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

(57) There is disclosed a silver halide photographic light sensitive material excellent in photosensitive speed and latent image preservability, comprising a silver halide emulsion characterized in that the silver halide grains having one or two development initiating points made present in each of the grains account for not less than 75% of the whole grain of the emulsion.

The term, 'development starting point' is recognized as a point at which a development is to be initiated. The points on a grain are preferable to be far away from each other, when two development points are made present in one and single grain.

The positions of the development initiating points are also preferable to be on the corner or edge of the grain and the neighborhood thereof. When the grain has twin plane(s), the development initiating positions are preferable to be either on a line formed by exposing the twin plane to the grain surface or in the neighborhood of the line.

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FIELD OF THE INVENTION

This invention relates to a silver halide photographic light sensitive material high in photosensitive speed and excellent in latent-image preservability.

BACKGROUND OF THE INVENTION

With the popularization of high-speed photographic light sensitive materials, picture-taking domain has been widened increasingly and pictures have readily been taken at present. On the other hand, there have often been the instances where it passes a long time from the day of taking pictures to the day of carrying out the development.

What the picture-taking domain has been widened results in the increase of the picture-taking frequency at under-exposure. High-speed photographic light sensitive materials have been still more demanded to avoid the above-mentioned increase.

In the case where it passes a long time from taking pictures to the development thereof, there arises a serious problem that a latent image produced by an exposure is faded out as time goes on, that is so-called a latent image fading. It is, therefore, one of the essential requirements for photographic light sensitive materials that a latent image preservability is to be excellent.

In the conventional techniques for making a photosensitivity, for example, the photosensitivity of tetradecahedral silver halide grains has been improved by making use of a compound (for example, a dye) having a characteristic of selectively working on a specific crystal face (the characteristic is hereinafter referred to as a face-selectivity) or by controlling a chemical sensitization to be caused on a specific face by making use of a sulfur sensitizer having a face-selectivity. Besides the above, there has been a proposal that tabular grains or octahedral grains are chemically sensitized in the presence of a silver halide-adsorptive material and the development starting points are controlled to be at the corner of the grains and in the neighborhood of the edge lines thereof, so that a photosensitivity and a graininess can be improved.

The above-mentioned conventional techniques are detailed in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP OPI Publication) Nos. 64-62631/1989, 64-62632/1989, 64-40938/1989, 64-74540/1989, 63-305343/1988, 64-77047/1989, 3-204633/1991 and so forth.

For the purpose of improving the photosensitivity relative to fog, silver halide grains such as those having each not more than 3 development initiating points in a certain development condition have been studied as disclosed in JP OPI Publication No. 3-204633/1991. However, these techniques are still not satisfactory from the viewpoints of improving both of a high photosensitivity and a latent image preservability.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a silver halide photographic light sensitive material high in photosensitivity and excellent in latent image preservability.

The above-mentioned object of the invention can be achieved with a silver halide photographic light sensitive material comprising a silver halide emulsion, wherein the silver halide emulsion contains silver halide grains having one or two development initiating points in each of the grains, accounting for less than 75% of the whole silver halide grain, based on number of grains.

DETAILED DESCRIPTION OF THE INVENTION

The silver halide emulsions relating to the invention may be those either having or not having a twin plane and the emulsions may also contain both of them. The emulsions may have any shapes including, for example, the so-called tabular, octahedral and tetradecahedral shapes. For more preferably displaying the effects of the invention, it is preferable to have a twinned-crystal plane.

The above-mentioned twin plane may be (111) twin plane, (100) twin plane or both of the above-mentioned two twin plane. Among them, the (111) twin plane is preferred. When each grain has not less than two twin planes, it is preferable that the twin planes are in parallel to each other. It is particularly preferable to be twinned crystal grains having each two parallel (111) twin planes (hereinafter abbreviated to 'parallel two-plane twinned crystal grains') are preferred.

In the case of the grains each having a twin plane, they may take any one of various shapes. However, in the case of parallel two-plane twinned crystal grains, it is preferred that the grains are tabular-shaped grains having each an aspect ratio of less than 3.0. The aspect ratios mentioned herein can be expressed as a ratio of the diameter of a circle correspondingly converted from a projected area (circular-equivalent diameter) to thickness of a tabular-shaped grain. The particularly preferable grains are twinned crystal grains having an aspect ratio within the range of 1.0 to 2.5. In the parallel two-plane twinned crystal grains having each an aspect ratio in the neighborhood of 1.0, the apparent shapes thereof are observed as the octahedron or one having the apices so scraped off as to be slightly distorted.

Concerning a tabular-shaped silver halide grain, the diameter thereof can be expressed by the diameter of a circle having the same projected area as that of the tabular-shaped silver halide grain when the same tabular-shaped silver halide grain is so oriented as to set horizontally the two principal planes facing each other to the plane. Such a diameter as mentioned above is to be within the range of, preferably 0.1 to 5.0μm, more preferably 0.2 to 4.0μm and particularly preferably 0.3 to 3.0μm.

In the silver halide emulsions relating to the invention, the grain size distribution is preferable to be monodispersive.

When making use of a monodispersive emulsion in the invention, the variation coefficient (v) is defined by the following formula;

v = (a standard diameter deviation/an average diameter)x100 = variation coefficient (%)

The variation coefficient (v) thus defined is preferably less than 20%, more preferably less than 18% and most preferably less than 15%.

The above-mentioned diameter can be obtained in the following manner that a silver halide emulsion containing the tabular-shaped silver halide grains of the invention is projected by magnifying 10,000 to 50,000 times through an electron microscope and the area of the grains projected on a print is practically measured, (provided that the numbers of the measured grains are to be not less than 1000 grains at random).

The silver halide emulsions relating to the invention may have any one of halogen compositions. However, the halogen compositions thereof are to be composed of silver iodobromide having an average silver iodide content within the range of, preferably 4 to 20 mol% and more preferably in particular 5 to 15 mol%.

When making use of a silver iodobromide emulsion, it is allowed to contain silver chloride, provided that the effects of the invention shall not be spoiled.

When making use of a core/shell type silver halide emulsion in the invention, the silver halide emulsion grains are to have a high silver iodide containing phase inside the grains thereof.

The silver iodide content of the high silver iodide containing phase is to be within the range of, preferably 15 to 45 mol%, more preferably 20 to 42 mol% and particularly preferably 25 to 40 mol%.

The silver halide grains relating to the invention and having a high silver iodide containing phase inside the grains are those comprising a high silver iodide containing phase covered by the other lower silver iodide containing phase having a silver iodide content lower than that of the former high silver iodide containing phase.

When an outer phase has a silver iodide content lower than in the other high silver iodide containing phase, the average silver iodide content of the outer phase is preferably not higher than 6 mol% and preferably in particular within the range of 0 to 4 mol%. It is also allowed to interpose a further silver iodide containing phase (that is called an intermediate phase) between the outer phase and the high silver iodide containing phase.

The silver iodide content of the intermediate phase is to be within the range of, preferably, 10 to 22 mol% and, more preferably in particular, 12 to 20 mol%.

Between the outermost phase and the intermediate phase and between the intermediate phase and the inside high silver iodide containing phase, the silver iodide contents are preferable to have a difference of not less than 6 mol% and preferable in particular to have a difference of not less than 10 mol%, respectively.

In the above-described embodiment, a further separate silver halide phase may be made present in the central portion of the internal high silver iodide containing phase, between the internal high silver iodide containing phase and the intermediate phase and between the intermediate phase and the outermost phase.

The volume of the outermost phase may be within the range of, preferably 4 to 70 mol% of the whole volume of the grain and, more preferably 10 to 50 mol% thereof. The volume of the high silver iodide containing phase is to be within the range of, preferably 10 to 80% of the whole volume of the grain, more preferably 20 to 50% thereof and, further preferably 20 to 45% thereof. The volume of the intermediate phase is to be within the range of, preferably 5 to 60% of the volume of the whole grain and, more preferably 20 to 55% thereof.

The above-mentioned phases may also be any one of a single phase having a uniform composition, the group consisting of the plural phases each having a uniform and stepwise varying composition, a continuous phase having a continuously varying composition in any desired phase and the combinations thereof.

The other embodiments of the silver halide emulsions of the invention include an embodiment in which silver iodide localized inside the grain does not form any substantially uniform phase, but the silver iodide content changes continuously from the center of each grain toward the outside. In this case, it is preferable that the silver iodide content is reduced monotonously from the point having a maximum silver iodide content inside the grain toward the outside of the grains.

At the point where the silver iodide content can be maximized, the silver iodide content is to be within the range of, preferably 15 to 45 mol% and, more preferably 25 to 40 mol%.

The silver iodide content in the grain surface phase is to be, preferably not more than 6 mol% and, more preferably within the range of 0 to 4 mol%.

The silver halide emulsions of the invention are preferable to satisfy at least one of the following requirements (1) through (4).

(1) When comparing an average silver iodide content (J_1) determined by X-ray fluorescence analysis to a grain surface silver iodide content (J_2) determined by X-ray excited photoelectron spectroscopy (hereinafter sometimes abbreviated as XPS), the relation of $J_1 > J_2$ is to be satisfied.

Now, the above-mentioned XPS will be detailed.

In advance of an XPS measurement, an emulsion is pretreated as follows. First, a pronase solution is added to the emulsion and the resulting mixture is stirred at 40°C for one hour to hydrolyze gelatin. Next, the emulsion grains are so centrifuged as to be precipitated. After the resulting supernatant liquid is removed, an aqueous pronase solution is added thereto and another gelatin hydrolysis is then carried out again under the above-mentioned conditions. The resulting sample is centrifuged again and, after the supernatant liquid is removed, distilled water is added to disperse the emulsion grains again in distilled water. The resulting dispersion is centrifuged and the supernatant liquid is removed. After the above-mentioned washing treatment is repeated three times, the emulsion grains are redispersed in ethanol. The resulting dispersion is thinly coated over a specularly-polished silicon wafer, so that a sample subject to measurement can be prepared.

The above-mentioned XPS measurements are carried out, for example, by making use of Model ESCA/SAM 560 manufactured by PHI Co. and under the conditions of Mg-Kα rays as the excitation X-rays, 15Kv of the X-ray source voltage, 40mA of the X-ray source current and 50eV of the pass energy.

