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(54) **Silver halide color photographic light-sensitive material.**

(57) A silver halide color photographic light-sensitive material is disclosed, comprising a support having thereon a silver halide emulsion layer, wherein the silver halide emulsion layer contains monodispersed tabular silver halide grains having an even number of twin planes in the grain, an aspect ratio of less than 5 and accounting for not less than 50% of total projected area of grains contained in the emulsion layer ; the tabular gains being internally reduction-sensitized and satisfying a specific relation between twin plane distances and grain thicknesses.

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Field of the invention

This invention relates to a silver halide color photographic light-sensitive material useful for the photographic field and, particularly, to a silver halide color photographic light-sensitive material high in sensitivity and excellent in latent image preservability.

Background of the invention

In recent years, there has been a strong demand for a silver halide color photographic light-sensitive material having a higher sensitivity and a superior image-quality, because of the popularization of a compact type camera, an automatically focusing type single-lens reflex camera and, in addition, a film cartridge attached with a lens. Therefore, a demand for improving the characteristics of a silver halide emulsion for photographic use has been getting more serious, and there has also been a high-level demand for the photographic characteristics such as a higher sensitivity, an excellent graininess and an excellent sharpness.

In response to the above-mentioned demands, US Patent Nos. 4,434,226, 4,439,520, 4,414,310, 4,433,048, 4,414,306 and 4,459,353 disclose the techniques applied with tabular-shaped silver halide grains (hereinafter sometimes referred simply to as tabular grains), whereby the following advantages have been known; namely, a sensitivity improvement including a spectral-sensitization efficiency with a sensitizing dye, the improvements in a sensitivity/graininess, a sharpness improvement made by the specific optical characteristics of tabular-shaped grains and a covering-power improvement. However, such a technique as mentioned above has still not been satisfiable, but any more performance improvements have still been demanded.

For improving a sensitivity to be made higher, a variety of analyses and technical developments have been tried so far. There have been various factors of a non-efficiency relating to the sensitivity of an emulsion. From the viewpoint of preventing a free electron and a positive hole from recombination thereof, that is, one of the above-mentioned factors. It has been known so far that a reduction-sensitization is effective to prevent such a recombination as mentioned above.

As described in Journal of Photographic Science, Vol. 25, pp. 19-27, (1977) and Photographic Science and Engineering, Vol. 23, pp. 113-117, (1979), a optimal reduction-sensitization has been considered to contribute to a sensitization when making an exposure, through the reactions represented by the following formulas, as described by Michell and Lowe in Photographishe Korrespondenz, Vol. 1, pp. 20-, (1957) and Photographic Science and Engineering, Vol. 19, pp. 49-55, (1975), respectively.

$$AgX + hv \rightarrow e^- + h^+ \qquad (1)$$

$$Ag_2 + h^+ \rightarrow Ag^+ + Ag \qquad (2)$$

$$Ag \rightarrow Ag^+ + e^-$$

wherein h^+ and e^- represent s free positive hole and a free electron produced upon exposure; hv represents a photon; and Ag_2 represents a reduction-sensitization nucleus. Based on assumption as above-mentioned, it can be considered that a reduction-sensitization nucleus can prevent an efficiency deterioration due to recombination of an electron and a positive hole so as to contribute to increase a sensitivity.

However, according to the descriptions in Photographic Science and Engineering, Vol. 10, pp. 35-42, (1971) and, ibid., Vol. 23, pp. 113-117, (1979), a reduction-sensitization nucleus has a capability of traping not only a positive hole but also an electron. Therefore, a sufficient explanation cannot always be made, based on only the above-mentioned theory.

Different from a sensitivity speck inherent in silver halide grains described above, the functions of reduction-sensitization of a spectrally sensitized silver halide in the spectral-sensitizing region is really difficult to be predicted.

In a spectrally sensitized silver halide emulsion, light is absorbed by a sensitizing dye, that is different from the case of the inherent sensitivity region. The primary stage of a photosensitization is represented by formula (4), instead of formula (1).

$$Dye + hv \rightarrow Dye^+ + e^- \qquad (4)$$

Transfer of a dye positive hole (Dye^+) and an electron (e^-) as described in the right side of the formula to a silver halide grain depends greatly upon the characteristics of the dye. Concerning a dye positive hole, it has generally been regarded that a sensitization efficiency may become better when a dye positive hole is not transferred to the inside of a grain.

For example, in Photographic Science and Engineering, Vol. 24, pp. 138-143, (1980), discussions was made in relation to an oxidation potential (Eox) of a dye.

However, Abstracts of International Congress of Photographic Science, pp. 159-162, (1978) and Photographic Science and Engineering, Vol. 17, pp. 235-244, (1973) suggest each that such a sensitizing dye as those in which a dye positive hole (Dye^+) produced upon exposure remains on the surface of the silver halide

grain and, thereby, a fog nucleus and a reduction-sensitization nucleus are bleached on the surface of the silver halide grain. In a conventional surface-latent image type emulsion, it may be expected that a latent image on the surface is bleach to result in a desensitization.

As described thus far, it has still been unknown, in a spectrally sensitized system, which is better to reduction-sensitize the surface of a silver halide grain or the inside thereof, and it has also still unknown what kinds of dyes are to be used in combination so as to display the effects of the combination use.

As for the reduction-sensitization processes, the following processes have been known; namely, a process in which a reduction-sensitization is applied to the surface of a silver halide grain or it is applied in the course of growing silver halide grains, or a process in which a seed crystal is reduction-sensitized in advance when making use of the seed crystal for growing up a grain.

When making combination use of the process of applying a reduction-sensitization to the surface of a grain and the other sensitization process (such as those in which a gold compound or a sulfur compound is used), an unacceptable fog is seriously increased so as not to be suitable for practical application. In contrast to the above, a process of applying a reduction-sensitization in the course of growing silver halide grains, that is to say, a process for applying a reduction-sensitization to the inside of a grain, has not such a defect as mentioned above even if making combination use of other sensitization processes.

Such a process as mentioned above is detailed in, for example, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP OPI Publication) Nos. 48-87825/1973 and 57-179835/1982. In these patents, however, there is no description on a spectrally sensitized system, though the improvement of the inherent sensitivity of silver halide is reported therein. The above-mentioned fact may be supposed that a dye positive hole remaining on the surface of silver halide may destroy a latent image formed on the silver halide surface. It is presumed that a reduction-sensitization cannot be effected, because a reduction-sensitization nucleus present inside a grain does not effectively trap a dye positive hole on the surface of the grain.

For the purpose of increasing the sensitivity of a surface latent image type silver halide by making combination use of a reduction-sensitization and a gold·sulfur sensitization, it has been known that the following problems still remaining unsolved, from the standpoint of improving a spectral sensitivity.

1. When applying a reduction-sensitization to the inside of a grain, there is mostly no effect on a spectral sensitization. When applying a reduction-sensitization to the surface of a grain, on the other hand, there is still no positive evidence on a spectral sensitization effect; and
2. When applying a reduction-sensitization to the surface of a grain, it is difficult to make combination use thereof with a gold·sulfur sensitization, because of a high fog.

In regard to the above-mentioned points, JP OPI Publication Nos. 2-105139/1990, 2-108038/1990, 2-125247/1990, 2-127636/1990, 2-130545/1990, 2-150837/1990, 2-168247/1990, 2-135043/1990, 4-232945/1992 and 4-32832/1992 disclose the techniques applicable particularly to a spectrally sensitized silver halide emulsion, such as that for increasing sensitivity, for improving preservability and for improving pressure resistance property.

However, the above-mentioned techniques have not been able to afford the practical application, because the resulting desensitization has been increased after making an exposure and then preserving under the conditions of a high temperature and a high humidity over a long period of time.

Summary of the invention

It is an object of the invention to provide a silver halide color photographic light-sensitive material improved in the above-mentioned problems, high in sensitivity and excellent in latent image preservability (that is the stability of sensitivity obtained after making an exposure and then preserving a subject under the conditions of high temperature and high humidity for a long time).

The above-mentioned object of the invention can be achieved by the following constitution.

A silver halide color photographic light-sensitive material comprising a support bearing thereon at least one silver halide emulsion layer containing silver halide grains, wherein the silver halide grain emulsion comprises tabular-shaped silver halide grains having a even number of twinned crystal planes parallel to the major faces thereof and an aspect ratio of less than 5, the tabular grains accounting for not less than 50% of the total projected area of the grains contained in the layer and satisfying the following requirements (A) through (C);

(A) A variation coefficient of grain-size distribution is to be not greater than 20%;

(B) Between a variation coefficient (x) of twin plane distances of the grains and a variation coefficient (y) of thicknesses of the grains, there is a relation of $0.7 \leqq y/x \leqq 2.0$; and

(C) The grains are internally reduction-sensitized.

Detailed description of the invention

The silver halide grains contained in a silver halide emulsion of the invention are to be tabular-shaped grains. Tabular-shaped grains are categorized crystallographically into a twinned crystal.

A twinned crystal is a silver halide crystal having not less than one twinned crystal planes in the grain thereof. The classifications of the twinned crystal shapes are detailed in Klein & Moiser, Photographishe Korrespondenz, Vol. 99, p. 100 and, ibid., Vol. 100, p. 57, respectively.

