin plane or two or more parallel twin planes. A twin plane refers to a (111) plane on the both sides of which ions at all lattice points bear a mirror image relationship.

In the tabular silver halide emulsion, an aspect ratio means the ratio of the diameter of a silver halide grain to its thickness. That is, the aspect ratio is a value obtained by dividing the diameter of each silver halide grain by its thickness. In this case, the diameter of a silver halide grain means the diameter of a circle having an area equivalent to the projected area of that grain when the grain is observed by a microscope or an electron microscope. An aspect ratio of 3 or more therefore means that the diameter of this circle is three times or more the thickness of the corresponding grain.

As an example of a method of measuring the aspect ratio, there is a method wherein a transmission electron micrograph is taken, and the equivalent-circle diameter and the thickness of each individual grain are obtained, according to a replica method. In this method, the thickness is calculated from the length of the shadow of the replica.

In the silver halide seed crystal grains of the present invention, 50% to 100%, preferably 60% to 100%, and more preferably 70% to 100% of a projected area are occupied by grains with an aspect ratio of 2 to 12. In grains obtained by growing these tabular seed crystal grains, 50% to 100%, preferably 60% to 100%, and more preferably 70% to 100% of a projected area are occupied by grains with an aspect ratio of 3 to 40.

The aspect ratio of the tabular seed crystal grains of the present invention is 2 to 12, preferably 5 to 12, and more preferably 8 to 12. The aspect ratio of grains obtained by growing these seed crystals is 3 to 40, preferably 6 to 40, and more preferably 10 to 40.

The variation coefficient of each of the tabular seed crystal grains of the present invention and the variation coefficient of the tabular grains obtained by growing the tabular seed crystal grains is preferably 8% to 22%, more preferably 8% to 20%, and most preferably 8% to 18%. The variation coefficient means a quotient obtained by dividing the standard deviation of the diameters of all silver halide grains by their average diameter.

The tabular silver halide emulsion grains of the present invention may be of any of silver bromide, silver iodobromide, silver chloride, silver chlorobromide, silver bromochloroiodide, and silver iodochloride.

The tabular silver halide emulsion grains of the present invention may have at least two-layered structure with essentially different halogen compositions inside grains or may have a homogeneous composition.

An emulsion having the layered structure with different halogen compositions can be either an emulsion containing a high-iodide layer in the core and a low-iodide layer in the outermost layer, or an emulsion containing the low-iodide layer in the core and the high-iodide layer in the outermost layer. The layered structure may consist of three or more layers, in which case it is preferred that the iodide content become lower toward the outermost layer.

A method of preparing the tabular seed crystal grains and a method of preparing the tabular grains obtained by growing the tabular seed crystal grains, according to the present invention, will be described.

The tabular seed crystal grains of the present invention are prepared by a process of simultaneously mixing water-soluble silver salt and halide salt aqueous solutions into a reactor vessel containing an aqueous gelatin solution, extinguishing grains except for tabular grains by ripening, and then growing the remaining grains. That is, seed crystal grains are obtained by forming tabular grains essentially small in size.

To obtain a large amount of tabular seed crystals in a single batch without impairing the monodispersity of the grains, the method of preparing tabular grains of the present invention produces a large amount of tabular nuclei in nucleation and extinguishes grains other than tabular grains by the use of a solvent. The remaining grains are then grown to a stable size as seed crystals, desalted, set, and stored. Tabular grains with a desired size can then be obtained by growing a portion of the seed crystals thus prepared. By checking the sizes of the seed crystal grains by using an electron microscope according to the replica method, it is possible to accurately determine the amount of silver halide further required to obtain grains with a desired size. This also eliminates variations in grain size among batches. Small size grains can be obtained by stopping the growth at an intermediate stage, which, however, can not fully use the volume of the reaction vessel, leading to a low yield. On the other hand, small size grains can be obtained by using seed crystals if the ratio of silver nitrated used for the growth is made small, and this results in an advantage that the volume of the reaction vessel can be used up to its upper limit.

In the present invention, seed grains are preferably grown such that each final grown tabular grain has a volume 4 or more times the volume of each seed grain on an average. The size of the grown grain varies depending on its intended use. Grains used in a color negative light-sensitive material vary in sizes depending on sensitivity. The size is small in a high-sensitivity material, and is large in a low-sensitivity material. Further, it is generally performed to use a plurality of different sensitivity grains in one light-sensitive material to provide a wide light sensitivity.

Grains of various desired sizes can be obtained by growing seed grains of a given size. One advantage of using seed grains resides in that the grown grains of plural batches can be stably obtained from the seed grains of one batch. Thus, it is preferred that the seed grains be used in an amount as small as possible, and grown large.

A time required for the formation of tabular grains is generally about 40 minutes in the stage of nucleation - ripening, which is 1/2 to 1/3 the time of the whole process. If grains finished before the growth are prepared in one batch according to the seed crystal method, the overall preparation time can be advantageously shortened as compared with that when the whole process is repeated from scratch many times.

In the present invention, in order to increase the generation ratio of twined crystal nuclei in the nucleation, iodide ions are added to the reaction solution or the aqueous silver salt solution added during the nucleation. The iodide ion concentration in the solution is 0.5 to 20 mol%, preferably 0.5 to 12 mol%, and more preferably 0.5 to 9 mol% of halide ions.

The purpose of the present invention is to form seed crystal grains with a narrow size distribution. As an effective method for this purpose, a method is known which uses gelatin having an average molecular weight of 70,000 or less in nucleation. In the present invention, it is unpreferable to use a silver halide solvent which increases the thickness of the grains, since the present invention aims at providing tabular grains having a high aspect ratio. Bromide ions are preferably used as the solvent in the present invention. For this reason, the use of a dispersion medium which achieves a higher tabular grain formation ratio is required in the present invention. The low molecular weight gelatin used in the present invention has an average molecular weight of 5,000 to 25,000, preferably 5,000 to 20,000, and more preferably 5,000 to 18,000.

When an aqueous silver nitrate solution and an aqueous potassium bromide solution are added to a reaction solution, precipitation of a silver halide occurs immediately. Although the number of fine silver halide grains formed increases while silver ions and bromide ions are added, it does not increase in proportion to time; the increase gradually becomes moderate, and finally stops and remains at a constant value. The silver halide fine grains produced by the precipitation starts growing immediately after being produced. Nuclei produced earlier grow more easily, and those produced later are more difficult to grow. If a variation occurs in size of nuclei during the nucleation, this variation is further increased by the subsequent Ostwald ripening. The spread of the size distribution of the nuclei occurring in the nucleation is determined by the nucleation time and the temperature of the reaction solution. The size distribution begins to spread when 90 seconds elapse in nucleation at 30°C. Polydispersion begins when 50 seconds elapse in nucleation at 45°C, and when 80 seconds elapse in nucleation at 60°C. The time before the size distribution starts spreading depends on the temperature of nucleation because this time reflects the time before the fine silver halide grains are dissolved. For this reason, a time for addition of the aqueous silver nitrate solution and the aqueous halide solution to the reactor vessel is preferably as short as possible. In addition, the nucleation temperature is practically, preferably as low as possible within a range in which the aqueous gelatin solution is not set. As a method of nucleation, there are two known methods: one is a so-called single-jet method in which only an aqueous silver nitrate solution is added to a halide salt solution, and the other is a so-called double-jet method in which an aqueous silver nitrate solution and an aqueous halide salt solution are added simultaneously. Since desirable nucleation conditions in the present invention require a high twined crystal generation probability, the double-jet method is preferred in which the degree of supersaturation in a stirmixing apparatus is high and hence nuclei are produced easily. Although the nucleation can be performed at a temperature between 20°C to 50°C, it is preferably performed at a temperature between 30°C to 40°C at which the twined crystal generation probability is high, and which is therefore suitable for the manufacture. After the nucleation, the temperature is raised, the pAg is adjusted to 7.6 to 10.0, and grains other than tabular grains are extinguished by using a silver halide solvent. After the tabular grains alone are thus obtained, desired tabular seed crystal grains are obtained by a grain growth process. In the grain growth process, it is desired to add silver and a halogen solution so as not to produce new crystal nuclei. The aspect ratio of the emulsion grains can be controlled by properly selecting the temperature and the pAg of the grain growth process, the addition rates of the aqueous silver nitrate solution and the aqueous halide solution, and the like.

Further, a method in which all or part of silver added in the process of the grain growth is supplied as fine silver halide grains as described in JP-A-62-99751 may be used.

The tabular silver halide emulsion of the present invention can be prepared with reference to known methods of preparing tabular silver halide emulsion, except for the shape of the seed crystals and the shape of the grains grown from the seed crystals as defined in the present invention. Tabular silver halide emulsions are described in, for example, the reports of Cugnac and Chateau; Duffin, "Photographic Emulsion Chemistry", Focal Press, New York, 1966, pp. 66-72; and P.H. Trivelli and W.F. Smith Ed. "Phot. Journal", 80, 1940, p. 285, and reference may be made of the methods described in, for example, JP-A-58-113927, JP-A-58-113928 and JP-A-58-127921.

