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(54) Silver halide photographic emulsion and photographic light-sensitive material using the same.

(57) A silver halide photographic emulsion contains tabular silver halide grains consisting of silver chloroiodobromide, silver iodobromide, silver chlorobromide, or silver bromide, having an aspect ratio of 3 or more and at least one dislocation line per grain, and chemically sensitized by at least one selenium sensitizer, at least one gold sensitizer, and at least one sulfur sensitizer. A photographic light-sensitive material comprises at least one silver halide emulsion layer on a support, wherein tabular silver halide grains described above account for at least 50% of a total projected area of silver halide grains in the silver halide emulsion layer.

The present invention relates to a silver halide photographic emulsion and a photographic light-sensitive material using the same.

A dislocation of a silver halide grain is described in, e.g., C.R. Berry, J. Appl. Phys., 27, 636 (1956), C.R. Berry, D.C. Skillman, J. Appl. Phys., 35, 2165 (1964), J.F. Hamilton, Phot. Sci. Emg., 11, 57 (1967), T. Shiozawa, J. Soc. Phot. Sci. Japan, 34, 16 (1971), and T. Shiozawa, J. Soc. Phot. Sci. Japan, 35, 213 (1972). These references describe that dislocations in a crystal can be observed by an X-ray diffraction method or a cryo- transmission electron microscopic method and various types of dislocations are produced in a crystal by intentionally distorting the crystal.

Many attempts have been conventionally made to intentionally control and form dislocations in a tabular silver halide grain, thereby improving various photographic characteristics. JP-A-63-220238 ("JP-A-" means published unexamined Japanese patent application) discloses a method of forming dislocation lines on the circumferential surface of a tabular grain. JP-A-1-102547 discloses a method of forming dislocation lines on the major faces of a tabular grain.

JP-B-44-15748 ("JP-B-" means published examined Japanese patent application) discloses a photographic silver halide emulsion sensitized by at least two types of different sensitizers, i.e., a noble metal sensitizer and an unstable selenium sensitizer. JP-B-43-13489 discloses a photographic silver halide emulsion sensitized by at least three types of different sensitizers, i.e., a noble metal sensitizer, an unstable selenium sensitizer, and an unstable sulfur sensitizer.

Summary of the Invention

It is an object of the present invention to provide a silver halide photographic emulsion comprising tabular silver halide grains having dislocation lines and an average aspect ratio of 3 or more and preferably less than 8 and having increased sensitivity.

It is another object of the present invention to provide a selenium-sensitized emulsion which has a good strage stability and whose fog is low.

The above objects of the present invention can be achieved by the following photographic emulsion and photographic material.

(1) A silver halide photographic emulsion containing tabular silver halide grains consisting of silver chloroiodobromide, silver iodobromide, silver chlorobromide, or silver bromide, having an aspect ratio of 3 or more, having at least one dislocation line per grain, and having been chemically sensitized by at least one selenium sensitizer, at least one gold sensitizer, and at least one sulfur sensitizer.

(2) A silver halide photographic emulsion described in item (1) above, wherein the tabular silver halide grains have 10 or more of dislocation lines per grain.

(3) A photographic light-sensitive material comprising at least one silver halide emulsion layer on a support, wherein the tabular silver halide grains described in item (1) above account for at least 50% of a total projected area of silver halide grains contained in the silver halide emulsion layer.

(4) A photographic light-sensitive material described in item (3) above, wherein the silver halide grains accounting at least 50% of the total projected area of the silver halide grains contained in the silver halide emulsion layer are the tabular silver halide grains described in item (1) above having an average aspect ratio of 3 or more and less than 8.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Figs. 1 to 3 are electron micrographs (× 100,000) showing crystal features, of silver halide grains in emulsions prepared in Example 1, more specifically, Figs. 1, 2, and 3 are cryo-transmission electron micrographs of typical silver halide grains in emulsions A, C, and D, respectively; and

Figs. 4 and 5 are electron micrographs (× 100,000) showing crystal features of silver halide grains in emulsions prepared in Example 2, more specifically, Figs. 4 and 5 are cryo-transmission electron micrographs of typical silver halide grains in emulsions E and F, respectively.

The present invention will be described in detail below.

An emulsion of the present invention preferably consists of tabular silver halide grains having aspect ratios of 3 or more and preferably 3 to less than 8, and most preferably, 4 or more and 7 or less. The tabular grain is a general term representing grains having one twin a crystal face or two or more parallel twin crystal faces. When ions at all lattice points at two sides of a (111) face are in a mirror image relationship, this (111) face is called a twin crystal face. When this tabular grain is viewed from the above, the shape of the grain is a triangle, a hexagon, or a circle which is rounded triangle or rounded hexagon. Triangular, hexagonal, and circular grains have triangular, hexagonal, and circular parallel surfaces, respectively.

In the present invention, an average aspect ratio of tabular grains having a grain size of 0.1 μm or more is an average value of values obtained by dividing grain sizes of the grains by their thicknesses. The thickness of each grain can be easily measured as follows. That is, a metal is obliquely deposited on a grain and a latex as a reference, and the length of a shadow is measured on an electron micrograph, thereby calculating the thickness of the grain in accordance with the length of the shadow of the latex.

In the present invention, the grain size is a diameter of a circle having an area equal to a projected area of parallel surfaces of a grain.

The projected area of a grain can be obtained by measuring an area on an electron micrograph and correcting a photographing magnification.

The diameter of the tabular grain is preferably 0.15 to 5.0 μm. The thickness of the tabular grain is preferably 0.05 to 1.0 μm.

An average aspect ratio is obtained as an arithmetic mean of aspect ratios of at least 100 silver halide grains. The average aspect ratio can also be obtained as a ratio of an average diameter to an average thickness of grains.

An emulsion of the present invention contains tabular silver halide grains having an aspect ratio of 3 or more and preferably 3 to less than 8, and these tabular silver halide grains account for 50% or more of a total projected area.

A ratio of the tabular grains in the total projected area is preferably 50% or more, and most preferably, 80% or more.

More preferable result may be obtained by using monodisperse tabular grains. Although a feature and a method of manufacturing the monodisperse tabular grains are described in, e.g., JP-A-63-151618, the feature of the grain will be briefly described below. That is, 70% or more of the total projected area of silver halide grains are occupied by hexagonal tabular silver halide grains in which a ratio of the length of an edge having a maximum length to the length of an edge having a minimum length is 2 or less and which has two parallel faces as outer surfaces. The hexagonal tabular silver halide grains are monodisperse, i.e., have a variation coefficient (a value obtained by dividing a variation (standard deviation) in grain sizes represented by a circle-equivalent diameter of a projected area by an average grain size) in grain size distribution of 20% or less.

The emulsion of the present invention has a dislocation line. A dislocation of a tabular grain can be observed by a direct method using a transmission electron microscope at a low temperature as described in, e.g., J. F. Hamilton, Phot. Sci. Eng., 11, 57, (1967) or T. Shiozawa, J. Soc. Phot. Sci. Japan, 35, 213, (1972). That is, a silver halide grain extracted from an emulsion so as not to apply a pressure which produces a dislocation in the grain, is placed on a mesh for electron microscope observation, and observation is performed by a transmission method while a sample is cooled to prevent a damage (e.g., print out) caused by an electron beam. In this case, since it becomes difficult to transmit an electron beam as the thickness of a grain is increased, the grain can be observed more clearly by using a high-voltage (200 kV or more with respect to a grain having a thickness of 0.25 μm) electron microscope. By using photographs of grains obtained by this method, the positions and number of dislocations of each grain when the grain is vertically viewed with respect to the major faces can be obtained.

The number of dislocation lines is one or more per grain, preferably, an average of 10 per grain, and more preferably, an average of 20 per grain. When dislocation lines are concentrated or cross each other upon observation, the number of dislocation lines per grain may not be correctly obtained. In these cases, however, dislocation lines can be roughly counted to confirm that, e.g., 10, 20, or 30 lines are present, and the dislocation lines counted in this manner can be clearly distinguished from only several dislocation lines. An average number of dislocation lines per grain is obtained as a number average calculated by counting dislocation lines of 100 grains or more.

Dislocation lines can be formed, e.g., in the neiborhood of the circumferential of a tabular grain. In this case, the direction of dislocations are substantially perpendicular to the circumferened, and each dislocation line starts from a position corresponding to x% of a distance from the center to the edge (circumference) of the tabular grain and extends toward the circumferential. The value of x is preferably 10 to less than 100, more preferably, 30 to less than 99, and most preferably, 50 to less than 98. In these cases, although a shape obtained by connecting the start positions of the dislocations is similar to the shape of the grain, it is not perfectly similar but may be distorted. A dislocation of this type is not found in a central region of a grain. Crystallographic directions of dislocation lines are generally (211) orientation. The directions, however, are often zigzagged or sometimes cross each other.

Dislocation lines may be uniformly present throughout the entire circumference of a tabular grain or present locally on the circumference. That is, in a hexagonal tabular silver halide grain, for example, dislocation lines may be concentrated about either six corners or only one of the six corners. To the contrary, dislocation lines can be concentrated to only edges except for the six corners.

Also, dislocation lines can be formed throughout a region including the centers of two parallel major faces of a tabular grain. When dislocation lines are formed throughout the entire major faces, crystallographic directions of the dislocation lines viewed in a direction perpendicular to the major faces are sometimes (211) orientation and sometimes (110) orientation or formed at random. The length of each dislocation line is also randomly formed, i.e., the line is sometimes observed as a short line on the major face and sometimes observed as a long line reaching the edge (circumference). The dislocation line is sometimes a straight line but is often zigzagged. In many cases, dislocation lines cross each other.

As described above, positions of dislocations may be concentrated on the circumference, the major faces, or a local position, or dislocations may be formed on two or more locations thereof. That is, dislocations may be simultaneously present on the circumference and the major faces.