In the invention, a tabular-shaped grain has even number of twin planes each parallel to the major face of the grain. The twin planes can be observed through a transmission type electron microscope. The concrete observation method is as follows. First, a sample is prepared in such a manner that a silver halide photographic emulsion containing tabular-shaped grains is coated on a support so that the major face of the tabular-shaped grains are oriented in parallel with the support. The resulting sample is cut and scraped by making use of a diamond cutter into a thinned cut piece having a thickness of the order of 0.1μm. When observing the resulting cut piece through a transmission type electron microscope, the presence of the twinned crystal planes can be confirmed.

In the invention, the twin plane distance is the shortest distance between two or more twin planes parallel to the major face. Thus, the twin plane distance is the distance between two twin planes in a grain when the grain has two twin planes, and it is the shortest distance among the distances between twin planes in a grain when the grain has four or more even-numbered twin planes.

In the invention, a mean value of twin plane distances can be obtained in the following manner. When observing a cut piece through a transmission type electron microscope as mentioned above, not less than 1000 tabular-shaped grains having a section almost vertical to the major face are selected at random. Among even-numbered twin planes parallel to the major face, the shortest distance between two twinned crystal planes is obtained from each grain, and the mean distance between twinned crystal planes of the grains can be obtained as an arithmetic mean of the shortest distances.

In the invention, the term, a variation coefficient (x) of twin plane distances, herein means a fluctuation of the twin plane distances of tabular-shaped grains. It expresses in terms of a percentage obtained by dividing a standard deviation value of the twin plane distances by a mean value of the twin plane distances.

In the invention, the mean twin plane distance is to be within the range of 0.01μm to 0.05μm and, preferably, 0.013μm to 0.03μm.

The mean thickness of tabular-shaped grains of the invention can be obtained in such a manner that the thickness of each grain is obtained by observing the cut piece of a subject sample through a transmission type electron microscope in the same manner as described above and the mean thickness of the grains can be obtained by averaging out the thickness of the grains as an arithmetic mean. The mean thickness of the tabular-shaped grains is to be within the range of 0.05μm to 1.5μm and, preferably, 0.15μm to 1.0μm.

In the invention, the term, a variation coefficient (y) of thicknesses of tabular-shaped grains, herein means fluctuation of the thicknesses among the tabular-shaped grains. It expresses in terms of a percentage obtained by dividing a standard deviation of grain thickness by a mean value of the grain thickness.

Tabular-shaped grains of the invention have the following relations;

Between a variation coefficient (x) of distances between the twin planes and a grain-thickness variation coefficient (y), there is a relation of $0.7 \leqq y/x \leqq 2.0$, preferably, $0.8 \leqq y/x \leqq 1.6$ and, most preferably, $0.9 \leqq y/x \leqq 1.3$.

A tabular-shaped grain of the invention is defined as those having an aspect ratio (a grain-size/a grain thickness) of lower than 5, preferably not higher than 4.0 and more preferably 3.0 to 1.0.

In the invention, the grain-size of a silver halide grain is indicated by a diameter equivalent to that of a circle having the same area as the projected area of the silver halide grain (i.e., a circular-equivalent diameter). It is to be within the range of, preferably, 0.1 to 5.0μm and, more preferably, 0.2 to 2.0μm.

A grain-size can be obtained, for example, in the following manner. A subject grain is magnified 10,000 to 70,000 times through an electron microscope and then photographed. The resulting diameter of the grain come out on a print or the projected area of the grain is practically measured, provided that the numbers of the grains subject to the measurement are to be not less than 1,000 at random.

An average grain-size r is herein defined as a grain-size ri when maximizing a product $ni \times ri^3$ in which ni represents a frequency of grains having a grain-size ri, provided that a significant figure is three columns and the figure in the lowest column is rounded.

A silver halide grain of the invention comprises a monodisperse type silver halide emulsion. As for the monodisperse type silver halide emulsions, the weight of silver halide having a grain-size within the scope of ±20% of an average grain-size r is to be, preferably, not less than 60% of the weight of the whole silver halide grain, more preferably, not less than 70% and, particularly, not less than 80%.

When defining a grain-size distribution width in the following formula,

(a standard deviation/an average grain - size) x 100 = a grain - size distribution width (a grain - size variation coefficient) [%]

a monodispersed type emulsion of the invention has a grain-size distribution width of not higher than 20%, more preferably not higher than 15% and, most preferably, not higher than 12%. An average grain-size and a standard deviation are herein obtained from the above-defined grain-size ri.

In the invention, a distance between twin planes may be controlled by suitably selecting the following various factors, which may give an influence on the supersaturated state in the nucleation stage, including for example a gelatin concentration, a gelatin type, a temperature, an iodide ion concentration, a pBr, a pH, an ion-supply rate, an rpm for stirring and a combination thereof. Generally, the higher supersaturation in the nucleation stage, the smaller becomes the distance between twin planes.

The details of the above-mentioned supersaturation factors may be referred to the descriptions appeared in JP OPI Publication No. 63-92924/1988 or, ibid., No. 1-213637/1989.

Silver halide grains of the invention are internally reduction-sensitized, thus, an internal portion of the grain is subjected to reduction sensitization. The word internal portion herein means an inner portion of 90% or less and preferably 70% or less of the grain, based on the volume. In other words, silver halide grains of the invention are subjected to reduction sensitization before 90% (preferably, 70%) of the ultimate grain volume of the grain is reached.

The above-mentioned reduction-sensitization is carried out by adding a reducing agent to a silver halide emulsion or a mixed solution during the growth of the grains. Or, it is carried out by ripening or grain-growing a silver halide emulsion or a mixed solution for growing grains under the conditions of a low pAg of not higher than pAg 7 or a high pH of not lower than pH 7. A process carried out by making combination use of the above-mentioned methods is also a preferable embodiment of the invention.

Preferable reducing agents include, for example, thiourea dioxide, ascorbic acid and the derivatives thereof, and stannous salt. Other suitable reducing agents include, for example, a borane compound, a hydrazine derivative, formamidine sulfinic acid, a silane compound, an amine and a polyamine, and a sulfite. They may be added preferably in an amount within the range of 10^{-2} to 10^{-8} mols per mol of silver halide used therein.

For performing a ripening treatment at a low pAg, a silver salt may be added. Among the silver salts for this purpose, a water-soluble silver salt is preferred. Among the water-soluble silver salts, silver nitrate is preferred. When carrying out a ripening treatment, the pAg is suitable to be not higher than 7, preferably, not higher than 6 and, particularly, within the range of 1 to 3, provided, pAg = -log[Ag^+].

A high pH ripening treatment may be carried out, for example, by adding an alkaline compound to a silver halide emulsion or a mixed solution for growing grains. The alkaline compounds applicable thereto include, for example, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate and ammonia. In a process for adding an ammoniacal silver nitrate for producing silver halide, an alkaline compounds except ammonia may preferably be used, because an ammonia effect may be deteriorated.

As for the process of adding a silver salt or an alkaline compound for making a reduction-sensitization, they may be rush added or may also be added by taking a given time. In the latter instance, it may be added at a certain flow rate or may also be added by varying acceleratedly the flow rate thereof. It is also allowed to add a necessary amount divided into several parts for the addition. In advance of adding a soluble silver salt and/or a soluble halide to a reaction chamber, the silver salts or an alkaline compound for a reduction-sensitization may be made present in the reaction chamber, or they are mixed in a soluble halide solution and then they may be added together with the halide. Besides the above, they may further be added, separately from the soluble silver salt and soluble halide.

For preparing a silver halide emulsion of the invention, a process of growing grains from seed grains is preferably used. To be more concrete, in the process, an aqueous solution containing protective colloid and seed grains are made present in a reaction chamber in advance and silver ions, halogen ions or silver halide fine grains are supplied thereto, so that the seed grains are grown up to final grains. Therein, the seed grains may be prepared by a single-jet process or a controlled double-jet process, which have been well-known in the art. Any halogen composition of the seed grains may be used therein, including any one of silver bromide, silver iodide, silver chloride, silver iodobromide, silver chloroiodide, silver chlorobromide and silver chloroiodobromide. Among them, silver bromide and silver iodobromide are preferred. In the case of silver iodobromide, the average silver iodide content thereof is preferably within the range of 1 mol% to 20 mol%.

To meet the afore-mentioned requirement $0.7 \leqq y/x \leqq 2.0$, a value of x is preferably to be small as possible. In order to decrease a value of x , silver halide grains are preferably to be grown from seed grains having narrow distance(s) between twin planes. In a preferred embodiment of the invention, the pBr of a reaction mother liquor is maintained at 2.5 or less (preferably, 1.0 to 2.0) at the nucleation stage in the course of forming seed grains to decease the distance between twin planes of the seed grains. It is further preferable that the resulting nucleus grains are subjected to ripening to dissolve grains other than those having even number of twin planes.