Further, reference can be made of the methods described in, for example, Cleve, "Photography Theory and Practice", 1930, p. 131; Gutoff, "Photographic Science and Engineering", Vol. 14, 1970, pp. 248-259; U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520; and British Patent 2,112,157.

Silver halide grains used in the present invention may be subjected to chemical sensitization represented by sulfur sensitization and gold sensitization. The sites to be chemically sensitized differ depending on the composition, structure and shape of the emulsion grains, or on the intended use of the emulsion. For example, chemical sensitization nuclei may be embedded in the interior of the grain, at a position shallow from the grain surface, or at the surface of the grain. In any case, the advantages of the present invention can be obtained. However, the chemical sensitization nuclei are preferably formed at a portion near the surface. That is, a surface latent image type emulsion is more effective than an internal latent image type emulsion.

The chemical sensitization can be carried out using activated gelatin, as described in T.H. James, "The Theory of the Photographic Process", 4th ed., Macmillan, 1977, pp. 67-76, or using sulfur, selenium, tellurium, gold, platinum, palladium, iridium, or a combination of these sensitizers at a pAg of 5 to 10, pH of 5 to 8 and a temperature of 30 to 80 ° C, as described in Research Disclosure, Vol. 120, April, 1974, 12008, Research Disclosure, Vol. 34, June, 1975, 13452, 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 1,315,755.

As a gold sensitizer used in the present invention, gold complexes (see, for example, U.S. Patent 2,399,083 specification) are particularly preferably used.

Of these, potassium chloroaurate, potassium aurithiocyanate, auric trichloride, sodium aurithiosulfate and 2-aurosulfobenzothiazole methochloride are particularly suitable.

The content of the gold sensitizer in the silver halide grain phase is preferably 10^{-9} to 10^{-3} mols, particularly 10^{-8} to 10^{-4} mols, per mol of silver halide.

In the present invention, sulfur sensitization is preferably combined with gold sensitization.

As a sulfur sensitization used, thiosulfate salts, thioureas, thiazoles, rhodanines, and the other compounds (specific examples are described in U.S. Patents 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,656,955, 4,030,928, and 4,067,740) may be cited, and thiosulfates, thioureas and rhodanines are particularly suitable of these.

The amount of the sulfur sensitizer can be optimally selected, depending on conditions such as the grain size, and the temperature, pAg and pH of the chemical sensitization. It is used in an amount of 10^{-7} to 10^{-3} mols, preferably 5×10^{-7} to 10^{-4} mols, more preferably 5×10^{-7} to 10^{-5} mols, per mol of silver halide.

The temperature of the chemical sensitization may be properly selected within a rage of 30-90 ° C, pAg may be selected within a range of 5-10, and pH may be selected within a range of 4 or more.

In the present invention, sensitization by metals such as iridium, platinum, rhodium or palladium (see, for example, U.S. Patents 2,448,060, 2,566,245 and 2,566,263) or selenium sensitization using selenium compounds may also be used.

The chemical sensitization can be effected in the presence of a chemical sensitization aid. As the chemical sensitization aid used, use may be made of compounds which are known to suppress fogs during chemical sensitization and increase sensitivity, such as azaindene, azapyridazine, and azapyrimidine. Examples of a modifier for chemical sensitization aids are described in U.S. Patents 2,131,038, 3,411,914 and 3,554,757, JP-A-58-126526, and the above-described Duffin's "Photographic Emulsion Chemistry", pp. 138-143.

Silver halide emulsions used in the present invention may be subjected to spectral sensitization by methine dyes or the other dyes. Useful dyes involve a cyanine dye, a merocyanine dye, a composite cyanine dye, a composite merocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye, and a hemioxonole dye. Most useful dyes are those belonging to a cyanine dye, a merocyanine dye, and a composite merocyanine dye. Any nucleus commonly used as a basic heterocyclic nucleus in cyanine dyes can be contained in these dyes. Examples of a nucleus are a pyrroline nucleus, an oxazoline nucleus, a pyrrole nucleus, an oxazole nucleus, nucleus, a selenazole nucleus, an imidazole uncleus, a tetrazole uncleus, and a pyridine nucleus; a nucleus in which an aliphatic hydrocarbon ring is fused to any of the above nuclei, and a nucleus in which an aromatic hydrocarbon ring is fused to any of the above nuclei, e.g., an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzthiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, and a quinoline nucleus. These nuclei may have a substitutent on a carbon atom.

It is possible for a merocyanine dye or a composite merocyanine dye to have a 5- or 6-membered heterocyclic nucleus as a nucleus having a ketomethylene structure, e.g., a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thiooxazolidine-2-4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus, and a thioharhituric acid nucleus.

Although these sensitizing dyes may be used singly, they can also be used in combination. The combination of sensitizing dyes is often used for a supersensitization purpose. Representative examples of the combination 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 1,344,281 and 1,507,803, JP-B-43-4936, JP-B-53-12375, JP-A-52-110618, and JP-A-52-109925.

The emulsions may contain, in addition to the sensitizing dyes, dyes having no spectral sensitizing effect or substances not essentially absorbing visible light and presenting supersensitization.

The sensitizing dyes can be added to an emulsion at any stage in preparation of an emulsion, which is conventionally known to be useful. Most ordinarily, the addition is performed after completion of chemical sensitization and before coating. However, it is possible to perform the addition at the same time as addition of chemical sensitizing dyes to perform spectral sensitization and chemical sensitization simultaneously, as described in U.S. Patents 3,628,969 and 4,225,666. It is also possible to perform the addition prior to chemical sensitization, as described in JP-A-58-113928, or before completion of formation of a silver halide grain precipitation to start spectral sensitization. Alternatively, as disclosed in U.S. Patent 4,225,666, these compounds described above can be added separately: a portion of the compounds may be added prior to chemical sensitization, while the remaining portion is added after that. That is, the compounds can be added at any timing during formation of silver halide grains, including the method disclosed in U.S. Patent 4,183,756.

The addition amount of the spectral sensitizing dye may be 4×10^{-6} to 8×10^{-3} mole per mole of silver halide.

The light-sensitive material of the present invention needs only to have at least one of silver halide emulsion layers, i.e., a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer, formed on a support. The number or order of the silver halide emulsion layers and the non-light-sensitive layers are particularly not limited. A typical example is a silver halide photographic light-sensitive material having, on a support, at least one unit light-sensitive layer constituted by a plurality of silver halide emulsion layers which are sensitive to essentially the same color but have different sensitivities or speeds. The unit light-sensitive layer is sensitive to blue, green or red light. In a multi-layered silver halide color photographic light-sensitive material, the unit light-sensitive layers are generally arranged such that red-, green-, and blue-sensitive layers are formed from a support side in the order named. However, this order may be reversed or a layer having a different color sensitivity may be sandwiched between layers having the same color sensitivity in accordance with the application.

Non-light-sensitive layers such as various types of interlayers may be formed between the silver halide light-sensitive layers and as the uppermost layer and the lowermost layer.

The interlayer may contain, e.g., couplers and DIR compounds as described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037, and JP-A-61-20038 or a color mixing inhibitor which is normally used.

As a plurality of silver halide emulsion layers constituting each unit light-sensitive layer, a two-layered structure of high- and low-speed emulsion layers can be preferably used as described in West German Patent 1,121,470 or British Patent 923,045. In this case, layers are preferably arranged such that the sensitivity or speed is sequentially decreased toward a support, and a non-light-sensitive layer may be formed between the silver halide emulsion layers. In addition, as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, layers may be arranged such that a low-speed emulsion layer is formed remotely from a support and a high-speed layer is formed close to the support.

More specifically, layers may be arranged from the farthest side from a support in an order of, for example, low-speed blue-sensitive layer (BL)/high-speed blue-sensitive layer (BH)/high-speed green-sensitive layer (GH)/low-speed green-sensitive layer (GL)/high-speed red-sensitive layer (RH)/low-speed red-sensitive layer (RL), an order of BH/BL/GL/GH/RH/RL, or an order of BH/BL/GH/GL/RL/RH.

In addition, as described in JP-B-55-34932, layers may be arranged from the farthest side from a support in an order of blue-sensitive layer/GH/RH/GL/RL. Furthermore, as described in JP-A-56-25738 and JP-A-62-63936, layers may be arranged from the farthest side from a support in an order of blue-sensitive layer/GL/RL/GH/RH.

As described in JP-B-49-15495, three layers may be arranged such that a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having sensitivity lower than that of the upper layer is arranged as an intermediate layer, and a silver halide emulsion layer having sensitivity lower than that of the intermediate layer is arranged as a lower layer. In other words, three layers having different sensitivities may be arranged such that the sensitivity is sequentially decreased toward the support. When a layer structure is constituted by three layers having different speeds, these layers may be arranged in an order of medium-speed emulsion layer/high-speed emulsion layer/low-speed emulsion layer from the farthest side from a support in a layer having the same color sensitivity as described in JP-A-59-202464.

Also, an order of high-speed emulsion layer/low-speed emulsion layer/medium-speed emulsion layer, or low-speed emulsion layer/medium-speed emulsion layer/high-speed emulsion layer may be adopted. Furthermore, the arrangement can be changed as described above even when four or more layers are formed.