For determining a surface halide composition, Ag3d, Br3d and I3d3/2 electrons are detected. The composition ratios are calculated from the integrated intensities of each peak and by making use of a relative photosensitive speed coefficient method. As the relative photosensitive speed coefficients of Ag3d, Br3d and I3d3/2, 5.10, 0.81 and 4,592 are used, thereby the composition ratios can be given by an atomic percentage as the unit, respectively.

(2) An average silver iodide content (J_1) is obtained in the aforementioned X-ray fluorescence analysis and an average silver iodide content (J_3) is measured, in an X-ray microanalysis, on a silver halide crystal 80% or more apart from the center in the grain diameter direction of a silver halide grain. The term, 'diameter', stated herein means the diameter of a circle circumscribed with a grain where the projected area of the grain can be maximized. When comparing the resulting (J_1) to (J_3), the relation of $J_1 > J_3$ is to be satisfied.

Now, the X-ray microanalysis will be detailed. Silver halide grains are dispersed to a grid for electron-microscopic observation use equipped with an electron microscope to which an energy-dispersion type X-ray analyzer was attached. The magnification is set so that one grain can be made to come within the range of the electron microscope by a liquid nitrogen cooling treatment. The intensities of AgLα and ILα rays are integrated for a certain time. A subject silver iodide content can then be calculated out by making use of the intensity ratio of the AgLα rays/the ILα rays and a calibration curve made out in advance.

(3) It is to be characterized in that a series of signals is made present continuously extending over not less than 1.5 degrees of the diffraction angle (2θ), at a height of 0.13 x the maximum peak of (420) diffraction signal when X-ray diffractometry is made using CuKα rays as the radiation sources are set to be. It is further preferable when the signals are made present continuously extending over not less than 1.5 degrees of the diffraction angle, at a height of 0.15 x the maximum peak of the signals. It is further preferable when the diffraction angles within which the signals are made present are extended over not less than 1.8 degrees. It is particularly preferable when the signals are made present extending over not less than 2.0 degrees. The expression, 'signals are made present', means that a subject signal intensity

is greater than at a height of 0.13 or 0.15 x the maximum peak.

Another preferable embodiment of the silver halide emulsions of the invention is that the above-mentioned (420) X-ray diffraction signal, in which CuKα rays are used as the radiation source, have two or three peaks and, more preferably in particular, three peaks.

As for the methods of investigating the structures of silver halide crystals, an X-ray diffraction method has been known.

As for the X-ray radiation sources, any X-rays having a variety of characteristics can be used. Among them, CuKα rays targeting for Cu have been used most popularly.

Silver iodobromide has a rock-salt structure and the (420) diffraction signal made out by CuKα rays is observed at an angle within the range of 71 to 74 degrees (2θ). As the signal intensity thereof is relatively strong and at a high angle, the resolving power is also excellent and it is optimum for investigating crystal structures.

When measuring the X-ray diffraction of a photographic emulsion, it is desired to remove gelatin and a standard sample such as silicon is mixed in, so that the measurement can be carried out in a powder method.

The methods of the measurements may be carried out with reference to "Kiso Bunsekikagaku Koza, 24 X-sen Bunseki" ("The Course of Basic Analytical Chemistry", 24, 'X-ray Analysis'), published by Kyoritsu Publishing Co. and so forth.

(4) When measuring each of the average silver iodide contents of individual silver halide grains in the above-mentioned X-ray microanalysis, the relative standard deviations of the measured values are each not more than 20%, preferably not more than 15% and, particularly not more than 12%.

The term, 'a relative standard deviation', stated herein shall be defined as a value (obtained as follows) x 100. When measuring the silver iodide contents of at least 100 emulsions, for example, the above-mentioned value can be obtained by dividing the standard deviation of the subject silver iodide contents by the average silver iodide content.

In the silver halide grains applicable to the color light sensitive materials of the invention, the requirement for growing the grains may be any one of acidic method, neutral method and ammoniacal method. It is allowed to use the known methods including, for example, those described in JP OPI Publication Nos. 61-6643/1986, 61-14630/1986, 61-112142/1986, 62-157024/1987, 62-18556/1987, 63-92942/1988, 63-151618/1988, 63-1613451/1988, 63-220238/1988 and 63-311244/1988.

When forming the silver halide grains applicable to the invention, a method of adding an aqueous solution of the water-soluble iodide may be used as one of the iodide supply methods. The grains can also be grown up in an Ostwald ripening treatment after adding it in the forms of fine silver halide grains (such as silver iodide or silver iodobromide). It is further preferable to use a method of supplying it in the form of fine silver halide grains.

When growing the silver halide grains of the invention, any known silver halide solvents such as ammonia, thioether and thiourea can be made present. It is further allowed to use a crystal-form controller.

A metal ion may be added to the above-mentioned silver halide grains in the courses of forming and/or growing the grains by making use of at least one selected from the group consisting of cadmium salts, zinc salts, the complex salts thereof, thallium salts including the complex salts thereof, iridium salts, rhodium salts and iron salts, so that the above-mentioned metal element can be contained in the inside of the grains and/or on the surfaces of the grains. When putting the grains in suitable reducible atmospheric conditions, reduction-sensitization nuclei can be provided to the inside of the grains and/or the surfaces of the grains.

From the above-mentioned silver halide emulsions, unnecessary soluble salts can be removed after completing the growth of the silver halide grains or they may still remain contained therein even thereafter. When removing the salts, it is possible to remove them according to the method described in Research Disclosure (hereinafter abbreviated to RD), No. 17643, Article 11.

The term, 'a development initiating point', is recognized as a point at which a development is initiated by developing silver halide grains, development-stopping and thereafter observing them. To be more concrete, it can be specified as follows.

To specify a development initiating point on grains, a light sensitive material comprising a support coated thereon with an photographic emulsion is treated as follows.

The light sensitive material is exposed to light and then developed with Kodak MAA-1 developer as below. The characteristic curve is made out of the resulting developed light sensitive material.

Metol-ascorbic acid developer (MAA-1)	
N-methyl para-aminophenol sulphate (Metol),	2.5 g
Ascorbic acid,	10.0 g
Potassium bromide,	1.0 g
Sodium metaborate ("Kodalk" alkali),	35.0 g
Distilled water to make	1 liter

Next, an exposure is made to light in an amount of 50 times as much as the exposure amount necessary to give the maximum density in the above-mentioned characteristic curve. Then, a development is carried out at 20 ° C by making use of Developer A such as shown below. The development has initiated and thereafter the light sensitive material is dipped in a 3% acetic acid solution to stop the development.

Developer (A)	
P-aminophenol methyl hydrogen sulfate	0.28 g/liter
Ascorbic acid	2.8 g/liter
Sodium metaborate tetrahydrate	4.0 g/liter
KBr	1.0 g/liter
Sodium-di(2-ethylhexyl)sulfosuccinate	0.1 g/liter
H_2O	1000 cc

The development processing requirements for specifying the development initiating point can suitably be so selected as to make the initiation point observation easier. In particular, the developing conditions are to be set so that developed silver may be grown up with developer (A) to have some extent of the length, so that the developed silver can be discriminated from a little bit of print-out silver produced in the course of an electron microscopic observation.

There is no limitation to the location of the development initiating point on a grain. When there are two development-initiating points on a single grain, it is preferable to locate each point as farther as possible.

The development initiating point(s) is preferable to be located at the corner or edge of grains, or in the neighborhood thereof.

When a grain has a twin plane, the development initiating point(s) is preferable to be located on a line formed by exposure of the twin plane in the surface of the grain, or in the neighborhood thereof.

The ratio of the grains having each one or two development-initiating points to the whole grains is preferably not less than 75% and, more preferably, not less than 85%.

In the invention, when a silver halide emulsion is chemically ripened, the pAg during the ripening treatment is within the range of, preferably not less than 8 and not more than 12, more preferably not less than 9 and not more than 11 and, particularly not less than 9.5 and not more than 10.5.

The temperature during the ripening treatment is within the range of, preferably not lower than 50 ° C and not higher than 75 ° C and, more preferably not lower than 60 ° C and not higher than 70 ° C.

The silver halide emulsions of the invention can be spectrally sensitized by making use of a sensitizing dye, and the emulsions can also be chemically sensitized.

The silver halide emulsions of the invention are preferable to be chemically sensitized in the presence of a sensitizing dye and, more preferably in the presence of not less than two kinds of sensitizing dyes.

When applying a chemical sensitizing treatment, it is preferable that a silver halide solvent is made present at the initial point of time for the chemical sensitizing treatment.

When applying a chemical sensitizing treatment to the silver halide emulsions of the invention, any known treatment methods such as a sulfur sensitizing method, a selenium sensitizing method, a reduction-sensitization method and a gold sensitizing method can be used, and these sensitizing methods may be used independently or in combination.

The above-mentioned gold sensitizing method is one of the typical noble-metal sensitizing methods. In this method, gold compounds including typically a gold complex salt are used. The preferable gold sensitizers include typically chloroauric acid and the salts thereof. It is also useful that a gold sensitization is enhanced by making combination use of thiocyanate. It is also allowed that the complex salts of other noble metals than gold, such as platinum, palladium and iridium, are used independently or in combination as a gold sensitizer. The concrete examples thereof are given in U.S. Patent No. 2,448,060, British Patent No. 618,061 and so forth.

The chalcogenite sensitizers applicable thereto include, for example, sulfur compounds contained in gelatin and, besides, various sulfur compounds such as inorganic sulfur compounds, e.g., thiosulfates, thioureas, thiazoles and rhodanines, a dithiacarbamic acid derivative, selenourea and tellurourea. The concrete examples are given in U.S. Patent Nos. 1,574,944, 2,278,947, 2,410,689, 2,728,668, 3,501,313 and 3,656,955.

Organic sulfur sensitizers including particularly thiourea type sulfur sensitizers are preferable for chemically sensitizing the silver halide emulsions of the invention. The compounds preferable for the thiourea sensitizers include, for example, the exemplified compounds given in JP OPI Publication Nos. 55-45016/1980, 58-80634/1983, 62-196645/1987 and 1-114839/1989.

The reduction sensitizers applicable thereto include, for example, stannous salts, amines, formamidine sulfinic acid and silane compounds.

The combination use of a sulfur sensitizer and a gold sensitizer is preferable for effectively displaying the advantages of the invention.

The sulfur sensitizers are used in an amount, that is converted into the active sulfur content, within the range of, preferably 1×10^{-7} mols to 1×10^{-4} mols and, further preferably, 1×10^{-6} mols to 5×10^{-5} mols, each per mol of silver halide used.

