



(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **93101342.9**

(51) Int. Cl.⁵: **G03C 1/035**, **G03C 1/005**,
G03C 5/29

(22) Date of filing: **29.01.93**

(30) Priority: **01.02.92 JP 46208/92**

(43) Date of publication of application:
15.09.93 Bulletin 93/37

(84) Designated Contracting States:
DE FR GB NL

(71) Applicant: **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome Shinjuku-ku
Tokyo(JP)

(72) Inventor: **Haraga, Hideaki, Konica Corporation**

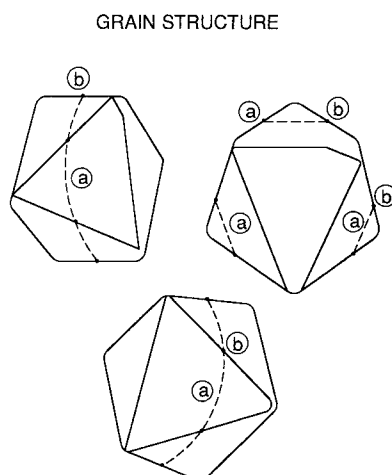
1 Sakura-machi
Hino-shi, Tokyo(JP)
 Inventor: **Tashiro, Kouji, Konica Corporation**
1 Sakura-machi
Hino-shi, Tokyo(JP)
 Inventor: **Nomiya, Makoto, Konica Corporation**
1 Sakura-machi
Hino-shi, Tokyo(JP)

(74) Representative: **Türk, Gille, Hrabal, Leifert**
Brucknerstrasse 20
D-40593 Düsseldorf (DE)

(54) **Silver halide photographic emulsion with high sensitivity and good processing stability and pressure resistance.**

(57) Disclosed is a silver halide photographic light-sensitive emulsion comprising grains having twin planes, wherein at least 60 % of projected area of the whole grains are occupied by said grains having twin planes, and part or all of said grains having twin planes each have a start point of development at a cross point or the vicinity of said cross point, wherein said cross point is formed by a line formed by a twin plane border lying bare to the grain surface, which intersects an ridge line of the grain.
 The silver halide photographic emulsion has a high sensitivity, high color forming performance, promising a good processing stability and good pressure resistance.

FIG. 1



FIELD OF THE INVENTION

The present invention relates to a silver halide photographic emulsion having a high sensitivity and high color forming performance and promising a good processing stability and good pressure resistance. More particularly it relates to a silver halide photographic emulsion that can provide a light-sensitive silver halide photographic material having a good processing stability and processing operability.

BACKGROUND OF THE INVENTION

With spread of light-sensitive silver halide photographic materials, there are increasing demands for photographing miss-free without regard to time and place and for speedy photofinishing service. For satisfying such demands, the improvement in performance of high-sensitivity light-sensitive photographic materials and the spread of what is called mini-labs installed at, e.g., storefronts of photo retailers play a great roll. Nonetheless, in the photographic processing in such mini-labs, problems are still unsettled in respect of deterioration of quality of finished products, caused by variations in composition of processing solutions and fogging by pressure (or pressure mark) caused by adhesion of foreign matters or improper handling of light-sensitive materials.

With regard to the achievement of higher sensitivity and the improvement of developability, techniques to intentionally control chemically sensitizing portions or start points of development on the surfaces of silver halide grains have been disclosed, as described in Japanese Patent Publications Open to Public Inspection [hereinafter referred to as Japanese Patent O.P.I. Publication(s)] No. 62631/1989, No. 62632/1989, No. 40938/1989, No. 74540/1989, No. 305343/1988, No. 77047/1989, No. 26838/1989 and No. 231739/1991.

In these conventional techniques, however, no satisfactory results have been obtained with regard to the improvement in the relationship between sensitivity and developability, and it has been impossible to achieve the processing adaptability such that a constant quality can be obtained even when the composition or concentration of a developing solution undergo changes to some extent.

As for the silver halide grains contained in light-sensitive materials, they are commonly responsive to pressure, and become sharply more responsive to pressure as they are made to have a higher sensitivity. In other words, they cause phenomena of fogging by pressure and desensitization by pressure to fatally affect photographic images, when light-sensitive material films are folded or have scratches on their surfaces. In particular, improper handling during the processing in mini-labs, or photographic processing carried out therein in the state any dirt or dust in the surroundings has adhered, brings about a serious problem of fogging by pressure.

As means for coping with this problem, Japanese Patent O.P.I. Publications No. 99433/1984, No. 301937/1988, No. 149641/1988, No. 106746/1988, No. 151618/1988, No. 220238/1988 and No. 231739/1991 disclose means for improving pressure resistance. Techniques disclosed therein, however, have achieved no enough improvements, and are still unsatisfactory.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a silver halide photographic emulsion having a high sensitivity and high color forming performance and promising a good processing stability and good pressure resistance, in particular, a silver halide photographic emulsion that can provide a light-sensitive silver halide photographic material having a good processing stability and processing operability.

The above object of the present invention can be achieved by a silver halide photographic emulsion comprising grains having a twin plane, wherein part or all of said grains each have a start point of development at a cross point at which a line formed by a twin-plane border lying bare to the grain surface intersects an edge of the grain, or the vicinity of said cross point.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 illustrates cross points (black spots (b)) at which lines (dotted lines (a)) formed by twin-plane borders lying bare to the grain surfaces intersect edges of each grain, in octahedral twinned crystals of grains of Em-3 in Example 1.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described below in detail.

The silver halide photographic emulsion according to the present invention is mainly comprised of
 5 grains having a twin plane (hereinafter "twinned grains"). What is meant by "mainly comprised of twinned grains" is that at least 60%, preferably not less than 70%, and more preferably not less than 80%, of projected areas of the whole grains is held by twinned crystals when subjected to chemical ripening.

The twin plane may be either {111} twin plane or {100} twin plane, or may be formed of the both. It may preferably be {111} twin plane. In instances in which a grain has two or more twin planes, these twin
 10 planes should preferably be parallel to each other. Twinned grains having two parallel {111} twin planes (hereinafter "parallelly double-twinned grains") are particularly preferred.

In particular, it is more preferred for the parallelly double-twinned grains to be in a percentage of not less than 50% based on the whole twinned grains, and most preferred for them to be in a percentage of not less than 80% based on the same.

15 The silver halide grains can be of various shapes so long as they have twin planes. In the case of the parallelly double-twinned grains, they should preferably be tabular grains having an aspect ratio of less than 5.0. Here, the aspect ratio is expressed as a diameter calculated as a circle corresponding to a projected area, taking the thickness of a tabular grain as a denominator. The twinned grains may preferably have an aspect ratio of not more than 3.5, and most preferably from 1.0 to 2.5. Here, as apparent shapes, a
 20 parallelly double-twinned grain having an aspect ratio of about 1.0 is observed as an octahedron, or an octahedron whose tops are cut away or rounded to give a slightly deformed shape.

The diameter of a tabular silver halide grain is expressed as a diameter of a circle having the same projected area as that of the tabular grain when tabular silver halide grains are aligned on a flat surface in the manner that the facing two main planes of each grain is parallel to this flat surface. This diameter may
 25 preferably be from 0.1 to 5.0 μm , more preferably from 0.2 to 4.0 μm , and particularly preferably from 0.3 to 3.0 μm .

The silver halide emulsion according to the present invention may preferably be monodisperse in its grain size distribution.

When such a monodisperse emulsion is used in the present invention, the emulsion may preferably
 30 have a coefficient of variation (ν) of less than 20%, more preferably less than 18%, and most preferably less than 15%. The coefficient of variation is defined as follows:

$$35 \quad \nu = \frac{\text{Diameter standard deviation}}{\text{Average diameter}} \times 100 = \text{coefficient of variation (\%)}$$

The diameter can be determined by photographing the silver halide emulsion containing the tabular
 40 silver halide grains of the present invention, by the use of an electron microscope at a magnification of 10,000 to 50,000, and actually measuring the projected areas of the grains on a print thus obtained. (The measurement is made on at least 1,000 grains counted at random.)

The silver halide emulsion according to the present invention may have any composition, and may preferably be comprised of silver iodobromide having a silver iodide content of from 4 to 20 mol%, and
 45 particularly preferably from 5 to 15 mol%.

In the case when such a silver iodobromide emulsion is used, the emulsion may contain silver chloride so long as the effect of the present invention is not lost.

When a core/shell silver halide emulsion is used in the present invention, the silver halide emulsion has inside its each grain a phase with a higher silver iodide content.

50 The phase with a higher silver iodide content may preferably have a silver iodide content of from 15 to 45 mol%, more preferably from 20 to 42 mol%, and particularly preferably from 25 to 40 mol%.

The silver halide grains of the present invention, having inside the grain the phase with a higher silver iodide content are grains in which the phase with a higher silver iodide content is covered with a phase with a lower silver iodide content, having a lower silver iodide content than the former.

55 The phase with a silver iodide content lower than the phase with a higher silver iodide content, the former of which forms an outermost phase, may preferably have an average silver iodide content of not more than 6 mol%, and particularly preferably from 0 to 4 mol%. Other silver iodide-containing phase (an intermediate phase) may also be present between the outermost phase and the phase with a higher silver

iodide content.

The intermediate phase may have a silver iodide content of from 10 to 22 mol%, and particularly preferably from 12 to 20 mol%.

In silver iodide content between the outermost phase and intermediate phase and between the intermediate phase and the inside phase with a higher silver iodide content, there may preferably be a difference of not less than 6 mol% each, and particularly preferably a difference of not less than 10 mol% each.

In the above embodiment, other silver halide phases may be further present at the center of the inside phase with a higher silver iodide content, between the inside phase with a higher silver iodide content and intermediate phase and between the intermediate phase and outermost phase, respectively.

The outermost phase should preferably have a volume of from 4 to 70 mol%, and more preferably from 10 to 50 mol%, based on that of the whole grain. The phase with a higher silver iodide content should have a volume of from 10 to 80%, preferably from 20 to 50%, and more preferably from 20 to 45%, based on that of the whole grain. The intermediate phase should preferably have a volume of from 5 to 60%, and more preferably from 20 to 55%.

These phases may each be a single phase with uniform composition, or may be a group of phases having composition stepwise changed, comprised of a plurality of phases with uniform composition. Alternatively, any of the phases may be a continuous phase having composition continuously changed, or may be a combination of these.

Another embodiment of the silver halide emulsion according to the present invention can be an embodiment in which the silver iodide localized in a grain does not form a substantially uniform phase and the silver iodide content continuously changes from the core of a grain toward the shell thereof. In this instance, it is preferable for the content of the silver iodide to monotonously decrease from a point at which the silver iodide content is maximum toward the shell of the grain.

The silver iodide content at the point where the silver iodide content is maximum may preferably be from 15 to 45 mol%, and more preferably from 25 to 40 mol%.

The silver iodide content in the grain surface phase may preferably be not more than 6 mol%, and particularly preferably from 0 to 4 mol%. Such silver iodobromide should be used.

The silver halide emulsion of the present invention may preferably satisfy at least one condition of the following (1) to (4).

(1) In comparison between an average silver iodide content (J_1) determined by fluorescent X-ray analysis and a grain surface silver iodide content (J_2) determined by X-ray photoelectric spectroscopy, the emulsion satisfies the relationship of $J_1 > J_2$.

Grain diameter herein referred to is the diameter of a circumcircle of a side on which a projected area of a grain is maximum.

The X-ray photoelectric spectroscopy will be described below.