To improve the color reproduction, a donor layer (CL) of an interlayer effect can be arranged directly adjacent to, or close to, a main light-sensitive layer such as BL, GL or RL. The donor layer has a spectral sensitivity distribution which is different from that of the main light-sensitive layer. Donor layers of this type are disclosed in U.S. Patent 4,663,271, U.S. Patent 4,705,744, U.S. Patent 4,707,436, JP-A-62-160448, and JP-A-63-89850.

As described above, various layer configurations and arrangements can be selected in accordance with the application of the light-sensitive material.

Next, silver halide grains other than the tabular grains of the present invention will be described. A preferable silver halide contained in photographic emulsion layers of the photographic light-sensitive material of the present invention is silver bromoiodide, silver chloroiodide, or silver chlorobromoiodide containing about 30 mol% or less of silver iodide. The most preferable silver halide is silver bromoiodide or silver chlorobromoiodide containing about 2 mol% to about 10 mol% of silver iodide.

Silver halide grains contained in the photographic emulsion may have regular crystals such as cubic, octahedral, or tetradecahedral crystals, irregular crystals such as spherical, or tabular crystals, crystals having defects such as twin planes, or composite shapes thereof.

The silver halide may consist of fine grains having a grain size of about 0.2 µm or less or large grains having a projected-area diameter of up to 10 µm, and the emulsion may be either a polydisperse emulsion or a monodisperse emulsion.

The silver halide photographic emulsion which can be used in the present invention can be prepared by methods described in, for example, Research Disclosure (RD) No. 17643 (December 1978), pp. 22 to 23, "I. Emulsion preparation and types", RD No. 18716 (November 1979), page 648, and RD No. 307105 (November 1989), pp. 863 to 865; P. Glafkides, "Chemie et Phisique 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.

Monodisperse emulsions described in, for example, U.S. Patents 3,574,628 and 3,655,394, and British Patent 1,413,748 are also preferred.

Also, tabular grains having an aspect ratio of about 3 or more can be used in the present invention. The tabular grains can be easily prepared by methods described in, e.g., Gutoff, "Photographic Science and Engineering", Vol. 14, PP. 248 to 257 (1970); U.S. Patents 4,434,226; 4,414,310; 4,433,048 and 4,499,520, and British Patent 2,112,157.

The crystal structure may be uniform, may have different halogen compositions in the interior and the surface thereof, or may be a layered structure. Alternatively, silver halides having different compositions may be joined by an epitaxial junction, or a compound other than a silver halide such as silver rhodanide or zinc oxide may be joined. A mixture of grains having various types of crystal shapes may be used.

The above emulsion may be of any of a surface latent image type in which a latent image is mainly formed on the surface of each grain, an internal latent image type in which a latent image is formed in the interior of each grain, and a type in which a latent image is formed on the surface and in the interior of each grain. However, the emulsion must be of a negative type. When the emulsion is of an internal latent image type, it may be a core/shell internal latent image type emulsion described in JP-A-63-264740. A method of preparing this core/shell internal latent image type emulsion is described in JP-A-59-133542. Although the thickness of a shell of this emulsion changes in accordance with development or the like, it is preferably 3 to 40 nm, and most preferably, 5 to 20 nm.

A silver halide emulsion layer is normally subjected to physical ripening, chemical ripening, and spectral sensitization steps before it is used. Additives for use in these steps are described in RD Nos. 17,643; 18,716 and 307,105 and they are summarized in the table represented later.

In the light-sensitive material of the present invention, two or more types of emulsions different in at least one of features such as a grain size, a grain size distribution, a halogen composition, a grain shape, and sensitivity can be mixed and used in the same layer.

Surface-fogged silver halide grains described in U.S. Patent 4,082,553, internally fogged silver halide grains described in U.S. Patent 4,626,498 or JP-A-59-214852, and colloidal silver can be preferably used in a light-sensitive silver halide emulsion layer and/or a substantially non-light-sensitive hydrophilic colloid layer. The internally fogged or surface-fogged silver halide grains are silver halide grains which can be uniformly (non-imagewise) developed despite the presence of a non-exposed portion and exposed portion of the light-sensitive material. A method of preparing the internally fogged or surface-fogged silver halide grain is described in U.S. Patent 4,626,498 or JP-A-59-214852.

The silver halides which form the core of the internally fogged or surface-fogged core/shell silver halide grains may be of the same halogen composition or different halogen compositions. Examples of the internally fogged or surface-fogged silver halide are silver chloride, silver bromochloride, silver bromoiodide, and silver bromochloroiodide. Although the grain size of these fogged silver halide grains is not particularly limited, an average grain size is preferably 0.01 to 0.75 µm, and most preferably, 0.05 to 0.6 µm. The grain shape is also not particularly limited, and may be a regular grain shape. Although the emulsion may be a polydisperse emulsion, it is preferably a monodisperse emulsion (in which at least 95% in weight or number of silver halide grains have a grain size falling within a range of ±40% of the average grain size).

In the present invention, a non-light-sensitive fine grain silver halide is preferably used. The non-light-sensitive fine grain silver halide means silver halide fine grains not sensitive upon imagewise exposure for obtaining a dye image and essentially not developed in development. The non-light-sensitive fine grain silver halide is preferably not fogged beforehand.

The fine grain silver halide contains 0 to 100 mol% of silver bromide and may contain silver chloride and/or silver iodide as needed. Preferably, the fine grain silver halide contains 0.5 to 10 mol% of silver iodide.

An average grain size (an average value of equivalent-circle diameters of projected areas) of the fine grain silver halide is preferably 0.01 to 0.5 µm, and more preferably, 0.02 to 0.2 µm.

The fine grain silver halide can be prepared by a method similar to a method of preparing normal light-sensitive silver halide. In this preparation, the surface of a silver halide grain need not be subjected to either chemical sensitization or spectral sensitization. However, before the silver halide grains are added to a coating solution, a known stabilizer such as a triazole compound, an azaindene compound, a benzothiazolium compound, a mercapto compound, or a zinc compound is preferably added. This fine grain silver halide grain-containing layer preferably contains colloidal silver.

A coating silver amount of the light-sensitive material of the present invention is preferably 6.0 g/m^2 or less, and most preferably, 4.5 g/m^2 or less.

Known photographic additives usable in the present invention are also described in the above three RDs, and they are summarized in the following Table:

	Additives	RD17643	RD18716	RD307105
1.	Chemical sensitizers	page 23	page 648, right column	page 866
2.	Sensitivity-increasing agents		page 648, right column	
3.	Spectral sensitizers, supersensitizers	pp. 23-24	page 648, right column to page 649, right column	pp. 866-868
4.	Brighteners	page 24	page 648, right column	page 868
5.	Antifoggants, stabilizers	pp. 24-25	page 649, right column	pp. 868-870
6.	Light absorbent, filter dye, ultraviolet absorbents	pp. 25-26	page 649, right column to page 650, left column	page 873
7.	Stain-preventing agents	page 25, right column	page 650, left-right columns	page 872

(Continued)

Additives	RD17643	RD18716	RD307105
8. Dye image-stabilizer	page 25	page 650, left column	page 872
9. Hardening agents	page 26	page 651, left column	pp. 874-875
10. Binder	page 26	page 651, left column	pp. 873-874
11. Plasticizers, lubricants	page 27	page 650, right column	page 876
12. Coating aids, surface active agents	pp. 26-27	page 650, right column	pp. 875-876
13. Antistatic agents	page 27	page 650, right column	pp. 876-877
14. Matting agent			pp. 878-879

In order to prevent degradation in photographic properties caused by formaldehyde gas, a compound described in U.S. Patent 4,411,987 or 4,435,503, which can react with formaldehyde and fix the same, is preferably added to the light-sensitive material.

The light-sensitive material of the present invention preferably contains a mercapto compound described in U.S. Patents 4,740,454 and 4,788,132, JP-A-62-18539, and JP-A-1-283551.

The light-sensitive material of the present invention preferably contains compounds which release, regardless of a developed silver amount produced by the development, a fogging agent, a development accelerator, a silver halide solvent, or precursors thereof, described in JP-A-1-106052.

The light-sensitive material of the present invention preferably contains dyes dispersed by methods described in International Disclosure WO 88/04794 and JP-A-1-502912 or dyes described in European Patent 317,308A, U.S. Patent 4,420,555, and JP-A-1-259358.

Various color couplers can be used in the present invention, and specific examples of these couplers are described in patents described in the above-mentioned RD No. 17643, VII-C to VII-G and RD No. 307105, VII-C to VII-G.

Preferable examples of yellow couplers are described in, e.g., U.S. Patents 3,933,501; 4,022,620; 4,326,024; 4,401,752 and 4,248,961, JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents

3,973,968; 4,314,023 and 4,511,649, and European Patent 249,473A.

Examples of a magenta coupler are preferably 5-pyrazolone type and pyrazoloazole type compounds, and more preferably, compounds described in, for example, U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,067, RD No. 24220 (June 1984), JP-A-60-33552, RD No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, U.S. Patents 4,500,630; 4,540,654 and 4,556,630, and WO No. 88/04795.