The gold sensitizers are used in an amount within the range of, preferably 1×10^{-7} mols to 1×10^{-4} mols and, further preferably 5×10^{-7} to 5×10^{-5} mols, each per mol of silver halide used.

When making combination use of a sulfur sensitizer and a gold sensitizer, the ratio of the former to the latter is preferably within the range of 3:1 to 1:1.

When making combination use of a sulfur sensitizer and a gold sensitizer, they may be mixed up together and then added or they may be added separately. It is preferable to add them separately. When adding them separately, they may be added at the same time or may also be added one first and then the other next. The effects of the invention can more advantageously be displayed when a sulfur sensitizer is added first.

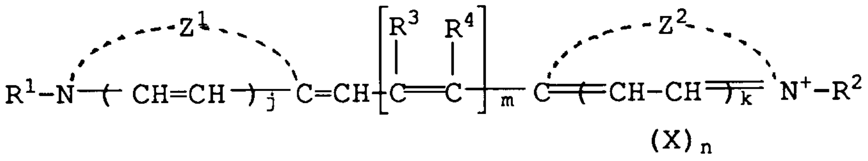
When chemically sensitizing the emulsions of the invention, it is allowed to make present the so-called silver halide solvent such as a thiocyanate, a thioether compound, thiazolidinethione and quadrisubstituted thiourea, when carrying out a chemical sensitization. Among them, thiocyanates, tetra-substituted thiourea and thioether are preferable solvents. These silver halide solvents may be made present when carrying out a chemical sensitization or any points of time. However, it is particularly effective to make them present before the chemical sensitization.

To the silver halide emulsions of the invention, a spectrally sensitizing dye is preferable to be added thereto, for the purpose of providing a spectral sensitivity to a desired light wavelength region.

The spectrally sensitizing dyes applicable thereto include, for example, a variety of dyes such as cyanine, merocyanine, holopolar cyanine, compounded cyanine, compounded merocyanine, oxonol, hemioxonol, styryl, merostyrol, streptocyanine and the group consisting of polymethine dyes containing pyrylium. Among them, cyanine dyes are particularly preferable.

The cyanine dyes preferably applicable thereto are represented by the following Formula [I].

Formula [I]



$$R^1-N\left(CH=CH\right)_j C=CH\left[\overset{R^3}{C}=\overset{R^4}{C}\right]_m C\left(=CH-CH\right)_k=N^+-R^2 \quad (X)_n$$

In the formula, Z^1 and Z^2 represent each the group consisting of the atoms necessary to form a heterocyclic nucleus.

The cyanine dyes represented by Formula [I] include S-1 through S-71 given in JP Application No. 3-231739/1991, in the upper right column of p.313 through the left lower column of p.318.

For performing a spectral sensitization with the above-mentioned sensitizing dyes, any commonly known methods may be used. To be more concrete, the following method may be used. A sensitizing dye is dissolved in a suitable solvent (that is methanol, ethanol, propanol, alcohol fluoride, 1-methoxyethanol, ethyl acetate, water or an aqueous acid or alkali solution having a suitable pH value) and, the resulting solution is adjusted to have a suitable concentration. The solution is then added into a silver halide emulsion or an aqueous hydrophilic colloid solution.

The above-mentioned solution is added in any desired step among the steps of preparing a silver halide emulsion. The preferred steps include, for example, a step before, during or after the silver halide grains are formed, a step during a physical ripening treatment, a step before, during or after a chemical ripening treatment and before or when a coating solution is prepared. It is regardless of the order for adding a stabilizer and an antifoggant, but they are preferable to be added when forming the grains or before a chemical sensitizing reaction is started in a chemical ripening treatment, thereby the chemical sensitization can be performed in the presence of a sensitizing dye (more preferably in the presence of two or more kinds of sensitizing dyes), so that the advantages of the invention can more effectively be displayed.

The above-mentioned sensitizing dyes may be used independently. It is, however, particularly effective when two or more kinds of sensitizing dyes are used in combination.

The amounts of the sensitizing dyes may be widely changed as the case may be. However, they are usually used in an amount within the range of, preferably $1x10^{-5}$ mols to $1x10^{-2}$ mols and, more preferably $1x10^{-4}$ mols to $1x10^{-3}$ mols, each per mol of silver halide used.

When spectrally sensitizing the silver halide emulsions of the invention, it is particularly preferable to add the spectrally sensitizing dyes in the combination capable of showing a supersensitization. As for the combination thereof capable of showing a supersensitization, two or more kinds of them are selected from the above-mentioned dyes so that they may be used in combination. Any compounds other than the above-mentioned compounds may be used as supersensitizers. For example, it is allowed to use a substance such as a dye that can be used together with sensitizing dyes, but does not have any spectrally sensitizing function in itself, or another substance incapable of substantially absorbing any visible rays of light, but capable of displaying a supersensitization.

The above-mentioned substances include, for example, aromatic organic acid formaldehyde condensates (such as those given in U.S. Patent No. 3,437,510), cadmium salts, azaindene compounds, and aminostilbene compounds each substituted with a nitrogen-containing heterocyclic group (such as those given in U.S. Patent Nos. 2,933,390 and 3,635,721). The combinations thereof given in U.S. Patent Nos. 3,615,613, 3,615,641, 3,617,295 and 3,635,721 are particularly useful.

It is preferable that the silver halide emulsions of the invention are chemically sensitized in the presence of the nitrogen-containing heterocyclic compounds described in JP OPI Publication No. 58-126526/1983. In particular, when a chemical sensitization is carried out in the presence of not less than two kinds of sensitizing dyes and the above-mentioned nitrogen-containing heterocyclic compound, the advantages of the invention can more effectively be displayed. The above-mentioned nitrogen-containing heterocyclic compound, that is to be applied thereto in the presence of two or more kinds of sensitizing dyes, is used in various amounts as the case may be. However, it may be ordinarily used in an amount within the range of, preferably $5x10^{-7}$ mols to $1x10^{-2}$ mols and, more preferably $1x10^{-6}$ mols to $1x10^{-3}$ mols, each per mol of silver halide used.

It is preferable that the silver halide fine grains, as described in JP Application No. 3-238444/1991, are added to the silver halide emulsion of the invention, in the course between a chemical ripening step and a coating step. It is particularly effective to use silver iodide grains.

When the average grain size of twinned crystal grains is regarded as d (μm), finely grained silver halide grains may be added in an amount of, preferably not more than 1/100d mols, more preferably within the range of 1/20000d to 1/300d mols and, most preferably 1/5000d to 1/500d mols, each per mol of the twinned crystal grains.

In the invention, a silver halide may be added at any point of time from a chemical ripening step to the point of time immediate before starting a coating step and, preferably during the chemical ripening step. It is particularly preferable to add finely grained silver halide before adding a sulfur sensitizer or within 30 minutes after adding the sulfur sensitizer.

For the purposes of stabilizing the emulsion characteristics and preventing any fog production, a stabilizer may be added to the silver halide emulsions of the invention.

The additives applicable to the above-mentioned steps are detailed in Research Disclosure Nos. 17643, 18716 and 308119 (hereinafter abbreviated to RD 17643, RD 18716 and RD 308119).

[Article]	[Page of RD 308119]	[RD 17643]	[RD 18716]
Antifoggant Stabilizer	998VI 998VI	24 to 25	649

The known photographic additives each applicable to the invention are also described in the above-given Research Disclosures.

The following table shows the places relevant thereto.

[Article]	[Page of RD 308119]	[RD 17643]	[RD 18716]
Color contamination preventive	1002 VII-I	25	650
Dye-image stabilizer	1002 VII-J	25	
Whitening agent	998 V	24	
UV absorbent	1003 VIIIC XIIIC	25 to 26	
Light absorbent	1003 VIII	25 to 26	
Light scattering agent	1003 VIII		
Filter dye	1003 VIII	25 to 26	
Binder	1003 IX	26	651
Antistatic agent	1006 XIII	27	650
Layer hardener	1006 X	26	651
Plasticizer	1006 XII	27	650
Lubricant	1006 XII	27	650
Activator • Coating aid	1005 XI	26 to 27	650
Matting agent	1007 XVI		
Developing agent (contained in light sensitive material)	1011 XXB		

When the silver halide emulsions of the invention are used in color photographic light sensitive materials, a variety of couplers may be used therein. The concrete examples of the couplers are detailed in the above-given Research Disclosures.

The following table shows the places relevant thereto.

[Article]	[Page of RD 308119]	[RD 17643]	[RD 18716]
Yellow coupler	1001 VII-D	VII C to G	
Magenta coupler	1001 VII-D	VII C to G	
Cyan coupler	1001 VII-D	VII C to G	
Colored coupler	1002 VII-G	VII G	
DIR coupler	1001 VII-F	VII F	
BAR coupler	1002 VII-F		
Other useful residual group	1001 VII-F		
Alkali-soluble coupler	1001 VII-E		

The additives applicable to the invention can be added in such a method as detailed in RD 308119, XIV.

In the invention, such a support as detailed in RD 17643, p.28, RD 18716, pp.647 to 648 and RD 308119, XVII can be used.

To the light sensitive materials of the invention, it can be provided with auxiliary layers such as a filter layer and an intermediate layer, as described in RD 308119, VII-K.

The light sensitive materials of the invention can have various layer-arrangements such as the regular, inverted and unit layer arrangements, as described in RD 308119, VII-K.

This invention can be applied to a variety of color light sensitive materials typified by color negative film for general or cinematographic use, color reversal film for slide or TV use, color paper, color positive film and color reversal paper.

The light sensitive materials of the invention can be developed in the ordinary processes described in RD 17643, pp.28 to 29, RD 18716, p.615 and RD 308119, XIX.

EXAMPLES

The invention will be detailed with reference to the following examples. It is, however, to be understood that the invention shall not be limited thereto.

Example 1

[Preparation of Emulsion Em-1]

According to the processes described in JP OPI Publication No. 3-228043/1991, silver halide emulsion Em-1 was prepared by making use of three kinds of aqueous solutions, an emulsion solution containing fine silver iodide grains, and seed grain emulsion (B), each detailed as follows.