In order to form dislocation lines on the circumference of a tabular grain, a specific high silver iodide layer can be formed inside the grain. In this case, to form the high silver iodide layer may include to form a discontinuous high silver iodide region. More specifically, after a substrate grain is prepared, a high silver iodide layer is formed, and a layer having a silver iodide content lower than that of the high silver iodide layer is formed to cover the high silver iodide layer. A silver iodide content of the substrate tabular grain is lower than that of the high silver iodide layer, preferably, 0 to 20 mol%, and more preferably, 0 to 15 mol%.

The high silver iodide layer inside a grain is a silver halide solid solution containing silver iodide. In this case, the silver halide is preferably silver iodide, silver iodobromide, or silver chloroiodobromide, and more preferably, silver iodide or silver iodobromide (silver iodide content = 10 to 40 mol%).

The high silver iodide layer inside a grain (to be referred to as an inner high silver iodide layer hereinafter) can be selectively formed on the edge or corner of a substrate grain by controlling formation conditions of the substrate grain and formation conditions of the inner high silver iodide layer. As the formation conditions of the substrate grain, a pAg (a logarithm of a reciprocal of a silver ion concentration), the presence/absence, the type, and the amount of a silver halide solvent, and a temperature are important factors. When a pAg is set to be 8.5 or less and more preferably 8 or less during growth of substrate grains, the inner high silver iodide layer can be selectively formed about the corner of a substrate grain. When the pAg is set to be 8.5 or more and more preferably 9 or more, the inner high silver iodide layer can be formed on the edge of a substrate grain. The threshold value of a pAg is increased or decreased in accordance with the temperature and the presence/absence, the type, and the amount of a silver halide solvent. When thiocyanate is used as the silver halide solvent, the pAg threshold value is increased. As the pAg during growth, a pAg in a final stage of substrate grain growth is most important. Even if the pAg during growth does not satisfy the above value, a position of the inner high silver iodide layer can be controled by adjusting the pAg to be the above value after substrate grains are grown and ripening the grains. In this case, effective examples of the silver halide solvent are ammonia, an amine compound, and thiocyanate salt.

The inner high silver iodide layer can be formed by a so-called conversion method. This method includes a method of adding a halogen ion having lower solubility in salt for forming a silver ion than that of a halogen ion which currently forms a grain or a portion near the surface of a grain. In the present invention, a predetermined amount (according to a halogen composition) or more of halogen ions having low solubility is preferably added with respect to the surface area of currently formed grains. For example, during grain formation, a predetermined amount or more of KI is preferably added with respect to the surface area of currently formed AgBr grains. More specifically, 8.2×10^{-5} mol/m^2 of iodide salt are preferably added.

A more preferable method of forming an inner high silver iodide layer is a method of adding an aqueous silver salt solution simultaneously with addition of an aqueous halide salt solution containing iodide salt.

For example, an aqueous $AgNO_3$ solution is added by double jet simultaneously with addition of an aqueous KI solution. In this case, addition start timings and addition end timings of the aqueous KI solution and the aqueous $AgNO_3$ may be shifted from each other. An addition molar ratio of the aqueous $AgNO_3$ solution with respect to the aqueous KI solution is preferably 0.1 or more, more preferably, 0.5 or more, and most preferably, 1 or more. A total addition molar amount of the aqueous $AgNO_3$ solution may fall within a silver excessive range with respect to halogen ions and added iodine ions in a system. A pAg during addition of the aqueous halide solution containing the iodine ions and addition of the aqueous silver salt solution performed by double jet, is preferably decreased as an addition time of the double jet elapses. A pAg before the addition is started is preferably 6.5 to 13, and more preferably, 7.0 to 11. A pAg at the end of the addition is most preferably 6.5 to 10.0.

When the above method is to be performed, the solubility of a silver halide in a mixing system is preferably minimized. The temperature of the mixing system during formation of the high silver iodide layer is therefore preferably 30° C to 70° C, and more preferably, 30° C to 50° C.

Formation of the inner high silver iodide layer can be most preferably performed by adding fine silver iodide grain (i.e., fine silver iodide, and "fine grain" has the same meaning hereinafter), fine silver iodobromide grain, fine silver chloroiodide grain, or fine silver chloroiodobromide grain. Most preferably, formation of the inner high silver iodide layer is performed by adding fine silver iodide grain. Although these fine grains normally have a grain size of 0.01 to 0.1 µm, fine grains having a grain size of 0.01 µm or less or 0.1 µm or more can be used. Methods of preparing fine silver halide grains are described in JP-A-1-251030, JP-A-2-44775, JP-A-78552, Japanese Patent Application No. 63-7853, JP-A-2-43534, and JP-A-43535. The inner high silver iodide layer can be formed by adding the fine grain silver halide and ripening. When the fine grains are to be dissolved to perform ripening, the above-mentioned silver halide solvent can be used. These added fine grains need not be immediately perfectly dissolved and disappear but may be dissolved and disappear when final grains are formed.

The silver iodide content of the outer layer covering the inner high silver iodide layer is lower than that of the high silver iodide layer, preferably, 0 to 30 mol%, more preferably, 0 to 20 mol%, and most preferably, 0 to 10 mol%.

A position of the inner high silver iodide layer, for example, is within the region ranging preferably 5 to less than 100 mol%, more preferably, 20 to less than 95 mol%, and most preferably, 50 to less than 90 mol%, with respect to a silver amount of all the grains, measured from the center of a projected hexagon. An amount (silver amount) of the silver halide for forming the inner high silver iodide layer is 50 mol% or less, and more preferably, 20 mol% or less with respect to a silver amount of all the grains. These values of the high silver iodide layer are not measured values obtained by measuring a halogen composition of a final grain by various types of analyzing methods, but formulated values in the manufacture of a silver halide emulsion. The inner high silver iodide layer often disappears from a final grain by, e.g., a recrystallization process, and the above description concerns only the manufacturing method.

In a final grain, therefore, although observation of dislocation lines can be easily performed by the above method, the inner high silver iodide layer formed to form dislocation lines is often cannot be clearly observed as a layer. For example, the entire circumference region of a tabular grain is sometimes observed as a high silver iodide layer. These halogen compositions can be observed by a combination of, e.g., X-ray diffraction, an EPMA (also called XMA) method (in which silver halide grains are scanned by an electron beam to detect a silver halide composition), and an ESCA (also called XPS) method (in which X rays are radiated to perform spectroscopy for photoelectrons emitted from the grain surface).

Although the temperature and the pAg during formation of the outer layer covering the inner high silver iodide layer can be arbitrarily selected, the temperature is preferably 30 ° C to 80 ° C, and most preferably 35 ° C to 70 ° C, and the pAg is preferably 6.5 to 11.5. The silver halide solvent described above can be sometimes preferably used, and a most preferable silver halide solvent is thiocyanate salt.

In order to form dislocation lines on the major face of a tabular grain, after a substrate grain is prepared, a silver halochloride is deposited on the major face and converted into a high silver bromide or a high iodide layer, and a shell is formed outside the layer. Examples of the silver halochloride are silver chloride, silver chlorobromide, and silver chloroiodobromide containing 10 mol% or more and preferably 60 mol% or more of silver chloride. The silver halide can be deposited on the major face of a substrate grain by independently or simultaneously adding an aqueous silver nitrate solution and an aqueous solution of a suitable alkali metal salt (e.g., potassium chloride) or by adding an emulsion comprising such a silver salt and ripening the emulsion to deposit. Although deposition of the silver halochloride can be performed in an arbitrary pAg range, the pAg is most preferably 5.0 to 9.5. In this method, a tabular grain is grown in mainly the direction of thickness. An amount (silver amount) of the silver halochloride layer is 1 to 80 mol%, and more preferably, 2 to 60 mol% with respect to the substrate grain. Dislocation lines can be formed on the major face of a tabular grain by converting the silver halochloride layer by an aqueous halide solution capable of forming a silver salt having lower solubility than that of a silver halochloride. For example, after the silver halochloride layer is converted by an aqueous KI solution, a shell can be grown to form a final grain. In this halogen conversion of the silver halochloride layer, not all the silver halochloride but preferably 5% or more, more preferably, 10% or more, and most preferably, 20% or more of the silver halochloride are replaced by a silver salt having lower solubility than that of the silver halochloride. Dislocation lines can be formed in a local portion on the major face by controlling a halogen structure of a substrate grain on which a silver halochloride layer is to be formed. For example, when a substrate tabular grain having an internally high silver iodide structure in the transverse direction of the substrate grain is used, dislocation lines can be formed on only a peripheral portion except for a central portion of the major face. When a substrate tabular grain having an externally high silver iodide structure in the transverse direction of the substrate grain is used, dislocation lines can be formed in only a central portion except for a peripheral portion of the major face. In addition, a site director of epitaxial growth of a silver halochloride, e.g., an iodide can be used to deposit the silver halochloride in only an areally limited portion, thereby forming dislocation lines in only the limited portion. The temperature during deposition of the silver halochloride is preferably 30° C to 70° C, and more preferably, 30° C to 50° C. Although the process can be performed such that conversion is performed after the silver halochloride is deposited and then a shell is grown, the halogen conversion may be performed while shell growth is performed after deposition of the silver halochloride.

The position of the inner silver halochloride layer formed substantially parallel to the major face is within the region ranging preferably 5 to less than 100 mol%, more preferably, 20 to less than 95 mol%, and most preferably, 50 to less than 90 mol%, from the center of the grain thickness to both sides, with respect to a silver amount of the entire grain.

The silver iodide content of the shell is preferably 0 to 30 mol% and more preferably 0 to 20 mol%. Although the temperature and the pAg during shell formation are arbitrarily selected, the temperature is preferably 30° C to 80° C and most preferably 35° C to 70° C, and the pAg is preferably 6.5 to 11.5. The silver halide solvent described above can be sometimes preferably used, and a most preferable silver halide solvent is thiocyanate salt. In a final grain, the inner silver halochloride layer subjected to the halogen conversion sometimes cannot be observed by the above-mentioned halogen composition analyzing methods, depending on the conditions such as a degree of the halogen conversion. Dislocation lines, however, can be clearly observed.