Examples of a cyan coupler are phenol type and naphthol type ones. Of these, preferable are those described in, for example, U.S. Patents 4,052,212; 4,146,396; 4,228,233; 4,296,200; 2,369,929; 2,801,171; 2,772,162; 2,895,826; 3,772,002; 3,758,308; 4,343,011 and 4,327,173, West German Patent Laid-open Application 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622; 4,333,999; 4,775,616; 4,451,559; 4,427,767; 4,690,889; 4,254,212 and 4,296,199, and JP-A-61-42658. Also, the pyrazoloazole type couplers disclosed in JP-A-64-553, JP-A-64-554, JP-A-64-555 and JP-A-64-556, and imidazole type couplers disclosed in U.S. Patent 4,818,672 can be used as cyan coupler in the present invention.

Typical examples of a polymerized dye-forming coupler are described in, e.g., U.S. Patents 3,451,820; 4,080,211; 4,367,282; 4,409,320 and 4,576,910, British Patent 2,102,173, and European Patent 341,188A.

Preferable examples of a coupler capable of forming colored dyes having proper diffusibility are those described in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570, and West German Laid-open Patent Application No. 3,234,533.

Preferable examples of a colored coupler for correcting unnecessary absorption of a colored dye are those described in RD No. 17643, VII-G, RD No. 30715, VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368. A coupler for correcting unnecessary absorption of a colored dye by a fluorescent dye released upon coupling described in U.S. Patent 4,774,181 or a coupler having a dye precursor group which can react with a developing agent to form a dye as a split-off group described in U.S. Patent 4,777,120 may be preferably used.

Those compounds which release a photographically useful residue upon coupling may also be preferably used in the present invention. DIR couplers, i.e., couplers releasing a development inhibitor, are preferably those described in the patents cited in the above-described RD No. 17643, VII-F and RD No. 307105, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350, and U.S. Patents 4,248,962 and 4,782,012.

RD Nos. 11449 and 24241, and JP-A-61-201247, for example, disclose couplers which release bleaching accelerator. These couplers effectively serve to shorten the time of any process that involves bleaching. They are effective, particularly when added to light-sensitive material containing tabular silver halide grains. Preferable examples of a coupler which imagewise releases a nucleating agent or a development accelerator are preferably those described in British Patents 2,097,140 and 2,131,188, JP-A-59-157638, and JP-A-59-170840. In addition, compounds releasing, e.g., a fogging agent, a development accelerator, or a silver halide solvent upon redox reaction with an oxidized form of a developing agent, described in JP-A-60-107029, JP-A-60-252340, JP-A-1-44940, and JP-A-1-45687, can also be preferably used.

Examples of other compounds which can be used in the light-sensitive material of the present invention are competing couplers described in, for example, U.S. Patent 4,130,427; poly-equivalent couplers described in, e.g., U.S. Patents 4,283,472, 4,338,393, and 4,310,618; a DIR redox compound releasing coupler, a DIR coupler releasing coupler, a DIR coupler releasing redox compound, or a DIR redox releasing redox compound described in, for example, JP-A-60-185950 and JP-A-62-24252; couplers releasing a dye which restores color after being released described in European Patent 173,302A and 313,308A; a ligand releasing coupler described in, e.g., U.S. Patent 4,553,477; a coupler releasing a leuco dye described in JP-A-63-75747; and a coupler releasing a fluorescent dye described in U.S. Patent 4,774,181.

The couplers for use in this invention can be introduced into the light-sensitive material by various known dispersion methods.

Examples of a high-boiling point organic solvent to be used in the oil-in-water dispersion method are described in, e.g., U.S. Patent 2,322,027. Examples of a high-boiling point organic solvent to be used in the oil-in-water dispersion method and having a boiling point of 175 °C or more at atmospheric pressure are phthalic esters (e.g., dibutylphthalate, dicyclohexylphthalate, di-2-ethylhexylphthalate, decylphthalate, bis-(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) isophthalate, bis(1,1-di-ethylpropyl) phthalate), phosphate or phosphonate esters (e.g., triphenylphosphate, tricresylphosphate, 2-ethylhexyldiphenylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, tributoxyethylphosphate, trichloropropylphosphate, and di-2-ethylhexylphenylphosphonate), benzoate esters (e.g., 2-ethylhexylbenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide, and N-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearyl alcohol and 2,4-di-tert-amylphenol), aliphatic carboxylate esters (e.g., bis(2-ethylhexyl) sebacate, dioctylazelate, glyceroltributyrate, isostearyllactate, and trioctylcitrate), an aniline derivative (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), and hydrocarbons (e.g., paraffin, dodecylbenzene, and diisopropylnaphthalene).

An organic solvent having a boiling point of about 30°C or more, and preferably, 50°C to about 160°C can be used as an auxiliary solvent. Typical examples of the auxiliary solvent are ethyl acetate, butyl acetate, ethyl propionate, methylethylketone, cyclohexanone, 2-ethoxyethylacetate, and dimethylformamide.

Steps and effects of a latex dispersion method and examples of a immersing latex are described in, e.g., U.S. Patent 4,199,363 and German Laid-open Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

Various types of antiseptics and fungicides agent are preferably added to the color light-sensitive material of the present invention. Typical examples of the antiseptics and the fungicides are phenethyl alcohol, and 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol, and 2-(4-thiazolyl)benzimidazole, which are described in JP-A-63-257747, JP-A-62-272248, and JP-A-1-80941.

The present invention can be applied to various color light-sensitive materials. Examples of the material are a color negative film for a general purpose or a movie, a color reversal film for a slide or a television, a color paper, a color positive film, and a color reversal paper.

A support which can be suitably used in the present invention is described in, e.g., RD. No. 17643, page 28, RD. No. 18716, from the right column, page 647 to the left column, page 648, and RD. No. 307105, page 879.

In the light-sensitive material of the present invention, the sum total of film thicknesses of all hydrophilic colloidal layers at the side having emulsion layers is preferably 28 μm or less, more preferably, 23 μm or less, much more preferably, 18 μm or less, and most preferably, 16 μm or less. A film swell speed $T_{1/2}$ is preferably 30 seconds or less, and more preferably, 20 seconds or less. The film thickness means a film thickness measured under moisture conditioning at a temperature of 25°C and a relative humidity of 55% (two days). The film swell speed $T_{1/2}$ can be measured in accordance with a known method in the art. For example, the film swell speed $T_{1/2}$ can be measured by using a swello-meter described by A. Green et al. in Photographic Science & Engineering, Vol. 19, No. 2, pp. 124 to 129. When 90% of a maximum swell film thickness reached by performing a treatment by using a color developer at 30°C for 3 minutes and 15 seconds is defined as a saturated film thickness, $T_{1/2}$ is defined as a time required for reaching 1/2 of the saturated film thickness.

The film swell speed $T_{1/2}$ can be adjusted by adding a film hardening agent to gelatin as a binder or changing aging conditions after coating. A swell ratio is preferably 150% to 400%. The swell ratio is calculated from the maximum swell film thickness measured under the above conditions in accordance with a relation:

(maximum swell film thickness - film thickness)/film thickness.

In the light-sensitive material of the present invention, a hydrophilic colloid layer (called back layer) having a total dried film thickness of 2 to 20 μm is preferably formed on the side opposite to the side having emulsion layers. The back layer preferably contains, e.g., the light absorbent, the filter dye, the ultraviolet absorbent, the antistatic agent, the film hardener, the binder, the plasticizer, the lubricant, the coating aid, and the surfactant, described above. The swell ratio of the back layer is preferably 150% to 500%.

The color photographic light-sensitive material according to the present invention can be developed by conventional methods described in RD. No. 17643, pp. 28 and 29, RD. No. 18716, the left to right columns, page 651, and RD. No. 307105, pp. 880 and 881.

A color developer used in development of the light-sensitive material of the present invention is an aqueous alkaline solution containing as a main component, preferably, an aromatic primary amine color developing agent. As the color developing agent, although an aminophenol compound is effective, a p-phenylenediamine compound is preferably used. Typical examples of the p-phenylenediamine compound are: 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, and the sulfates, hydrochlorides and p-toluenesulfonates thereof. Of these compounds, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline sulfates are preferred in particular. These compounds can be used in a combination of two or more thereof in accordance with the application.

In general, the color developer contains a pH buffering agent such as a carbonate, a borate or a phosphate of an alkali metal, and a development restrainer or an antifoggant such as a chloride, a bromide, an iodide, a benzimidazole, a benzothiazole, or a mercapto compound. If necessary, the color developer may also contain a preservative such as hydroxylamine, diethylhydroxylamine, a sulfite, a hydrazine such as N,N-biscarboxymethylhydrazine, a phenylsemicarbazide, triethanolamine, or a catechol sulfonic acid; an organic solvent such as ethyleneglycol or diethyleneglycol; a development accelerator such as benzylalcohol, polyethyleneglycol, a quaternary ammonium salt or an amine; a dye-forming coupler; a competing coupler; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a viscosity-imparting agent; and a chelating agent such as an aminopolycarboxylic acid, an aminopolyphosphonic acid, an alkylphosphonic acid, or a phosphonocarboxylic acid. Examples of the chelating agent are ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and ethylenediamine-di(o-hydroxyphenylacetic acid), and salts thereof.