Aqueous solution (b-1)	
Gelatin	231.9 g
A 10% methanol solution of compound [I] detailed below	30.0 ml
Aqueous ammonia (in a 28% solution)	1056 ml
Add water to make	11827 ml

Aqueous solution (b-2)	
$AgNO_3$	1587 g
Aqueous ammonia (in a 28% solution)	1295 ml
Add water to make	2669 ml

Aqueous solution (b-3)	
KBr	1572 g
Add water to make	3774 ml

Emulsion solution containing fine silver iodide grains (b-4)	
A finely grained silver iodide emulsion (detailed later)	1499.3 g
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	5.2 g
An aqueous 10% potassium hydroxide solution	14.75 ml
Add water to make	1373 ml

At a temperature of 60 °C, seed emulsion (B) in an amount equivalent to 0.407 mols was added to violently stirred aqueous solution (b-1) having the above-mentioned composition. The pH and pAg of the resulting solution were adjusted by making use of acetic acid and an aqueous KBr solution.

After that, while the pH and pAg were kept controlled as shown in Table 1, aqueous solutions (b-2) and (b-3) and emulsion solution (b-4) containing fine grains of silver iodide were each added thereto in a triple-jet method at the flow rates shown in Tables 2, 3 and 4, respectively.

After completing the addition thereof, an aqueous solution of phenyl carbamyl gelatin was added. The grains were precipitated and coagulated by controlling the pH of the resulting mixed solution and the desalting and washing treatments were then carried out. After that, the pH was adjusted to be 5.80 at 40 °C.

In the above-mentioned processes, a monodispersed silver iodobromide emulsion having an average grain size of 0.99μm, an average silver iodide content of 8.0 mol% and a grain size distribution of 11.2% was prepared. The resulting emulsion is herein named Em-1.

Table 1

Grain-growth conditions 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

wherein, → indicates that pH/pAg were kept constant,

↘ indicates that pH/pAg were lowered continuously, and

↓ indicates that pH &pAg were rapidly lowered.

Table 2

Pattern of adding (b-2)	
Time (min.)	Adding rate (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

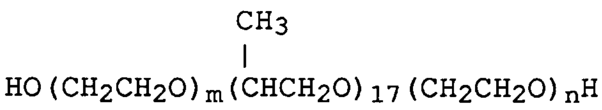
Table 3

Pattern of adding (b-3)	
Time (min.)	Adding rate (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	263.8
132.7	141.8
147.7	230.0

Table 4

Pattern of adding (b-4)	
Time (min.)	Adding rate (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

Compound [I]



$$\mathrm{HO(CH_2CH_2O)_m(\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2O)_{17}(CH_2CH_2O)_nH}$$

(Average molecular weight ≒ 1300)

[Preparation of seed emulsion (B)]

A silver iodobromide emulsion containing silver iodide in a proportion of 2.0 mol% was prepared in a controlled•double-jet method under the conditions of 40 ° C, pH8.0 and pAg 9.0. The resulting emulsion was then so washed as to remove the excessive salts therefrom.

The resulting grains were proved to have an average grain size of 0.335µm and a grain size distribution of 12.5%.

The resulting emulsion is herein named Seed Emulsion (B).

(Preparation of fine grain silver iodide emulsion)

An aqueous solution containing gelatin of 5 wt% was added into a reaction chamber, and 1 mol each of both aqueous 3.5N solutions of silver nitrate solution and potassium iodide solution were then added thereto at a fixed rate by taking a time for 30 minutes, with stirring at 40 ° C.

The pAg of the mixed solution was kept to be 13.5 during the addition of the solutions, by making use of an ordinary pAg controlling means.

The resulting fine grains of silver iodide were proved to be a mixture of β-AgI and γ-AgI having an average grain size of 0.06µm.

The resulting emulsion was made to contain silver in the amount equivalent to 400g of silver nitrate, and the emulsion was then prepared to be a finely grained silver iodide. The completed amount thereof was 4178 g.

[Preparation of Emulsion Em-2]

According to the method described hereunder, Emulsion Em-2 having an average silver iodide content of 8.0% was prepared by making use of each of the following solutions.

A_2	
Ossein gelatin	76.8 g
Potassium bromide	3.0 g
Disodium propyleneoxy•polyethyleneoxy• disuccinate	24 g
(A 10% methanol solution)	10 ml
Globular-shaped seed emulsion (A)	Equivalent to 0.191 mols
Nitric acid (having a specific gravity of 1.38)	4.5 ml
Add water to make	4.0 liters

B_{2-1}	
Silver nitrate	137.2 g
Nitric acid (having a specific gravity of 1.38)	3.3 ml
Add water to make	978 ml

C_{2-1}	
Ossein gelatin	39.1 g
Potassium bromide	62.4 g
Potassium iodide	46.8 g
Add water to make	978 ml

B_{2-2}	
Silver nitrate	137.7 g
Nitric acid (having a specific gravity of 1.38)	3.3 ml
Add water to make	982 ml

C_{2-2}	
Ossein gelatin	39.3 g
Potassium bromide	70.4 g
Potassium iodide	36.3 g
Add water to make	982 ml

B_{2-3}	
Silver nitrate	135.1 g
Nitric acid (having a specific gravity of 1.38)	1.4 ml
Add water to make	397 ml

C_{2-3}	
Ossein gelatin	15.8 g
Potassium bromide	75.6 g
Potassium iodide	26.4 g
Add water to make	397 ml

B_{2-4}	
Silver nitrate	758.4 g
Nitric acid (having a specific gravity of 1.38)	7.8 ml
Add water to make	2232 ml

C_{2-4}	
Ossein gelatin	89.3 g
Potassium bromide	526 g
Potassium iodide	7.41 g
Add water to make	2232 ml

By making use of the equipment described in JP OPI Publication No. 62-160128/1987, 6 pieces each of supply nozzles were provided respectively for supplying B_2 group solutions (which are used by switching B_{2-1} solution over to B_{2-3} solution and vice versa) and for supplying C_2 group solutions (which are used by switching C_{2-1} solution over to C_{2-3} solution and vice versa) to the lower part of the propeller of a mixing stirrer, so that the supply solutions could be split into 6 supply flows.

To the solution A_2 that was being stirred at 75 °C and 450 rpm, solutions B_{2-1} and C_{2-1} were each added in a double-jet method so that the addition rate thereof could be 11.62 ml/min at the beginning of the addition and 22.9 ml/min at the completion of the addition. The addition rate thereof during the addition was linearly increased to the adding time and the pAg thereof was kept at 8.3. After completing the addition of solutions B_{2-1} and C_{2-1}, the stirring speed was increased to 500 rpm.

In succession, solutions B_{2-2} and C_{2-2} were added to the above-mentioned stirred solution in a double-jet method so that the addition rate could be 22.91 ml/min at the beginning of the addition and 30.27 ml/min at the completion of the addition. The rate during the addition was increased linearly to the adding time and the pAg was kept at 8.3. After completing the addition of solutions B_{2-2} and C_{2-2}, the pAg was adjusted to be 8.6 with an aqueous 3.5N potassium bromide solution.

Next, solutions B_{2-3} and C_{2-3} were added to the above-mentioned stirred solution in a double-jet method so that the addition rate could be 16.71 ml/min at the beginning of the addition and 18.63 ml/min at the completion of the addition. The rate during the addition was increased linearly to the adding time and the pAg was kept at 8.6. After completing the addition of solutions B_{2-3} and C_{2-3}, the stirring speed was increased to be 550 rpm.

Further, solutions B_{2-4} and C_{2-4} were added to the above-mentioned stirred solution in a double-jet method so that the addition rate could be 41.19 ml/min at the beginning of the addition and 68.14 ml/min at the completion of the addition. The rate during the addition was increased linearly to the adding time and the pAg was kept at 8.6.

After completing the addition, the pH was adjusted to be 6.0 by making use of an aqueous (1.78N) potassium hydroxide solution and a desalting treatment was carried out in an ordinary method.

when the resulting emulsion was observed through an electron microscope, it was proved to have an average grain size of 1.24μm and a grain size distribution of 13.9%.

It was also proved that, of the twinned crystal grains having even-numbered twin plane of the resulting emulsion, the average ratio of the twinned crystal grain diameters to the thicknesses thereof was 2.9.

[Preparation of twinned crystal, monodisperse type emulsion Em-3]

Monodisperse type globular-shaped seed emulsion [A] was prepared in the following procedures.

A:	
Ossein gelatin	80 g
Potassium bromide	47.4 g
A 10% methanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	20 ml
Add water to make	8 liters

B:	
Silver nitrate	1.2 kg
Add water to make	1.6 liters

C:	
Ossein gelatin	32.2 g
Potassium bromide	840 g
Add water to make	1.6 liters

D:	
Aqueous ammonia	470 ml

Solutions B and C were added to solution A vigorously stirred at 40°C in a double-jet method by taking 11 minutes, so that the nuclei could be produced. In the courses thereof, the pBr was kept at 1.60.

After that, the temperature was lowered to 30°C by taking 12 minutes, and a ripening treatment was carried out for 18 minutes. Further, solution D was added thereto by taking one minute and another ripening treatment was successively carried out for 5 minutes. In the course of the ripening treatment, KBr concentration was 0.07 mols/liter and the ammonia concentration was 0.63 mols/liter.

After completing the ripening treatment, the pH was adjusted to be 6.0 and a desalting treatment was then carried out in an ordinary method. When the resulting seed emulsion was observed through an electron microscope, it was proved to be a globular-shaped emulsion having a couple of twin plane parallel to each other and an average grain size of 0.318µm. In the above-described procedures, the objective globular-shaped emulsion (A) could be prepared.

Octahedral, twinned crystal and monodisperse type emulsion Em-3 was prepared by making use of the following 7 kinds of solutions.

(Solution A)

Ossein gelatin	268.2 g
Distilled water	4.0 liters
A 10% methanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	1.5 ml
Seed emulsion [A]	0.286 mols
An aqueous 28 wt% ammonia solution	528.0 ml
An aqueous 56 wt% acetic acid solution	795.0 ml
A methanol solution containing iodine in an amount of 0.001 mols	50.0 ml
Add distilled water to make	5930.0 ml

(Solution B)

An aqueous 3.5N ammoniacal silver nitrate solution, (provided therein, the pH was adjusted to be 9.0 with ammonium nitrate)

(Solution C)

An aqueous 3.5N potassium bromide solution containing gelatin in a proportion of 4.0 wt%

(Solution D)

Fine grain emulsion comprising gelatin in a proportion of 3 wt% and silver iodide grains (having an average grain size of 0.05µm)	0.844 mols

The preparation procedures of Solution D will be detailed hereunder.