Dislocation lines can also be formed by arbitrarily combining the method of forming dislocation lines in an arbitrary position on the major face of a tabular grain and the method of forming dislocation lines in an arbitrary position on the circumference of a tabular grain.

A silver halide emulsion which can be used in the present invention may comprise any silver halide of silver bromide, silver iodobromide, silver iodochlorobromide, and silver chlorobromide. A preferable silver halide is silver iodobromide or silver iodochlorobromide containing 30 mol% or less of silver iodide.

The tabular grain of the present invention can be easily prepared by methods described in, e.g., Cleve, "Photography Theory and Practice", (1930), P. 131; Gutoff, "Photographic Science and Engineering", vol. 14, PP. 248 to 257, (1970); and U.S. Patents 4,434,226, 4,414,310, 4,433,048, and 4,439,520 and British Patent 2,112,157.

In the silver halide emulsion used in the present invention, a crystal structure may be uniform, may have different halogen compositions between the inner and outer portions of a crystal, or may be layered structure. These emulsion grains are disclosed in, e.g., British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877, and Japanese Patnet Application No. 58-248469. In addition, a silver halide having different compositions may be bonded by an epitaxial junction, or a compound other than a silver halide such as silver rhodanate or zinc oxide may be bonded.

The silver halide emulsion of the present invention preferably has a distribution or structure of a halogen composition in its grain. A typical example is a core-shell type or double structured grain having different halogen compositions in the interior and surface layer of the grain as disclosed in, e.g., JP-B-43-13162, JP-A-61-215540, JP-A-60-222845, and JP-A-61-75337. In such a grain, the shape of a core portion is sometimes identical to or sometimes different from that of the entire grain with a shell. In addition, not a simple double structure but a triple structure as disclosed in JP-A-60-222844 or a multilayered structure of more layers can be formed, or a thin film of a silver halide having a different composition can be formed on the surface of a core-shell double structure grain.

In order to give a structure inside the grain, a grain having not only the above surrounding structure but a so-called junction structure can be made. Examples of such a grain are disclosed in, e.g., JP-A-59-133540, JP-A-58-108526, EP 199290A2, JP-B-58-24772, and JP-A-59-16254. A crystal to be bonded having composition different from that of a host crystal can be produced and bonded to an edge, corner, or face portion of the host crystal. Such a junction crystal can be formed regardless of whether the host crystal has a homogeneous halogen composition or a core-shell structure.

The junction structure can be naturally made by a combination of silver halides. In addition, the junction structure can be made by combining a silver salt compound not having a rock salt structure, e.g., silver rhodanate or silver carbonate with a silver halide. A non-silver salt compound such as PbO can also be used as long as the junction structure can be made.

In a silver iodobromide grain having the above structure, e.g., in a core-shell type grain, the silver iodide content may be high at a core portion and low at a shell portion or vice versa. Similarly, in a grain having the junction structure, the silver iodide content may be high in a host crystal and relatively low in a junction crystal or vice versa.

In a grain having the above structure, a boundary portion between different halogen compositions may be clear or unclear due to a crystal mixture formed by a composition difference. Alternatively, a continuous structure change may be positively made.

The silver halide emulsion for use in the present invention can be subjected to a treatment for rounding a grain as disclosed in, e.g., EP-0096727BI and EP-0064412BI or a treatment of modifying the surface of a grain as disclosed in DE-2306447C2 and JP-A-60-221320.

The silver halide emulsion for use in the present invention is preferably of a surface latent image type. An internal latent image type emulsion, however, can be used by selecting a developing solution or development conditions as disclosed in JP-A-59-133542. In addition, a shallow internal latent image type emulsion covered with a thin shell can be used in accordance with an application.

A silver halide solvent can be effectively used to promote ripening. For example, in a known conventional method, an excessive amount of halogen ions are supplied in a reaction vessel in order to promote ripening. Therefore, it is apparent that ripening can be promoted by only supplying a halide salt solution into a reaction vessel. In addition, another ripening agent can be used. In this case, a total amount of these ripening agents can be mixed in a dispersion medium in the reaction vessel before a silver salt and a halide salt are added therein, or they can be added in the reaction vessel together with one or more halide salts, a silver salt or a deflocculant. Alternatively, the ripening agents can be added in separate steps during process of adding a halide salt and a silver salt.

Examples of the ripening agent other than the halogen ion are ammonia, an amine compound, and a thiocyanate such as an alkali metal thiocyanate, especially sodium or potassium thiocyanate and ammonium thiocyanate.

In the emulsion of the present invention, a silver iodide content between grains is preferably more uniform. The uniformity of the silver iodide content between grains can be determined by the EPMA (Electron-Probe Micro Analyzer) method described above.

In this method, a sample is dispersed well so that emulsion grains are not in contact with each other, and an electron beam is radiated on the sample. Element analysis of a very small portion can be performed by X-ray diffraction based on electron beam excitation.

In the EPMA method, a halogen composition of each grain can be determined by obtaining characteristic X-ray intensities of silver and iodine radiated from the grain.

When a distribution of the silver iodide content between grains is measured by the EPMA method, a relative standard deviation is preferably 50% or less, more preferably, 35% or less, and most preferably, 20% or less.

In a process of formation or physical ripening of silver halide grains, the silver halide emulsion of the present invention may contain a cadmium salt, a zinc salt, a thallium salt, an iridium salt or its complex salt, rhodium salt or its complex salt, and an iron salt or its complex salt. Most preferably, the silver halide emulsion contains the iridium salt.

The emulsion of the present invention has been chemically sensitized by different sensitizers of at least one selenium sensitizer, at least one gold sensitizer, and at least one sulfur sensitizer.

Selenium sensitization is performed by a conventional method. That is, an labile selenium compound and/or a non-labile selenium compound are/is added to an emulsion, and the emulsion is stirred at a high temperature of preferably 40°C or more for a predetermined time period. Selenium sensitization using labile selenium sensitizers described in JP-B-44-15748 is preferably performed. Examples of the unstable selenium sensitizer are an aliphatic isoselenocyanate such as allylisoselenocyanates, selenoureas, selenoketones, selenoamides, selenocarboxylic acids and esters, and selenophosphates. Most preferable examples of the labile selenium compound are as follows.

I. Colloidal metal selenium

II. Organic selenium compound (in which a selenium atom is double-bonded to a carbon atom of an organic compound by covalent bonding)

a. Isoselenocyanates e.g., aliphatic isoselenocyanate such as allylisoselenocyanate

b. Selenoureas (including an enol type) e.g., selenoured; aliphatic selenourea such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, dioctyl, tetramethyl, N-(β-carboxyethyl)-N', N'-dimethyl, N,N-dimethyl, diethyl, and dimethyl selenourea; an aromatic selenourea having one or more aromatic groups such as phenyl and tolyl; a heterocyclic selenourea having a heterocyclic group such as pyridyl and benzothiazolyl

c. Selenoketones e.g., selenoacetone, selenoacetophenone, selenoketone in which an alkyl group is bonded to

$$>\mathrm{C}=\mathrm{Se},$$

and selenobenzophenone
d. Selenoamides e.g., selenoacetoamide
e. Selenocarboxylic acids and esters e.g., 2-selenopropionic acid, 3-selenobutyric acid, and methyl 3-selenobutyrate

III. Others
a. Selenides e.g., diethylselenide, diethyldiselenide, and triphenylphosphineselenide
b. Selenophosphates e.g., tri-p-tolylselenophosphate and tri-n-butylselenophosphate

Although the preferable type of the labile selenium compound are enumerated above, the compound is not limited to the above examples. It is generally understood by those skilled in the art that the structure of the labile selenium compound as a sensitizer of a photographic emulsion is not so important as long as selenium is labile and that an organic portion of a selenium sensitizer molecule has no function except for a function of carrying selenium and allowing selenium to be present in an labile state in an emulsion. In the present invention, the labile selenium compound in such a wide range of general idea is effectively used.

Selenium sensitization using non-labile selenium sensitizers described in JP-B-46-4553, JP-B-52-34492, and JP-B-52-34491 is also performed. Examples of the non-labile selenium compound are selenious acid, potassium selenocyanide, selenazoles, a quaternary ammonium salt of a selenazole, diarylselenide, diaryldiselenide, 2-thioselenazolizinedione, 2-selenooxozinethione, and derivatives of these compounds.

A non-labile selenium sensitizer and a thioselenazolizinedione compound described in JP-B-52-38408 are also effective.

These selenium sensitizers are dissolved in water, an organic solvent such as methanol or ethanol, or a solvent mixture thereof and added upon chemical sensitization. Preferably, the sensitizers are added before chemical sensitization is started. The labile sensitizers need not be used singly but may be used in combination of two or more types thereof. The labile and non-labile selenium compounds can be preferably used in combination.

Although an addition amount of the selenium sensitizer for use in the present invention differs in accordance with the activity of the selenium sensitizer or the temperature and time of ripening, it is preferably 1×10^{-8} mol or more, and more preferably, 1 × 10-7 to 5×10^{-5} mol per mol of a silver halide. When the selenium sensitizer is used, the temperature of chemical ripening is preferably 45° C or more, and more preferably, 50° C to 80° C. A pAg and a pH may take arbitrary values. For example, the effect of the present invention can be obtained throughout a wide pH range of 4 to 9.

In the present invention, selenium sensitization can be performed more effectively in the presence of a silver halide solvent.

Examples of the silver halide solvent which can be used in the present invention are (a) organic thioethers described in, e.g., U.S. Patents 3,271,157, 3,531,289, and 3,574,628, JP-A-54-1019, and JP-A-54-158917; (b) thiourea derivatives described in, e.g., JP-A-53-82408, JP-A-55-77737, and JP-A-55-2982; (c) a silver halide solvent having a thiocarbonyl group sandwiched by an oxygen or sulfur atom and a nitrogen atom described in JP-A-53-144319; (d) imidazoles described in JP-A-54-100717; (e) sulfite; and (f) thiocyanate.

Practical compounds of the solvent are listed in Table A.

Most preferable examples of the solvent are thiocyanate and tetramethylthiourea. An amount of the solvent changes in accordance with the type of a solvent. For example, a preferable amount of thiocyanate is 1×10^{-4} to 1×10^{-2} mol per mol of a silver halide.