In order to perform reversal development, black-and-white development is performed and then color development is performed. As a black-and-white developer, a well-known black-and-white developing agent, e.g., a dihydroxybenzene such as hydroquinone, a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone, and an aminophenol such as N-methyl-p-aminophenol can be used singly or in a combination of two or more thereof. The pH of the color and black-and-white developers is generally 9 to 12. Although the quantity of replenisher of the developers depends on a color photographic light-sensitive material to be processed, it is generally 3 liters or less per m^2 of the light-sensitive material. The quantity of replenisher can be decreased to be 500 mℓ or less by decreasing a bromide ion concentration in a replenisher. When the quantity of the replenisher is decreased, a contact area of a processing tank with air is preferably decreased to prevent evaporation and oxidation of the solution upon contact with air.

The contact area of the processing solution with air in a processing tank can be represented by an aperture defined below:

Aperture = [contact area (cm^2) of processing solution with air]/[volume (cm^3) of the solution]

The above aperture is preferably 0.1 or less, and more preferably, 0.001 to 0.05. In order to reduce the aperture, a shielding member such as a floating cover may be provided on the surface of the photographic processing solution in the processing tank. In addition, a method of using a movable cover described in JP-A-1-82033 or a slit developing method descried in JP-A-63-216050 may be used. The aperture is preferably reduced not only in color and black-and-white development steps but also in all subsequent steps, e.g., bleaching, bleach-fixing, fixing, washing, and stabilizing steps. In addition, the quantity of replenisher can be reduced by using a means of suppressing storage of bromide ions in the developing solution.

A color development time is normally 2 to 5 minutes. The processing time, however, can be shortened by setting a high temperature and a high pH and using the color developing agent at a high concentration.

The photographic emulsion layer is generally subjected to bleaching after color development. The bleaching may be performed either simultaneously with fixing (bleach-fixing) or independently thereof. In addition, in order to increase a processing speed, bleach-fixing may be performed after bleaching. Also, processing may be performed in a bleach-fixing bath having two continuous tanks, fixing may be performed before bleach-fixing, or bleaching may be performed after bleach-fixing, in accordance with the application. Examples of the bleaching agent are compounds of a polyvalent metal, e.g., iron (III); peracids; quinones; and nitro compounds. Typical examples of the bleaching agent are an organic complex salt of iron (III), e.g., a complex salt with an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, and 1,3-diaminopropanetetraacetic acid, and glycoletherdiaminetetraacetic acid; or a complex salt with citric acid, tartaric acid, or malic acid. Of these compounds, an iron (III) complex salt of an aminopolycarboxylic acid such as an iron (III) complex salt of ethylenediaminetetraacetic acid or 1,3-diaminopropanetetraacetic acid is preferred because it can increase a processing speed and prevent an environmental contamination. The iron (III) complex salt of an aminopolycarboxylic acid is useful in both the bleaching and bleach-fixing solutions. The pH of the bleaching or bleach-fixing solution using the iron (III) complex salt of an aminopolycarboxylic acid is normally 4.0 to 8. In order to increase the processing speed, however, processing can be performed at a lower pH.

A bleaching accelerator can be used in the bleaching solution, the bleach-fixing solution, and their pre-bath, if necessary. Examples of a useful bleaching accelerator are: compounds having a mercapto group or a disulfide group described in, for example, U.S. Patent 3,893,858, West German Patents 1,290,812 and

2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, and RD No. 17129 (July, 1978); thiazolidine derivatives described in JP-A-50-140129; thiourea derivatives described in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735, and U.S. Patent 3,706,561; iodide salts described in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds descried in West German Patents 966,410 and 2,748,430; polyamine compounds described in JP-B-45-8836; compounds descried in JP-A-49-40943, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506, and JP-A-58-163940; and a bromide ion. Of these compounds, a compound having a mercapto group or a disulfide group is preferable since the compound has a large accelerating effect. In particular, compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630 are preferred. A compound described in U.S. Patent 4,552,834 is also preferable. These bleaching accelerators may be added in the light-sensitive material. These bleaching accelerators are useful especially in bleach-fixing of a photographic color light-sensitive material.

The bleaching solution or the bleach-fixing solution preferably contains, in addition to the above compounds, an organic acid in order to prevent a bleaching stain. The most preferable organic acid is a compound having an acid dissociation constant (pKa) of 2 to 5, e.g., acetic acid, propionic acid, or hydroxy acetic acid.

Examples of the fixing agent used in the fixing solution or the bleach-fixing solution are a thiosulfate salt, a thiocyanate salt, a thioether-based compound, a thiourea and a large amount of an iodide. Of these compounds, a thiosulfate, especially, ammonium thiosulfate, can be used in the widest range of applications. In addition, a combination of a thiosulfate with a thiocyanate, a thioether-based compound or thiourea is preferably used. As a preservative of the fixing solution or the bleach-fixing solution, a sulfite, a bisulfite, a carbonyl bisulfite adduct, or a sulfinic acid compound described in European Patent 294,769A is preferred. Further, in order to stabilize the fixing solution or the bleach-fixing solution, various types of aminopolycarboxylic acids or organic phosphonic acids are preferably added to the solution.

In the present invention, 0.1 to 10 moles, per liter, of a compound having a pKa of 6.0 to 9.0 are preferably added to the fixing solution or the bleach-fixing solution in order to adjust the pH. Preferable examples of the compound are imidazoles such as imidazole, 1-methylimidazole, 1-ethylimidazole, and 2-methylimidazole.

The total time of a desilvering step is preferably as short as possible as long as no desilvering defect occurs. A preferable time is one to three minutes, and more preferably, one to two minutes. A processing temperature is 25 °C to 50 °C, and preferably, 35 °C to 45 °C. Within the preferable temperature range, a desilvering speed is increased, and generation of a stain after the processing can be effectively prevented.

In the desilvering step, stirring is preferably as strong as possible. Examples of a method of intensifying the stirring are a method of colliding a jet stream of the processing solution against the emulsion surface of the light-sensitive material described in JP-A-62-183460, a method of increasing the stirring effect using rotating means described in JP-A-62-183461, a method of moving the light-sensitive material while the emulsion surface is brought into contact with a wiper blade provided in the solution to cause disturbance on the emulsion surface, thereby improving the stirring effect, and a method of increasing the circulating flow amount in the overall processing solution. Such a stirring improving means is effective in any of the bleaching solution, and the bleach-fixing solution. It is assumed that the improvement in stirring increases the speed of supply of the bleaching agent and the fixing agent into the emulsion film to lead to an increase in desilvering speed. The above stirring improving means is more effective when the bleaching accelerator is used, i.e., significantly increases the accelerating speed or eliminates fixing interference caused by the bleaching accelerator.

An automatic developing machine for processing the light-sensitive material of the present invention preferably has a light-sensitive material conveyer means described in JP-A-60-191257, JP-A-60-191258, or JP-A-60-191259. As described in JP-A-60-191257, this conveyer means can significantly reduce carry-over of a processing solution from a pre-bath to a post-bath, thereby effectively preventing degradation in performance of the processing solution. This effect significantly shortens especially a processing time in each processing step and reduces the quantity of replenisher of a processing solution.

The photographic light-sensitive material of the present invention is normally subjected to washing and/or stabilizing steps after desilvering. An amount of water used in the washing step can be arbitrarily determined over a broad range in accordance with the properties (e.g., a property determined by the substances used, such as a coupler) of the light-sensitive material, the application of the material, the temperature of the water, the number of water tanks (the number of stages), a replenishing scheme representing a counter or forward current, and other conditions. The relationship between the amount of water and the number of water tanks in a multi-stage counter-current scheme can be obtained by a method described in "Journal of the Society of Motion Picture and Television Engineering", Vol. 64, PP. 248 - 253 (May, 1955). In the multi-stage counter-current scheme disclosed in this reference, the amount of water used for washing can be greatly decreased. Since washing water stays in the tanks for a long period of time, however, bacteria multiply and floating substances may be adversely attached to the light-sensitive material. In order to solve this problem in the process of the color photographic light-sensitive material of the present invention, a method of decreasing calcium and magnesium ions can be effectively utilized, as described in JP-A-62-288838. In addition, a germicide such as an isothiazolone compound and a cyabendazole described in JP-A-57-8542, a chlorine-based germicide such as chlorinated sodium isocyanurate, and germicides such as benzotriazole, described in Hiroshi Horiguchi et al., "Chemistry of Antibacterial and Antifungal Agents", (1986), Sankyo Shuppan, Eiseigijutsu-Kai ed., "Sterilization, Antibacterial, and Antifungal Techniques for Microorganisms", (1982), Kogyogijutsu-Kai, and Nippon Bokin Bobai Gakkai ed., "Dictionary of Antibacterial and Antifungal Agents", (1986), can be used.