Before measurement by the X-ray photoelectric spectroscopy, the emulsion is pretreated as follows: First, a pronase solution is added to the emulsion, followed by stirring at 40 °C for 1 hour to effect decomposition of gelatin. Next, centrifugal separation is carried out to settle emulsion particles. After the supernatant is removed, a pronase solution is added, and then gelatin is again decomposed under the above conditions. The sample thus obtained is again subjected to centrifugal separation. After the supernatant is removed, distilled water is added and the emulsion particles are again dispersed in the distilled water, followed by centrifugal separation and then removal of the supernatant. This washing is repeated three times, and thereafter the emulsion particles are again dispersed in ethanol. The resulting dispersion is thinly coated on a mirror-polished silicon wafer to give a sample to be measured.

The measurement by X-ray photoelectric spectroscopy is carried out using, for example, ESCA/SAM 560 Type, manufactured by PHI Co., as a measuring apparatus and using Mg-K α rays as exciting X-rays under conditions of an X-ray source voltage of 15 kV, an X-ray source current of 40 mA and a pass energy of 50 eV.

In order to determine the surface halide composition, Ag3d, Br3d and I3d3/2 electrons are detected. Compositional ratio is calculated by the coefficient of relative sensitivity method, using integral strength at each peak. As Ag3d, Br3d and I3d3/2 coefficients of relative sensitivity, 5.10, 0.84 and 4.592 are respectively used, and thus the compositional ratio is given as a unit of atom percent.

(2) In comparison between the average silver iodide content (J_1) determined by the fluorescent X-ray analysis and an average value (J_3) of the measurements of silver iodide content measured by X-ray microanalysis on each silver halide crystal at its position distant by 80% or more from the center with respect to the direction of grain diameter of a silver halide grain, the emulsion satisfies the relationship of $J_1 > J_3$.

The X-ray microanalysis will be described. Silver halide grains are scattered over a grid for electron microscope observation made using an electron microscope equipped with an energy-dispersive X-ray analyzer. The microscopic observation is made by liquid nitrogen cooling and magnification is set so that one grain comes in sight of CRT, and strengths of $\text{AgL}\alpha$ - and $\text{IL}\alpha$ -rays are integrated for a given time.

The silver iodide content can be calculated using a strength ratio of $\text{IL}\alpha$ to $\text{AgL}\alpha$ and a calibration curve prepared in advance.

(3) The emulsion is characterized in that a signal is continuously present over 1.5 degrees or more of the diffraction angle, at maximum peak height $\times 0.13$ of a signal obtained by diffraction of (420) X-rays from the output of a ray source $\text{CuK}\alpha$ -rays, and preferably a signal is continuously present over 1.5 degrees or more of the diffraction angle, at maximum peak height $\times 0.18$ of the signal. More preferably the diffraction angle over which the signal is present is 1.8 degrees or more, and particularly preferably 2.0 degrees or more. The presence of the signal indicates the presence of a signal that shows a signal strength not lower than the height at the maximum peak height $\times 0.13$ or 0.15.

In a more preferred embodiment of the silver halide emulsion according to the present invention, the above (420) X-ray diffracted signal has two or three peaks. Particularly preferably it has three peaks.

X-ray diffraction is known as a method by which the crystal structure of silver halides is examined.

X-rays with various characteristics can be used as an X-ray source. In particular, the $\text{CuK}\alpha$ -rays generated using Cu as a target are most widely used.

Silver iodobromide has a rock salt structure, and the (420) diffracted beam of $\text{CuK}\alpha$ -rays is observed at 2θ 71 to 74 degrees. Since its signal has a relatively large strength and is at a high angle, the dissolution is so good that its crystal structure can be examined most suitably.

In the measurement of X-ray diffraction of photographic emulsions, it is necessary to remove gelatin, mix a standard sample such as silicon and make the measurement by the powder process.

The measurement may be made by making reference to, e.g., KISO BUNSEKI KAGAKU KOZA 24 (Basic Analytical Chemistry Course 24), "X-ray Analysis" (Kyoritsu Shuppan).

(4) In measurement of average silver iodide content of individual silver halide grains by the X-ray microanalysis described above, the relative standard deviation of measurements is not more than 20%, preferably not more than 15%, and particularly preferably not more than 12%.

Herein the relative standard deviation is obtained in the following way: The standard deviation of silver iodide content in the measurement of silver iodide content in, for example, at least 100 emulsion grains is divided by the average silver iodide content determined in that measurement, and the resulting value is multiplied by 100.

The silver halide grains used in the light-sensitive material of the present invention may be grown by any of the acid method, the neutral method and the ammonia method. It is possible to use known methods as disclosed in Japanese Patent O.P.I. Publications No. 6643/1986, No., 14630/1986, No. 112142/1986, No. 157024/1987, No. 18556/1987, No. 92942/1988, No. 151618/1988, No.1613451/1988, No. 220238/1988, No. 311244/1988 and so forth.

When the silver halide grains used in the present invention are formed, iodide can be fed using a method in which an aqueous solution of its soluble salt is added, or by adding it in the form of fine silver halide grains as exemplified by fine silver iodide or silver iodobromide grains followed by Ostwald ripening to make them grow. The method in which it is fed in the form of fine silver halide grains is preferred.

The growth of the silver halide grains of the present invention may be made in the presence of a known silver halide solvent such as ammonia, thioether or thiourea. A crystal form control agent may also be used.

In the course of the formation and/or growth of grains, metal ions may be added to the silver halide grains by the use of at least one selected from a cadmium salt, a zinc salt, a lead salt, a thallium salt (including complex salts thereof), an iridium salt, a rhodium salt and an iron salt so that any of these metal elements can be incorporated in grain insides and/or grain surfaces. The silver halide grains may also be placed in an appropriate reducing atmosphere so that reducingly sensitizing nuclei can be imparted to the grain insides and/or grain surfaces.

From the silver halide emulsion described above, excess soluble salts may be removed after the growth of the silver halide grains has been completed, or they may remain unremoved. In the case when the salts are removed, they can be removed by the method described in Research Disclosure No. 17643, paragraph II.

In the present invention, the portion at which development is started on a grain (in the present specification "start point of development" or "development start point") must be specified.

The "start point of development" or "development start point" is a point recognized as a point at which development is started, when developing and stopping are carried out and observation is made thereon. Stated specifically, it can be specified as follows:

To specify development start points on grains, light-sensitive materials comprising a support coated thereon with a photographic emulsion to be noted are processed in the following way.

A part of the light-sensitive materials is subjected to wedge exposure, followed by conventional photographic processing to obtain the characteristic curve. Then the remaining light-sensitive materials are exposed in the amount of exposure that corresponds to $(\text{maximum density} - \text{minimum density}) \times 3/4$ on the characteristic curve to the amount of exposure that is 50 times that amount, and then developed using developing solutions having substantially the same composition. After the developing is started, the light-sensitive materials are immersed in a 3% acetic acid solution, and the developing is stopped.

Conditions for the photographic processing to specify the start points of development, as exemplified by temperature, time, and concentration of processing solutions, may be appropriately selected so as to enable easy observation of the start points of development.

The present invention is characterized in that part or all of the twinned grains described above each have a start point of development at a cross point at which a line formed by a twin-plane border lying bare to the grain surface intersects an edge of the grain, or the vicinity of said cross point (the cross point or the vicinity thereof is abridged to "cross area").

Herein at least 70% of the total sum of development start points on a grain are present in its cross areas when the development start points of twinned grains are observed by the above exposure and developing method. Preferably, 80% or more of all the development start points should be present in the cross areas.

The "line formed by a twin-plane border lying bare to the grain surface" can be readily recognized from its grain form in the case when the twin-plane border forms a clear ridge line on the grain surface in the case when, for example, the grain has only a single twin plane. In the case of the parallelly double-twinned grains whose twin-plane borders form substantially no ridge lines on the grain surfaces, the stated line can be readily recognized when a scanning electron microscope having a high resolving power is used at a low accelerating voltage to observe the grains.

What is meant by the "cross point at which a line formed by a twin-plane border lying bare to the grain surface intersects an edge of the grain, or the vicinity of said cross point" is a point at which the line formed by a twin-plane border lying bare to the surface of a grain crosses an edge thereof not parallel to that line, or the vicinity of that point. What is meant by "the vicinity of that point" is the area of a circle around the aforesaid cross point (the center of the cross area), having a radius corresponding to about $1/3$, and preferably $1/4$, of grain thickness. A greater effect can be brought about when the area has a radius corresponding to $1/5$ of grain thickness.

In the case when the line formed by a twin-plane border lying bare to the grain surface forms a clear ridge line or in the case when a plurality of ridge lines not parallel thereto cross at the same time, the center of the cross area forms a top. In such cases, resistance to the fogging by pressure as aimed in the present invention may become slightly poor compared with the case when the center of the cross area does not form a top, but is clearly superior to the case when the start point of development is present at a top including no twin-plane border.

The "edge" and "top" of the grain are meant by portions crystallographically judged to be substantially an edge and a top.

When the position of the start point of development is specified in the present invention, it is preferable that a scanning electron microscope having a high resolving power is used at a low accelerating voltage like the case when the line formed by a twin-plane border lying bare to the grain surface is observed. If necessary, the observation may be made in the state the sample is cooled, whereby much better results of observation can be obtained. Transmission electron microscopes can only obtain two-dimensional flat information in respect of the development start points of the tabular grains, and it is difficult for them to obtain three-dimensional information. It is also difficult for them to specify the line formed by a twin-plane border lying bare to the grain surface. Thus they can be of no use.

Japanese Patent O.P.I. Publications No. 305343/1988 and No. 77047/1989 discloses techniques in which development start points of tabular grains are specified at edges and tops and the vicinities thereof. In these techniques, however, substantially two-dimensional information only is obtained in respect of the development start points of tabular grains. In other words, they do not specifically state whether or not the start point of development are present at the cross point at which the line formed by a twin-plane border lying bare to the grain surface intersects an edge of the grain, or the vicinity of the cross point. In this regard, the present invention is a technique in which the position of the start point of development is more precisely specified, and therefore not only a greater sensitizing effect and an improvement in photographic processing stability have been achieved but also an improvement in resistance to fogging by pressure has been achieved.

The silver halide emulsion of the present invention may be spectrally sensitized using a spectral sensitizer. It may also be chemically sensitized.

The silver halide emulsion of the present invention may preferably be chemically sensitized in the presence of a spectral sensitizer. More preferably it should be chemically sensitized in the presence of two or more kinds of spectral sensitizers.

When chemically sensitized, a silver halide solvent may preferably be present at the time when the chemical sensitization is started.

The silver halide emulsion of the present invention can be chemically sensitized by any known methods such as sulfur sensitization, selenium sensitization, reduction sensitization and gold sensitization, any of which may be used alone or in combination.

The gold sensitization is a typical method of noble metal sensitization, where a gold compound, chiefly a gold complex salt, is used. Preferable gold sensitizers are typified by chlorauric acid and salts thereof. It is also useful to use a thiocyanate in combination to increase gold sensitization. Noble metals other than gold, as exemplified by complex salts of platinum, palladium, iridium or the like may also be used alone or in combination with gold sensitizers. Examples thereof are disclosed in U.S. Patent No. 2,448,060, British Patent No. 618,061 and so forth.