In chemical sensitization of the emulsion of the present invention, sulfur sensitization and gold sensitization are performed jointly.

Sulfur sensitization is generally performed by adding a sulfur sensitizer to an emulsion and stirring the emulsion at a high temperature of preferably 40° C or more for a predetermined time period.

Gold sensitization is generally performed by adding a gold sensitizer to an emulsion and stirring the emulsion at a high temperature of 40° C or more for a predetermined time period.

Known compounds can be used as the sulfur sensitizer in sulfur sensitization. Examples of the sulfur sensitizer are thiosulfate, allylthiocarbamidothiourea, allylisothiacyanate, cystine, p-toluenethiosulfonate, and rhodanine. In addition, sulfur sensitizers described in e.g., U.S. Patents 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313, and 3,656,955, West German Patent 1,422,869, JP-B-56-24937, and JP-A-55-45016 can be used. An addition amount of the sulfur sensitizer need only be an amount sufficient to effectively increase the sensitivity of the emulsion. Although the amount changes throughout a wide range in accordance with various conditions such as a pH, a temperature, and the size of a silver halide grain, it is preferably 1×10^{-7} to 5×10^{-5} mol per mol of a silver halide.

An oxidation number of gold of a gold sensitizer for use in gold sensitization of the present invention may be +1 or +3, and gold compounds which are normally used as a gold sensitizer can be used in the present invention. Typical examples of the gold compound are chloroaurate, potassium chloroaurate, aurictrichloride, potassium auricthiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, and pyridyltrilorogold.

Although an addition amount of the gold sensitizer changes in accordance with various conditions, it is preferably 1 × 10^{-7} to 5 × 10^{-5} mol per mol of a silver halide.

In chemical ripening, addition times and an addition order of the silver halide solvent, the selenium sensitizer, the sulfur sensitizer, and the gold sensitizer need not be particularly limited. For example, the above compounds can be added simultaneously or at different addition timings in (preferably) an initial stage of chemical ripening or during chemical ripening. The compounds are dissolved in water, an organic solvent, which can be mixed in water, such as methanol, ethanol, or acetone, or a solution mixture thereof and added to an emulsion.

The silver halide emulsion of the present invention, preferably, has been subjected to reduction sensitization during grain formation.

"Reduction sensitization is performed during grain formation of a silver halide emulsion" basically means that reduction sensitization is performed during nucleation, ripening, and growth or precipitation. Reduction sensitization may be performed upon any of nucleation as an initial stage of grain formation, physical ripening, or precipitation. Most preferably, reduction sensitization is performed during precipitation of silver halide grains. In this case, reduction sensitization may be performed while silver halide grains are physically ripened or grown upon addition of water-soluble silver salt and water-soluble alkali halide. Alternatively, reduction sensitization may be performed by temporarily stopping growth, and growth may be performed again.

Reduction sensitization may be any of a method of adding a known reduction sensitizer to a silver halide emulsion, a method called silver ripening in which grains are grown or ripened in a low-pAg atmosphere having a pAg of 1 to 7, and a method called high-pH ripening in which grains are grown or ripened in a high-pH atmosphere having a pH of 8 to 11. These methods can be used in combination of two or more thereof.

The method of adding a reduction sensitizer is preferable since the level of reduction sensitization can be finely controlled.

Examples of the reduction sensitizer are stannous chloride, a amines and polyamines, hydrazine derivatives, formamidinesulfinic acid, silane compounds, and borane compounds. In the present invention, these compounds may be selectively used or used in combination of two or more types thereof. Preferable compounds as the reduction sensitizer are stannous chloride, thiourea dioxide, dimethylamineborane, ascorbic acid, and asoorbic acid derivatives. Although an addition amount of the reduction sensitizer depends on emulsion manufacturing conditions, it is preferably 10^{-8} to 10^{-3} mol per mol of a silver halide.

The reduction sensitizer can be dissolved in water or a solvent such as alcohols, glycols, ketones, esters, or amides and added during grain formation. Although the reduction sensitizer may be added to a reaction vessel beforehand, it is preferably added at an arbitrary timing during grain formation. The reduction sensitizer may be added to an aqueous solution of water-soluble silver salt or water-soluble alkali halide, and the resultant aqueous solution may be used in grain formation. In addition, a solution of a reduction sensitizer may be added continuously or a plurality of times as grain formation progresses.

More preferably, a palladium compound in an amount of 5 × 10^{-5} mol or more per mol of a silver halide is added to the silver halide emulsion of the present invention after grain formation is finished and preferably before desalting is started.

In this case, the palladium compound is a palladium divalent or tetravalent salt. The palladium compound is preferably represented by R_2PdX_6 or R_2PdX_4 wherein R represents hydrogen atom, alkali metal atom, or ammonium group and X represents halogen atom, i.e., chlorine, bromine, or iodine.

Preferable examples of the palladium compound are $K_2PdC\ell_4$, $(NH_4)_2PdC\ell_6$, $Na_2PdC\ell_4$, $(NH_4)_2PdC\ell_4$, $Li_2PdC\ell_4$, $Na_2PdC\ell_6$, and K_2PdBr4.

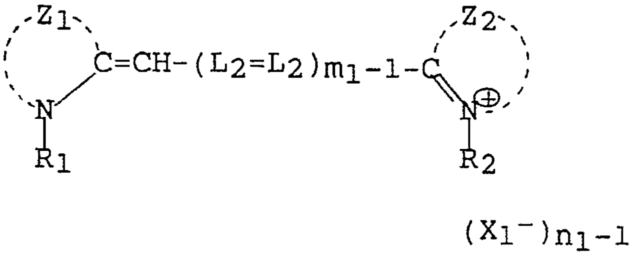
Most preferably, the palladium compound is used in combination of thiocyanate ions in an amount five times that of the palladium oompound.

The silver halide emulsion of the present invention is preferably spectrally sensitized and used.

A methine dye is normally used as a spectral sensitizing dye for use in the present invention. The methine dye includes a cyanine dye, a merocyanine dye, a complex dye, a complex merocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye, and a hemioxonol dye. In these dyes, any nucleus normally used as a basic heterocyclic nucleus in cyanine dyes can be used. Examples of the nucleus are pyrroline, oxazoline, thiazoline, pyrrole, oxazole, thiazole, selenazole, imidazole, tetrazole, and pyridine; a nucleus obtained by fusing an alicyclic hydrocarbon ring to each of the above nuclei; and a nucleus obtained by fusing an aromatic hydrocarbon ring to each of the above nuclei, e.g., indolenine, benzindolenine, indole, benzoxadole, naphthooxadole, benzothiazole, naphthothiazole, benzoselenazole, benzimidazole, and quinoline. These nuclei may have substituent group on a carbon atom.

For a merocyanine dye or complex merocyanine dye, a 5- or 6-membered heterocyclic nucleus, e.g., pyrazoline-5-one, thiohydantoin, 2-thiooxazoline-2,4-dione, thiazoline-2,4-dione, rhodanine, or thiobarbituric acid can be used as a nucleus having a ketonmethylene structure. Of the above dyes, a dye most effectively used in the present invention is a cyanine dye. An example of a cyanine dye effectively used in the present invention is a dye represented by the following formula (I):

Formula (I)



wherein each of Z_1 and Z_2 independently represents an atom group required to form a heterocyclic nucleus normally used in a cyanine dye, such as thiazole, thiazoline, benzothiazole, naphthothiazole, oxazole, oxazoline, benzooxazole, naphthooxazole, tetrazole, pyridine, quinoline, imidazoline, imidazole, benzoimidazole, naphthoimidazole, selenazoline, selenazole, benzoselenazole, naphthoselenazole, or indolenine. These nuclei may be substituted by a lower alkyl group such as methyl, halogen atom, phenyl, hydroxyl, alkoxy having 1 to 4 carbon atoms, carboxyl, alkoxycarbonyl, alkylsulfamoyl, alkylcarbamoyl, acetyl, acetoxy, cyano, trichloromethyl, trifluoromethyl, and nitro.

L_1 or L_2 represents a methine group and a substituted methine group. Examples of the substituted methine group are a methine group substituted by, e.g., a lower alkyl group such as methyl and ethyl, phenyl, substituted phenyl, methoxy, and ethoxy.

Each of R_1 and R_2 independently represent alkyl having 1 to 5 carbon atoms; substituted alkyl having a carboxy group; substituted alkyl having a sulfo group such as β-sulfoethyl, γ-sulfopropyl, δ-sulfobutyl, 2-(3-sulfopropoxy)ethyl, 2-(2-(sulfopropoxy)ethoxy)ethyl, and 2-hydroxysulfopropyl, an allyl group or a substituted alkyl group normally used as an N-substituting group of a cyanine dye. m_1 represents 1, 2, or 3. $X_1^{\ominus}$ represents an acid anion group normally used in a cyanine dye such as an iodide ion, a bromide ion, a p-toluenesulfonate ion, or a perchlorate ion. n_1 represents 1 or 2. When it is a betaine structure, n_1 is 1.

In addition to the above sensitizing dyes, examples of the spectral sensitizing dye are described in, e.g., West German Patent 929,080, U.S. Patents 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,656,956, 3,672,897, 3,694,217, 4,025,349, 4,046,572, 2,688,545, 2,977,229, 3,397,060, 3,552,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,814,609, 3,837,862, and 4,026,344, British Patents 1,242,588, 1,344,281, and 1,507,803, JP-B-44-14030, JP-B-52-24844, JP-B-43-4936, JP-B-53-12375, JP-A-52-110618, JP-A-52-109925, and JP-A-50-80827.

An amount of the sensitizing dye to be added during preparation of the silver halide emulsion changes in accordance with the type of additive or a silver halide amount. However, substantially the same amount as that added in conventional methods can be used.

That is, an addition amount of the sensitizing dye is preferably 0.001 to 100 mmol, and more preferably, 0.01 to 10 mmol per mol of a silver halide.