To 5000 ml of a 6.0 wt% gelatin solution containing potassium iodide in an amount of 0.06 mols, 2000 ml each of both of an aqueous solution containing 7.06 mols of silver nitrate and the other aqueous solution containing 7.06 mols of potassium iodide were added by taking 10 minutes. In the course of producing the fine grains, the pH was controlled to be 2.0 by making use of nitric acid and the temperature was controlled to be 40 ° C. After producing the grains, the pH was adjusted to be 6.0 by making use of an aqueous sodium carbonate solution.

(Solution E)

Fine grain emulsion comprising (an average grain size of 0.04µm) silver iodobromide grains each containing silver iodide content 1 mol%, that was prepared in the same manner as in the fine grains silver iodide emulsion of Solution D as described above, 2.20 mols, provided therein the temperature was controlled to be 3.0 ° C in the course of producing the fine grains.

(Solution F)

An aqueous 1.75N potassium bromide solution

(Solution G)

An aqueous 56 wt% acetic acid solution

To Solution A kept at 70 ° C in a reaction chamber, Solutions B, C and D were added by a double-jet method over a period of 163 minutes. Successively, Solution E was independently added at a constant rate over a period of 12 minutes, so that the seed crystals were grown up to be 1.0μm in an average size.

Solutions B and C were each added at an accelerated adding-rate to meet the critical growth rate and neither to produce any other smaller grains than the growing seed crystals nor to polydisperse the resulting emulsion in an Ostward ripening treatment. When supplying Solution D of a fine silver iodide grain emulsion, the addition rate ratio (mol ratio) thereof to the aqueous ammoniacal silver nitrate solution (Solution D) were changed in proportion to the grain sizes (or the adding time) as shown in the following Table 5. Thereby, a core/shell type silver halide emulsion having a multilayered structure was prepared.

By making use of Solutions F and G, the pAg and pH in the course of growing the crystals were controlled as shown in Table 5. The pAg and pH were measured in an ordinary method by making use of a silver sulfide electrode and a glass electrode.

After producing the grains, a desalting treatment was carried out in the method detailed in JP Application No. 3-41314/1991. Thereafter, gelatin was added thereto and then a dispersing treatment was carried out. The pH and pAg were adjusted to be 5.80 and 8.06 each at 40 ° C, respectively.

When the resulting emulsion grains were observed through an electron microscope, they were proved to be 100% twinned crystal grains and, more concretely, slightly distorted octahedral, twinned crystal, monodispersed grains each having not less than two parallel twin plane, a twinned crystal proportion of 85%, a grain size distribution of 10% and an average grain size of 1.0μm. Emulsion Em-3 was prepared as described above.

Table 5

	Adding time (min)	Grain size (μm)	Addition rate-ratio	pH	pAg
Internal 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

Emulsions Em-1 through Em-3 prepared in Example 1 were each subjected to the following chemical sensitization [A] through [D], so that Emulsions [1-A] through [3-D] could be prepared.

Chemical sensitization [A]

A part of Emulsion Em-1 was heated up to 65 ° C to be dissolved. Thereto added with sensitizing dyes (SD-1) in an amount of $1.2\text{x}10^{-4}$ mols, (SD-3) in an amount of $1.5\text{x}10^{-5}$ mols and (SD-2) in an amount of $1.4\text{x}10^{-4}$ mols, each per mol of silver halide used. Thirty (30) minutes thereafter, sodium thiosulfate pentahydrate in an amount of $3.4\text{x}10^{-6}$ mols was added and, further 10 minutes after, chloroauric acid in an amount of $3.6\text{x}10^{-6}$ mols and ammonium thiocyanate in an amount of $5.0\text{x}10^{-4}$ mols were mixedly added. A ripening treatment was then carried out for a suitable time.

When completing the ripening treatment, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added as a stabilizer and the resulting mixture was cooled down to be solidified, so that Emulsion [1-A] could be obtained.

By making use of Emulsions Em-2 and Em-3, Emulsions [2-A] and [3-A] were each obtained in the same manner as in the case of the above-described Emulsion [1-A].

Chemical sensitization [B]

A part of Emulsion Em-1 was heated up to 65 ° C to be dissolved and a KBr solution was added to the resulting solution to adjust the pAg to be 10. Thereto added with sensitizing dyes (SD-1) in an amount of $1.2\text{x}10^{-4}$ mols, (SD-3) in an amount of $1.5\text{x}10^{-5}$ mols and (SD-2) in an amount of $1.4\text{x}l0^{-4}$ mols, each per mol of silver halide used. Thirty (30) minutes thereafter, sodium thiosulfate pentahydrate was added in an amount of $2.0\text{x}10^{-5}$ mols and, further 10 minutes after, chloroauric acid in an amount of $3.6\text{x}10^{-6}$ mols and ammonium thiocyanate in an amount of $5.0\text{x}10^{-4}$ mols were mixedly added thereto. A ripening treatment was then carried out for a suitable time.

When completing the ripening treatment, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added as a stabilizer and the resulting mixture was cooled down to be set, so that Emulsion [1-B] was obtained.

By making use of Emulsions Em-2 and Em-3, Emulsions [2-B] and [3-B] were each obtained in the same manner as in the case of the above-described Emulsion [1-B].

Chemical sensitization [C]

A part of Emulsion Em-1 was heated up to 65 ° C to be dissolved. Thereto added with sensitizing dyes (SD-1) in an amount of $1.2\text{x}10^{-4}$ mols, (SD-3) in an amount of $1.5\text{x}10^{-5}$ mols and (SD-2) in an amount of $1.4\text{x}10^{-4}$ mols, each per mol of silver halide used. Thirty (30) minutes thereafter, 1-ethyl-3-thiazolylthioureawas added in an amount of $3.7\text{x}10^{-6}$ mols and, further 10 minutes after, chloroauric acid in an amount of $3.6\text{x}10^{-6}$ mols and ammonium thiocyanate in an amount of $5.0\text{x}10^{-4}$ mols were mixedly added thereto. A ripening treatment was then carried out for a suitable time.

When completing the ripening treatment, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added as a stabilizer and the resulting mixture was cooled down to be set, so that Emulsion [1-C] was obtained.

By making use of Emulsions Em-2 and Em-3, Emulsions [2-C] and [3-C] were each obtained in the same manner as in the case of the above-described Emulsion [1-C].

Chemical sensitization [D]

A part of Emulsion Em-1 was heated up to 65 ° C to be dissolved and a KBr solution was added thereto to adjust the pAg to be 10. Thereto added with sensitizing dyes (SD-1) in an amount of $1.2\text{x}10^{-4}$ mols, (SD-3) in an amount of $1.5\text{x}10^{-5}$ mols and (SD-2) in an amount of $1.4\text{x}10^{-4}$ mols, each per mol of silver halide used. Thirty (30) minutes thereafter, 1-ethyl-3-thiazolylthioureawas added in an amount of $3.7\text{x}10^{-6}$ mols and, further 10 minutes after, chloroauric acid in an amount of $3.6\text{x}10^{-6}$ mols and ammonium thiocyanate in an amount of $5.0\text{x}10^{-4}$ mols were mixedly added thereto. A ripening treatment was then carried out for a suitable time.

When completing the ripening treatment, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added as a stabilizer and the resulting mixture was cooled down to be set, so that Emulsion [1-D] was obtained.

By making use of Emulsions Em-2 and Em-3, Emulsions [2-D] and [3-D] were each obtained in the same manner as in the case of the above-described Emulsion [1-D].

[Preparation of Coated Samples of Single-layered Emulsion Layers]

Samples 101 through 112 were each prepared in the manner that Emulsions [1-A] through [3-D] prepared in the aforementioned procedures were coated and then dried on subbed triacetyl cellulose film supports in the following coating formula, respectively. In all the following examples of silver halide photographic light sensitive materials, the amounts of the materials thereof will be indicated in terms of grams per sq.meter, unless otherwise expressly stated. The silver halides used therein will be indicated in terms of the silver contents thereof.

[Coating Formula]

The coating treatments were carried out in the order from the support side. (The chemical formulas of the compounds used therein will be collectively given in Example 3.)

Layer 1	
Emulsion	2.0
High-boiling solvent (Oil-1)	0.15
Gelatin	1.5

Layer 2: A protective layer	
Gelatin	1.0

Besides the above-given compositions, coating-aid Su-1, dispersion-aid Su-2 and layer-hardener H-1 were each added.

[Sensitometric evaluation & Development starting point number measurement]

The resulting coated samples 101 through 112 were each exposed wegdewise to red light and were then developed at 20°C for 10 minutes with Kodak Formula MAA-1 developer. From the characteristic curves made out of the resulting developed samples, the minimum exposure amounts necessary to obtain the maximum densities were obtained, respectively.

Next, For observing the development-initiating points, coated samples 101 through 112 were each exposed to light respectively having the light quantities each 50 times as much as the minimum light quantities necessary to obtain the maximum densities each already obtained as mentioned above. The exposed samples were developed and stopped in the following processing steps.

Processing steps (at 20°C)	
Developing (with developer [A])	15min.00sec.
Stopping (in an aqueous 3% acetic acid solution)	2min.00sec.
Washing	5min.
Drying	

After completing the developing and development stopping treatments, the resulting samples were each gelatin-decomposed by making use of enzyme. The development initiating points were observed by observing the silver halide grains of each sample through a high-resolution scanning type electron microscope (Model S-900 manufactured by Hitachi, Ltd.).

Of 200 grains each of the samples, all the numbers of the development initiating points made present in each grain were counted and the ratios of the development initiating points made present in each grain were then obtained. The results thereof are shown in Table 6 given hereunder.

Table 6

Em No.	Development initiating point (%)					Remarks
	0	1	2	3≦	1 + 2	
101 [1-A]	20	22	23	35	45	Comparison
102 [1-B]	8	40	42	10	82	Invention
103 [1-C]	10	40	40	10	80	Invention
104 [1-D]	6	42	43	9	85	Invention
105 [2-A]	31	30	20	19	50	Comparison
106 [2-B]	11	45	40	4	85	Invention
107 [2-C]	10	43	37	10	80	Invention
108 [2-D]	7	45	45	3	90	Invention
109 [3-A]	15	33	32	20	65	Comparison
110 [3-B]	6	50	35	9	85	Invention
111 [3-C]	8	45	35	12	80	Invention
112 [3-D]	4	53	40	3	93	Invention

From the results shown in Table 6, it was proved that the emulsions of the invention were obtained by applying the chemical ripening treatments B, C and D to Emulsions Em-1 through Em-3.