The ripenining is carried out at 30°C (preferably, 18 to 26°C) and in the presence of a silver halide solvent such as ammonia, thioether, or thiocyanate. In the case when using ammonia as the solvent, the amount thereof may be 0.10 mol/l or more, preferably, 0.2 to 2.0 mol/l. In the present invention, x is preferably 20% or less, more preferably 15% or less.

In the process of growing crystals from seed grains, it is preferable that ripening treatment at a low pAg is carried out by adding silver nitrate thereto, that is to say, the ripening treatment is preferably carried out by adding silver nitrate in the course between the point of time immediately before desalting the seed grain emulsion and the time after completing the desalting treatment thereof. It is particularly preferable to add silver nitrate after desalting and then ripening the seed grains. The ripening temperature is preferable to be kept not lower than 40°C, that is, within the range of 50°C to 80°C. The ripening time is preferable to be taken for not shorter than 30 minutes, that is, within the range of 50 to 150 minutes.

In the system of carrying out a grain growing treatment by making use of seed grains and when carrying out ripening treatment at a high pH therein, it is necessary to grow the grains by subjecting them to an environment having a pH of not lower than 7 at least once, before 70% of the ultimate grain volume of the grown-up grains is reached. It is more preferable to grow up the grains by subjecting them to an environment having a pH of not lower than 7 at least once, before 50% of the ultimate grain volume of the grown-up grains is reached. It is particularly preferable to grow up the grains by subjecting them to an environment having a pH of not lower than 8 at least once, before 40% of the ultimate grain volume of the grown-up grains is reached.

An oxidizing agent may be applied to a silver halide emulsion of the invention. The oxidizing agent applicable thereto include, for example, the following ones.

Hydrogen peroxide (in an aqueous solution) and the adducts thereof such as H_2O_2, $NaBO_2$-H_2O_2-$3H_2O_1$, $Na_4P_2O_7$-$2H_2O_2$ and $2Na_2SO_4$-H_2O_2-$2H_2O$; peroxy acid salt such as $K_2S_2O_3$, $K_2C_2O_3$, $K_4P_2O_3$ and $K_2[Ti(O_2)C_2O_4]$-$3H_2O$; peracetic acid; ozone; iodine; bromine; and a thiosulfonic acid derivative.

The above-mentioned oxidizing agent applicable to the invention may be added preferably in an amount within the range of 10^{-2} to 10^{-5} mols per mol of a reducing agent used therein, provided, however, that such an adding amount thereof as mentioned above may be varied, according to the kind of reducing agent used, the conditions of a reduction-sensitization, a addition time of an oxidizing agent and the condition of adding the oxidizing agent.

The oxidizing agent may be added optimally at a time during the course of preparing a silver halide emulsion. It is also allowed to add it in advance of adding a reducing agent.

It is further allowed to newly add a reducible substance after adding an oxidizing agent so that an excessive oxidizing agent may be neutralized. Such a reducible substances as mentioned above are those capable of reducing the above-mentioned oxidizing agent, and the reducible substances include, for example, a sulfinic acid, a di- and tri-hydroxybenzene, a chroman, a hydrazine and hydrazide, a p-phenylenediamine, an aldehyde, an aminophenol, an endiol, an oxime, a reducible sugar, a phenidone, a sulfite and an ascorbic acid derivative. These reducible substances may be added preferably in an amount within the range of 10^{-3} to 10^{3} mols per mol of an oxidizing agent used.

A silver halide grain of the invention comprises substantially silver iodobromide. However, it is allowed to contain silver chloride therein, provided that the effects of the invention shall not be deteriorated thereby.

It is preferable that silver halide grains of the invention have a silver iodobromide phase containing not less than 5 mol% of silver iodide inside the grain. It is more preferable that a silver halide grain of the invention has a silver iodobromide phase containing silver iodide in a proportion within the range of 10 mol% to 40 mol%. The expression, graind have a silver iodobromide phase inside the grain, herein means an internal portion co 90% or more inside of the grain and preferably 50% or more inside thereof, based on the ultimate volume of the grain.

Silver halide grains of the invention are preferable to be the so-called core/shell type grains containing silver iodide localized inside the grain.

A silver halide grain of the invention is to be comprised of silver iodobromide having an average silver iodide content within the range of, preferably, 1 mol% to 20 mol% and, more preferably, 3 to 15 mol%.

As for the means for preparing a silver halide emulsion of the invention, a variety of means having been well-known in the field of the art may be used. The following means can be used in any combination, namely, a single-jet precipitation, a controlled double-jet precipitation, a controlled triple-jet precipitation and so forth. However, for obtaining a highly monodisperse type grains of the invention, it is essential to control a pAg in a solution, in which silver halide grains are produced, so as to meet the silver halide grain growth rate. Such a pAg value as mentioned above is used in the region within the range of 7.0 to 10.5, preferably, 7.5 to 10.0 and, more preferably, 8.0 to 9.5.

In the afore-mentioned requirement, $0.7 \leqq y/x \leqq 2.0$, a value of y is preferably small as possible to meet the requirement. To decease y, it is essential to control the pAg of a solution. The pAg is preferably within the

range of 7.5 to 10.0, more preferably 8.0 to 9.5. In the present invention, y is 20% or less, preferably 15% or less.

When determining an addition rate, JP OPI Publication Nos. 54-48521/1979 and 58-49938/1983 may be referred to.

It is allowed to make present a well-known silver halide solvent such as ammonia, thioether and thiourea, or no silver halide solvent may be used, when preparing silver halide grains of the invention.

Silver halide grains of the invention may be either those capable of forming a latent image mainly on the surface thereof, or those capable of forming a latent image mainly inside the grain. In the present invention, is preferable a surface latent image-forming silver halide emulsion.

Silver halide grains of the invention are prepared in the presence of a dispersion medium, that is, in an aqueous solution containing the dispersion medium. The expression, an aqueous solution containing a dispersion medium, herein means an aqueous solution in which a protective colloid is formed of a substance capable of constituting hydrophilic colloid (that is, for example, a substance capable of serving as a binder) such as gelatin, and it also preferably means an aqueous solution containing a protective colloidal gelatin.

When the invention is embodied by making use of gelatin as the above-mentioned protective colloid, the gelatin may be either lime-treated or acid-treated. Details of the gelatin preparation is referred to Arthur Veis, The Macromolecular Chemistry of Gelatin, Academic Press, 1964.

The hydrophilic colloids other than gelatin, which can be used as a protective colloid, include, for example, the following substances; namely, a protein such as a gelatin derivative, a graft polymer of gelatin and other polymer, albumin and casein; a cellulose derivative such as hydroxyethyl cellulose, carboxymethyl cellulose and a cellulose sulfate; a sugar derivative such as sodium alginate and a starch derivative; and various kinds of synthetic hydrophilic macromolecular substance such as a monomer or copolymer of polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinyl pyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole or polyvinyl pyrazole.

In the case of making use of gelatin, it is preferable to make use of those having a jelly strength of not lower than 200 in AGI's method.

Silver halide grains of the invention can contain a metal ion inside the grain and/or on the surface of the grain by adding a metal ion to the grain by making use of at least one selected from the group consisting of a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iron salt, a rhodium salt, an iridium salt and an indium salt (including the complex salts thereof), in the courses of forming the grain and/or growing the grain.

A silver halide grain of the invention may be a grain from which any unnecessary soluble salts are removed after completing the growth of the silver halide grain, or may also be a grain remaining contained.

As in the method described in JP OPI Publication No. 60-138538/1985, a desalting treatment can be performed at any point in the course of preparing silver halide. When trying to remove the above-mentioned salts, they can be removed in the method described in Research Disclosure (hereinafter abbreviated to RD) No. 17643, Article II. To be more detailed, for removing a soluble salt from an emulsion after completing precipitation or physical ripening, it is allowed to make use of a noodle-washing method in which gelatin is gelled, or to make use of a flocculation method in which an inorganic salt, an anionic surfactant, an anionic polymer (such as polystyrene sulfonic acid) or a gelatin derivative (such as acylated gelatin and carbamoylated gelatin) is utilized.

A silver halide grain of the invention can be chemically sensitized in an ordinary method. To be more concrete, a sulfur sensitization method, a selenium sensitization method, a noble-metal sensitization method in which gold or other noble metal compound is used, and so forth may be used singly or in combination.

Silver halide grains of the invention can be spectrally sensitized to any desired wavelength region by making use of a dye that has been known as a sensitizing dye in the photographic field. Such a sensitizing dye as mentioned above may be used singly or in combination. It is also allowed that an emulsion is to contain, together with a sensitizing dye, a supersensitizer capable of enhancing the sensitizing effect of a sensitizing dye, that is a dye having no spectral sensitizing function in itself, or, that is a compound substantially incapable of absorbing any visible rays of light.

An antifoggant or stabilizer may be added to a silver halide grain emulsion of the invention.

As for a binder applicable to the invention, it is advantageous to use gelatin. An emulsion layer and other hydrophilic colloidal layers may be hardened and, a plasticizer and a water-insoluble or water-soluble synthetic polymer dispersion (so-called a latex) may also be contained therein.