The pH of the water for washing the photographic light-sensitive material of the present invention is 4 to 9, and preferably, 5 to 8. The water temperature and the washing time can vary in accordance with the properties and applications of the light-sensitive material. Normally, the washing time is 20 seconds to 10 minutes at a temperature of 15°C to 45°C, and preferably, 30 seconds to 5 minutes at 25°C to 40°C. The light-sensitive material of the present invention can be processed directly by a stabilizing agent in place of water-washing. All known methods described in JP-A-57-8543, JP-A-58-14834, and JP-A-60-220345 can be used in such stabilizing processing.

In some cases, stabilizing is performed subsequently to washing. An example is a stabilizing bath containing a dye stabilizing agent and a surface-active agent to be used as a final bath of the photographic color light-sensitive material. Examples of the dye stabilizing agent are an aldehyde such as formalin or glutaraldehyde, an N-methylol compound, hexamethylenetetramine, and an adduct of aldehyde sulfite. Various chelating agents and fungicides can be added to the stabilizing bath.

An overflow solution produced upon washing and/or replenishment of the stabilizing solution can be reused in another step such as a desilvering step.

In the processing using an automatic developing machine or the like, if each processing solution described above is concentrated by evaporation, water is preferably added to correct the concentration.

The silver halide color light-sensitive material of the present invention may contain a color developing agent in order to simplify processing and increases a processing speed. For this purpose, various types of precursors of a color developing agent can be preferably used. Examples of the precursor are an indoaniline-based compound described in U.S. Patent 3,342,597, Schiff base compounds described in U.S. Patent 3,342,599 and RD Nos. 14850 and 15159, an aldol compound described in RD No. 13924, a metal salt complex described in U.S. Patent 3,719,492, and a urethane-based compound described in JP-A-53-135628.

The silver halide color light-sensitive material of the present invention may contain various 1-phenyl-3-pyrazolidones in order to accelerate color development, if necessary. Typical examples of the compound are described in JP-A-56-64339, JP-A-57-144547, and JP-A-58-115438.

Each processing solution in the present invention is used at a temperature of 10°C to 50°C. Although a normal processing temperature is 33°C to 38°C, processing may be accelerated at a higher temperature to shorten a processing time, or image quality or stability of a processing solution may be improved at a lower temperature.

Further, the silver halide light-sensitive material of the present invention can be applied also to a heat-developing light-sensitive material as disclosed in, e.g., U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056, and European Patent 210,660A2.

The present invention will be described in more detail below by way of its examples, but the invention is not limited to these examples.

Reference Example

Spherical grains with an average grain size of 0.28 µm and a variation coefficient of a grain size distribution of 23% were formed as seed crystals in accordance with the method of the embodiment described in JP-B-3-46811.

A reactor vessel containing the spherical seed emulsion equivalent to 0.083 mol, 1,533 cc of distilled water, 14.2g of inert gelation, 19.2g of potassium bromide, 14 cc of 56% acetic acid, and 23.3 cc of 28% ammonia water was heated up to 75°C, and 717 cc of an aqueous 2.1 mols/liter silver nitrate solution and 717 cc of an aqueous 2.1 mols/liter potassium bromide solution were added. The addition was performed by a method in which the flow rate increased with time. The addition of both the aqueous silver nitrate solution and the aqueous potassium bromide solution was started at a rate of 2.33 cc/min, and the addition rate was so controlled as to increase by 0.47 cc per minute while the pAg during growth was kept at 7.4, thereby preparing an emulsion A-1. In addition, emulsions A-2, A-3, and A-4 were prepared by maintaining the pAg during the growth at 8.0, 8.3, and 8.6, respectively.

The emulsions A-1 to A-4 thus prepared are summarized in Table 1 below. Table 1 shows that when the spherical grains were used as seed crystals and grown at a low pAg at which the grain thickness increased, an emulsion with a narrow grain size distribution was obtained, but the aspect ratio was low. When the grains were grown while the pAg was kept at a high value so as not to increase the grain thickness, the grain size distribution broadened. It is thus seen that when a spherical emulsion is used as seed crystals, it is impossible to obtain grains with a high aspect ratio while maintaining their monodispersity.

Table 1

Emulsion No.	pAg during growth	Equivalent-circle diameter (µm)	Thickness (µm)	Ratio occupied in projected area by grains with aspect ratio of 3 or more	Variation coefficient of grain size
A-1 (Comparative example)	7.4	0.85	0.50	0	12%
A-2 (")	8.0	0.90	0.45	47	14%
A-3 (")	8.3	1.05	0.38	76	23%
A-4 (")	8.6	1.10	0.30	97	34%

Example 1

An aqueous solution of 11g of inert, low molecular weight (average molecular weight 15,000) gelatin and 6.0g of potassium bromide dissolved in 1 liter of distilled water was stirred at 40 °C, and an aqueous 1.9 M silver nitrate solution and an aqueous 1.9 M solution of potassium bromide and potassium iodide (molar ratio 95/5) were added to the solution at a flow rate of 100 cc/min for 40 seconds. Thereafter, the pAg was raised to 10, and 32g of inert gelatin were added to the resultant solution. The solution was then ripened for 20 minutes while the temperature was raised to 75° C. Subsequently, the pAg was adjusted to 7.5, and 100 cc of an aqueous ammonium nitrate solution (50 wt%) and 100 cc of sodium hydroxide (1 N) were added to produce ammonia in the reaction solution, thereby performing ammonia ripening. After 20 minutes, the solution was neutralized with acetic acid until the pH became 4.0. Subsequently, 340 cc of an aqueous 1.9 M silver nitrate solution and an aqueous 1.9 M potassium bromide solution were added with the pAg kept at 7.4. The aqueous silver nitrate solution was first added at a rate of 10.0 cc/min and then added over 28 minutes and 22 seconds such that the addition flow rate increased by 0.14 cc per minute. Thus, an emulsion B-1 was obtained.

In the emulsion B-1, grains with an aspect ratio of 2 or more occupied 42% of the total projected area of silver halide grains, and an average aspect ratio was 1.5. The variation coefficient of all silver halide grains was 11%.

Emulsions B-2, B-3, and B-4 were prepared following the same procedures as for the emulsion B-1 except that the pAg during growth was kept at 8.0, 8.3, and 8.6, respectively. The emulsions B-1 to B-4 thus prepared are shown in Table 2 below.

Table 2

Emulsion No.	pAg during growth	Equivalent-circle diameter (µm)	Thickness (µm)	Aspect ratio	Ratio occupied in projected area by grains with aspect ratio of 2 or more	Variation coefficient (%) of equivalent-circle diameter
B-1 (Comparative example)	7.4	0.30	0.20	1.5	28%	11%
B-2 (")	8.0	0.42	0.10	4.2	85%	13%
B-3 (")	8.3	0.48	0.08	6.0	96%	15%
B-4 (")	8.6	0.54	0.06	9.0	98%	18%

Grain growth was performed by using the seed crystal emulsions obtained as described above. 300g of the seed emulsion B-1 and 25g of inert gelation were added to a reactor vessel, and distilled water was added to make 1 liter as a total quantity. 506 cc of 1.9 M silver nitrate and 1.9 M potassium bromide were added at 75 °C under stirring with the pAg kept at 7.4. The silver nitrate solution was first added at a rate of 8.6 cc/min and then added such that the flow rate increased by 0.114 cc per minute. Thus, an emulsion C-1 was obtained.

When the emulsion C-1 was observed by an electron microscope, tabular grains with an average equivalent-circle diameter of 1.12 µm, an average thickness of 0.62 µm, and an aspect ratio of 3 or more occupied 8% of the total projected area of silver halide grains. The aspect ratio was 2.2 on average, and the variation coefficient of all silver halide grains was 12%.

Emulsion grains C-2 and C-3 were formed following the same procedures as for the emulsion C-1 except that the pAg during growth was adjusted to 8.0 and 8.3, respectively. The results are summarized in Table 3 below.

In addition, emulsions C-4 to C-12 were formed by using the seed emulsions B-2, B-3, and B-4 following the same procedures as for the emulsion C-1 except that the pAg during growth was adjusted to 7.4, 8.0, and 8.3.

As can be seen from Table 3, each emulsion grown by using the seed emulsion B-1 having a low aspect ratio could not have a high aspect ratio and a high monodispersity at the same time even when the pAg during the growth was changed.

When the seed emulsion B-2 having a high aspect ratio was used, on the other hand, the grain size distribution of the resultant grains was narrower than that of the grains formed by using the seed emulsion B-1 for the same aspect ratio. This tendency was established for the seed emulsions B-3 and B-4 with higher aspect ratios. This demonstrates that the use of high-aspect-ratio tabular grains as a seed emulsion makes it possible to form an emulsion having both a high aspect ratio and a high monodispersity.

Each resultant emulsion was desalted by a regular flocculation process, subjected to optimal gold-sulfur sensitization, and stored.