EXAMPLE 3

[Preparation of Multilayer-coated Samples]

Multilayered color photographic light sensitive material samples 201 through 212 were each prepared by coating each of the layers having the following compositions in the order from the side of a triacetyl cellulose film-made support, wherein Emulsions [1-A] through [3-D] prepared in Example 2 were used as the high speed red-sensitive emulsions for Layer 5, respectively.

The amounts of each of the compositions added thereto will be indicated by grams per sq.meter. The colloidal silver amounts added thereto will be each indicated by the silver contents thereof. The sensitizing dye amounts added thereto will be indicated by mols per mol of the silver halides used therein.

Layer 1: An antihalation layer (HC-1)	
Black colloidal silver	0.16
UV absorbent (UV-1)	0.20
High-boiling solvent (Oil-1)	0.16
Gelatin	1.23

Layer 2: An intermediate layer	
Compound (SC-1)	0.15
High-boiling solvent (Oil-2)	0.17
Gelatin	1.27

Layer 3: A low-speed red-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.38μm and a silver iodide content of 8.0 mol%)	0.50
Silver iodobromide emulsion (having an average grain size of 0.27μm and a silver iodide content of 2.0 mol%)	0.21
Sensitizing dye (SD-1)	2.8×10^{-4}
Sensitizing dye (SD-2)	1.9×10^{-4}
Sensitizing dye (SD-3)	1.9×10^{-5}
Sensitizing dye (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

Layer 4: A medium-speed red-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.52μm and a silver iodide content of 8.0 mol%)	0.62
Silver iodobromide emulsion (having an average grain size of 0.38μm and a silver iodide content of 8.0 mol%)	0.27
Sensitizing dye (SD-1)	2.3×10^{-4}
Sensitizing dye (SD-2)	1.2×10^{-4}
Sensitizing dye (SD-3)	1.6×10^{-5}
Sensitizing dye (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	1.93

Layer 5: A high-speed red-sensitive layer	
Silver iodobromide emulsion that was prepared in Example 2)	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

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 (having an average grain size of 0.38µm and a silver iodide content of 8.0 mol%)	0.61
Silver iodobromide emulsion (having an average grain size of 0.27µm and a silver iodide content of 2.0 mol%)	0.20
Sensitizing dye (SD-4)	$7.4x10^{-5}$
Sensitizing dye (SD-5)	$6.6x10^{-4}$
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

Layer 8: A medium-speed green-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.59µm and a silver iodide content of 8.0 mol%)	0.87
Sensitizing dye (SD-6)	$1.6x10^{-4}$
Sensitizing dye (SD-7)	$1.6x10^{-4}$
Sensitizing dye (SD-8)	$1.6x10^{-4}$
Magenta coupler (M-1)	0.058
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

Layer 9: A high-speed green-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 1.00µm and a silver iodide content of 8.0 mol%)	1.27
Sensitizing dye (SD-6)	$9.4x10^{-5}$
Sensitizing dye (SD-7)	$9.4x10^{-5}$
Sensitizing dye (SD-8)	$9.4x10^{-5}$
Magenta coupler (M-2)	0.084
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)	0.12
Gelatin	1.00

Layer 10: A yellow filter layer	
Yellow colloidal silver	0.08
Color-stain preventive (SC-2)	0.15
Formalin scavenger (HS-1)	0.20
High-boiling solvent (Oil-2)	0.19
Gelatin	1.10

Layer 11: An intermediate layer	
Formalin scavenger (HS-1)	0.20
Gelatin	0.60

Layer 12: A low-speed blue-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.38µm and a silver iodide content of 8.0 mol%)	0.22
Silver iodobromide emulsion (having an average grain size of 0.27µm and a silver iodide content of 2.0 mol%)	0.03
Sensitizing dye (SD-9)	$4.2\text{x}10^{-4}$
Sensitizing dye (SD-10)	$6.8\text{x}10^{-5}$
Yellow coupler (Y-1)	0.75
DIR compound (D-1)	0.010
High-boiling solvent (Oil-2)	0.30
Gelatin	1.20

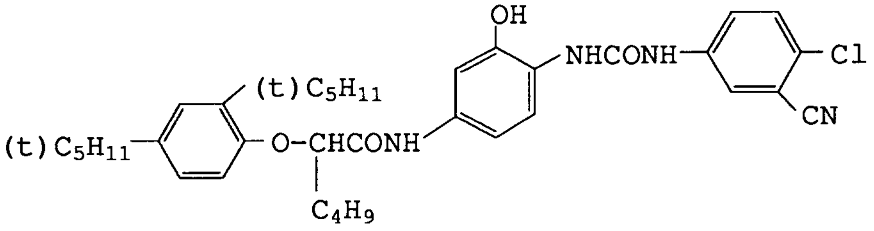
Layer 13: A medium-speed blue-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.59µm and a silver iodide content of 8.0 mol%)	0.30
Sensitizing dye (SD-9)	$1.6\text{x}10^{-4}$
Sensitizing dye (SD-11)	$7.2\text{x}10^{-5}$
Yellow coupler (Y-1)	0.10
DIR compound (D-1)	0.010
High-boiling solvent (Oil-2)	0.046
Gelatin	0.47

Layer 14: A high-speed blue-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 1.00µm and a silver iodide content of 8.0 mol%)	0.85
Sensitizing dye (SD-9)	$7.3\text{x}10^{-5}$
Sensitizing dye (SD-11)	$2.8\text{x}10^{-5}$
Yellow coupler (Y-1)	0.11
High-boiling solvent (Oil-2)	0.046
Gelatin	0.80

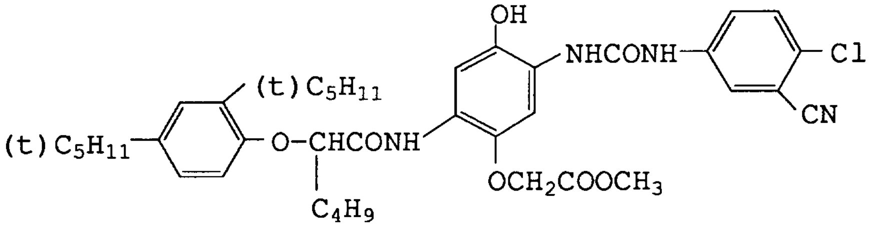
Layer 15: Protective layer 1	
Silver iodobromide emulsion (having an average grain size of 0.08µm and a silver iodide content of 1.0 mol%)	0.40
UV absorbent (UV-1)	0.026
UV absorbent (UV-2)	0.013
UV absorbent (UV-3)	0.013
UV absorbent (UV-4)	0.013
High-boiling solvent (Oil-1)	0.07
High-boiling solvent (Oil-3)	0.07
Formalin scavenger (HS-1)	0.40
Gelatin	1.31

Layer 16: Protective layer 2	
An 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