As sulfur sensitizers, various sulfur sensitizers can be used besides a sulfur compound contained in gelatin, which are exemplified by thiosulfates, thioureas, thiazoles and rhodanines. Specific examples thereof are those disclosed in U.S. Patents No. 1,574,944, No. 2,278,947, No. 2,410,689, No. 2,728,668, No. 3,501,313 and No. 3,656,955.

Organic sulfur sensitizers, in particular, thiourea type sulfur sensitizers are preferable as sensitizers used when the silver halide emulsion of the present invention is chemically sensitized. Examples of preferable compounds of the thiourea type sulfur sensitizers are exemplary compounds disclosed in Japanese Patent O.P.I. Publications No. 45016/1980, No. 196645/1987 and No. 114839/1989.

As reduction sensitizers, stannous salts, amines, formamidinesulfinic acids, silane compounds and so forth can be used.

Use of a sulfur sensitizer and a gold sensitizer in combination is preferable for making the present invention effective.

The sulfur sensitizer may be used preferably in an amount of from 1×10^{-7} mol to 1×10^{-4} mol, and more preferably from 1×10^{-6} mol to 5×10^{-5} mol, per mol of silver halide, in terms of active sulfur.

The gold sensitizer may be used preferably in an amount of from 1×10^{-7} mol to 1×10^{-4} mol, and more preferably from 5×10^{-7} mol to 5×10^{-5} mol, per mol of silver halide.

In the case when the sulfur sensitization and gold sensitization are used in combination, they may preferably be used in a ratio of from 3:1 to 1:1.

In the case when the sulfur sensitization and gold sensitization are used in combination, the sulfur sensitizer and gold sensitizer may be added in the form of a mixture, or may be separately added. It is preferred for them to be separately added. In the case when they are separately added, they may be added at the same time or one of them may be added first. The present invention can be more effective when the sulfur sensitizer is added first.

In the case when the sulfur sensitizer is added first, it is common to use a method in which the sulfur sensitizer is added, then the gold sensitizer is added and thereafter the reaction of the sulfur sensitizer is further continued. The present invention can be made more effective by a method in which, after the reaction has been allowed to proceed to a certain extent using only the sulfur sensitizer, the emulsion temperature is dropped to about 40°C until the reactivity of the sulfur sensitizer is lowered, whereupon the gold sensitizer is slowly reacted.

When the emulsion of the present invention is chemically sensitized, what is called the silver halide solvent such as a thiocyanate, a thioether compound, a thiazolidinethione or a four-substituted thiourea may be made present during chemical sensitization. In particular, a thiocyanate, a four-substituted thiourea and a thioether compound are preferred solvents. Any of these silver halide solvents may be made present at any time during the chemical sensitization. It is particularly effective for it to be made present before the chemical sensitization is started.

To the silver halide emulsion of the present invention, a spectral sensitizer should be added so that spectral sensitivity to light in the desired wavelength region can be imparted to the emulsion.

As the spectral sensitizer, it is possible to use various dyes including polymethine dyes including cyanine dyes, merocyanine dyes, holopolar cyanine dyes, complex cyanine dyes, complex merocyanine dyes, oxonol dyes, hemioxonol dyes, styryl dyes, merostyryl dyes, streptocyanine dyes and pyrylium dyes. Cyanine dyes are particularly preferred.

Cyanine dyes preferably used are the cyanine dyes represented by Formula I, described in Japanese Patent O.P.I. Publication No. 231739/1991, from page 313, right upper column to page 318, left lower column, which are denoted by S-1 to S-71.

Spectral sensitization using any of these spectral sensitizers may be carried out by conventionally well known methods. More specifically, it is carried out by a method in which the spectral sensitizer is dissolved in a suitable solvent such as methanol, ethanol, propanol, fluorinated alcohol, 1-methoxyethanol, ethyl acetate, water or an aqueous acid or alkali solution having a suitable pH value to form a solution with a suitable concentration, and the solution is added to the silver halide emulsion or an aqueous hydrophobic colloid solution.

The aforesaid solution is added at any step in the course of the preparation of the silver halide emulsion. For example, it may be added at any step before the formation of the silver halide grains, during the formation thereof, after the formation thereof and during physical ripening, before chemical ripening, during chemical ripening, after the chemical ripening and before the preparation of a coating solution, or at the preparation of the coating solution, without regard to the order in which a stabilizer and an antifoggant are added. It may preferably be added when grains are formed or before chemical sensitization reaction is initiated at the time of chemical ripening, to carry out the chemical sensitization in the presence of a spectral sensitizer, and more preferably in the presence of two or more kinds of spectral sensitizers. The present invention can thereby be made more effective.

These dyes may each be used alone. Alternatively, two or more kinds of dyes may be used in combination. The latter is particularly effective.

The amount in which these spectral sensitizers are added may vary over a wide range as occasion calls. In usual instances, they may be used in an amount ranging from 1×10^{-6} mol to 1×10^{-2} mol, and more preferably from 5×10^{-6} mol to 1×10^{-3} mol, per mol of silver halide. This can make the present invention more effective.

In terms of coverage on the grain surface, the spectral sensitizer may be added by from 40% to 80%, preferably from 50% to 80%, and more preferably from 55% to 75%, based on the amount of saturated monomolecular layer adsorption.

When the silver halide emulsion of the present invention is spectrally sensitized, the spectral sensitizers to be added may preferably be used in such a combination that gives supersensitization. As the combination that gives supersensitization, two or more kinds may be selected from the dyes described above, to form the desired combination. Compounds other than the above may also be used as supersensitizers. For example, it is possible to use a dye having no spectrally sensitizing action in itself, or a substance capable of absorbing substantially no visible light and showing supersensitization. Such a substance may include, for example, aromatic organic acid formaldehyde condensates as exemplified by those disclosed in U.S. Patent No. 3,437,517, cadmium salts, azaindene compounds, and aminostilbene compounds substituted with a nitrogen-containing heterocyclic group as exemplified by those disclosed in U.S. Patents No. 2,933,390 and No. 3,635,721. The combinations disclosed in U.S. Patents No. 3,615,613, No. 3,615,641, No. 3,617,295 and No. 3,635,721 are particularly useful.

The silver halide emulsion of the present invention may preferably be chemically sensitized in the presence of the nitrogen-containing heterocyclic compound disclosed in Japanese Patent O.P.I. Publication No. 126526/1983. In particular, the emulsion may be chemically sensitized in the presence of both the two or more kinds of spectral sensitizers and the above nitrogen-containing heterocyclic compound, whereby the present invention can be made more effective. The amount of the nitrogen-containing heterocyclic compound used together with the two or more kinds of spectral sensitizers may vary over a wide range as occasion calls. In usual instances, they may be used in an amount ranging from 5×10^{-7} mol to 1×10^{-2} mol, and more preferably from 1×10^{-6} mol to 1×10^{-3} mol, per mol of silver halide.

To the silver halide emulsion of the present invention, the fine-grain silver halide (fine silver halide grains) disclosed in Japanese Patent O.P.I. Publication No. 238444/1991 may preferably be added in the course of from the step of chemical ripening to the step of coating. In particular, it is very effective to use fine-grain silver iodide (fine silver halide grains)

The fine-grain silver halide may preferably be added in an amount of not more than $1/100$ d mol per mol of twinned grains where an average grain diameter of the twinned grains is represented by d (μm), more preferably in an amount ranging from $1/20,000$ d to $1/300$ d mol per mol of mother grains, and most preferably from $1/5,000$ d to $1/500$ d mol per mol of mother grains.

The fine-grain silver halide in the present invention may be added at any steps of from the step of chemical ripening to the step right before coating. It may preferably be added at the step of chemical ripening. The fine-grain silver halide may particularly preferably be added before the addition of a sulfur sensitizer or within 30 minutes after the addition of a sulfur sensitizer.

To the silver halide emulsion of the present invention, having been chemically sensitized, an antifoggant and a stabilizer may be added for the purposes of stabilizing emulsion performance and preventing fog.

The additives used in such steps are disclosed in Research Disclosures No. 17643, No. 18716 and No. 308119 (hereinafter "RD17643", "RD18716" and "RD308119", respectively).

Related items and paragraphs thereof are shown in the following:

Items	Page of RD308119, RD17643, RD18716		
Antifoggant	998 Par. VI	24-25	649
Stabilizer	998 Par. VI		

Known photographic additives usable in the present invention are also disclosed in the above Research Disclosures. Related items and paragraphs thereof are shown in the following table.

Table 1

Items	Page of RD308119, RD17643, RD18716		
Color contamination preventive agent	1002 Par. VII-I	25	650
Color image stabilizer	1002 Par. VII-J	25	
Brightening agent	998 V	24	
Ultraviolet absorbent	1003 Par. VIIIC XIIIC	25-26	
Light absorbing agent	1003 Par. VIII	25-26	
Light scattering agent	1003 Par. VIII		
Filter dye	1003 Par. VIII	25-26	
Binder	1003 Par. IX	26	651
Antistatic agent	1006 Par. XIII	27	650
Hardening agent	1004 Par. X	26	651
Plasticizer	1006 Par. XII	27	650
Lubricant	1006 Par. XII	27	650
Surfactant, coating aid	1005 Par. XI	26-27	650
Matting agent	1007 Par. XVI		
Developing agent	1011 Par. XX-B		
(contained in light-sensitive materials)			

When the silver halide emulsion of the present invention is used in light-sensitive color photographic materials various couplers can be used. Examples thereof are described in the above Research Disclosures.

Related items and paragraphs thereof are shown in the following:

Items	Page of RD308119	RD17643
Yellow coupler	1001 Par. VII-D	Par. VII-C-G
Magenta coupler	1001 Par. VII-D	Par. VII-C-G
Cyan coupler	1001 Par. VII-D	Par. VII-C-G
Colored coupler	1002 Par. VII-G	Par. VII-G
DIR coupler	1001 Par. VII-F	Par. VII-F
BAR coupler	1002 Par. VII-F	
Other useful residual group releasing coupler	1001 Par. VII-F	
Alkali-soluble coupler	1001 Par. VII-E	

The additives used in the present invention can be added by the dispersion method as described in RD308119, paragraph XIV.

In the present invention, the supports as described in the above RD17643, page 28, RD18716, pages 647 to 648 and RD308119, paragraph XVII can be used.

The light-sensitive material of the present invention may also be provided with the auxiliary layers such as filter layers and intermediate layers as described in RD308119, paragraph VII-K.

The light-sensitive material used in the present invention may have various layer structures such as regular layer order, inverse layer order or unit structure as described in the above RD308119, paragraph VII-K.

The present invention can be preferably applied to various color light-sensitive materials as typified by color negative films for general use or motion picture, color reversal films for slide or television, color photographic papers, color positive films and color reversal papers.

The light-sensitive material of the present invention can be photographically processed by the conventional methods as disclosed in the above RD17643, pages 28-29, RD18716, page 615 and RD308119, paragraph XIX.

EXAMPLES

Example 1

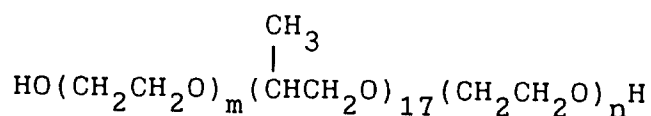
Preparation of regular-crystal monodisperse emulsion Em-1:

A silver iodobromide emulsion containing 2.0 mol% of silver iodide was prepared by double jet precipitation under conditions of 40°C, pH 8.0 and pAg 9.0, followed by washing with water to remove excess salts. The resulting emulsion was comprised of grains with an average grain size of 0.27 μm and a grain size distribution [(standard deviation/average grain size) × 100] of 12.0%. This emulsion was formed into an emulsion containing silver in an amount corresponding to 1,200 g in terms of silver nitrate, to give a seed emulsion A. The seed emulsion A was in an amount of 4,160 g as a finished product.