The sensitizing dye is added after or before chemical ripening. For the silver halide grains of the present invention, the sensitizing dye is most preferably added during chemical ripening or before chemical ripening (e.g., during grain formation or during physical ripening).

In addition to the sensitizing dye, a dye not having a spectral sensitizing effect or a substance essentially not absorbing visible light but exhibiting supersensitization may be added to the emulsion. Examples of the substance are an aminostylyl compound substituted by a nitrogen-containing heterocyclic group (described in, e.g., U.S. Patent 2,933,390 or 3,635,721), an aromatic organic acid formaldehyde condensate (described in, e.g., U.S. Patent 3,743,510), cadmium salt, and an azaindene compound. Combinations described in U.S. Patents 3,615,613, 3,615,641, 3,617,295, and 3,635,721 are most effective.

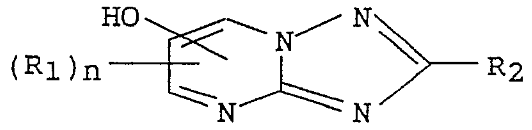
The photographic emulsion for use in the present invention can contain various compounds in order to prevent fog during manufacture, storage, or a photographic treatment of the light-sensitive material or to stabilize photographic properties. Examples of the compound known as an antifoggant or stabilizer are azoles such as benzothiazolium salt, nitroindazoles, triazoles, benzotriazoles, and benzimidazoles (especially a nitro- or halogen-substituted form); a heterocyclic mercapto compound such as mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiazoles, mercaptotetrazoles (especially 1-phenyl-5-mercaptotetrazole), and mercaptopyrimidines; the heterocyclic mercapto compound having a water-soluble group such as a carboxyl group or a sulfone group; a thioketo compound such as oxazolinethiones; azaindenes such as tetraazaindenes (especially 4-hydroxy-substituted(1,3,3a,7) tetraazaindenes); benzenethiosulfonic acids; and benzenesulfinic acids.

Although these antifoggants or stabilizers are normally added after chemical ripening is performed, they may be more preferably added during chemical ripening or before start of chemical ripening. That is, in a silver halide emulsion grain formation process, the antifoggants or stabilizers can be added during addition of a silver salt solution, after the addition and before start of chemical ripening, or during chemical ripening (within preferably 50%, and more preferably, 20% of a chemical ripening time from the start of chemical ripening).

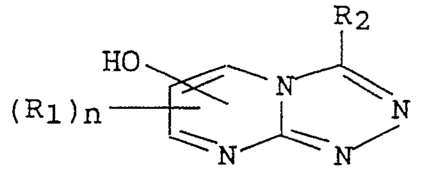
More specifically, examples of the antifoggant or stabilizer are a hydroxyazaindene compound, a benzotriazole compound, and a heterocyclic compound substituted by at least one mercapto group and having at least two aza-nitrogen atoms in a molecule.

A preferable example of the hydroxyazaindene compound is represented by the following formula (II) or (III):

Formula (II)



Formula (III)



wherein R_1 and R_2 may be the same or different and independently represent a hydrogen atom; an aliphatic moiety (e.g. an alkyl group (e.g., methyl, ethyl, propyl, pentyl, hexyl, octyl, isopropyl, sec-butyl, t-butyl, cyclohexyl, cyclopentylmethyl, and 2-norbornyl); an alkyl group substituted by an aromatic moiety (e.g., benzyl, phenethyl, benzhydryl, 1-naphthylmethyl, and 3-phenylbutyl); an alkyl group substituted by an alkoxy group (e.g., methoxymethyl, 2-methoxyethyl, 3-ethoxypropyl, and 4-methoxybutyl); and alkyl group substituted by a hydroxy group, a carbonyl group, or an alkoxycarbonyl group (e.g., hydroxymethyl, 2-hydroxymethyl, 3-hydroxybutyl, carboxymethyl, 2-carboxyethyl, and 2-(methoxycarbonyl)ethyl) or an aromatic moiety (an aryl group (e.g., phenyl and 1-naphthyl); an aryl group having a substituting group (e.g., p-tolyl, m-ethylphenyl, m-cumenyl, mesityl, 2,3-xylyl, p-chlorophenyl, o-bromophenyl, p-hydroxyphenyl, 1-hydroxy-2-naphthyl, m-methoxyphenyl, p-ethoxyphenyl, p-carboxyphenyl, o-(methoxycarbonyl) phenyl, m-(ethoxycarbonyl)phenyl, and 4-carboxy-1-naphthyl).

A total number of carbon atoms of R_1 and R_2 is preferably 12 or less.

n represents 1 or 2.

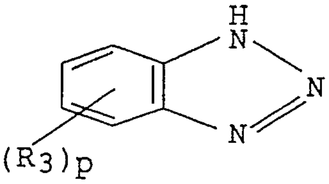
Examples of a hydroxytetraazaindene compound represented by formula (II) or (III) will be listed below. However, the compound for use in the emulsion of the present invention is not limited to the following examples.

II-1	4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene
II-2	4-hydroxy-1,3,3a,7-tetraazaindene
II-3	4-hydroxy-6-methyl-1,2,3a,7-tetraazaindene
II-4	4-hydroxy-6-phenyl-1,3,3a,7-tetraazaindene

II-5	4-methyl-6-hydroxy-1,3,3a,7-tetraazaindene
II-6	2,6-dimethyl-4-hydroxy-1,3,3a,7-tetraazaindene
II-7	4-hydroxy-5-ethyl-6-methyl-1,3,3a,7-tetraazaindene
II-8	2,6-dimethyl-4-hydroxy-5-ethyl-1,3,3a,7-tetraazaindene
II-9	4-hydroxy-5,6-dimethyl-1,3,3a,7-tetraazaindene
II-10	2,5,6-trimethyl-4-hydroxy-1,3,3a,7-tetraazaindene
II-11	2-methyl-4-hydroxy-6-phenyl-1,3,3a,7-tetraazaindene
II-12	4-hydroxy-6-ethyl-1,3,3a,7-tetraazaindene
II-13	4-hydroxy-6-phenyl-1,2,3a,7-tetraazaindene
II-14	4-hydroxy-1,2,3a,7-tetraazaindene
II-15	4-methyl-6-hydroxy-1,2,3a,7-tetraazaindene
II-16	5,6-trimethylene-4-hydroxy-1,3,3a,7-' tetraazaindene

An example of a benzotriazole compound is a compound represented by the following formula IV:

Formula (IV)



wherein p represents 0 or an integer of 1 to 4 and R_3 represents a halogen atom (chlorine, bromine, or iodine) or an aliphatic group (including saturated and non-saturated aliphatic groups), e.g., a nonsubstituted alkyl group preferably having 1 to 8 carbon atoms (e.g., methyl, ethyl, n-propyl, or hexyl); a substituted alkyl group in which an alkyl radical (moiety) preferably has 1 to 4 carbon atoms, e.g., a vinylmethyl group, an aralkyl group (e.g., benzyl or phenethyl), a hydroxyalkyl group (e.g., 2-hydroxyethyl, 3-hydroxypropyl, or 4-hydroxylbutyl), an acetoxyalkyl group (e.g., 2-acetoxyethyl or 3-acetoxypropyl), an alkoxyalkyl group (e.g., 2-methoxyethyl or 4-methoxybutyl); or an aryl group (e.g., phenyl). More preferably, R_3 is a halogen atom (chlorine or iodine) or an alkyl group having 1 to 3 carbon atoms (methyl, ethyl, or propyl).

Examples of a benzotriazole compound for use in the emulsion of the present invention will be listed below. However, the benzotriazole compound used in the present invention is no limited to the following compounds.

IV-1	benzotriazole
IV-2	5-methyl-benzotriazole
IV-3	5,6-dimethylbenzotriazole
IV-4	5-bromo-benzotriazole
IV-5	5-chloro-benzotriazole
IV-6	5-nitro-benzotriazole
IV-7	4-nitro-6-chlorobenzotriazole
IV-8	5-nitro-6-chlorobenzotriazole

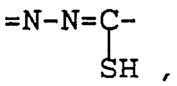
A heterocyclic compound substituted by at least one mercapto group and having at least two aza-nitrogen atoms in a molecule (to be referred to as a nitrogen-containing heterocyclic compound having a mercapto group hereinafter) will be described below. A heterocyclic ring of such a compound may have different types of atoms bisides a nitrogen atom, such as oxygen, sulfur, and selenium. A preferable compound is a two 5- or 6-membered mono-heterocyclic compound having at least aza-nitrogen atoms or a 2- or 3-heterocyclic compound which is obtained by condensing two or three heterocyclic rings each having at least one nitrogen atom, in which a mercapto group is substituted on a carbon atom adjacent to aza-nitrogen.

In the nitrogen-containing heterocyclic compound having a mercapto group which can be used in the present invention, examples of the heterocyclic ring are pyrazole, 1,2,4-triazole, 1,2,3-triazole, 1,3,4-thiadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,2,3,4-tetrazole, pyridazine, 1,2,3-triazine, 1,2,4-triazine, 1,3,5-triazine, and a ring obtained by condensing two or three of the above rings, e.g., triazolotriazole, diazaindene, triazaindene, tetrazaindene,. and pentazaindene. In addition, a heterocyclic ring obtained by condensing a monoheterocyclic ring and an aromatic ring, e.g., a phthalazine ring and an indazole ring can be used.

Of these rings, preferable rings are 1,2,4-triazole, 1,3,4-thiadiazole, 1,2,3,4-tetrazole, 1,2,4-triazine, triazolotriazole, and tetrazaindene.

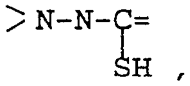
Although a mercapto group may be substituted on any carbon atom of the ring, the following bonds are preferably formed.

a)



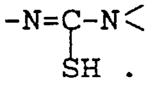
$=N-N=\underset{SH}{C}-$,

b)



$>N-N-\underset{SH}{C}=$,

c)



$-N=\underset{SH}{C}-N<$.