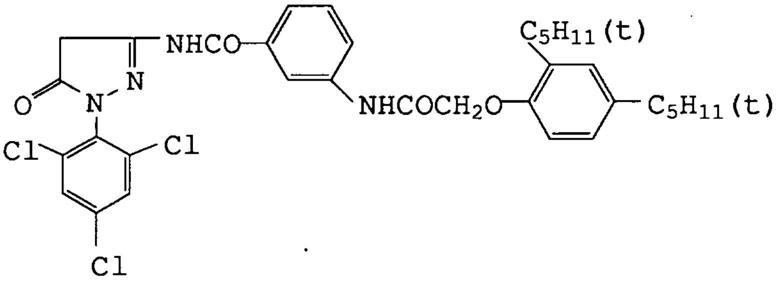
C-1



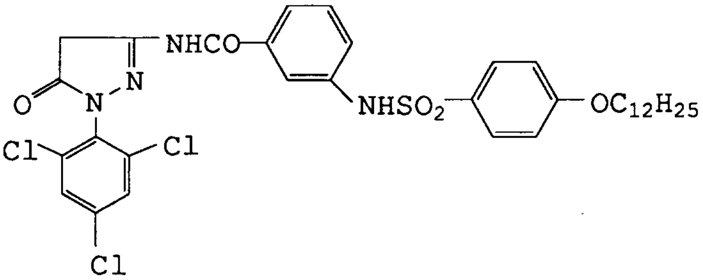
C-2



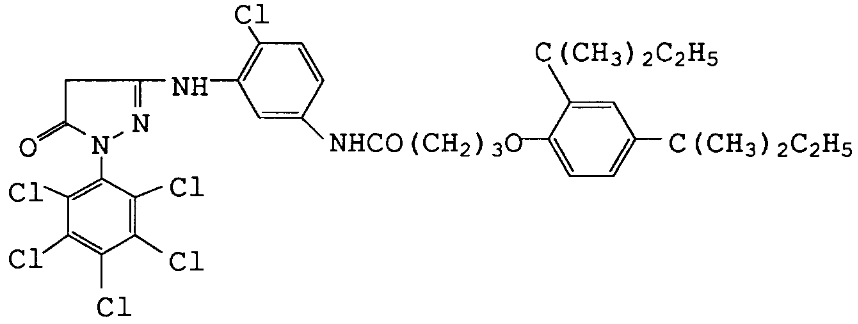
M-1



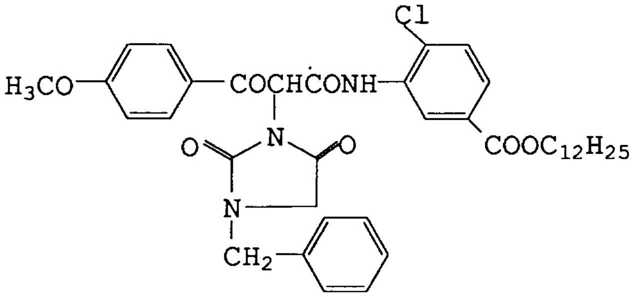
M-2



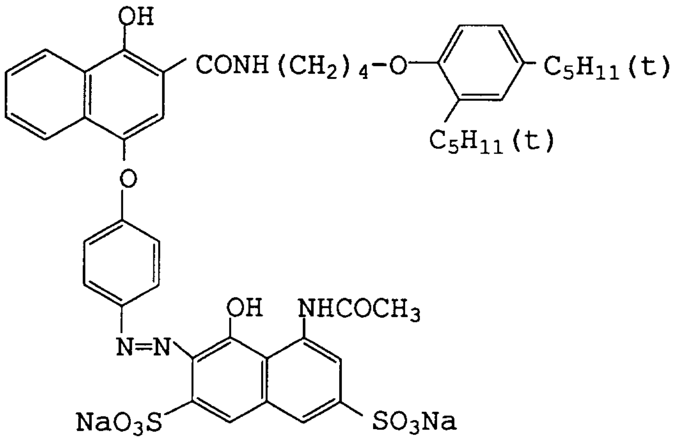
M-3



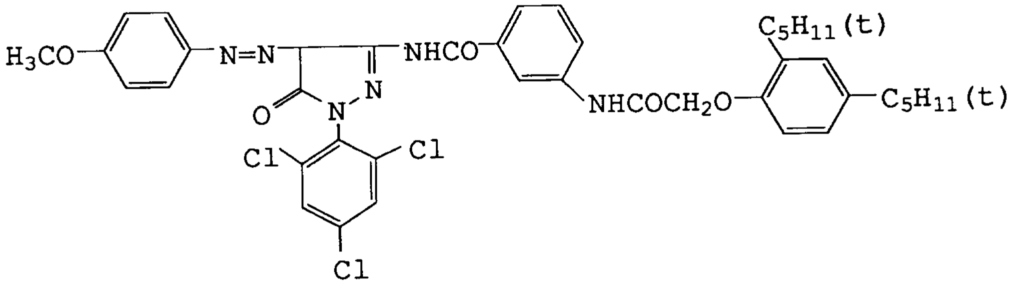
Y-1



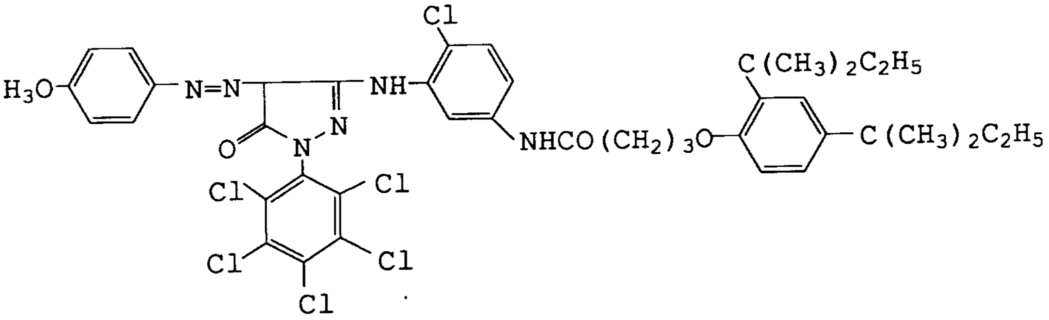
CC-1



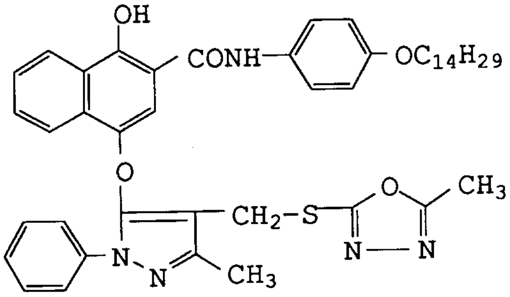
CM-1


H3CO
N=N
NHCO
N
N
O
Cl
Cl
Cl
C5H11(t)
NHCOCH2O
C5H11(t)

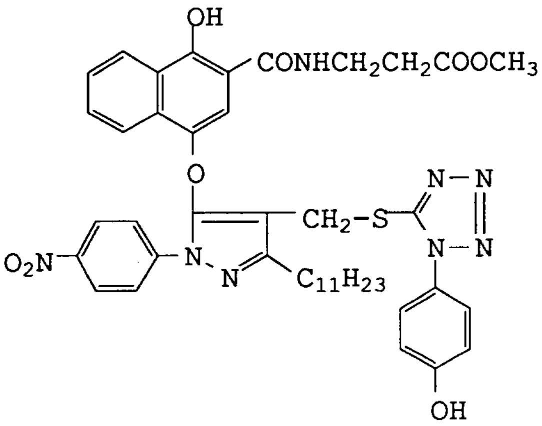
CM-2


H3O
N=N
NH
Cl
N
N
O
Cl
Cl
Cl
Cl
Cl
C(CH3)2C2H5
NHCO(CH2)3O
C(CH3)2C2H5

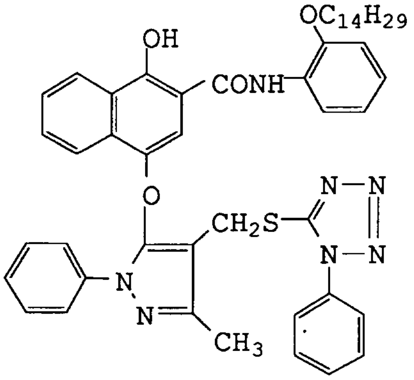
D-1


OH
CONH
OC14H29
O
CH2-S
O
CH3
N
N
N
N
CH3

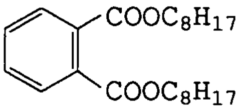
D-2



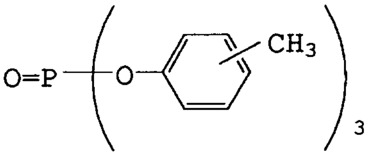
D-3



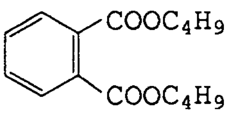
Oil-1



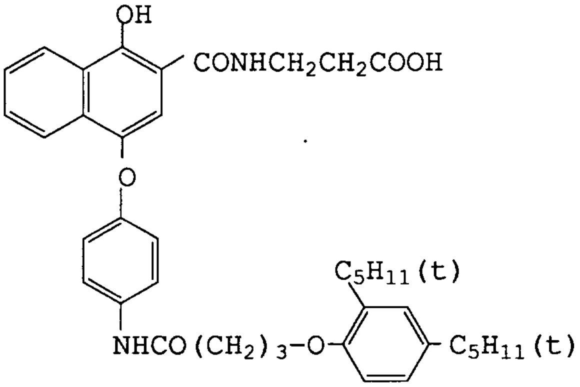
Oil-2



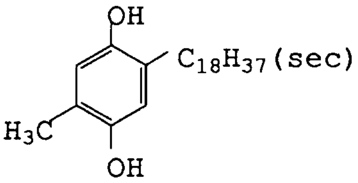
Oil-3



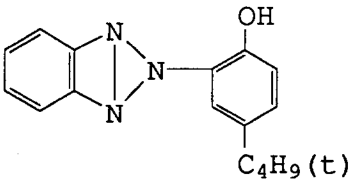
SC-1



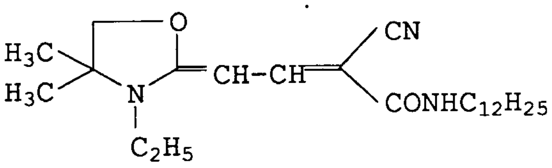
SC-2



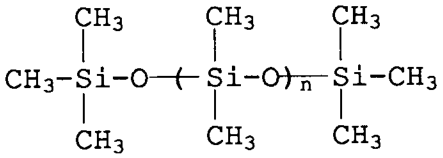
UV-1



UV-2



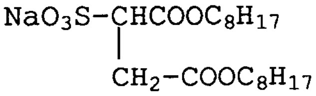
WAX-1



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-(\overset{CH_3}{\underset{CH_3}{Si}}-O)_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

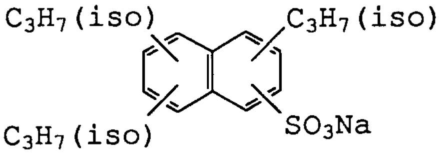
Weight average molecular weight $M_W = 3,000$