A coupler is used in an emulsion layer of a silver halide color photographic light-sensitive material of the invention. It is also allowed to use a competing coupler having a color correction effect and a compound capable of releasing such a photographically useful fragment as a development accelerator, a developing agent, a silver halide solvent, a color toner, a layer hardener, a foggant, an antifoggant, a chemical sensitizer, a spectral sensitizer and a desensitizer, through a coupling reaction with the oxidized product of a developing agent.

To a silver halide color photographic light-sensitive material of the invention, an auxiliary layer such as a filter layer, an antihalation layer and an anti-irradiation layer may be provided. In the above-mentioned layer and/or an emulsion layer, it is also allowed to contain a dye capable of being dissolved out of a light-sensitive material or being bleached, in the course of carrying out the development treatment.

To a silver halide color photographic light-sensitive material of the invention, may be added a matting agent, a lubricant, an image stabilizer, a formalin scavenger, a UV absorbent, a fluorescent whitening agent, a surfactant, a development accelerator and a development retarder.

As for the supports applicable to the invention, a sheet of paper laminated thereon with polyethylene or the like, polyethylene terephthalate film, baryta paper and cellulose triacetate film may be used.

Examples

The invention will now be detailed with reference to the following examples. However, the embodiments of the invention shall not be limited thereto.

Example 1

(Preparation of twinned crystal emulsion T-1)

According to the following process, a seed emulsion having two parallel twin planes was prepared.

(Solution A)

Ossein gelatin	80.0 g
Potassium bromide	47.4 g
A 10 wt% methanol solution of $HO(CH_2CH_2O)_m[CH(CH_3)CH_2O]_{19.8}(CH_2CH_2O)_nH$ ($m+n=9.77$)	0.48 ml
Add distilled water to make	8000.0 ml

(Solution B)

Silver nitrate	1200.0 g
Add distilled water to make	1600.0 ml

(Solution C)

Ossein gelatin	32.2 g
Potassium bromide	790.0 g
Potassium iodide	70.34 g
Add distilled water to make	1600.0 ml

(Solution D)

Aqueous ammonia	470.0 ml

Solution A was violently stirred at 40°C and Solutions B and C were added to Solution A in a double-jet method for 7 minutes so as to produce nuclei. During the addition thereof, the pBr of the mixture was kept at

1.60. Thereafter, the temperature of the mixture was lowered to be 20°C by taking 30 minutes. Further, Solution D was added thereto by taking one minute and, successively, the mixture thereof was ripened for 5 minutes. While the mixture was being ripened, the KBr concentration and ammonia concentration were 0.03 mols/liter and 0.66 mols/liter, respectively.

After completing the ripening treatment, the pH was adjusted to be 6.0 and a desalting treatment was carried out in an ordinary method. To the resulting emulsion was added an aqueous 10 wt% gelatin solution and the emulsion was then stirred to be dispersed at 60°C for 30 minutes. Thereafter, distilled water was added thereto, so that 5360 g of an emulsion was made up.

When observing the resulting seed emulsion grains through an electron microscope, they were proved to be tabular-shaped grains having two twin planes parallel to each other.

It was also proved that the average grain-size of the seed emulsion grains was 0.217μm and that the grains having two parallel crystal planes amounted to 75% (in number) of the whole grain.

(Preparation of twinned crystal, seed grain emulsion T-2 ripened at a low pAg)

In the process for preparing seed emulsion T-1, 1884 ml of an aqueous 10 wt% gelatin solution was added to a desalted emulsion and was then stirred the emulsion to be dispersed at 60°C for 15 minutes. Then, 130 ml of an aqueous solution containing 21 g of silver nitrate was added thereto and the pAg value of the emulsion was then adjusted to be 1.88. Successively, a ripening treatment was carried out by stirring the emulsion at 60°C for 80 minutes. Thereafter, 193 ml of an aqueous solution containing 14.5 g of potassium bromide was added. The emulsion temperature was lowered to 40°C and distilled water was added, so that 5360 g of an emulsion could be prepared.

When observing the resulting seed emulsion grains through an electron microscope, they were proved to be the tabular-shaped grains having two twin planes parallel to each other.

It was also proved that the average grain-size of the seed emulsion grains was 0.217μm and that the grains having two parallel crystal planes amounted to 75% (in number) of the whole grain.

(Preparation of Emulsion EM-1 of the invention)

Tabular-shaped emulsion EM-1 of the invention was prepared by making use of the following 7 kinds of solutions, (among them, Solution A contained seed emulsion T-2 subjected to a low pAg ripening treatment).

(Solution A)

Ossein gelatin	67.0 g
Distilled water	3176 ml
A 10 wt% methanol solution of $HO(CH_2CH_2O)_m[CH(CH_3)CH_2O]_{19.8}(CH_2CH_2O)_nH$ ($_m^+{}_n$=9.77)	2.50 ml
Seed emulsion (T-2)	98.51 g
Add distilled water to make	3500.0 ml

(Solution B)

An aqueous 0.5N silver nitrate solution	948 ml

(Solution C)

Potassium bromide	52.88 g
Ossein gelatin	35.55 g
Add distilled water to make	948 ml

(Solution D)

An aqueous 3.5N silver nitrate solution	4471 ml

(Solution E)

Potassium bromide	1862.2 g
Ossein gelatin	200 g

(Solution F)

A fine-grain emulsion(*) comprising 3 wt% of gelatin and silver iodide grains (having an average grain-size of 0.05μm)	2465.5 g

(*) The preparation process thereof will be detailed below.

An aqueous solution containing 7.06 mols of silver nitrate and an aqueous solution containing 7.06 mols of potassium iodide were each added in an amount of 2000ml to 5000ml of a 6.0 wt%-gelatin solution containing 0.06 mols of potassium iodide by taking 10 minutes, respectively. The pH and temperature were controlled with nitric acid so as to be 2.0 and 40°C while the fine grains were being produced. After the grains were formed, the pH was adjusted with an aqueous sodium carbonate solution so as to be 6.0. The finished amount by weight was proved to be 12.53 kg.

(Solution G)

An aqueous 1.75N potassium bromide solution

Solution A was added to a reactor vessel. Solutions B through F were added thereto, with stirring, by a double-jet method in accordance with the combination shown in Table 1, and the seed crystals were grown up, so that a core/shell type silver halide grain emulsion was prepared.

Therein, (1) the adding rates of Solutions (B), (C) and (F), (2) the adding rates of Solutions (D), (E) and (F), and (3) the adding rates of Solutions (D) and (E) were optimally controlled to meet the critical growth rate of silver halide grains so that any small grains other than the growing seed crystal grains were neither produced nor polydispersed in an Ostwald's ripening.

Extending over the whole region of growing crystals, the temperature and pAg of each of the solutions were controlled to be 75°C and 8.8 in the reactor vessel, respectively. For controlling the pAg, Solution G was added when necessary.

Table 1 shows the grain-sizes at the points of time corresponding to each of the time of adding the solutions, and the silver iodide contents of the silver halide phases capable of forming each of the grain surfaces.

After growing up the grains, a desalting treatment was carried out according to the method described in JP Application No. 3-41314/1991 and a redispersion treatment was carried out by adding gelatin. The pH and pAg of the emulsion were controlled to be 5.80 and 8.06 at 60°C, respectively. From the electronmicrograph of the resulting emulsion grains, the resulting grains were proved to be the tabular-shaped grains having an average grain-size of 1.23μm, an average aspect ratio of 2.0 and an average grain-size distribution of 12.0%.

Table 1

Solution added	Time of adding a solution (min.)	Grain-size (μm)	AgI content (mol%)
(1) B,C,F	0.00	0.217	6.0
(1) B,C,F	12.50	0.318	8.4
(1) B,C,F	22.83	0.370	10.8
(1) B,C,F	30.98	0.410	13.2
(2) D,E,F	30.99	0.410	13.2
(2) D,E,F	52.82	0.499	20.4
(2) D,E,F	76.69	0.584	30.0
(2) D,E,F	122.33	0.715	30.0
(2) D,E,F	150.56	0.780	30.0
(2) D,E,F	155.12	0.790	27.5
(2) D,E,F	176.38	0.836	15.1
(2) D,E,F	187.90	0.860	7.7
(3) D,E	188.00	0.862	0.0
(3) D,E	210.46	0.959	0.0
(3) D,E	224.92	1.062	0.0
(3) D,E	233.55	1.133	0.0
(3) D,E	243.00	1.230	0.0

(Preparation of emulsion EM-2 of the invention)

Emulsion EM-2 was prepared in the same manner as in the process of preparing emulsion EM-1, except that 10 ml of an aqueous solution containing 2.0 g of potassium hydroxide was added to seed emulsion T-1 at the point of time 65 minutes after starting the addition of a solution for growing the crystals so that the pH of the emulsion was adjusted to be 8.7 in a reaction system. At the point of time when completing the addition of the reactive solution for growing the crystals, the pH of the emulsion was lowered to be 5.8.

From the scanning type electron microscopic photograph of the resulting emulsion grains, the grains were proved to be the tabular-shaped grains having an average grain-size of 1.24μm, an average aspect ratio of 2.1 and a grain-size distribution of 12.5%.