The heterocyclic ring may have a substituting group other than the mercapto group. Examples of the substituting group are alkyl having 8 or less carbon atoms (e.g., methyl, ethyl, cyclohexyl, and cyclohexylmethyl), substituted alkyl (e.g., sulfoethyl and hydroxymethyl), alkoxy having 8 or less carbon atoms (e.g., methoxy and ethoxy), alkylthio having 8 or less carbon atoms (e.g., methylthio and butylthio), hydroxy, amino, hydroxyamino, alkylamino having 8 or less carbon atoms (e.g., methylamino and butylamino), dialkylamino having 8 or less carbon atoms (e.g., dimethylamino and diisopropylamino), arylamino (e.g., anilino), acylamino (e.g., acetylamino), halogen (e.g., chlorine and bromine), cyano, carboxy, sulfo, sulfato, and phospho.

Examples of the nitrogen-containing heterocyclic compound having a mercapto group which can be used in the present invention will be listed in Table B. However, the compound is not limited to these examples.

Although an addition amount of the antifoggant or stabilizer for use in the present invention changes in accordance with an addition method or a silver halide amount, it is preferably 10^{-7} to 10^{-2} mol, and more preferably, 10^{-5} to 10^{-2} mol per mol of a silver halide.

The emulsion of the present invention can be used as a mixture with another emulsion. Two or more types of the emulsions of the present invention can be used in the form of a mixture, or the emulsion of the present invention can be used as a mixture with one or more types of other emulsions. Emulsions having different grain sizes can be mixed, emulsions having different halogen compositions can be mixed, and emulsions having different grain shapes can be mixed. Monodisperse emulsions can be mixed, polydisperse emulsions can be mixed, and monodisperse and polydisperse emulsions can be mixed. The silver halide emulsion of the present invention is preferably contained by at least 50%, more preferably 60% or more, with respect to the total projected area.

The above various additives are used in the light-sensitive material of the present invention. In addition to the above additives, however, various additives can be used in accordance with applications.

These additives are described in Research Disclosures, Item 17643 (Dec. 1978) and Item 18716 (Nov. 1979) and they are summarized in the following table.

	Additives	RD No.17643	RD No.18716
1.	Chemical sensitizers	page 23	page 648, right column
2.	Sensitivity increasing agents		do
3.	Spectral sensitizers, super sensitizers	pages 23-24	page 648, right column to page 649, right column
4.	Brighteners	page 24	
5.	Antifoggants and stabilizers	pages 24-25 pages 24-25	page 649, right column
6.	Light absorbent, filter dye, ultraviolet absorbents	pages 25-26	page 649, right column to page 650, left column
7.	Stain preventing agents	page 25, right column	page 650, left to right columns
8.	Dye image stabilizer	page 25	
9.	Hardening agents	page 26	page 651, left column
10.	Binder	page 26	do
11.	Plasticizers, lubricants	page 27	page 650, right column
12.	Coating aids, surface active agents	pages 26-27	do
13.	Antistatic agents	page 27	do

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

The photographic emulsion of the present invention is preferably used in a color light-sensitive material, and various color couplers can be used. Specific examples of these couplers are described in above-described Research Disclosure (RD), No. 17643, VII-C to VII-G as patent references.

Preferred examples of a yellow coupler are described in, e.g., U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752, and 4,248,961, JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023, and 4,511,649, and EP 249,473A.

Examples of a magenta coupler are preferably 5-pyrazolone and pyrazoloazole type compounds, and more preferably, compounds described in, e.g., U.S. Patents 4,310,619 and 4,351,897, EP 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June 1984), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, and JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654, and 4,565,630, and WO No. 04795/88.

Examples of a cyan coupler are phenol and naphthol type couplers, and preferably, those described in, e.g., U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,343,011, and 4,327,173, EP Disclosure 3,329,729, EP 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,994, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199 and JP-A-61-42658.

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

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

Typical examples of a polymerized dye-forming coupler are described in U.S. Patents 3,451,820, 4,080,221, 4,367,288, 4,409,320, and 4,576,910, and British Patent 2,102,173.

Couplers releasing a photographically useful residue upon coupling are preferably used in the present invention. DIR couplers, i.e., couplers releasing a development inhibitor are described in the patents cited in the above-described Research Disclosure No. 17643, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350, and U.S. Patents 4,248,962 and 4,782,012.

Examples of a coupler which can be used in the light-sensitive material of the present invention are competing couplers described in, e.g., U.S. Patent 4,130,427; poly-equivalent couplers described in, e.g., U.S. Patents 4,283,472, 4,338,393, and 4,310,618; a DIR redox compound releasing coupler, a DIR coupler releasing coupler, a DIR coupler releasing redox compound, or a DIR redox releasing redox compound described in, e.g., JP-A-60-185950 and JP-A-62-24252; couplers releasing a dye which turns to a colored form after being released described in EP 173,302A and 313,308A; bleaching accelerator releasing couplers described in, e.g., RD. Nos. 11,449 and 24,241 and JP-A-61-201247; a legand releasing coupler described in, e.g., U.S. Patent 4,553,477; a coupler releasing a leuco dye described in JP-A-63-75747; and a coupler releasing a fluorescent dye described in U.S. Patent 4,774,181.

Various types of an antiseptic agent or a mildewproofing agent are preferably added to the color light-sensitive material of the present invention. Examples of the antiseptic agent and the mildewproofing agent are 1,2-benzisothiazoline-3-one, n-butyl-p-hydroxybenzoate, 2-phenoxyethanol, and 2-(4-thiazolyl) benzimidazole described in JP-A-63-257747, JP-A-62-272248, and JP-A-1-80941.

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

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

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

The color photographic light-sensitive material according to the present invention can be developed by conventional methods described in RD. No. 17643, pp. 28 and 29 and RD. No. 18716, the left to right columns, page 615.

In order to perform reversal development, black-and-white development is performed and then color development is performed. As a black-and-white developer, well-known black-and-white developing agents, e.g., a dihydroxybenzene such as hydroquinone, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, and an aminophenol such as N-methyl-p-aminophenol can be used singly or in a combination of two or more thereof.

The photographic light-sensitive material of the present invention is normally subjected to washing and/or stabilizing steps after desilvering. An amount of water used in the washing step can be arbitrarily determined over a broad range in accordance with the properties (e.g., a property determined by use of a coupler) of the light-sensitive material, the application of the material, the temperature of the water, the number of water tanks (the number of stages), a replenishing scheme representing a counter or forward current, and other conditions. The relationship between the amount of water and the number of water tanks in a multi-stage counter-current scheme can be obtained by a method described in "Journal of the Society of Motion Picture and Television Engineering", Vol. 64, PP. 248 - 253 (May, 1955).

According to the above-described multi-stage counter-current scheme, the amount of water used for washing can be greatly decreased. Since washing water stays in the tanks for a long period of time, however, bacteria multiply and floating substances may be undesirably attached to the light-sensitive material. In order to solve this problem in the process of the color photographic light-sensitive material of the present invention, a method of decreasing calcium and magnesium ions can be effectively utilized, as described in JP-A-62-288838. In addition, a germicide such as an isothiazolone compound and cyabendazole described in JP-A-57-8542, a chlorine-based germicide such as chlorinated sodium isocyanurate, and germicides such as benzotriazole described in Hiroshi Horiguchi, "Chemistry of Antibacterial and Antifungal Agents", (1986), Eiseigijutsu-Kai ed., "Sterilization, Antibacterial, and Antifungal Techniques for Microorganisms", (1982), and Nippon Bokin Bokabi Gakkai ed., "Dictionary of Antibacterial and Antifungal Agents".

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

Stabilizing is sometimes performed subsequently to the washing. An example is a formalin bath used as a final bath of a photographic color light-sensitive material.

When the light-sensitive material of the present invention is to be used in the form of a roll, it is preferably housed in a cartridge. A most general cartridge is a 135-format patrone which is currently used. In addition, cartridges proposed in the following patents can be used. JU-A-58-67329, JP-A-58-181035, JP-A-58-182634, JP-A-58-195236, U.S. Patent 4,221,479, JP-A-1-231045, JP-A-2-124564, JP-A-2-170150, Japanese Patent Application Nos. 1-21862, 1-25362, 1-30246, 1-20222, 1-21863, 1-37181, 1-33108, 1-85198, 1-172595, 1-172594, 1-172593, and U.S. Patents 4,846,418, 484,693, and 4,832,275.)

EXAMPLES

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

EXAMPLE 1

(Preparation Method of Emulsion A)

1,000 mℓ of an aqueous solution containing 10.5 g of gelatin and 3.0 g of KBr were stirred at a temperature of 60° C. An aqueous silver nitrate solution (containing 8.2 g of $AgNO_3$) and an aqueous halide solution (containing 5.7 g of KBr and 0.35 g of KI) were added to the resultant solution by a double jet method over one minute. After 21.5 g of gelatin were added, the resultant solution was heated up to 75° C. An aqueous silver nitrate solution (containing 136.3 g $AgNO_3$) and an aqueous halide solution (containing 4.2 mol% of KI with respect to KBr) were added by the double jet method over 51 minutes while a flow rate was accelerated. During this addition, a silver potential was maintained at 0 mV with respect to a saturated calomel electrode. The temperature was decreased to 40° C, and an aqueous silver nitrate solution (containing 28.6 g of $AgNO_3$) and an aqueous KBr solution were added by the double jet method over 5.35 minutes, while the silver potential was maintained at -50 mV with respect to the saturated calomel electrode. The prepared emulsion was desalted by a flocculation method, and gelatin was added. Thereafter, the pH and the pAg were adjusted to be 5.5 and 8.8, respectively, to prepare emulsion A. The emulsion A was a tabular grain emulsion having an average circle-equivalent diameter of 1.14 μm, an average thickness of 0.189 μm, an average aspect ratio of 6.03, and a variation coefficient of a circle-equivalent diameter of 28%.

(Preparation Method of Emulsion B)

An emulsion B was prepared following the same procedures as for the emulsion A except that the aqueous halide solution (containing 4.2 mol% of KI with respect to KBr) was changed to an aqueous halide solution (containing 8.4 mol% of KI with respect to KBr) in the second stage. The emulsion B was a tabular grain emulsion having an average circle-equivalent diameter of 1.17 μm, an average thickness of 0.190 μm, an average aspect ratio of 6.16, and a variation coefficient of a circle-equivalent diameter of 31%.