SU-1

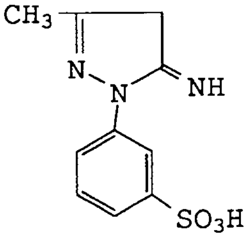


$$NaO_3S-\underset{CH_2-COOC_8H_{17}}{CHCOOC_8H_{17}}$$

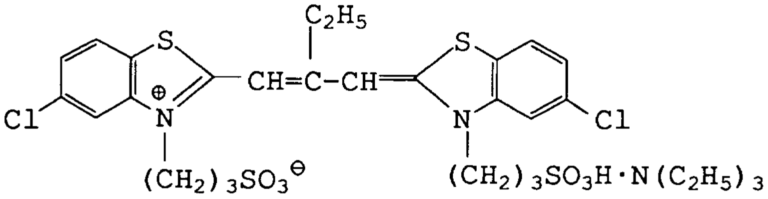
SU-2



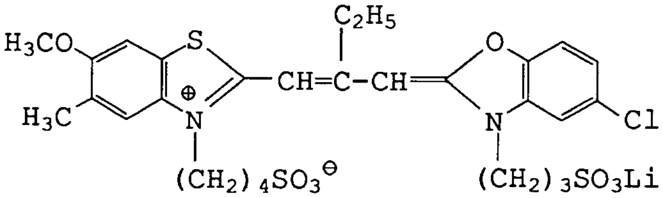
HS-1



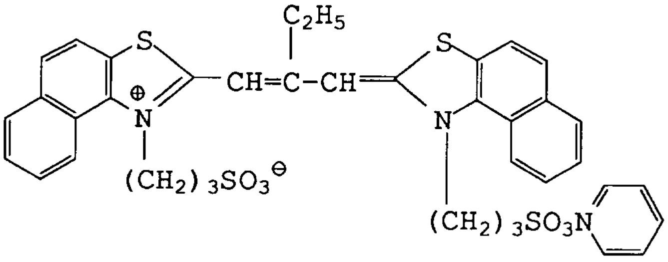
SD-1



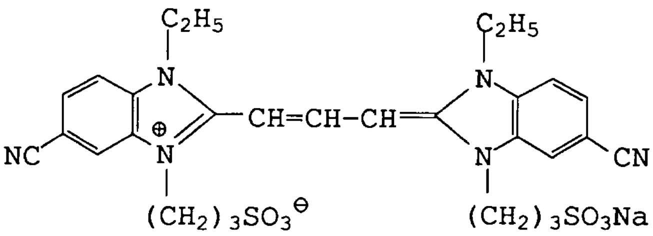
SD-2



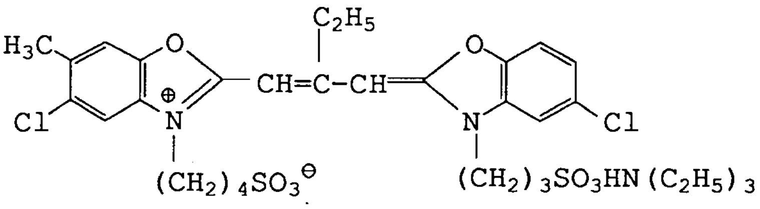
SD-3



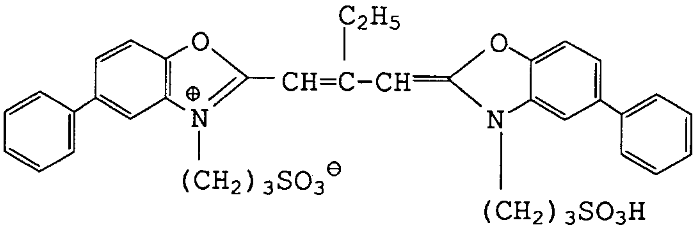
SD-4



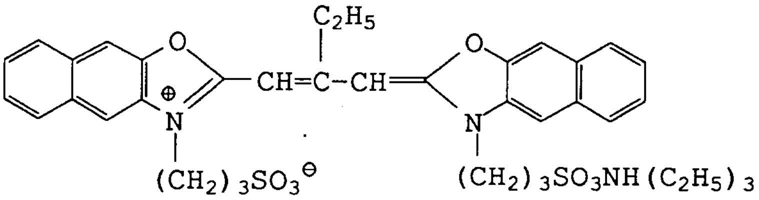
SD-5



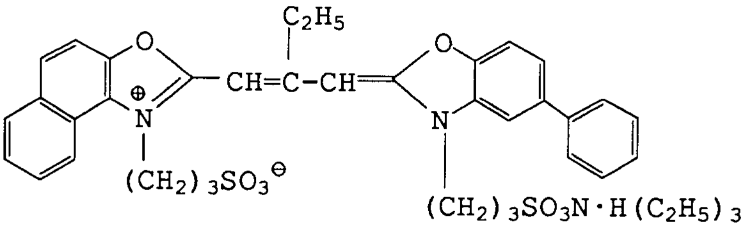
SD-6



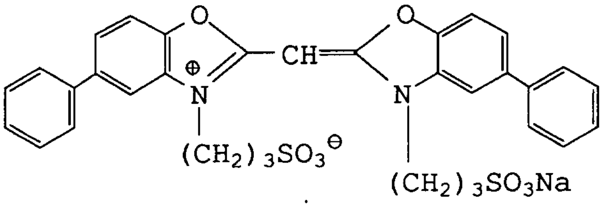
SD-7



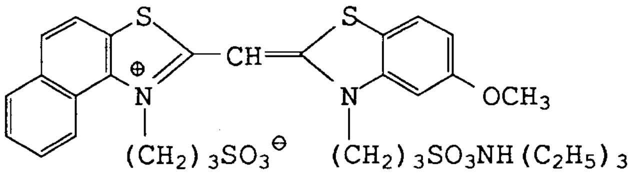
SD-8



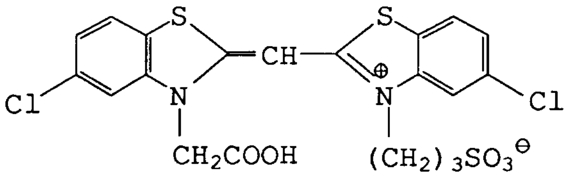
SD-9



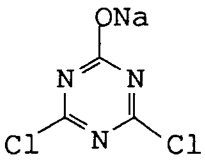
SD-10



SD-11



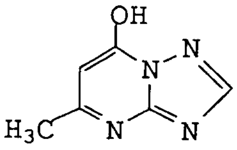
H-1



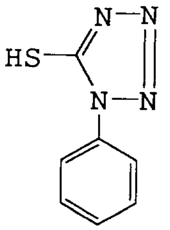
H-2

$(CH_2=CHSO_2CH_2)_2O$

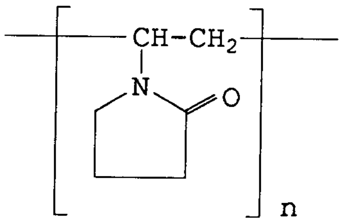
ST-1



AF-1

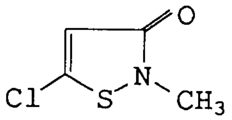


AF-2



n: Polymerization degree

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



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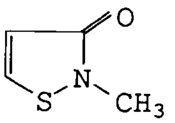

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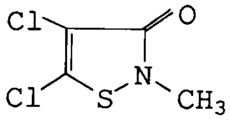

(Component A) (Component B) (Component C)

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

After exposing wedgewise the resulting coated samples 201 through 212 to red light, the samples were each treated in the following processing steps. The characteristic curves thereof were then made out to obtain the relative sensitivities (expressed by the relative values of the reciprocals of the exposure amounts capable of giving the densities of fog + 0.1).

Processing steps (at 38 ° C)	
Color developing	3min.15sec.
Bleaching	6min.30sec.
Washing	3min.15sec.
Fixing	6min.30sec.
Washing	3min.15sec.
Stabilizing	1min.30sec.
Drying	

The compositions of the processing solutions each 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, anhydrous	4.25 g
Hydroxyamine•$\frac{1}{2}$ sulfate	2.0 g
Potassium carbonate, anhydrous	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	10.0

[Bleach]	
Ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml
Add water to make	1 liter
Adjust pH with aqueous ammonia to be	6.0

[Fixer]	
Ammonium thiosulfate	175.0 g
Sodium sulfite, anhydrous	8.5 g
Sodium metasulfite	2.3 g
Add water to make	1 liter
Adjust pH with acetic acid to be	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

Further, 4 sets each of samples 201 through 212 were prepared and they were exposed wedgewise to light for 1/100th seconds. One set each thereof was preserved for 3 days under the conditions of 55°C and 55%RH, and another set each thereof was preserved for 30 days under the conditions of 23°C and 55%RH. The remaining two sets each thereof were preserved in a freezer as the control samples. They were developed in the same manner as mentioned above and were then evaluated on the latent image preservabilities.

The resulting latent image preservabilities thereof were expressed by the relative values of their photosensitive speeds so that the control photosensitive speeds of these samples were each regarded as a value of 100.

Table 7 shows the relative red sensitivities and those obtained after the latent images were each preserved.

Table 7

Sample No.	Relative speed*	Latent image preservability**		Remarks
		For 30 days at 23 °C/55%RH	For 3 days at 55 °C/55%RH	
201	100	77	70	Comparison
202	105	90	85	Invention
203	104	88	81	Invention
204	110	93	87	Invention
205	98	78	69	Comparison
206	111	96	86	Invention
207	105	92	82	Invention
208	115	98	88	Invention
209	100	78	70	Comparison
210	115	98	90	Invention
211	110	97	88	Invention
212	118	100	92	Invention

* : A relative speed when regarding the speed of sample 201 as a value of 100.
** : A relative speed when regarding the control speed of each sample as a value of 100.

From Table 7, it was proved that the samples of the invention each can be higher in photosensitive speed and superior in latent image preservability, as compared to the comparative samples, when the samples of the invention contain such an emulsion containing the silver halide grains having one or two development initiating points, in each of the grains, in an amount of not less than 75% of the whole grain of the emulsion.

EXAMPLE 4

Similar to the case of Example 2, samples 301 through 312 each provided with a single-coated layer were prepared by making use of the emulsions prepared in the same manners as in Samples 101 through 112, except that the sensitizing dyes were replaced by the sensitizing dyes used in Layer 9 of Example 3, respectively.

Similar to the case of Example 2, samples 401 through 412 each provided with a single-coated layer were prepared by making use of the emulsions prepared in the same manners as in Samples 101 through 112, except that the sensitizing dyes were replaced by the sensitizing dyes used in Layer 14 of Example 3, respectively.

When the development initiating points of Samples 301 through 312 and 401 through 412 were evaluated in the same manner as in Example 2, almost the same results were obtained as in Example 2.

EXAMPLE 5

Multilayered sample 501 was prepared by making use of the emulsion used in Layer 5 of Sample 209, the emulsion used in Layer 9 of Sample 309 and the emulsion used in Layer 14 of Sample 409, each prepared in Example 3.

Similar to the above, multilayered samples 502, 503 and 504 were each prepared by making use of the emulsion used in Samples 210, 310 and 410, the emulsion used in Samples 211, 311 and 411, and the emulsion used in Samples 212, 312 and 412, respectively.

In the same manner as in Example 3, the resulting photosensitive speeds and latent image preservabilities of the resulting 4 samples of this example were evaluated. It was resultingly proved that Samples 502 through 504 could get more excellent results of the photosensitive speeds and latent image preservabilities in the blue, green and red sensitive layers, as compared to Sample 501, respectively.

As described above, the silver halide photographic emulsions of the invention can display a high photosensitive speed and an excellent latent image preservability. The light sensitive material applied therewith can also similarly display the excellent advantages.

Claims

1. A silver halide photographic light sensitive material comprising a support having thereon a silver halide emulsion layer, wherein said silver halide emulsion contains silver halide grains having one or two development-initiating points in each of grains and accounting for at least 75% of total number of the grains.

2. The photographic material of claim 1, wherein said silver halide grains are twinned crystal grains.

3. The photographic material of claim 1, wherein said silver halide grains are silver iodobromide grains having a high iodide-containing phase in the internal portion.thereof.

4. The photographic material of claim 3, wherein said silver halide grains are prepared by supplying iodide in the form of silver iodide-containing fine grains.

5. The photographic material of claim 1, wherein said silver halide grains are chemically sensitized under the condition of pAg of 8 to 12.

6. The photographic material of claim 5, wherein said silver halide grains are chemically sensitized under the condition of pAg of 9 to 11.

7. The photographic material of claim 1, wherein said silver halide grains are chemically sensitized in the presence of a sensitizing dye.