Also, in the process of preparing emulsion EM-1, emulsion EM-3 for comparative use was prepared in the same manner as in the case of emulsion EM-1, except that seed emulsion T-1 was used and the pAg in the course of growing the crystals was controlled to be 11.0.

Further, in the process of preparing emulsion EM-2, emulsion EM-4 for comparison use was prepared in the same manner as in emulsion EM-2, except that potassium hydroxide was not added in the course of growing the crystals.

Still further, Emulsions EM-5 through EM-9 were each prepared by replacing seed emulsions, by changing the conditions for ripening the seed emulsions at a low pAg, by omitting or applying a high-pH ripening treatment in the course of growing the crystals, by altering the positions of adding potassium hydroxide in the course of growing the crystals or by varying the pAg control values in the course of growing the crystals.

For determining the distance between twin planes and the grain thickness, they were observed at a temperature of -120°C, through a transmission type electron microscope Model JEM-2000FX manufactured by Japan Electron Co., Ltd at an acceleration voltage of 200KV.

Table 2 collectively shows the conditions for preparing emulsions EM-1 through EM-9 and the results ob-

tained.

Table 2

Emulsion (Inv. or Comp.)	Seed emulsion low-pAg ripened or not		High-pH ripened or not, while growing crystals			pAg value while growing crystals	Average grain-size (μm)	Average aspect ratio	Grain-size distri-bution width (%)	y/x
	Ripened/ not ripened	pAg	Ripened/ not ripened	pH	KOH adding position					
EM-1 (Inv.)	Ripened	1.88	Not ripened	-	-	8.8	1.23	2.0	12.0	1.15
EM-2 (Inv.)	Not ripened	-	Ripened	8.7	11.0	8.8	1.24	2.1	12.5	1.22
EM-3 (Comp.)	Not ripened	-	Not ripened	-	-	11.0	1.43	3.5	28.5	3.20
EM-4 (Comp.)	Not ripened	-	Not ripened	-	-	8.8	1.25	2.2	13.1	1.30
EM-5 (Comp.)	Ripened	1.88	Not ripened	-	-	11.4	1.46	3.7	31.0	3.10
EM-6 (Comp.)	Not ripened	-	Ripened	8.7	11.0	11.2	1.44	3.6	29.0	3.10
EM-7 (Inv.)	Ripened	2.70	Not ripened	-	-	8.8	1.23	2.1	12.4	1.21
EM-8 (Inv.)	Not ripened	-	Ripened	8.7	32.0	8.8	1.24	2.1	13.0	1.22
EM-9 (Inv.)	Ripened	1.88	Ripened	8.7	11.0	8.8	1.23	2.0	12.4	1.19

In the table, the KOH adding positions represent in terms of (the volume of a grain at the point of time when

adding KOH / the volume of the grain after growing the crystal) × 100; and y/x represents a variation coefficient (y) of a grain thickness / a variation coefficient (x) of a distance between twinned crystal planes.

As is obvious from Table 2, when the pAg of an emulsion was controlled to not lower than 11.0 in the course of growing crystals, the grain-size distribution was widened and the y/x value was increased. This fact indicates that the dispersion of the grain thickness was increased, as well as that the grains-sizes were dispersed. On the other hand, an emulsion which was controlled to a pAg value of 8.8 in the course of growing the grains, the grain-size distribution was narrowed and the y/x value was also decreased. It was very interesting discovery that fluctuations in the grain-size and grain thickness depended upon a pAg value obtained when growing the grains.

Example 2 (Preparation of a silver halide color photographic light-sensitive material sample)

A silver halide color photographic light-sensitive material of the invention was prepared in the following manner. An optimum gold-sulfur sensitization was applied to each of emulsions EM-1 through EM-9. By making use of the resulting emulsions, each of the layers having the following compositions was formed on a tricetyl cellulose support in order from the side of the support.

In every description herein given, every addition into amount of a silver halide photographic light-sensitive material is indicated in terms of grams per sq.meter, unless otherwise expressly stated. Amounts of silver halide and colloidal silver are each indicated by the silver contents converted therefrom. The amount of the sensitizing dyes is indicated in terms of mols per mol of silver halide used therein.

The constitution of silver halide color photographic light-sensitive material sample 101 of the invention (in which emulsion EM-1 of the invention was used) was as follows.

Sample 101

Layer 1 : An antihalation layer

Black colloidal silver	0.16
UV absorbent (UV-1)	0.20
High boiling solvent (OIL-1)	0.16
Gelatin	1.60

Layer 2 : An intermediate layer

Compound (SC-1)	0.14
High boiling solvent (OIL-2)	0.17
Gelatin	0.80

Layer 3 : A low-speed red-sensitive layer

Silver iodobromide emulsion A	0.15
Silver iodobromide emulsion B	0.35

Sensitizing dye (SD-1)	2.0×10^{-4}
Sensitizing dye (SD-2)	1.4×10^{-4}
Sensitizing dye (SD-3)	1.4×10^{-5}
Sensitizing dye (SD-4)	0.7×10^{-4}
Cyan coupler (C-1)	0.53
Colored cyan coupler (CC-1)	0.04
DIR compound (D-1)	0.025
High boiling solvent (OIL-3)	0.48
Gelatin	1.09

Layer 4 : A medium-speed red-sensitive layer

Silver iodobromide emulsion B	0.30
Silver iodobromide emulsion C	0.34
Sensitizing dye (SD-1)	1.7×10^{-4}
Sensitizing dye (SD-2)	0.86×10^{-4}
Sensitizing dye (SD-3)	1.15×10^{-5}
Sensitizing dye (SD-4)	0.86×10^{-4}
Cyan coupler (C-1)	0.33
Colored cyan coupler (CC-1)	0.013
DIR compound (D-1)	0.02
High boiling solvent (OIL-1)	0.16
Gelatin	0.79

Layer 5 : A high-speed red-sensitive layer

Emulsion EM-1	0.95
Sensitizing dye (SD-1)	1.0×10^{-4}
Sensitizing dye (SD-2)	1.0×10^{-4}
Sensitizing dye (SD-3)	1.2×10^{-5}

Cyan coupler (C-2)	0.14
Colored cyan coupler (CC-1)	0.016
High boiling solvent (OIL-1)	0.16
Gelatin	0.79

Layer 6 : An intermediate layer

Compound (SC-1)	0.09
High boiling solvent (OIL-2)	0.11
Gelatin	0.80

Layer 7 : A low-speed green-sensitive layer

Silver iodobromide emulsion A	0.12
Silver iodobromide emulsion B	0.38
Sensitizing dye (SD-4)	4.6×10^{-5}
Sensitizing dye (SD-5)	4.1×10^{-4}
Magenta coupler (M-1)	0.14
Magenta coupler (M-2)	0.14
Colored magenta coupler (CM-1)	0.06
High boiling solvent (OIL-4)	0.34
Gelatin	0.70

Layer 8 : An intermediate layer

Gelatin	0.41

Layer 9 : A medium-speed green-sensitive layer

Silver iodobromide emulsion B	0.30
Silver iodobromide emulsion C	0.34
Sensitizing dye (SD-6)	1.2×10^{-4}
Sensitizing dye (SD-7)	1.2×10^{-4}
Sensitizing dye (SD-8)	1.2×10^{-4}

Magenta coupler (M-1)	0.04
Magenta coupler (M-2)	0.04
Colored magenta coupler (CM-1)	0.017
DIR compound (D-2)	0.025
DIR compound (D-3)	0.002
High boiling solvent (OIL-4)	0.12
Gelatin	0.50

Layer 10: A high-speed green-sensitive layer

Silver iodobromide emulsion D	0.95
Sensitizing dye (SD-6)	7.1×10^{-5}
Sensitizing dye (SD-7)	7.1×10^{-5}
Sensitizing dye (SD-8)	7.1×10^{-5}
Magenta coupler (M-1)	0.09
Colored magenta coupler (CM-1)	0.011
High boiling solvent (OIL-4)	0.11
Gelatin	0.79

Layer 11: A yellow filter layer

Yellow colloidal silver	0.08
Compound (SC-1)	0.15
High boiling solvent (OIL-2)	0.19
Gelatin	1.10

Layer 12: A low-speed blue-sensitive layer

Silver iodobromide emulsion A	0.12
Silver iodobromide emulsion B	0.24
Silver iodobromide emulsion C	0.12
Sensitizing dye (SD-9)	6.3×10^{-5}

Sensitizing dye (SD-10)	1.0×10^{-5}
Yellow coupler (Y-1)	0.50
Yellow coupler (Y-2)	0.50
DIR compound (D-4)	0.04
DIR compound (D-5)	0.02
High boiling solvent (OIL-2)	0.42
Gelatin	1.40

Layer 13: A high-speed blue-sensitive layer

Silver iodobromide emulsion C	0.15
Silver iodobromide emulsion E	0.80
Sensitizing dye (SD-9)	8.1×10^{-5}
Sensitizing dye (SD-11)	3.1×10^{-5}
Yellow coupler (Y-1)	0.12
High boiling solvent (OIL-2)	0.05
Gelatin	0.79

Layer 14: A protective layer-1

A silver iodobromide emulsion (having an average grain-size of 0.08μm and a silver iodide content of 1.0 mol%)	0.40
UV absorbent (UV-1)	0.065
High boiling solvent (OIL-1)	0.07
High boiling solvent (OIL-3)	0.07
Gelatin	0.65

Layer 15: A protective layer-2

Alkali-soluble matting agent (having an average particle-size of 2μm)	0.15
Polymethyl methacrylate (having an average particle-size of 3μm)	0.04
Lubricant (WAX-1)	0.04
Gelatin	0.55

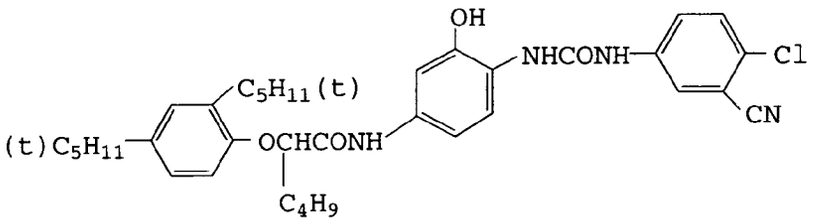
Besides the above-given compositions, there added coating aid Su-1, dispersion aid Su-2, a viscosity controller, layer hardeners H-1 and H-2, stabilizer ST-1, antifoggants AF-1 having an average molecular weight of 10,000 and AF-2 having an average molecular weight of 1,100,000, and preservative DI-1, respectively.