(Preparation Method of Emulsion C)

The same procedures as for the emulsion A is performed until an aqueous silver nitrate solution was added in the second stage and the temperature was decreased to 40° C in the procedures for the emulsion A. An aqueous silver nitrate solution (containing 3.2 g of $AgNO_3$) and an aqueous KI solution (containing 2.3 g of KI) were added over five minutes. Thereafter, an aqueous silver nitrate solution (containing 25.4 g of $AgNO_3$) and an aqueous KBr solution were added by the double jet method over 5.35 minutes, while the silver potential was maintained at -50 mV with respect to a saturated calomel electrode. The same procedures as for the emulsion A were performed from flocculation to prepare emulsion C. The emulsion C was a tabular grain emulsion having an average circle-equivalent diameter of 1.09 μm, an average thickness of 0.196 μm, an average aspect ratio of 5.56, and a variation coefficient of a circle-equivalent diameter of 29%.

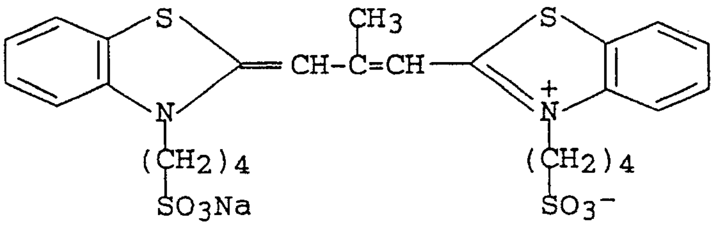
(Preparation Method of Emulsion D)

The the same procedures as for the emulsion A is performed until the aqueous silver nitrate solution was added in the first stage and the temperature was increased to 75° C. Thereafter, an aqueous silver nitrate solution (containing 136.3 g of $AgNO_3$) and an aqueous halogen solution (containing 4.2 mol% of KI with respect to KBr) were added by the double jet method over 51 minutes, while a flow rate was accelerated. During this addition, the silver potential was maintained at 0 mV with respect to a saturated calomel electrode for the first 46 minutes and then changed to +90 mV. The temperature was decreased to 40° C, and an aqueous silver nitrate solution (containing 3.2 g of $AgNO_3$) and an aqueous KI solution (containing 2.3 g of KI) were added over five minutes. Thereafter, an aqueous silver nitrate solution (containing 25.4 g of $AgNO_3$) and an aqueous KBr solution were added by the double jet method over 5.35 minutes. During this addition, the silver potential was maintained at - 50 mV with respect to the saturated calomel electrode. The same procedures as for the emulsion A were performed from flocculation to prepare emulsion D. The emulsion D was a tabular grain emulsion having an average circle-equivalent diameter of 1.21 μm, an average thickness of 0.197 μm, an average aspect ratio of 6.14, and a variation coefficient of a circle-equivalent diameter of 27%.

When the emulsions A to D were observed at a liquid nitrogen temperature by a 200-kV transmission electron microscope, most grains of the emulsions A and B had no dislocation lines. A large number of dislocation lines, however, were found on the entire circumferential surface area of each tabular grain of the emulsion C. In the emulsion D, a large number of dislocation lines are locally concentrated about the six corners of each hexagonal tabular grain. Although an average number of dislocation lines per grain could not be correctly counted in each of the emulsions C and D, 20 or more dislocation lines were apparently present per grain in each emulsion. Figs. 1 to 3 show typical photographs of the grains in the emulsions A, C, and D, respectively.

The emulsions A to D were subjected to gold-sulfur sensitization as follows. That is, each emulsion was heated up to 72° C, and 1×10^{-3} mol/mol Ag of a sensitizing dye Dye-1 to be described below, 7×10^{-5} mol/mol Ag of an antifoggant V-8 described in Table B (to be presented later), 1.1×10^{-5} mol/mol Ag of sodium thiosulfate, 1.0×10^{-5} mol/mol Ag of chloroauric acid, and 8.0×10^{-4} mol/mol Ag of potassium thiocyanate were sequentially added to the emulsion, thereby optimally performing chemical sensitization. In this case, "optimal chemical sensitization" means chemical sensitization in which the highest sensitivity was obtained when exposure was performed for 1/10 second after the chemical sensitization.

Dye-1



The emulsions A to D were subjected to gold-sulfur-selenium sensitization as follows. That is, each emulsion was heated up to 72° C, and 1×10^{-3} mol/mol Ag of the above sensitizing dye Dye-1, 1×10^{-4} mol/mol Ag of the antifoggant V-8 described in Table B, 1.0×10^{-5} mol/mol Ag of sodium thiosulfate, 1.5×10^{-5} mol/mol Ag of chloroauric acid, 2.4×10^{-3} mol/mol Ag of potassium thiocyanate, and 1.0×10^{-5}

mol/mol Ag of N,N-dimethylselenourea were sequentially added to the emulsion, thereby optimally performing chemical sensitization.

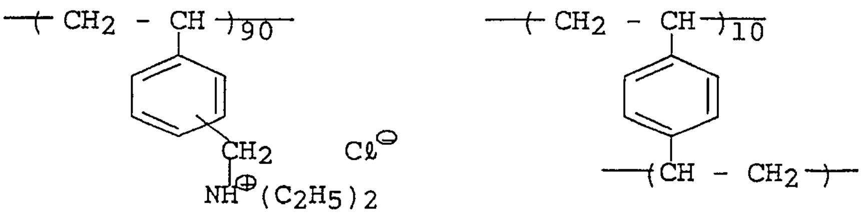
Layers having the following formulations were sequentially formed on a triacetylcellulose support from the support side, thereby forming a coated sample. In this case, the emulsion chemically sensitized as described above were used as the emulsion layer 2 to form sample Nos. 1 to 8.

(Lowermost Layer)

Binder: Gelatin 1 g/m^2

Fixing accelerator:

E-1



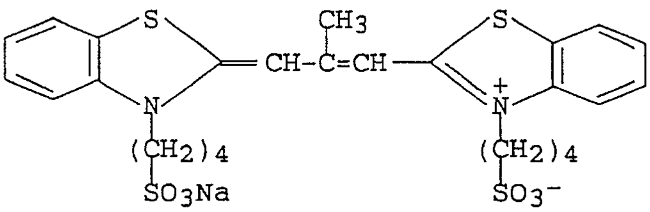
(Emulsion Layer 1)

Emulsion: Spherical monodisperse silver iodobromide grains having circle-equivalent diameter of 0.4 µm, variation coefficient = 13%, silver iodide content = 3 mol%

Coating silver amount: 1.5 g/m^2

Binder: Gelatin 1.6 g/Ag 1 g

Sensitizing dye: 8×10^{-6} mol/Ag 1 g



Additive: $C_{18}H_{35}O(CH_2CH_2O)_{20}H$ 5.8 mg/Ag 1 g

Coating aid: Sodium dodecylbenzenesulfonate 0.07 mg/m^2

Potassium poly p-styrenesulfonate 0.7 mg/m^2

(Emulsion layer 2)

Emulsion: Various types of emulsions

Coating silver amount: 4.0 g/m^2

Binder, additive, and coating aid: the same as in emulsion 1

(Surface Protective Layer)

Binder: Gelatin 0.7 g/m^2

Coating aid: Sodium N-oleoyl-N-methyltaurate 0.2 mg/m^2

Mat agent: Polymethylmethacrylate fine grains (average grain size = 3 µm) 0.13 mg/m^2

These samples were preserved at a temperature of 25° C and a humidity of 65% RH for seven days after coating. Each sample was exposed to a tungsten light (color temperature = 2,854 K) through a continuous wedge for 1/10 second, developed at 20° C for seven minutes by using a D-76 developing solution, fixed by a fixing solution (FUJI FIX: available from Fuji Photo Film Co., Ltd.), and washed and dried.

The sensitivity of the obtained emulsion is represented by a relative value of a reciprocal of an exposure amount required for an optical density to be fog + 0.1.

The graininess of each sample was evaluated as follows.

Each sample was exposed to an amount of light for giving a density of fog + 0.5 and developed as described above, and an RMS graininess was measured by a method described in Macmillan Co., "The Theory of The Photographic Process", page 619.

In addition, storage stability of each sample was evaluated as follows. That is, for evaluation of the storage stability, each sample was stored at a temperature of 50° C and a relative humidity of 30% for six days before exposure.

The obtained results are summarized in Table 1.

Table 1

Sample No.	Emulsion	Silver Iodide Content (mol%)	Aspect Ratio	Dislocation Lines	Chemical Sensitization	Relative Sensitivity	Fog	Relative Graininess	Relative Sensitivity After Storage	Fog After Storage
1 (Comparative Example)	A	3.5	6.03	~ 0	Gold·Sulfur	100	0.14	100	78	0.18
2 (Comparative Example)	A	3.5	6.30	~ 0	Gold·Sulfur·Selenium	110	0.19	104	73	0.28
3 (Comparative Example)	B	6.8	6.16	~ 0	Gold·Sulfur	107	0.14	93	81	0.17
4 (Comparative Example)	B	6.8	6.16	~ 0	Gold·Sulfur·Selenium	114	0.20	98	74	0.33
5 (Comparative Example)	C	4.9	5.56	20 or more	Gold·Sulfur	123	0.14	93	105	0.17

(Continued)

Sample No.	Emulsion	Silver Iodide Content (mol%)	Aspect Ratio	Disloction Lines	Chemical Sensitization	Relative Sensitivity	Fog	Relative Graininess	Relative Sensitivity After Storage	Fog After Storage
6 (Comparative Example)	C	4.9	5.56	20 or more	Gold·Suflur·Selenium	151	0.14	95	141	0.19
7 (Comparative Example)	D	4.9	6.14	20 or more	Gold·Suflur	129	0.12	94	110	0.16
8 (Comparative Example)	D	4.9	6.14	20 or more	Gold·Sulfur·Selenium	162	0.13	95	151	0.18

As is apparent from Table 1, sample of emulsion of the present invention each had high sensitivity. In addition, the fog was low, and changes in fog and sensitivity were small after it was stored.