Table 3

Emulsion No.	Speed emulsion	pAg during growth	Equivalent-circle diameter (µm)	Thickness (µm)	Average aspect ratio	Ratio (%) occupied in projected area by grains with aspect ratio of 3 or more	Variation coefficient of grain size	
C-1	B-1	7.4	1.19	0.54	2.2	8	12%	Comparative example
C-2	B-1	8.0	1.25	0.50	5.6	64	25%	"
C-3	B-1	8.3	1.63	0.29	7.4	84	38%	"
C-4	B-2	7.4	1.65	0.28	5.6	96	14%	Present Invention
C-5	B-2	8.0	1.79	0.24	7.4	98	18%	"
C-6	B-2	8.3	2.05	0.18	11.2	98	22%	"
C-7	B-3	7.4	1.79	0.24	7.4	97	16%	"
C-8	B-3	8.0	2.05	0.18	11.1	98	18%	"
C-9	B-3	8.3	2.19	0.16	13.7	97	24%	"
C-10	B-4	7.4	2.06	0.18	11.3	99	17%	"
C-11	B-4	8.0	2.19	0.16	13.6	99	22%	"
C-12	B-4	8.3	2.40	0.12	20.0	99	26%	"

Example 2

In this example, various seed crystal emulsions were formed by changing the nucleation conditions in the process of preparing seed crystal emulsions in Example 1, and then grown.

Seed Emulsion D-1 & Emulsion E-1

An aqueous solution of 11g of inert, low molecular weight (average molecular weight 15,000) gelatin and 6.0g of potassium bromide dissolved in 1 liter of distilled water was stirred at 40 ° C, and an aqueous 1.9 M silver nitrate solution and an aqueous 1.9 M solution of potassium bromide and potassium iodide (molar ratio 95/5) were added to the solution at a flow rate of 100 cc/min for 40 seconds. Thereafter, the pAg was raised to 10, and 32g of inert gelation were added to the resultant solution. The solution was then ripened for 20 minutes while the temperature was raised to 75 ° C. Subsequently, the pAg was adjusted to 7.5, and 100 cc of an aqueous ammonium nitrate solution (50 wt%) and 100 cc of sodium hydroxide (1 N) were added to produce ammonia in the reaction solution, thereby performing ammonia ripening. After 20 minutes, the resultant solution was neutralized with acetic acid until the pH became 4.0. Subsequently, 340 cc of an aqueous 1.9 M silver nitrate solution and an aqueous 1.9 M potassium bromide solution were added with the pAg kept at 8.3. The aqueous silver nitrate solution was first added at a rate of 10.0 cc/min and then added over 28 minutes and 22 seconds such that the addition flow rate increased by 0.14 cc per minute. Thus, a seed emulsion D-1 was obtained.

300g of the seed emulsion D-1 and 25g of inert gelation were added to a reactor vessel, and distilled water was added to make 1 liter as a total quantity. 506 cc of 1.9 M silver nitrate and 1.9 M potassium bromide were added at 75 ° C under stirring with the pAg kept at 8.0. The silver nitrate solution was first added at a rate of 8.6 cc/min and then added such that the flow rate increased by 0.114 cc per minute. Thus, an emulsion E-1 was obtained.

When the emulsion E-1 was observed by an electron microscope, tabular grains with an average equivalent-circle diameter of 2.05 µm, an average thickness of 0.18 µm, and an aspect ratio of 3 or more occupied 98% of the total projected area of silver halide grains. The aspect ratio was 2.2 on average, and the variation coefficient of all silver halide grains was 18%.

Seed Emulsion D-2 & Emulsion E-2

A seed emulsion D-2 was formed following the same procedures as for the emulsion D-1 except that gelation with an average molecular weight of 100,000 was used in the nucleation. The seed emulsion D-2 was grown following the same procedures as for the emulsion E-1, preparing an emulsion E-2.

Seed Emulsion D-3 & Emulsion E-3

A seed emulsion D-3 was formed following the same procedures as for the emulsion D-1 except that the temperature of nucleation was changed to 60 ° C. The seed emulsion D-3 was grown following the same procedures as for the emulsion E-1, preparing an emulsion E-3.

Seed Emulsion D-4 & Emulsion E-4

A seed emulsion D-4 was formed following the same procedures as for the emulsion D-1 except that the aqueous halide solution used in the nucleation was changed to an aqueous 1.9 M potassium bromide solution containing no iodide ions. The seed emulsion D-4 was grown following the same procedures as for the emulsion E-1, preparing an emulsion E-4.

Seed Emulsion D-5 & Emulsion E-5

A seed emulsion D-5 was formed following the same procedures as for the emulsion D-1 except that the addition time of the aqueous $AgNO_3$ solution and the aqueous halide solution added during the nucleation was changed from 40 seconds to 80 seconds. The seed emulsion D-5 was grown following the same procedures as for the emulsion E-1, preparing an emulsion E-5.

The seed emulsions D-1 to D-5 thus prepared and the emulsions E-1 to E-5 grown from these seed emulsions are shown in Tables 4 and 5 below, respectively.

The seed crystal D-2 obtained by performing nucleation by using gelatin with a molecular weight of 100,000, instead of low molecular weight gelatin, had a broad size distribution and was further polydispersed by the growth.

The seed emulsion D-3 obtained by performing nucleation at a temperature of 60 ° C had a size distribution broader than that of the seed emulsion D-1 and was therefore inadequate as seed crystals. The size distribution of the emulsion E-3 obtained by growing the seed emulsion D-3 was further broadened.

In the seed emulsion D-4 formed by using the solution containing no iodide ions as an aqueous halide solution added during nucleation, non-twined crystal grains remained, and the ratio occupied in the projected area by tabular grains with an aspect ratio of 2 or more was significantly low. The reason for this is assumed that the generation probability of twined crystals in the nucleation lowered largely. In the emulsion E-4 obtained by growing the seed emulsion D-4, the ratio occupied in the projected area by grains with an aspect ratio of 3 or more was low. The emulsion E-4 therefore cannot be expected to achieve a high performance as a tabular emulsion.

The seed emulsion D-5 obtained by performing the nucleation for 80 seconds had a broad grain size distribution. In addition, the mixing amount of non-twinned crystals and non-parallel twined crystals was large, and the ratio occupied in the projected area by grains with an aspect ratio of 2 or more was low. In the emulsion E-5 obtained by growing the seed emulsion D-5, the spread of the size distribution of tabular grains was significant. Furthermore, the non-twinned crystals and the non-parallel twined crystals contained in the seed crystals also grew to lower the ratio occupied in the projected area by tabular grains. Therefore, the emulsion E-5 cannot be expected to achieve a high performance as a tabular emulsion.

Table 4

Seed emulsion name	Average molecular weight of gelatin	Temperature (°C) during nucleation	Iodide ion concentration in added solution	Addition time (sec) during necleation	Ratio (%) occupied in projected area by grains with aspect ratio of 2 or more	Variation coefficient (%) of equivalent-circle diameter	
D-1	15.000	40	5 mol%	40	96	15	Present invention
D-2	100.000	40	5 mol%	40	75	29	Present invention
D-3	15.000	60	5 mol%	40	61	38	Present invention
D-4	15.000	40	0 mol%	40	43	39	Comparative example
D-5	15.000	40	5 mol%	80	48	35	Comparative example

Table 5

		Ratio occupied in projected area by grains with aspect ratio of 3 or more	Variation coefficient (%) of equivalent-circle diameter	
E-1	D-1	98%	18%	Present invention
E-2	D-2	78%	31%	Present invention
E-3	D-3	48%	46%	Comparative example
E-4	D-4	42%	47%	Comparative example
E-5	D-5	39%	42%	Comparative example

Example 3

This example shows reproducibility when grain formation was performed continuously from nucleation to grain growth and reproducibility when grain growth was performed by using seed crystals.

An aqueous solution prepared by dissolving 8.0g of inert, low molecular weight (average molecular weight 15,000) gelatin and 6.4g of potassium bromide in 1 liter of distilled water was stirred at 40 ° C, and an aqueous 1.9 M silver nitrate solution and an aqueous 1.9 M solution of potassium bromide and potassium iodide (molar ratio 95/5) were added to the solution at a flow rate of 20 cc/min for 40 seconds. Thereafter, the pAg was raised to 10, and 32g of inert gelation were added to the resultant solution. The solution was then ripened for 20 minutes while the temperature was raised to 75 ° C. Subsequently, the pAg was adjusted to 7.5, and 100 cc of aqueous ammonium nitrate solution (50 wt%) and 100 cc of sodium hydroxide (1 N) were added to produce ammonia in the reaction solution, thereby performing ammonia ripening. After 20 minutes, the resultant solution was neutralized with acetic acid until the pH became 4.0. Subsequently, 340 cc of an aqueous 1.9 M silver nitrate solution and an aqueous 1.9 M potassium bromide solution were added with the pAg kept at 7.7. The aqueous silver nitrate solution was first added at a rate of 10.0 cc/min and then added over 28 minutes and 22 seconds such that the addition flow rate increased by 0.14 cc per minute. Thus, a seed emulsion F-1 was obtained.