A regular-crystal monodisperse emulsion Em-1 was prepared using the following three kinds of aqueous solutions, the following emulsion solution containing fine silver iodide grains and the seed emulsion A.

Aqueous solution a-1:	
Gelatin	231.9 g
10 vol% Methanol solution of the compound I shown below	30.0 ml
28% Ammonia water	1,056 ml
Made up to 11,827 ml by adding water.	

Compound I:



(Average molecular weight: about 1,300)

Aqueous solution a-2:	
AgNO ₃	1,587 g
28% Ammonia water	1,295 ml
Made up to 2,669 ml by adding water.	

Aqueous solution a-3:	
KBr	1,572 g
Made up to 3,774 ml by adding water.	

Emulsion solution a-4 containing fine silver iodide grains:	
Fine-grain silver iodide emulsion	1,499.3 g
4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene	5.2 g
Aqueous 10% sodium hydroxide solution	14.75 ml
Made up to 1,373 ml by adding water.	

To the aqueous solution a-1 having the above composition, vigorously stirred at a temperature of 60 °C, the emulsion A was added in an amount corresponding to 0.40 mol, and the pH and pAg were adjusted using acetic acid and an aqueous KBr solution.

Thereafter, while the pH and pAg were controlled as shown in Table 2, the aqueous solutions a-2 and a-3 and the emulsion solution a-4 containing fine silver iodide grains were added by triple jet precipitation at the flow rates as shown in Tables 3, 4 and 5.

After the addition was completed, an aqueous phenylcarbamyl gelatin solution was added, and the pH of the mixed solution was adjusted to cause sedimentation and flocculation of grains, followed by washing with water to effect desalting. Thereafter, the pH and pAg was adjusted to 5.80 and 8.06, respectively, at 40 °C.

Thus, an octahedral regular crystal monodisperse silver iodobromide emulsion with an average grain size of 1.0 μm , an average silver iodide content of 8.0 mol% and a grain size distribution of 11% was obtained.

This emulsion was designated as Em-1.

Table 2
Conditions for grain growth of Em-1

Ag(%) :	0		29		29		56		100
pH:	7.0	→	7.0	↓	6.0	→	6.0	→	6.0
pAg:	7.8	→	7.8	↓	9.7	↓	10.1	→	10.1

→ : The pH and pAg were kept constant.

↓ : Continuously lowered.

↓ : Abruptly lowered.

Table 3

Addition pattern of a-2	
Time (min)	Rate of addition (ml/min)
0	12.2
25.6	13.0
42.6	12.9
43.9	8.4
67.5	11.0
97.3	14.8
97.7	20.6
105.0	22.3
105.4	25.4
112.3	32.1
112.6	35.1
129.4	90.3
145.7	194.2
145.7	200.5
147.4	203.9

Table 4

Addition pattern of a-3	
Time (min)	Rate of addition (ml/min)
0	10.9
25.6	11.7
42.6	11.6
43.9	7.6
97.3	13.3
97.7	18.6
105.0	20.0
105.0	36.5
112.0	56.2
112.3	60.6
121.2	106.0
121.4	91.4
132.4	263.3
132.7	141.8
147.4	230.0

Table 5

Addition pattern of a-4	
Time (min)	Rate of addition (ml/min)
0	0
43.9	0
43.9	73.6
51.7	80.6
52.5	28.5
84.3	40.4
84.9	11.6
97.7	13.0
105.0	14.1
105.4	16.3
112.3	20.6
112.6	6.2
130.4	17.5
132.7	22.1
145.7	34.4

Preparation of twinned monodisperse emulsion Em-2:

A monodisperse spherical seed emulsion B was prepared using the following solutions A1 to D1 by the method disclosed in Japanese Patent O.P.I. Publication No. 6643/1986.

EP 0 560 036 A2

A1:	
Ossein gelatin	150 g
Potassium bromide	53.1 g
Potassium iodide	24 g
Made up to 7.2 lit. by adding water.	

B1:	
Silver nitrate	1,500 g
Made up to 6 lit. by adding water.	

C1:		
Potassium bromide		1,327 g
1-Phenyl-5mercaptotetrazole (dissolved using methanol)		0.3 g
Made up to 3 lit. by adding water.		

D1:	
Ammonia water (28%)	705 ml

To the solution A1 vigorously stirred at 40 °C, the solutions B1 and C1 were added by double jet precipitation in 30 seconds to form nuclei. During this addition, the pBr was 1.09 to 1.15.

After 1 minute 30 seconds, the solution D1 was added in 20 seconds, followed by ripening for 5 minutes. At the time of the ripening, KBr was in a concentration of 0.071 mol/lit. and ammonia was in a concentration of 0.63 mol/lit.

Thereafter the pH was adjusted to 6.0, immediately followed by washing with water to effect desalting. The resulting seed emulsion B was observed using an electron microscope to reveal that it was a monodisperse spherical emulsion comprised of grains with an average grain size of 0.36 μm and a grain size distribution of 18%.

Then, a twinned monodisperse emulsion Em-2 according to the present invention was prepared using the following seven kinds of solutions.

Solution A:

Ossein gelatin	268.2 g
Distilled water	4.0 lit
Polyisopropylene-polyethyleneoxy-disuccinic acid ester sodium salt 10% methanol solution	1.5 ml
Seed emulsion B	0.332 mol
Aqueous 28% by weight ammonia solution	528.0 ml
Aqueous 56% by weight acetic acid solution	795.0 ml
Methanol solution containing 0.001 mol of iodide	50.0 ml
Made up to 5,930.0 ml using distilled water.	

Solution B:

Aqueous 3.5N ammoniacal silver nitrate solution
(Its pH was adjusted to 9.0 using ammonium nitrate)

Solution C:

Aqueous 3.5N potassium bromide solution containing 4.0% by weight of gelatin

Solution D:

Fine-grain emulsion comprised of 3% by weight of gelatin and silver iodide grains (average grain sizes: 0.05 μm)	2.39 mol
--	----------

This solution was prepared in the following way.

To 5,000 ml of 6.0% by weight gelatin solution containing 0.06 mol of potassium iodide, 2,000 ml each of an aqueous solution containing 7.06 mol of silver nitrate and an aqueous solution containing 7.06 mol of potassium iodide were added over a period of 10 minutes. In the course of the formation of fine grains, the pH was adjusted to 2.0 using nitric acid and the temperature was controlled to be 40 °C. After the formation of grains, the pH was adjusted to 6.0 using an aqueous sodium carbonate solution.

Solution E:

Fine-grain emulsion comprised of silver iodobromide grains (average grain size: 0.04 μm) containing 1 mol% of silver iodide, prepared in the same manner as the fine-grain silver iodide emulsion described for the solution D.	6.24 mol
---	----------

In the course of the formation of the fine grains, the temperature was controlled to be 30 °C.

Solution F:

Aqueous 1.75N potassium bromide solution

Solution G:

Aqueous 56% by weight acetic acid solution

To the solution A maintained at 70 °C in a reaction vessel, the solutions B, C and D were added by double jet precipitation over a period of 133 minutes, and thereafter the solution E was subsequently added alone at a constant rate over a period of 12 minutes to make the seed grains grow into 1.2 μm grains.

At this stage, the solutions B and C were added by accelerated flow rate precipitation, so accelerated with respect to time as to be in accordance with the critical growth rate, at an appropriate rate of addition so that no minute grains other than the growing seed grains were produced and no emulsion became polydisperse as a result of Ostwald ripening. The solution D, i.e., the fine-grain silver iodide emulsion was fed while its feed rate ratio (molar ratio) to the aqueous ammoniacal silver nitrate solution was changed with respect to grain size (time of addition) as shown in Table 6. A core/shell silver halide emulsion having a multiple structure was thus prepared.

Using the solutions F and G, the pAg and pH in the course of the growth of grains were controlled as also shown in Table 6. The pAg and pH were measured by a conventional method, using a silver sulfide electrode and a glass electrode.

After the formation of grains, desalting was carried out according to the method disclosed in Japanese Patent O.P.I. Publication No. 4003/1991. Thereafter gelatin was added to carry out redispersion, and the pH and pAg were adjusted to 5.80 and 8.06, respectively, at 40 °C.

Table 6

Time of addition	Grain size	Flow rate ratio of solution D	pH	pAg
(min)	(μm)			
Intermediate phase:				
0.0	0.391	10.3	7.2	7.8
25.1	0.533	10.3	7.2	7.8
40.1	0.609	10.3	7.2	7.8

Core:				
53.0	0.663	30.0	7.2	7.8
82.5	0.795	30.0	7.2	7.8
82.5	0.795	30.0	6.5	9.4

Shell:				
100.5	0.873	10.3	6.5	9.4
105.3	0.895	10.3	6.5	9.4
116.9	0.967	7.7	6.5	9.4
116.9	0.967	0.0	6.5	9.4
133.0	1.147	0.0	6.5	9.7

The emulsion grains thus obtained were observed using an electron microscope to reveal that they were comprised of edge-round octahedral twinned monodisperse grains deformed extendedly in the direction of twin planes, which were comprised of the twinned grains by 100% and in which their twin-plane percentage of grains having two or more parallel twin planes was 65%, grain size distribution was 14%, average grain size was 1.2 μm and average aspect ratio was 1.3.

EP 0 560 036 A2

Preparation of twinned monodisperse emulsion Em-3:

A monodisperse spherical seed emulsion C was prepared in the following way.

5	A:		
	Ossein gelatin		80 g
	Potassium bromide		47.4 g
	Polyisopropylene-polyethyleneoxy-disuccinic acid ester sodium salt 10% methanol solution		20 ml
10	Made up to 8.0 lit. by adding water.		

15	B:	
	Silver nitrate	1.2 kg
	Made up to 1.6 lit. by adding water.	

20	C:	
	Ossein gelatin	32.2 g
	Potassium bromide	840 g
	Made up to 1.6 lit. by adding water.	

30	D:	
	Ammonia water	470 ml

To the solution A vigorously stirred at 40°C, the solutions B and C were added by double jet precipitation in 11 seconds to form nuclei. During this addition, the pBr was kept at 1.60.

Thereafter, taking 12 minutes the temperature was dropped to 30°C, and ripening was carried out for further 18 minutes. Then the solution D was added in 1 minute, followed by ripening for 5 minutes. At the time of the ripening, KBr was in a concentration of 0.07 mol/lit. and ammonia was in a concentration of 0.63 mol/lit.

After the ripening was completed, the pH was adjusted to 6.0, followed by desalting according to a conventional method to give a seed emulsion. This seed emulsion was observed using an electron microscope to reveal that it was a spherical emulsion comprised of grains with an average grain size of 0.318 μm , having two twin planes parallel to each other.

An octahedral twinned-crystal monodisperse emulsion Em-3 according to the present invention was prepared using the following seven kinds of solutions.

Solution A:

5	Ossein gelatin	268.2 g
	Distilled water	4.0 lit
	Polyisopropylene-polyethyleneoxy-disuccinic acid ester sodium salt 10% methanol solution	1.5 ml
	Seed emulsion C	0.286 mol
	Aqueous 28% by weight ammonia solution	528.0 ml
10	Aqueous 56% by weight acetic acid solution	795.0 ml
	Methanol solution containing 0.001 mol of iodide	50.0 ml
Made up to 5,930.0 ml using distilled water.		