The emulsions used in the above-mentioned sample were as follows. Each of the emulsions was subjected to the optimum gold/sulfur sensitization.

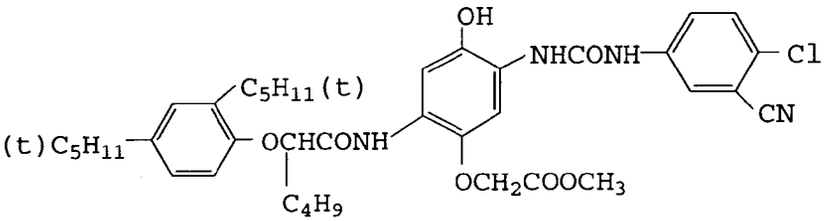
Table 3

Emulsion	Average AgI content (in mol%)	Average grain-diameter (in μm)	Crystal shape	Ratio of Diameter/Thickness	Remarks
Emulsion A	4.0	0.41	Regular crystal	1	
Emulsion B	6.0	0.57	Regular crystal	1	
Emulsion C	6.0	0.75	Regular crystal	1	
Emulsion D	6.0	1.16	Tabular twinned crystal	4	
Emulsion E	6.0	1.30	Tabular twinned crystal	4	

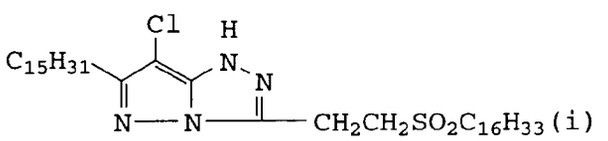
C-1



C-2



M-1



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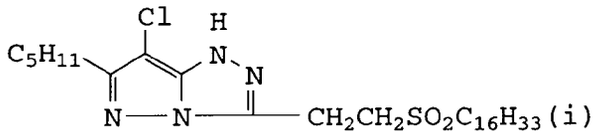
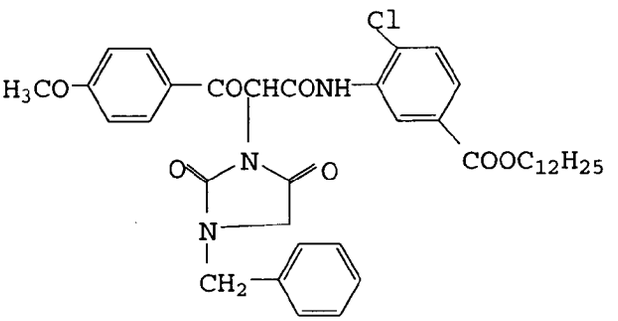


Y-1



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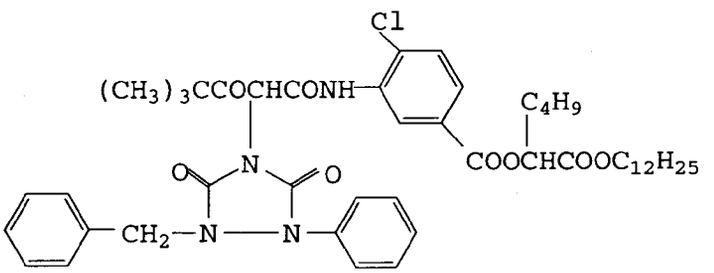
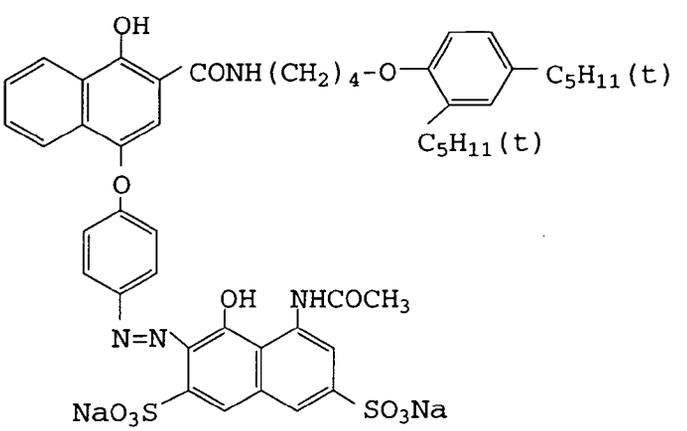


CC-1



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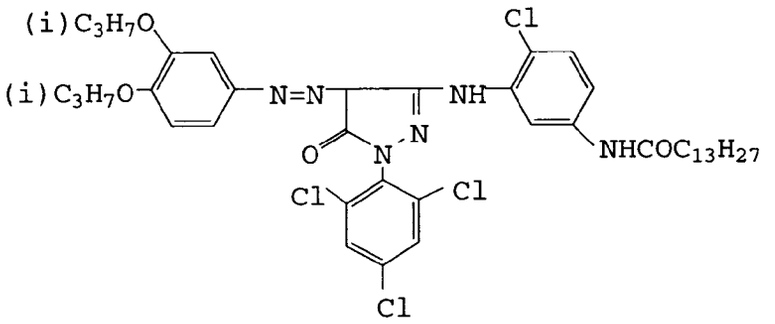

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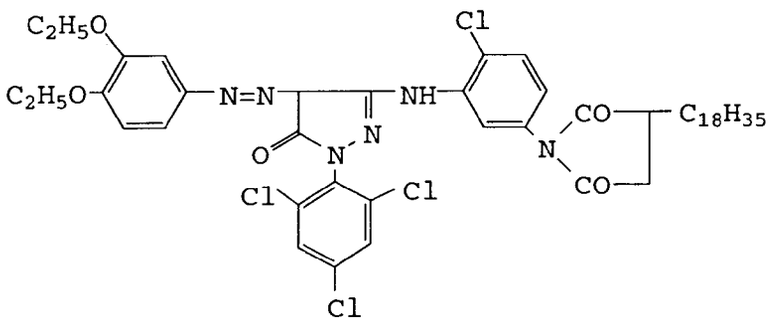
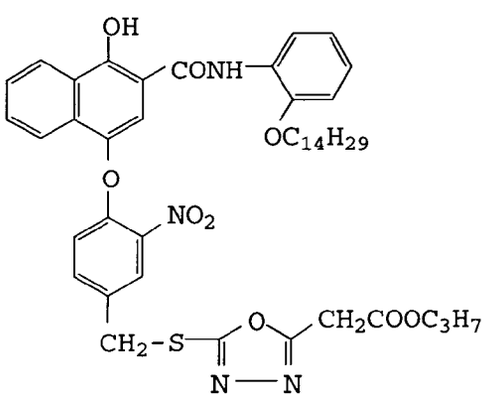


D-1



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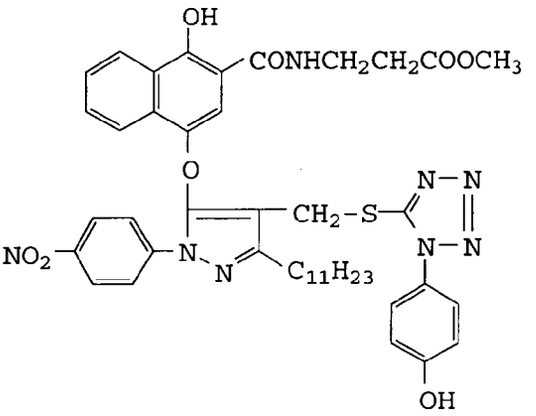

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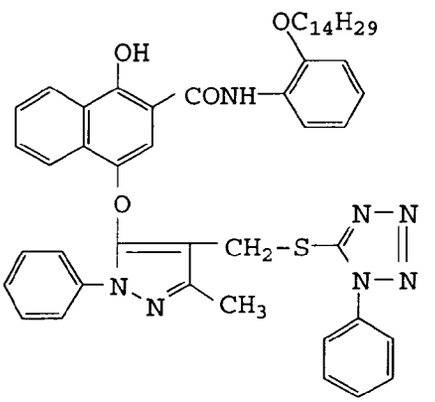