Emulsions F-2 to F-6 were obtained following exactly the same procedures as described above. The grains thus prepared did not exhibit a perfectly identical shape, i.e., differed in average grain size, thickness, aspect ratio, and variation coefficient. The emulsions F-1 to F-6 are summarized in Table 6 below.

Subsequently, the emulsion C-5 obtained in Example 1 and having substantially the same size as that of the emulsion F-1 was repeatedly prepared six times under the same conditions. The result is also shown in Table 6.

As is apparent from Table 6, when the steps from nucleation to grain growth were performed continuously, a variation occurred each time the process was performed, impairing the repetitive reproducibility. Each emulsion formed by performing grain growth by using seed crystals, on the other hand, had a high repetitive reproducibility and hence could be formed stably.

Table 6

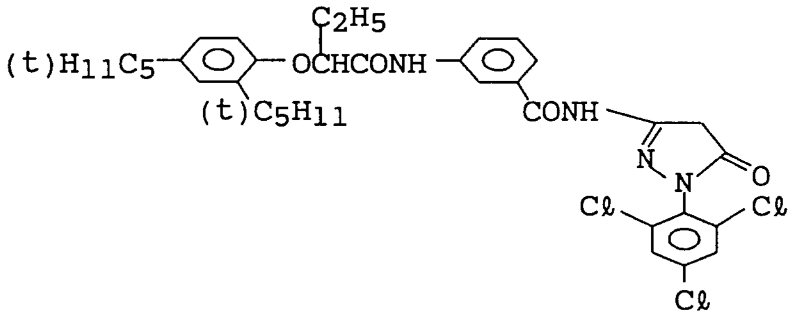
Emulsion No.	Average equivalent-circle diameter (μm) of projected area	Grain thickness (μm)	Variation coefficient of equivalent-circle diameter
F-1	2.00	0.19	5.4% by F-1 to F-6
F-2	2.06	0.18	
F-3	2.20	0.19	
F-4	2.20	0.17	
F-5	1.90	0.18	
F-6	2.17	0.19	
C-81	2.12	0.18	1.9% by C-81 to C-86
C-82	2.00	0.19	
C-83	2.10	0.18	
C-84	2.11	0.19	
C-85	2.08	0.18	
C-86	2.10	0.18	

Example 4

Layers of the emulsions prepared in Examples 1 and 2 and a protective layer were coated in coating amounts shown below on a triacetylcellulose film support having an undercoat layer.

(1) Emulsion layers... emulsions C-1 to C-12 shown in Table 3
emulsions F-1 and C-81 shown in Table 6
(silver 1.7×10^{-2} mol/m^2)
Coupler indicated below (1.5×10^{-3} mol/m^2)
·Tricresylphosphate (1.10 g/m^2)
·Gelatin (2.30 g/m^2)
(2) Protective layer
·2.4-dichloro-6-hydroxy-S-triazine sodium salt (0.08 g/m^2)
·Gelatin (1.80 g/m^2)

Coupler:



These samples were subjected to sensitometry exposure for 1/100 second and color development.

Each processed sample was then subjected to densitometric measurement through a green filter to check the sensitivity and the gradation of the sample. The sensitivities were compared in terms of an exposure amount by which an optical density of (fog + 0.2) was given, and evaluated as relative sensitivities assuming that the sensitivity of a sample 101 was 100.

The gradations were compared in terms of a value obtained by subtracting (fog + 0.2) from an optical density obtained by giving an exposure amount 10 times the exposure amount by which the optical density of (fog + 0.2) was given, and evaluated as relative values assuming that the gradation of the sample 101 was 100.

The development was performed in accordance with the following method.

Processing Method		
Step	Processing time	Processing temperature
Color development	2 min. 45 sec.	38 °C
Bleaching	6 min. 30 sec.	38 °C
Washing	2 min. 10 sec.	24 °C
Fixing	4 min. 20 sec.	38 °C
Washing (1)	1 min. 05 sec.	24 °C
Washing (2)	1 min. 00 sec.	24 °C
Stabilization	1 min. 05 sec.	38 °C
Drying	4 min. 20 sec.	55 °C

The compositions of the processing solutions used were as follows.

(Color developer)	
	(g)
Diethylenetriaminepentaacetic acid	1.0
1-hydroxyethylidene-1,1-diphosphonic acid	3.0
Sodium sulfite	4.0
Potassium carbonate	30.0
Potassium bromide	1.4
Potassium iodide	1.5 mg
4-[N-ethyl-N-β-hydroxyethylamino]-2-methylaniline sulfate	4.5
Water to make	1.0 liter
pH	10.05

(Bleaching solution)	
	(g)
Ferric ammonium ethylenediaminetetraacetate dihydrate	100.0
Disodium ethylenediaminetetraacetate	10.0
Ammonium bromide	140.0
Ammonium nitrate	30.0
Ammonia water (27%)	6.5 mℓ
Water to make	1.0 liter
pH	

(Fixing solution)	
	(g)
Disodium ethylenediaminetetraacetate	0.5
Sodium sulfite	7.0
Sodium bisulfite	5.0
Aqueous ammonium thiosulfate solution (70%)	170.0 mℓ
Water to make	1.0 liter
pH	6.7

(Stabilizer)	
Formalin (37%)	2.0 mℓ
Polyoxyethylene-p-monononylphenyl ether (average polymerization degree 10)	0.3
Disodium ethylenediamine tetraacetate	0.05
Water to make	1.0 liter
pH	5.0 - 8.0

The results are summarized in Table 7 below.

Table 7

Sample No.	Emulsion No.	Sensitivity	RMS granularity value
101 (Comparative example)	C-1	100	0.020
102 (")	C-2	165	0.024
103 (")	C-3	201	0.027
104 (Present invention)	C-4	180	0.022
105 (")	C-5	225	0.027
106 (")	C-6	292	0.028
107 (")	C-7	241	0.027
108 (")	C-8	310	0.028
109 (")	C-9	321	0.028
110 (")	C-10	310	0.028
111 (")	C-11	335	0.029
112 (")	C-12	400	0.030
113 (Comparative example)	F-1	295	0.028
114 (Present invention)	C-82	310	0.028

Table 7 reveals that each color photosensitive material of the present invention had a high sensitivity. When samples formed by coating emulsions with equivalent grain volumes and aspect ratios were compared, grains grown by using seed crystals with a high aspect ratio had a higher sensitivity and a higher granularity value.

Comparison between the emulsion F-1 formed continuously from nucleation to grain formation and the emulsion C-82 obtained by the use of the seed crystal method in Example 3 shows that the grains obtained by the seed crystal method had a higher sensitivity.

Although the present inventors did not expect the above result, the reason for this is estimated that nuclei ripened by ammonia ripening are small in grains using seed crystals, and so fog nuclei are limited to the centers of the individual grains, thereby lowering the internal sensitivity. The details of this mechanism, however, are still unknown.

According to the present invention as has been described in detail above, tabular grains with a high aspect ratio and a narrow size distribution can be obtained stably by using, as seed crystals, a silver halide emulsion in which tabular silver halide grains with an aspect ratio of 2 to 12 account for 50% to 100% of the total projected area of all silver halide grains.

Claims

1. A method of preparing a tabular silver halide emulsion, comprising growing a silver halide seed emulsion in which tabular silver halide grains having an aspect ratio of 2 to 12 account for 50% to

100% of a total projected area of all silver halide grains of the seed emulsion, to prepare a grown tabular silver halide emulsion in which tabular silver grains having an aspect ratio of 3 to 40 account for 50% to 100% of a total projected area of all silver halide grains of the grown emulsion.

2. The method according to claim 1, characterized in that a variation coefficient of equivalent-circle diameters of projected areas of all the tabular grains in said grown emulsion is 8% to 22%.

3. The method according to claim 1, characterized in that a variation coefficient of equivalent-circle diameters of projected areas of all the tabular grains in said seed emulsion is 8% to 22%.

4. The method according to claim 1, characterized in that the seed emulsion is prepared by a process including a nucleation step in which a low molecular weight gelatin having an average molecular weight of 5,000 to 25,000 is used as a dispersion medium, an aqueous halide salt solution added during the nucleation contains 0.5 to 20 mol% of iodide ions, a nucleation temperature is 20°C to 50°C, and a nucleation time is 5 to 60 seconds.

5. The method according to claim 1, characterized in that the seed emulsion grains are grown such that each grown emulsion grain has a volume at least 4 times that of each seed emulsion grain on an average.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 12 1086

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	EP-A-0 484 927 (KONICA CORPORATION) * example 1 * ---	1-5	G03C1/005
X	US-A-4 879 208 (S.URABE) * example 1 * ---	1-5	
X	EP-A-0 391 560 (MINNESOTA MINING AND MANUFACTURING COMPANY) * claims * ---	1-5	
X	EP-A-0 263 508 (E.I. DU PONT DE NEMOURS AND COMPANY) * claims * ---	1-5	
X	EP-A-0 263 507 (E.I. DU PONT DE NEMOURS AND COMPANY) * claims * ---	1-5	
X	EP-A-0 374 853 (FUJI PHOTO FILM COMPANY LTD.) * page 5, line 41 - line 43; example 1 * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 May 1994	Buscha, A

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
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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