15 Solution B:

Aqueous 3.5N ammoniacal silver nitrate solution
(Its pH was adjusted to 9.0 using ammonium nitrate)

20 Solution C:

Aqueous 3.5N potassium bromide solution containing 4.0% by weight of gelatin

25 Solution D:

Fine-grain emulsion comprised of 3% by weight of gelatin and silver iodide grains (average grain sizes: 0.05 μm)	2.39 mol
--	----------

30

This solution was prepared in the following way.

To 5,000 ml of 6.0% by weight gelatin solution containing 0.06 mol of potassium iodide, 2,000 ml each of an aqueous solution containing 7.06 mol of silver nitrate and an aqueous solution containing 7.06 mol of potassium iodide were added over a period of 10 minutes. In the course of the formation of fine grains, the pH was adjusted to 2.0 using nitric acid and the temperature was controlled to be 40 °C. After the formation of grains, the pH was adjusted to 6.0 using an aqueous sodium carbonate solution.

40 Solution E:

Fine-grain emulsion comprised of silver iodobromide grains (average grain size: 0.04 μm) containing 1 mol% of silver iodide, prepared in the same manner as the fine-grain silver iodide emulsion described for the solution D.	6.24 mol
---	----------

45

In the course of the formation of the fine grains, the temperature was controlled to be 30 °C.

Solution F:

50 Aqueous 1.75N potassium bromide solution

Solution G:

55 Aqueous 56% by weight acetic acid solution

To the solution A maintained at 70 °C in a reaction vessel, the solutions B, C and D were added by double jet precipitation over a period of 163 minutes, and thereafter the solution E was subsequently added alone at a constant rate over a period of 12 minutes to make the seed grains grow into 1.0 μm grains.

At this stage, the solutions B and C were added by accelerated flow rate precipitation, so accelerated with respect to time as to be in accordance with the critical growth rate, at an appropriate rate of addition so that no minute grains other than the growing seed grains were produced and no emulsion became polydisperse as a result of Ostwald ripening. The solution D, i.e., the fine-grain silver iodide emulsion was fed while its feed rate ratio (molar ratio) to the aqueous ammoniacal silver nitrate solution was changed with respect to grain size (time of addition) as shown in Table 7. A core/shell silver halide emulsion having a multiple structure was thus prepared.

Using the solutions F and G, the pAg and pH in the course of the growth of grains were controlled as also shown in Table 7. The pAg and pH were measured by a conventional method, using a silver sulfide electrode and a glass electrode.

After the formation of grains, desalting was carried out according to the method disclosed in Japanese Patent Application No. 41314/1991. Thereafter gelatin was added to carry out redispersion, and the pH and pAg were adjusted to 5.80 and 8.06, respectively, at 40 °C.

The emulsion grains thus obtained were observed using an electron microscope to reveal that they were comprised of slightly deformed octahedral twinned monodisperse grains, which were comprised of the twinned grains by 100% and in which their twin-plane percentage of grains having two or more parallel twin planes was 85%, grain size distribution was 10% and average grain size was 1.0 μm .

Table 7

	Time of addition	Grain size	Flow rate ratio of solution D	pH	pAg
	(min)	(μm)			
	Intermediate phase:				
	0.0	0.318	10.3	7.2	7.8
	23.1	0.432	10.3	7.2	7.8
	38.0	0.495	10.3	7.2	7.8

	Core:				
	50.1	0.538	30.0	7.2	7.8
	82.6	0.657	30.0	7.2	7.8
	82.6	0.657	30.0	6.5	9.4

	Shell:				
	112.7	0.706	10.3	6.5	9.4
	122.0	0.723	10.3	6.5	9.4
	141.6	0.781	7.7	6.5	9.4
	141.6	0.781	0.0	6.5	9.4
	163.0	0.925	0.0	6.5	9.7

Example 2

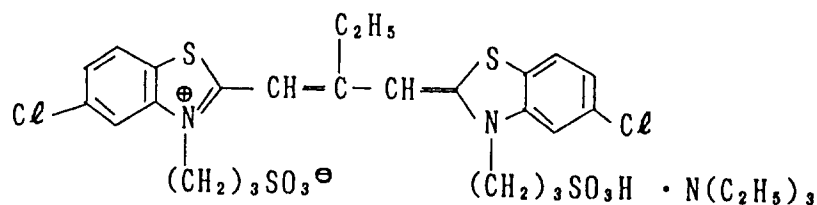
The emulsions Em-1 to Em-3 obtained in Example 1 was subjected to the following chemical ripening to give emulsions 1-A to 1-D.

Preparation of emulsion 1-A:

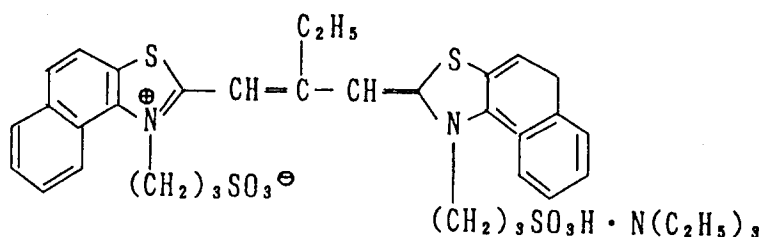
A portion of the emulsion Em-1 was heated to 50°C and dissolved, which was then subjected to ripening with addition of 1.0×10^{-5} mol of sodium thiosulfate pentahydrate, 3.6×10^{-6} mol of chloroauric acid and 5.0×10^{-4} mol of ammonium thiocyanate. The chloroauric acid and ammonium thiocyanate were used in the form of a mixed solution, which was added simultaneously with the sodium thiosulfate

pentahydrate. After ripening for 100 minutes, spectral sensitizers A, B and C were added in amounts of 1.3×10^{-4} mol, 1.6×10^{-5} mol and 1.3×10^{-4} mol, respectively, per mol of silver halide, for their adsorption for 15 minutes, followed by addition of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene as a stabilizer and then cooling to set to gel. An emulsion 1-A was thus obtained.

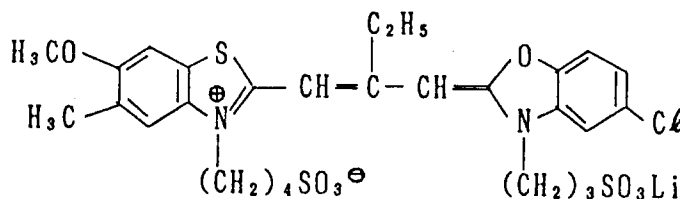
Spectral sensitizer A



Spectral sensitizer B



Spectral sensitizer C



Preparation of emulsion 1-B:

A portion of the emulsion Em-1 was heated to 50 °C and dissolved, to which the spectral sensitizers A, B and C were added in amounts of 1.3×10^{-4} mol, 1.6×10^{-5} mol and 1.3×10^{-4} mol, respectively, per mol of silver halide, for their adsorption for 15 minutes, followed by addition of 1.0×10^{-5} mol of sodium thiosulfate pentahydrate, 3.6×10^{-6} mol of chloroauric acid and 5.0×10^{-4} mol of ammonium thiocyanate to carry out ripening. The chloroauric acid and ammonium thiocyanate were used in the form of a mixed solution, which was added simultaneously with the sodium thiosulfate pentahydrate. After ripening for 100 minutes, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added as a stabilizer, followed by cooling to set to gel. An emulsion 1-B was thus obtained.

Preparation of emulsion 1-C:

A portion of the emulsion Em-1 was heated to 50 °C and dissolved, to which, 10 minutes before the addition of spectral sensitizers, ammonium thiocyanate was first added in an amount of 4×10^{-4} mol per mol of silver halide. Then, the procedure as in the preparation of the emulsion 1-B was repeated, except that 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added as the nitrogen-containing heterocyclic compound in an amount of 1×10^{-4} mol per mol of silver halide at the same time with the addition of the spectral sensitizers. An emulsion 1-C was thus prepared.

Preparation of emulsion 1-D:

A portion of the emulsion Em-1 was heated to 50 °C and dissolved, to which, 10 minutes before the addition of spectral sensitizers, ammonium thiocyanate was first added in an amount of 4×10^{-4} mol per mol of silver halide. Then, the procedure as in the preparation of the emulsion 1-B was repeated, except that silver iodide grains comprised of a mixture of β -Agl and γ -Agl with an average grain size of 0.06 μm were added as the fine silver iodide grains in an amount of 3×10^{-4} mol per mol of silver halide at the same time with the addition of the spectral sensitizers. An emulsion 1-D was thus prepared.

Subsequently, using the emulsion Em-2, the procedures for the preparation of the emulsions 1-A to 1-D were respectively repeated to give emulsions 2-A to 2-D.

Further, using the emulsion Em-3, the procedures for the preparation of the emulsions 1-A to 1-D were respectively repeated to give emulsions 3-A to 3-D.

Production of coated samples comprising single emulsion layer:

The emulsions 1-A to 3-D thus obtained were coated on subbed triacetyl cellulose film supports under the following coating formulation, followed by drying to give samples 101 to 112. In all the following examples, the amount of each compound added in the light-sensitive silver halide photographic materials is indicated as gram number per 1 m². The amount of silver halide is in terms of silver weight.

- Coating formulation -

The following layers are successively formed from the support side (chemical formulas of compounds used are set out together in Example 3).

First layer:	
Emulsion	2.0
Cyan coupler C-2	0.15
High-boiling solvent Oil-1	0.15
Gelatin	1.5

Second layer: Protective layer	
Gelatin	1.0

In addition to the foregoing compositions, coating aid Su-1, dispersion aid Su-2 and hardening agent H-1 were added.

Evaluation by sensitometry and measurement of start point of development:

The coated samples 101 to 112 were each subjected to wedge exposure using red light, and thereafter processed according to the following processing steps. For each sample, the characteristic curve was obtained, and maximum density relative sensitivity (a reciprocal of the amount of exposure that gives a density of fog + 0.1 is indicated as a relative value) and minimum amount of exposure that is necessary for obtaining a maximum density were determined.

EP 0 560 036 A2

Processing steps (38 ° C):

5

10

Color developing	1 min 45 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec
Drying	

Processing solutions used in the respective processing steps had the following composition.

15

20

25

- Color developing solution -	
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Made up to 1 liter by adding water and adjusted to pH 10.0 using sodium hydroxide.	

30

35

- Bleaching solution -	
Ferric ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml
Made up to 1 liter by adding water, and adjusted to pH 6.0 using ammonium water.	

40

45

- Fixing solution -	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metarsulfite	2.3 g
Made up to 1 liter by adding water, and adjusted to pH 6.0 using acetic acid.	

50

- Stabilizing solution -	
Formalin (aqueous 37% solution)	1.5 ml
KONIDAX (trade name; available from KONICA CORPORATION)	7.5 ml
Made up to 1 liter by adding water.	

Next, in order to observe the start point of development, the coated samples 101 to 112 were each exposed in the minimum amount of exposure, previously determined, that is necessary for obtaining a maximum density, and the developing and stopping were carried out according to the following processing steps.

Processing steps (38 ° C):

5

Color developing (1/10 dilute solution)	30 sec
Stopping	1 min 00 sec
Washing	3 min 15 sec
Drying	

10

In the color developing, a solution having the same composition as the one used when the characteristic curve was obtained, but diluted to 1/10 by adding water, was used.