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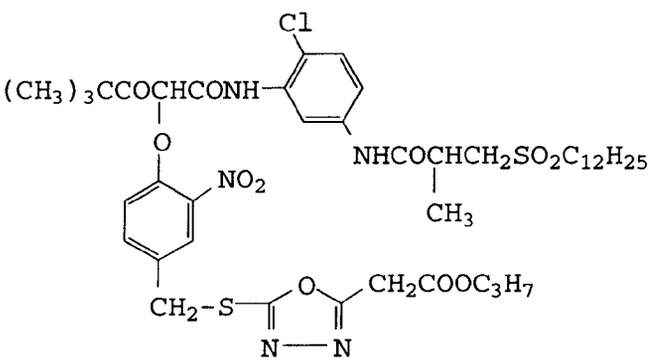

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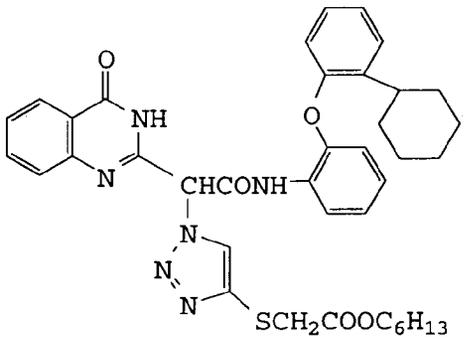

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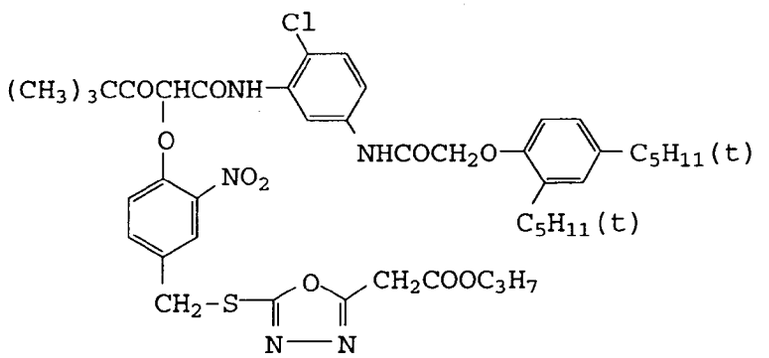

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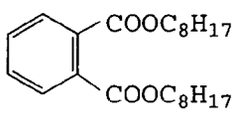

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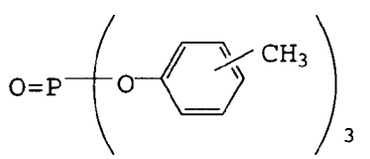

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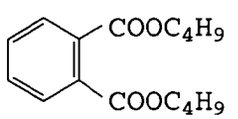

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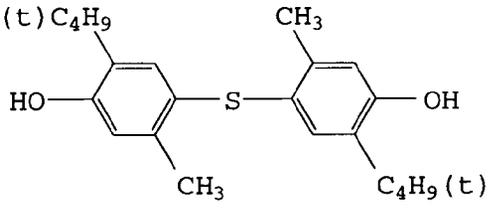

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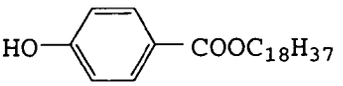
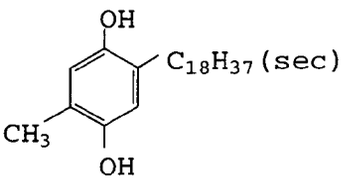
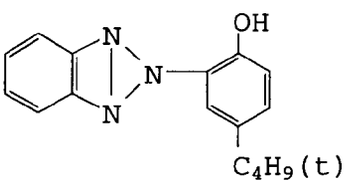


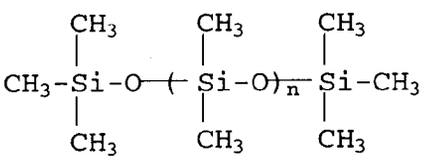
SC-1



UV-1

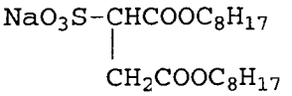


WAX-1

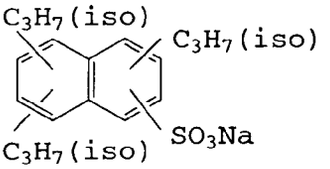


Weight average molecular weight Mw=3,000

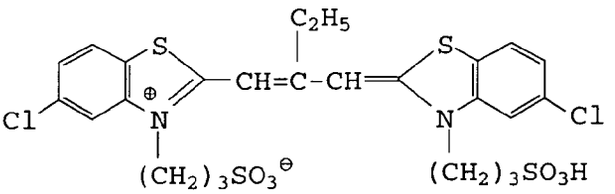
Su-1



Su-2



SD-1



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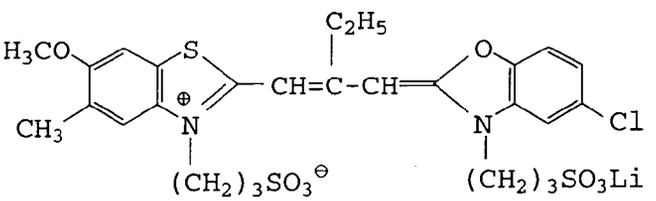
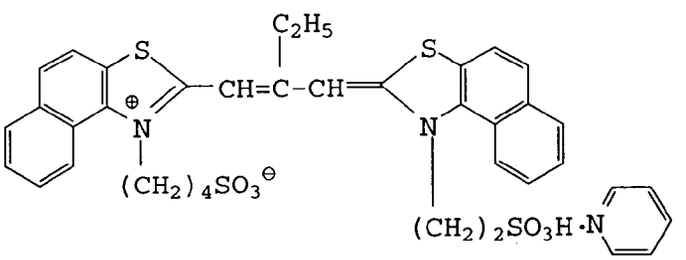
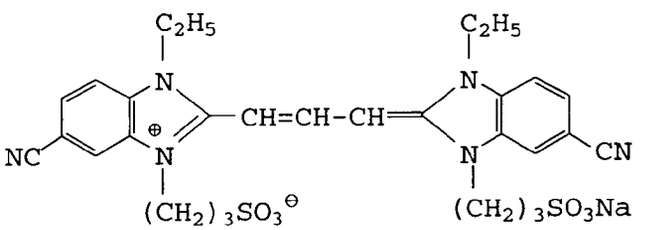