As a bath for the stopping, aqueous 3% acetic acid solution was used.

15

On the samples having been thus subjected to the developing and stopping, decomposition of gelatin was made by an enzyme, and the silver halide grains were observed using a high-resolving power scanning electron microscope to observe their start points of development. In respect of each sample, 400 to 500 start points of development were all counted and the percentage of the development start points in cross areas, held therein was determined.

20

Next, using a scratch hardness tester with a needle of 0.3 mm needle point, a load of 3 g was applied to unexposed samples 101 to 112. Thereafter the same photographic processing as for the sensitometric evaluation was carried out, and the density at which the fogging by pressure occurred was measured using a microdensitometer. Evaluation of the extent of fogging by pressure was made on the basis of the density of fog increase ascribable to fogging by pressure.

Table 8 shows the relative sensitivity, maximum density, extent of fogging by pressure (pressure mark), and development start points in cross areas of each sample.

25

Table 8

30

Sample No.	Emulsion used	*1 Relative sensi-tivity	Maximum density	*2 Pressure mark	Percentage of development start point in cross area (%)	Remarks
101	1-A	100	0.55	0.26	0	X
102	1-B	105	0.58	0.29	0	X
103	1-C	100	0.57	0.33	0	X
104	1-D	95	0.55	0.31	0	X
105	2-A	105	0.58	0.27	42	X
106	2-B	105	0.55	0.29	54	X
107	2-C	115	0.62	0.23	65	Y
108	2-D	110	0.60	0.20	76	Y
109	3-A	110	0.63	0.21	67	Y
110	3-B	125	0.66	0.18	80	Y
111	3-C	130	0.66	0.19	86	Y
112	3-D	125	0.68	0.16	83	Y
X: Comparative Example						
Y: Present Invention						

45

*1 Sensitivity is indicated as a relative value assuming the sensitivity of sample 101 as 100.

*2 (Red color density at 3 g loaded part) - (red color density at non-loaded part)

50

As is seen from Table 8, the emulsions of the present invention have made it possible to achieve the performances that the light-sensitive materials have a high sensitivity and good color forming performance and cause less fogging by pressure.

55

Example 3

Samples 201 to 209 were produced using each of the emulsions obtained in Example 2, as a high-speed red sensitive emulsion for the fifth layer in a multi-layer light-sensitive photographic material comprising a triacetyl cellulose film support and, successively provided thereon from the support side, layers having the composition shown below.

In the following, the amount of each compound added is indicated as gram number per 1 m² unless particularly noted. The amounts of silver halide and colloidal silver are in terms of silver weight. Those of spectral sensitizers are each indicated as molar number per mol of silver.

- Sample 101 -

First layer: Anti-halation layer	
Black colloidal silver	0.16
Ultraviolet absorbent UV-1	0.20
High-boiling solvent Oil-1	0.16
Gelatin	1.23

Second layer: Intermediate layer	
Compound SC-1	0.15
High-boiling solvent Oil-2	0.17
Gelatin	1.27

Third layer: Low-speed red-sensitive emulsion layer		
Silver iodobromide emulsion (average grain size: 0.38 μm; silver iodide content: 8.0 mol%)		0.50
Silver iodobromide emulsion (average grain size: 0.27 μm; silver iodide content: 2.0 mol%)		0.21
Spectral sensitizer SD-1		2.8×10^{-4}
Spectral sensitizer SD-2		1.9×10^{-4}
Spectral sensitizer SD-3		1.9×10^{-5}
Spectral sensitizer SD-4		1.0×10^{-4}
Cyan coupler C-1		0.48
Cyan coupler C-2		0.14
Colored cyan coupler CC-1		0.021
DIR compound D-1		0.020
High-boiling solvent Oil-1		0.53
Gelatin		1.30

Fourth layer: Medium-speed red-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.52 μm ; silver iodide content: 8.0 mol%)	0.62
Silver iodobromide emulsion (average grain size: 0.38 μm ; silver iodide content: 8.0 mol%)	0.27
Spectral sensitizer SD-1	2.3×10^{-4}
Spectral sensitizer SD-2	1.2×10^{-4}
Spectral sensitizer SD-3	1.6×10^{-5}
Spectral sensitizer SD-4	1.2×10^{-4}
Cyan coupler C-1	0.15
Cyan coupler C-2	0.18
Colored cyan coupler CC-1	0.030
DIR compound D-1	0.013
High-boiling solvent Oil-1	0.30
Gelatin	0.93

Fifth layer: High-speed red-sensitive emulsion layer

Silver iodobromide emulsion Em-1-B	1.27
Cyan coupler C-2	0.12
Colored cyan coupler CC-1	0.013
High-boiling solvent Oil-1	0.14
Gelatin	0.91

Sixth layer: Intermediate layer

Compound SC-1	0.09
High-boiling solvent Oil-2	0.11
Gelatin	0.80

Seventh layer: Low-speed green-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.38 μm ; silver iodide content: 8.0 mol%)	0.61
Silver iodobromide emulsion (average grain size: 0.27 μm ; silver iodide content: 2.0 mol%)	0.20
Spectral sensitizer SD-4	7.4×10^{-5}
Spectral sensitizer SD-5	6.6×10^{-4}
Magenta coupler M-1	0.18
Magenta coupler M-2	0.44
Colored magenta coupler CM-1	0.12
High-boiling solvent Oil-2	0.75
Gelatin	1.95

Eighth layer: Medium-speed green-sensitive emulsion layer		
5	Silver iodobromide emulsion (average grain size: 0.59 μm ; silver iodide content: 8.0 mol%)	0.87
	Spectral sensitizer SD-6	1.6×10^{-4}
	Spectral sensitizer SD-7	1.6×10^{-4}
	Spectral sensitizer SD-8	1.6×10^{-4}
	Magenta coupler M-1	0.058
10	Magenta coupler M-2	0.13
	Colored magenta coupler CM-2	0.070
	DIR compound D-2	0.025
	DIR compound D-3	0.002
	High-boiling solvent Oil-2	0.50
	Gelatin	1.00

15

Ninth layer: High-speed green-sensitive emulsion layer		
20	Silver iodobromide emulsion (average grain size: 1.00 μm ; silver iodide content: 8.0 mol%)	1.27
	Spectral sensitizer SD-6	9.4×10^{-5}
	Spectral sensitizer SD-7	9.4×10^{-5}
	Spectral sensitizer SD-8	9.4×10^{-5}
	Magenta coupler M-2	0.084
25	Magenta coupler M-3	0.064
	Colored magenta coupler CM-2	0.012
	High-boiling solvent Oil-1	0.27
	High-boiling solvent Oil-2	0.012
	Gelatin	1.00

30

Tenth layer: Yellow filter layer		
35	Yellow colloidal silver	0.08
	Color stain preventive agent SC-2	0.15
	Formalin scavenger HS-1	0.20
	High-boiling solvent Oil-2	0.19
	Gelatin	1.10

40

Eleventh layer: Intermediate layer		
45	Formalin scavenger HS-1	0.20
	Gelatin	0.60

45

Twelfth layer: Low-speed blue-sensitive emulsion layer		
50	Silver iodobromide emulsion (average grain size: 0.38 μm ; silver iodide content: 8.0 mol%)	0.22
	Silver iodobromide emulsion (average grain size: 0.27 μm ; silver iodide content: 2.0 mol%)	0.03
	Spectral sensitizer SD-9	4.2×10^{-4}
	Spectral sensitizer SD-10	6.8×10^{-5}
	Yellow coupler Y-1	0.75
55	DIR compound D-1	0.010
	High-boiling solvent Oil-2	0.30
	Gelatin	1.20

Thirteenth layer: Medium-speed blue-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.59 μm ; silver iodide content: 8.0 mol%)	0.30
Spectral sensitizer SD-9	1.6×10^{-4}
Spectral sensitizer SD-11	7.2×10^{-5}
Yellow coupler Y-1	0.10
DIR compound D-1	0.010
High-boiling solvent Oil-2	0.046
Gelatin	0.47

Fourteenth layer: High-speed blue-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 1.00 μm ; silver iodide content: 8.0 mol%)	0.85
Spectral sensitizer SD-9	7.3×10^{-5}
Spectral sensitizer SD-11	2.8×10^{-5}
Yellow coupler Y-1	0.11
High-boiling solvent Oil-2	0.046
Gelatin	0.80

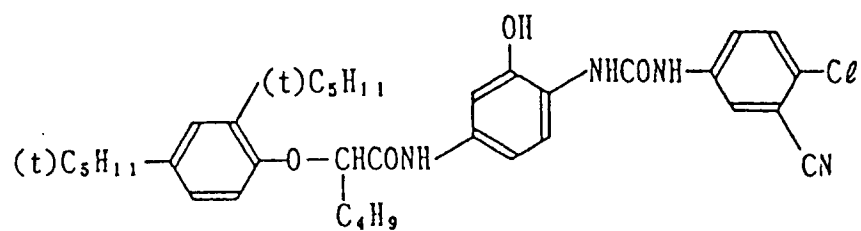
Fifteenth layer: First protective layer

Silver iodobromide emulsion (average grain size: 0.08 μm ; silver iodide content: 1.0 mol%)	0.40
Ultraviolet absorbent UV-1	0.026
Ultraviolet absorbent UV-2	0.013
Ultraviolet absorbent UV-3	0.013
Ultraviolet absorbent UV-4	0.013
High-boiling solvent Oil-1	0.07
High-boiling solvent Oil-3	0.07
Formalin scavenger HS-1	0.40
Gelatin	1.31

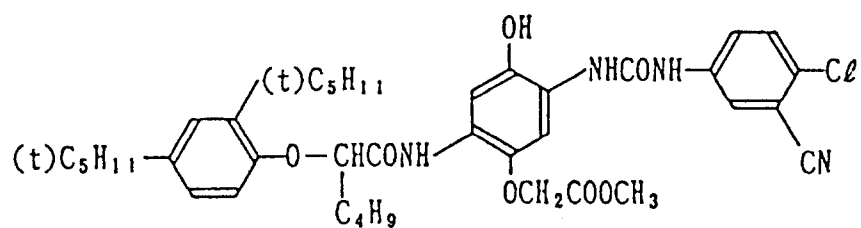
Sixteenth layer: Second protective layer

Alkali-soluble matting agent (average particle diameter: 2 μm)	0.15
Polymethyl methacrylate (average particle diameter: 3 μm)	0.04
Lubricant WAX-1	0.04
Gelatin	0.55