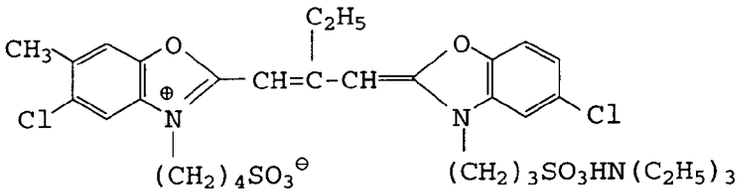
SD-3



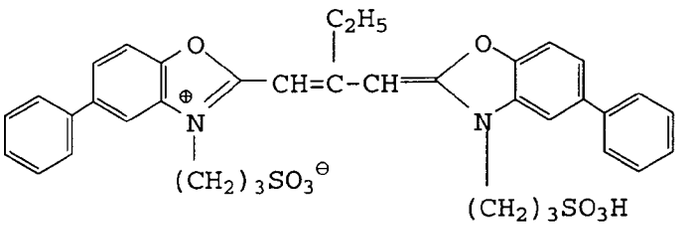
SD-4



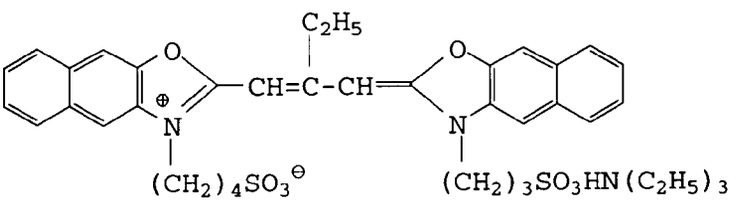
SD-5



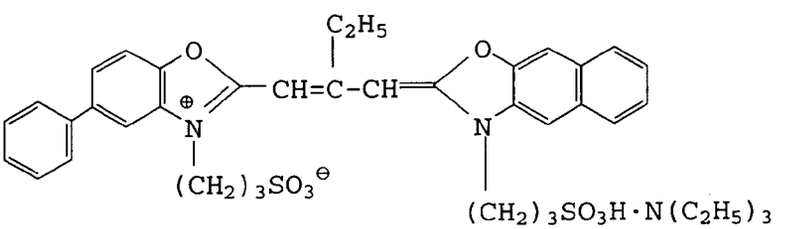
SD-6



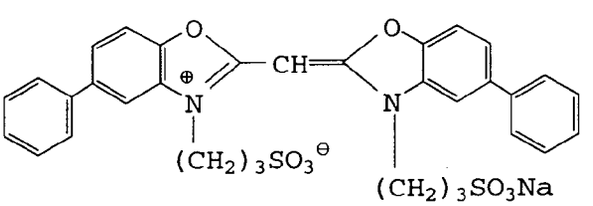
SD-7



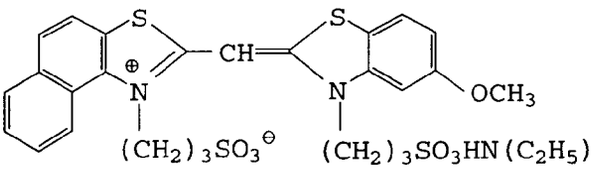
SD-8



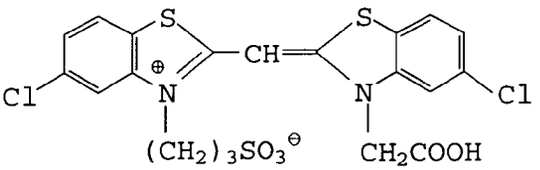
SD-9



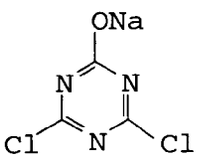
SD-10



SD-11



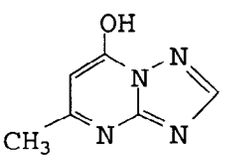
H-1



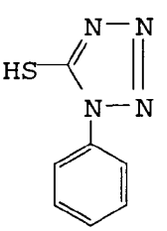
H-2

$(CH_2=CHSO_2CH_2)_2O$

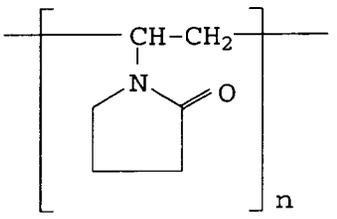
ST-1



AF-1

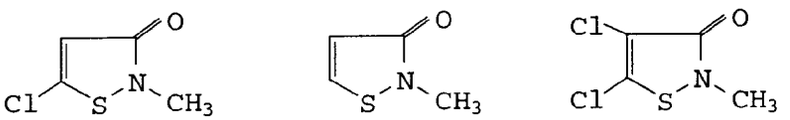


AF-2



n : Polymerization degree

DI-1 (A mixture of the following 3 components)



(Component A) (Component B) (Component C)

Component A:B:C = 50:46:4 (in mol ratio)

Silver halide color photographic light-sensitive material samples 102 through 109 were also prepared in the same manner as described above, except that emulsion EM-1 of sample 101 was replaced by emulsions EN-2 through EM-9 as shown in Table 4.

Table 4

Sample	102	103	104	105	106	107	108	109
Emulsion used	EM-2	EM-3	EM-4	EM-5	EM-6	EM-7	EM-8	EM-9

Each of the resulting samples were exposed to light through a optical wedge in an ordinary manner and were then processed in the following processing steps.

Processing steps

1. Color developing	3min.15sec.	38.0±0.1°C
2. Bleaching	6min.30sec.	38.0±3.0°C
3. Washing	3min.15sec.	24°C to 41°C
4. Fixing	6min.30sec.	38.0±3.0°C
5. Washing	3min.15sec.	24°C to 41°C
6. Stabilizing	3min.15sec.	38.0±3.0°C
7. Drying		≥50°C

The compositions of the processing solutions used in the above-mentioned processing steps were as follows.

<Color developer>	
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline·sulfate	4.75 g
Sodium sulfite anhydride	4.25 g
Hydroxylamine·½sulfate	2.0 g
Potassium carbonate anhydride	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Add water to make	1 liter
Adjust pH to be	pH=10.1

<Bleacher>	
Iron ammonium ethylenediamine tetraacetate	100.0 g
Diammonium ethylenediamine tetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
Add water to make	1 liter
Adjust pH with aqueous ammonia to be	pH=6.0

<Fixer>	
Ammonium thiosulfate	175.0 g
Sodium sulfite anhydride	8.5 g
Sodium metasulfite	2.3 g
Add water to make	1 liter
Adjust pH with acetic acid to be	pH=6.0

<Stabilizer>	
Formalin (in an aqueous 37% solution)	1.5 ml
Konidux (manufactured by Konica Corp.)	7.5 ml
Add water to make	1 liter

Each of the resulting samples was exposed (for 1/200") to red light (R) through a sensitometric wedge, and the resulting relative sensitivity and latent image preservability of the samples were evaluated.

The results thereof will be shown in Table 5 given below.

The relative sensitivity of a fresh sample was obtained in such a manner that the sample was color-developed within one minute after exposure and a relative value of the reciprocal of the exposure amount capable of giving a density of Dmin (the minimum density)+0.15 is obtained as the relative sensitivity of the sample. The sensitivity of the sample is indicated by a value relative to the sensitivity of sample 101 that is set to 100, (in other words, it means that the more is a value, the higher is the sensitivity.) The latent image preservability of a sample was obtained in such a manner that the sample was exposed to light and then allowed to stand at a relative humidity of 80% for 7 days. Thereafter, it was color-developed and the relative sensitivity thereof was then obtained as a value relative to the sensitivity obtained from sample 101 that was set to 100.

Table 5

Sample	Invention or Comparison	Red-sensitive layer	
		Real-time relative sensitivity	Relative sensitivity obtained after preserving a latent image
101	Invention	100	92
102	Invention	101	93
103	Comparison	77	42
104	Comparison	97	61
105	Comparison	75	65
106	Comparison	76	67
107	Invention	99	86
108	Invention	100	88
109	Invention	102	99

As is obvious from the results shown in Table 5, samples 101, 102 and 107 through 109 each relating to the invention, which contained an emulsion of the invention, have a high sensitivity and improved in latent image preservability.

Among the samples, sample 109 is particularly superior, because it used emulsion EM-9 satisfying the best combination of the invention.

As is apparent from Table 5, the grain-size distribution of the invention and the y/x effect thereof are displayed on the sensitivity of fresh.

On the other hand, it can be understood that the effect of the internally reduction-sensitized grains is displayed on the sensitivity obtained after preserving an latent image. As described above, the invention can provide a silver halide photographic light-sensitive material and a silver halide color photographic light-sensitive material each high in sensitivity and excellent in latent image preservability.

Claims

1. A silver halide color photographic light-sensitive material comprising a support having thereon a silver halide emulsion layer comprising silver halide emulsion, wherein said silver halide emulsion contains tabular silver halide grains having an even number of twin planes in the grain and an aspect ratio of grain diameter to thickness of less than 5, said tabular grains accounting for not less than 50% of total projected area of grains contained in the emulsion layer and satisfying the following requirements (a) to (c),
   (a) a variation coefficient of grain-size distribution of not more than 20%,
   (b) $0.7 \leqq y/x \leqq 2.0$, in which x is a variation coefficient of twin plane distances of the grains and y is a variation coefficient of grain thicknesses, and
   (c) said grains being internally reduction-sensitized.

2. The color photographic material of claim 1, wherein a mean twin plane distance of said tabular grains is 0.01 to 0.05 μm.

3. The color photographic material of claim 1, wherein a mean thickness of the tabular grains is 0.05 to 1.5 μm.

4. The color photographic material of claim 1, wherein said tabular grains are comprised of silver iodobromide grains having an average iodide content of 1 to 20 mol%.

5. The color photographic material of claim 4, wherein said grains have a silver iodobromide phase containing 5 mol% or more iodide within the grain.

6. A silver halide photographic emulsion wherein said silver halide emulsion comprises tabular silver halide grains having an even number of twin planes in the grain and an aspect ratio of grain diameter to thickness of less than 5, said tabular grains accounting for not less than 50% of the total projected area of grains contained in the emulsion layer and satisfying the following requirements (a) to (c),

(a) a variation coefficient of grain-size distribution of not more than 20%,

(b) $0.7 \leqq y/x \leqq 2.0$, in which x is a variation coefficient of twin plane distances of the grains and y is a variation coefficient of grain thicknesses, and

(c) said tabular grains being internally reduction-sensitized; and

said tabular grains obtainable by a process comprising the steps of

(i) forming nuclear grains by adding a water-soluble silver salt and water-soluble halide to a mother liquor,

(ii) forming seed grains by ripening the nuclear grains,and

(iii) growing the seed grains to form the tabular grains by adding a water-soluble silver salt and water-soluble halide, or silver halide.

7. The silver halide emulsion of claim 6, wherein, during the nuclear grain formation of step (i), the pBr of the mother liquor is maintained at 2.5 or less.

8. The silver halide emulsion of claim 6, wherein, in step (ii), the ripening is carried out in the presence of a silver halide solvent.

9. The silver halide emulsion of claim 8, wherein, after the seed grains are formed, the grains are further ripened at a pAg of 7.0 or less.

10. The silver halide emulsion of claim 6, wherein, in step (iii), the seed grains are grown at the pAg of 7.0 to 10.5.

11. The silver halide emulsion of claim 6, wherein, in step (iii), a reduction sensitization is carried out, before 90% of the ultimate grain volume of the grain is reached, by adding a reducing agent, a water-soluble silver salt or an alkaline compound.