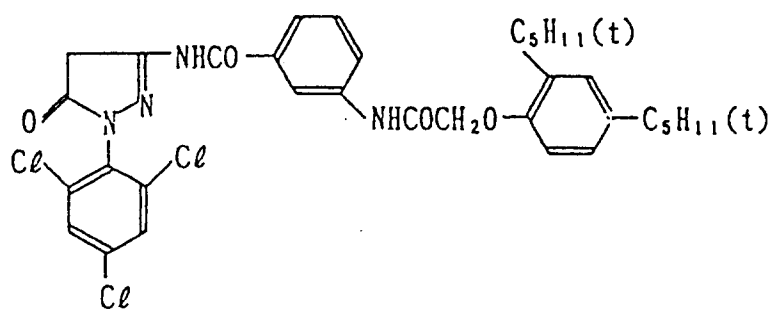
C - 1



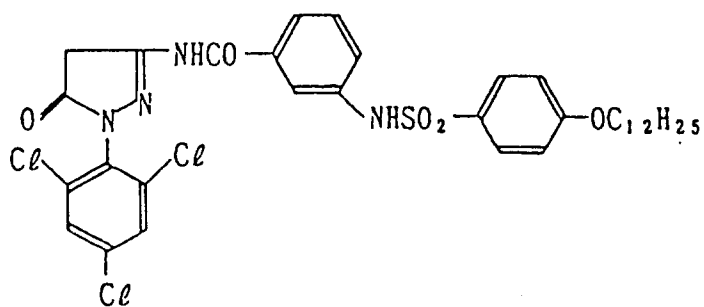
C - 2



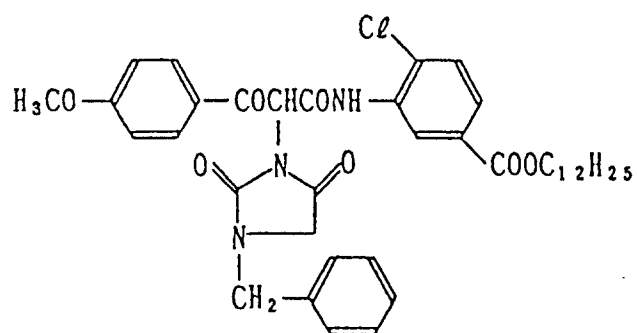
M - 1



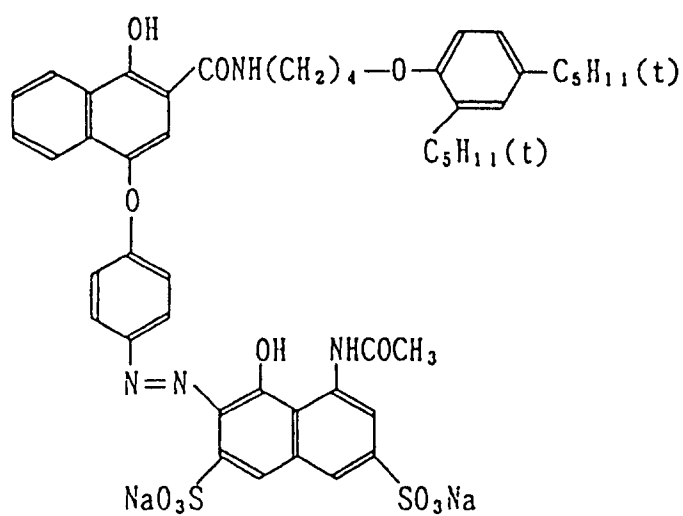
M - 2



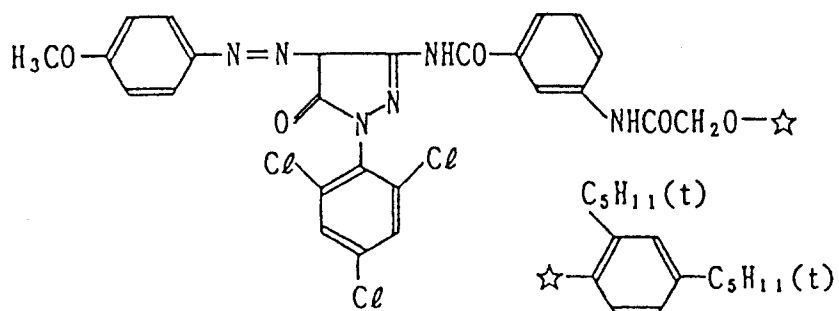
Y - 1



CC - 1

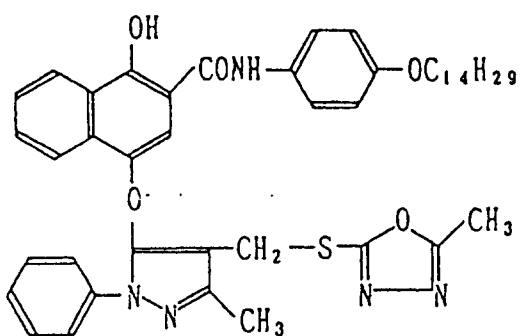


CM - 1



D - 1

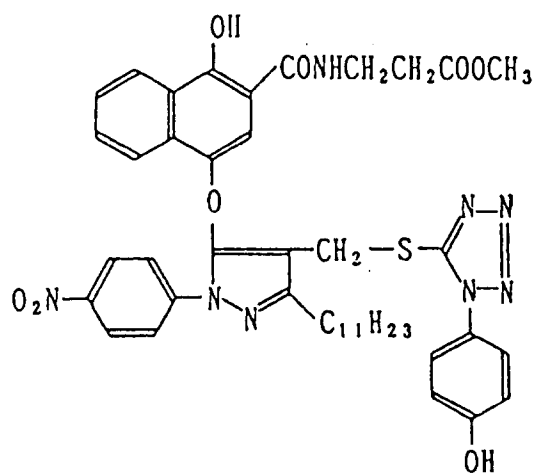
5



10

15 D - 2

20

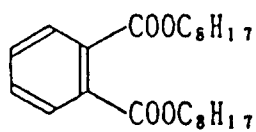


25

30

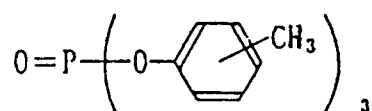
35 Oil - 1

40



45 Oil - 2

50



Oil - 3

55



15



30



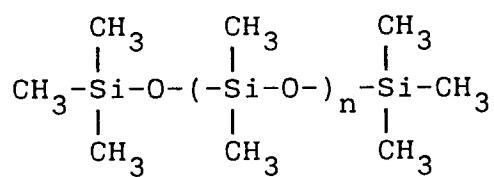
40



50

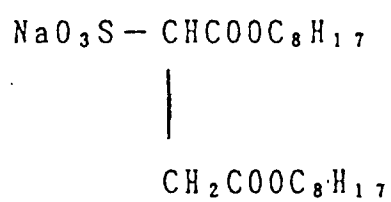


WAX-1

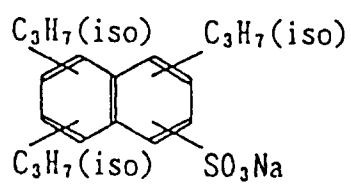


Weight average molecular weight Mw: 30,000

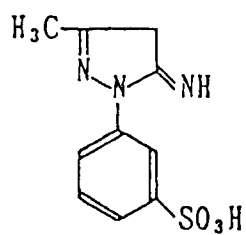
S u - 1



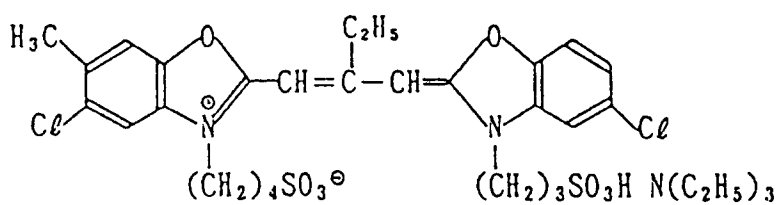
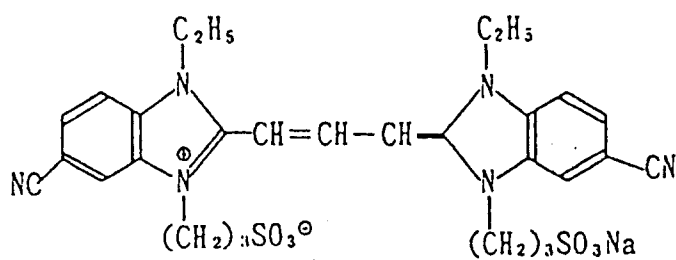
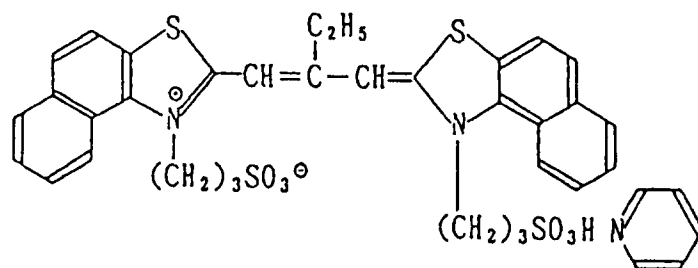
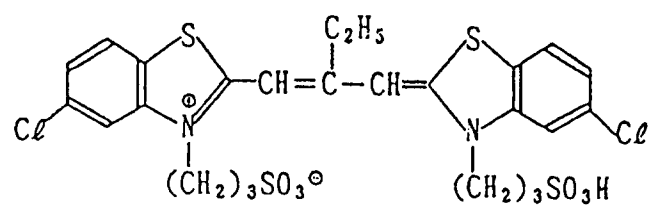
S u - 2

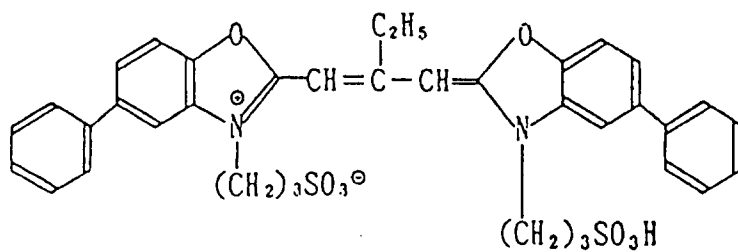


H S - 1

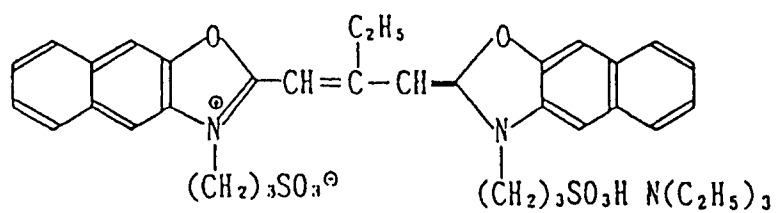


S D - 1

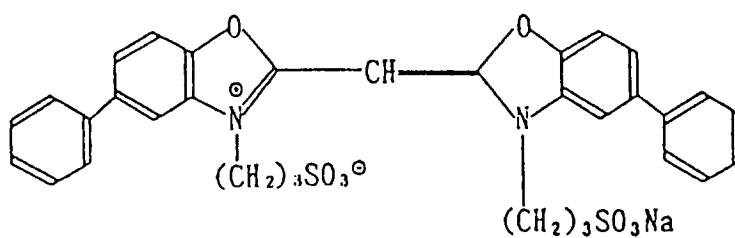




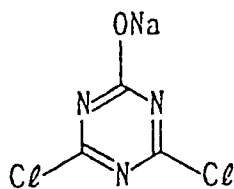
S D - 7



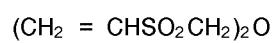
S D - 9



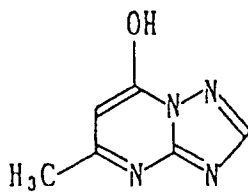
H - 1



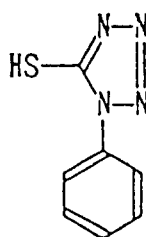
H - 2



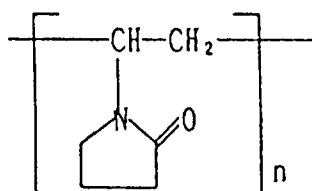
ST - 1



AF - 1



AF-2



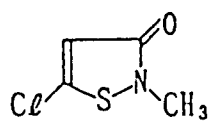
n: Degree of polymerization

DI-2

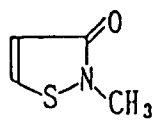
(Component A)

(Component B)

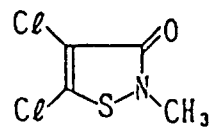
(Component C)



,



,



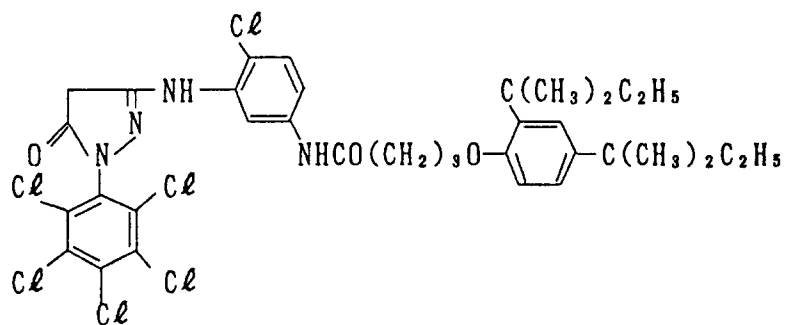
Components A:B:C is 50:46:4 (molar ratio)

M - 3

5

10

15

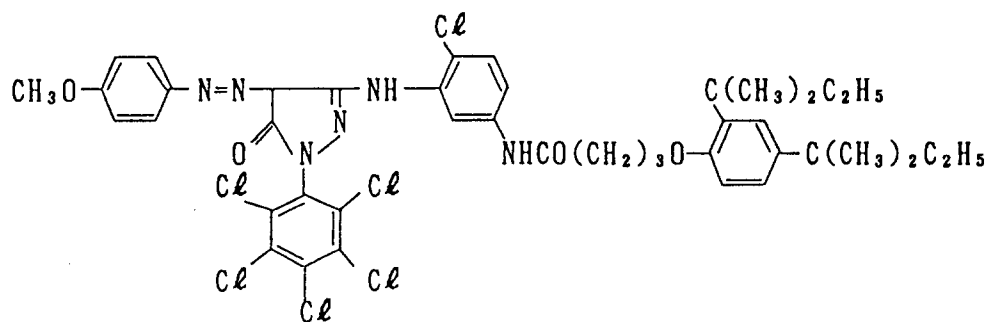


C M - 2

20

25

30

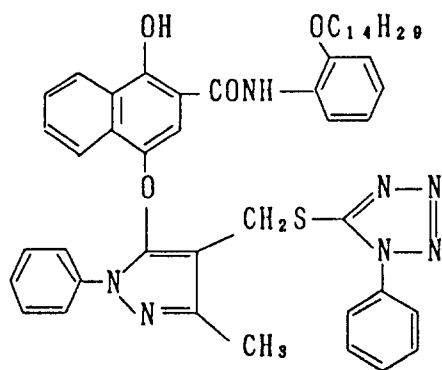


D - 3

35

40

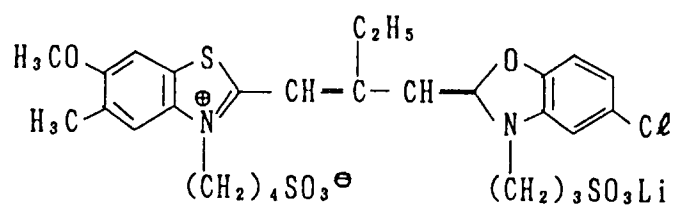
45



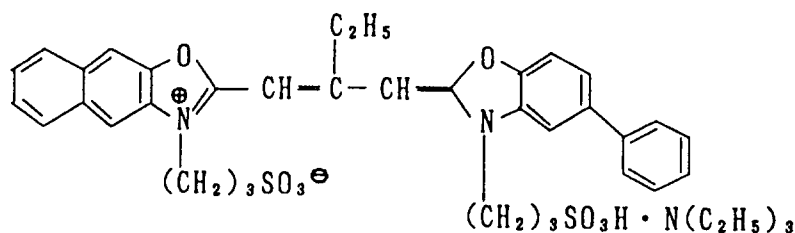
S D - 2

50

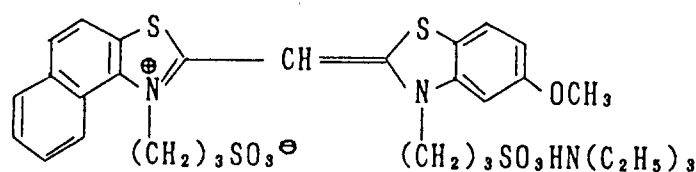
55



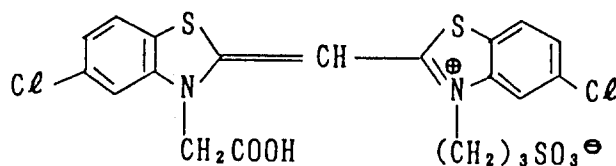
SD - 8



SD - 10



SD - 11



Samples 202 to 209 were produced by replacing as shown in Table 9 the fifth-layer red-sensitive emulsion 1-B in the sample 201 with other emulsions used in Example 2.

The samples 201 to 209 thus obtained were each subjected to wedge exposure using white light, and thereafter processed according to the following processing steps in which three kinds of color developing solutions containing developing agents in different concentrations were used. For each sample, the characteristic curve was obtained, and logarithmic values of the amounts of exposure that correspond to a minimum density + 0.2 and a minimum density + 0.7 in red densities, i.e., log E (0.2) and log E (0.7), respectively, were determined. The slope γ of the characteristic curve was defined as shown below and the values thereof were calculated.

$$\gamma = \frac{\log E (0.7) - \log E (0.2)}{0.5}$$

The γ values of the samples processed using developing solutions I, II and III were determined as γ_I , γ_{II} and γ_{III} , respectively, and values of γ_I/γ_{II} and γ_{III}/γ_{II} were calculated. Results obtained are shown in Table 9.

Processing A

Processing steps (38 ° C):

5

10

Color developing	3 min 15 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec
Drying	

15

Processing solutions used in the respective processing steps had the following composition.

20

25

- Color developing solution I -	
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline sulfate	3.56 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Made up to 1 liter by adding water (pH: 10.1).	

30

35

- Bleaching solution -	
Ferric ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml
Made up to 1 liter by adding water, and adjusted to pH 6.0 using ammonium water.	

40

45

- Fixing solution -	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasilicate	2.3 g
Made up to 1 liter by adding water, and adjusted to pH 6.0 using acetic acid.	

50

- Stabilizing solution -	
Formalin (aqueous 37% solution)	1.5 ml
KONIDAX (trade name; available from KONICA CORPORATION)	7.5 ml
Made up to 1 liter by adding water.	

55

At the same time, dye images were formed by carrying out processing under the same conditions as in Processing A except that the color developing solution I was replaced with color developing solutions II and III shown below.

- Color developing solution II -	
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Made up to 1 liter by adding water (pH: 10.1).	

- Color developing solution III -	
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline sulfate	5.93 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Made up to 1 liter by adding water (pH: 10.1).	

Table 9

Sample No.	Emulsion used in 5th layer	γ_I	γ_{II}	γ_{III}	γ_I/γ_{II}	γ_{III}/γ_{II}	Remarks
201	1-B	0.50	0.53	0.58	0.94	1.09	X
202	2-A	0.48	0.52	0.55	0.92	1.06	X
203	2-B	0.53	0.56	0.60	0.95	1.07	X
204	2-C	0.53	0.55	0.58	0.96	1.05	Y
205	2-D	0.53	0.55	0.56	0.96	1.02	Y
206	3-A	0.55	0.56	0.58	0.98	1.04	Y
207	3-B	0.58	0.58	0.60	1.00	1.03	Y
208	3-C	0.58	0.58	0.59	1.00	1.02	Y
209	3-D	0.56	0.57	0.57	0.98	1.00	Y
X: Comparative Example Y: Present Invention							

As is clear from Table 9, the samples making use of the emulsions of the present invention are characterized by causing a small change in the slope of the characteristic curve even with a change in concentration of the developing agent and hence giving a constant print quality.

As described above, the present invention can provide a silver halide photographic emulsion having a high sensitivity and high color forming performance and promising a good processing stability and good pressure resistance. In particular, it can provide a light-sensitive silver halide photographic material having a good processing stability and processing operability.

Claims

1. A silver halide photographic light-sensitive emulsion comprising grains having twin planes, wherein at least 60 % of projected area of the whole grains are occupied by said grains having twin planes, and part or all of said grains having twin planes each have a start point of development at a cross point or the vicinity of said cross point, wherein said cross point is formed by a line formed by a twin plane border lying bare on the grain surface, which intersects an ridge line of the grain.

2. The emulsion of claim 1, wherein said twin grains comprise at least one plane selected from the group consisting of {111} plane and {100} plane.
3. The emulsion of claim 2, wherein said twin grains comprise two or more twin planes per one grain,
5 wherein said twin planes are parallel to each other.
4. The emulsion of claim 3, wherein said twin grains comprise two parallel twin planes.
5. The emulsion of claim 4, wherein said twin grains comprise tabular grains having an aspect ratio of not
10 less than 5.0.
6. The emulsion of claim 3, wherein said twin grains having two parallel twin planes, are not less than 50 % of projected area of the whole twinned grains.
7. The emulsion of claim 3, wherein said twin grains having two parallel twin planes, are not less than 80
15 % of projected area of the whole twinned grains.
8. The emulsion of claims 1 or 2 to 7, wherein said emulsion is monodispersed emulsion in grain size distribution.
9. The emulsion of claims 1 or 2 to 8, wherein said emulsion is comprised of silver iodobromide having a
20 silver iodide content of from 4 to 20 mol%.
10. The emulsion of claims 1 or 2 to 9, wherein said emulsion has a relationship of $J_1 > J_2$, wherein J_1 is
25 an average silver iodide content measured by fluorescent X-ray analysis, and J_2 is a grain surface silver iodide content measured by X-ray photoelectric spectroscopy.
11. The emulsion of claims 1 or 2 to 10, wherein said emulsion has a relationship of $J_1 > J_3$, wherein J_1 is
30 an average silver iodide content measured by fluorescent X-ray analysis, and J_3 is an average value of the measurements of silver iodide content measured by X-ray microanalysis on each silver halide crystal at its position distant by 80 % or more the center with respect to the direction of grain diameter of a silver halide grain.
12. The emulsion of claims 1 or 2 to 11, wherein said emulsion has a signal being continuously present
35 over 1.5 degrees or more of the diffraction angle, at maximum peak height $\times 0.13$ of a signal obtained by diffraction of (420) X-rays from the output of a ray source $\text{CuK}\alpha$ -rays.
13. The emulsion of claims 1 or 2 to 12, wherein an average silver iodide content of each silver halide
40 grains of said emulsion, is measured by X-ray microanalysis, and the relative standard deviation of the measurements of the silver halide grains is not more than 20 %.
14. The emulsion of claims 1 or 2 to 13, wherein a percentage of development start point in cross area
(%), is not less than 60 %.
15. A silver halide photographic light-sensitive emulsion comprising grains having twin planes, wherein not
45 less than 70 % of projected area of the whole grains are occupied by said grains having twin planes, and part or all of said grains having twin planes each have a start point of development at a cross point or the vicinity of said cross point, wherein said cross point is formed by a line formed by a twin plane border lying bare to the grain surface, which intersects an ridge line of the grain.

50

55

FIG. 1

GRAIN STRUCTURE