EXAMPLE 2

(Preparation Method of Emulsion E)

2,000 mℓ of an aqueous solution containing 16 g of gelatin and 21.4 g of KBr were stirred at a temperature of 30° C. An aqueous silver nitrate solution (containing 10.2 g of $AgNO_3$) and an aqueous KBr solution (containing 7.1 g of KBr) were added to the solution by a double jet method. The resultant solution was heated up to 75° C, and 40 g of gelatin were added. Thereafter, the silver potential of the reaction solution was adjusted to be +10 mV with respect to a saturated calomel electrode. After 1.0 mg of thiourea dioxide was added, an aqueous silver nitrate solution (containing 104 g of $AgNO_3$) were added at an accelerated flow rate (a flow rate at the end of the addition was 10 times that at the beginning) over 60 minutes, and an aqueous KBr solution was simultaneously added by the double jet method. During this addition, the silver potential was maintained at +10 mV with respect to the saturated calomel electrode until 93.6 g of $AgNO_3$ was added, and then it was maintained at +90 mv. Thereafter, an aqueous silver nitrate solution (containing 46g of $AgNO_3$) and an aqueous KBr solution (containing 3.0 mol% of KI with respect to KBr) were added by the double jet method. During this addition, the silver potential was maintained at 0 mv with respect to the saturated calomel electrode. After 3.0×10^{-4} mol/mol Ag of $(NH_4)_2PdC\ell_4$ and 1.5×10^{-3} mol/mol Ag of potassium thiocyanate were added, the resultant solution was desalted by a flocculation method, and gelatin was added. Thereafter, a pH and a pAg were adjusted to be 6.9 and 8.0, respectively, to prepare emulsion E. The emulsion E was a monodisperse tabular grain emulsion having an average circle-equivalent diameter of 1.20 µm, an average thickness of 0.20 µm, an average aspect ratio of 6.0, and a variation coefficient of a circle-equivalent diameter of 15%.

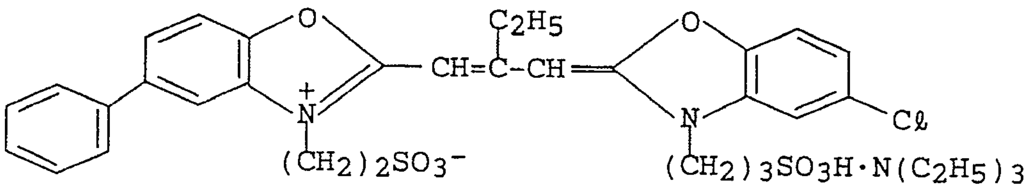
(Preparation Method of Emulsion F)

2,000 mℓ of an aqueous solution containing 16 g of gelatin and 21.4 g of KBr were stirred at a temperature of 30° C. An aqueous silver nitrate solution (containing 10.2 of $AgNO_3$) and an aqueous KBr solution (containing 7.1 g of KBr) were added to the solution by the double jet method. The resultant solution was heated up to 75° C, and 40 g of gelatin were added. Thereafter, the silver potential of the reaction solution was adjusted to be +10 mv with respect to a saturated calomel electrode. After 1.0 mg of thiourea dioxide was added, an aqueous silver nitrate solution (containing 104 g of $AgNO_3$) was added at an accelerated flow rate (a flow rate at the end of the addition was 10 times that at the beginning) over 50 minutes, and an aqueous KBr solution was simultaneously added by the double jet method. During this addition, the silver potential was maintained at +10 mV with respect to the saturated calomel electrode until 93.6 g of $AgNO_3$ were added and then it was maintained at +90 mV. Thereafter, an aqueous silver nitrate solution (containing 4.8 g of $AgNO_3$) and an aqueous KI solution (containing 3.5 g of KI) were added by the double jet method over 10 minutes. Thereafter, an aqueous silver nitrate solution (containing 41.2 g of $AgNO_3$) and an aqueous KBr solution were added by the double jet method over five minutes. During this addition, the silver potential was maintained at 0 mV with respect to the saturated calomel electrode. After 3.0×10^{-4} mol/mol Ag of $(NH_4)_2PdC\ell_4$ and 1.5×10^{-3} mol/mol Ag of potassium thiocyanate were added, the resultant solution was desalted by a flocculation method, and gelatin was added. Thereafter, a pH and a pAg were adjusted to be 6.9 and 8.0, respectively, to prepare emulsion F. The emulsion F was a monodisperse tabular grain emulsion having an average circle-equivalent diameter of 1.14 µm, an average thickness of 0.21 µm, an average aspect ratio of 5.4, and a variation coefficient of a circle-equivalent diameter of 16%.

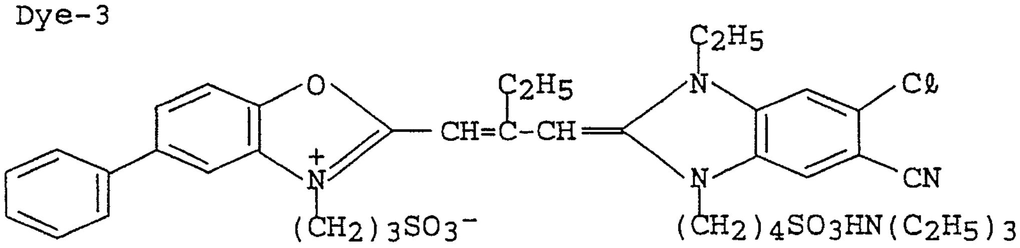
When the emulsions E and F were observed at a liquid nitrogen temperature by a 200-kV transmission electron microscope, most grains of the emulsion E had no dislocation lines. In the emulsion F, however, a large number of dislocation lines are locally concentrated about the six corners of each hexagonal tabular grain. Although an average number of dislocation lines per grain could not be correctly counted in the emulsion F, 20 or more dislocation lines were apparently present per grain in the emulsion. Figs. 4 and 5 show typical photographs of the emulsions E and F, respectively.

The emulsions E and F were subjected to gold-sulfur sensitization as follows. That is, each emulsion was heated up to 64° C, and 4.3×10^{-3} mol/mol Ag of sensitizing Dye-2, 1.3×10^{-4} mol/mol Ag of sensitizing Dye-3, 1.8×10^{-4} mol/mol Ag of sensitizing dyes Dye-4, 2×10^{-4} mol/mol Ag of the above antifoggant II-1, 5.5×10^{-6} mol/mol Ag of sodium thiosulfate, 1.0×10^{-5} mol/mol Ag of chloroauric acid, and 1.2×10^{-3} mol/mol Ag of potassium thiocyanate were sequentially added to the emulsion, thereby optimally performing chemical sensitization. In this case, "optimal chemical sensitization" means chemical sensitization in which the highest sensitivity was obtained when exposure was performed for 1/100 second after the chemical sensitization.

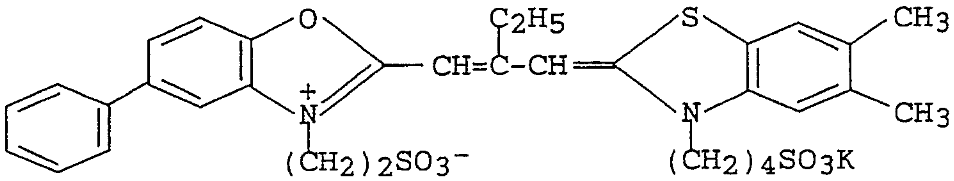
Dye-2



Dye-3



Dye-4

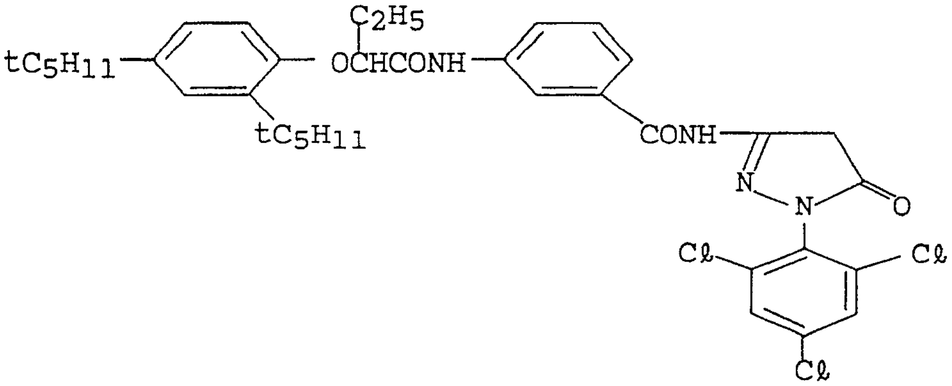


The emulsions E and F were subjected to gold-selenium sensitization as follows. That is, each emulsion was heated up to 64°C, and 4.3×10^{-4}, 1.3×10^{-4}, and 1.8×10^{-4} mol/mol Ag of the above sensitizing dyes Dye-2, Dye-3, and Dye-4, respectively, 6×10^{-4} mol/mol Ag of the antifoggant II-1, 2.0×10^{-5} mol/mol Ag of chloroauric acid, 2.4×10^{-3} mol/mol Ag of potassium thiocyanate, and 1.1×10^{-5} mol/mol Ag of selenourea were sequentially added to the emulsion, thereby optimally performing chemical sensitization.

The emulsions E and F were subjected to gold-sulfur-selenium sensitization as follows. That is, each emulsion was heated up to 64°C, and 4.3×10^{-4}, 1.3×10^{-4} and 1.8×10^{-4} mol/mol Ag of the above sensitizing dyes Dye-2, Dye-3, and Dye-4, respectively, 6×10^{-4} mol/mol Ag of the antifoggant II-1, 5.5×10^{-6} mol/mol Ag of sodium thiosulfate, 1.8×10^{-5} mol/mol Ag of chloroauric acid, 2.4×10^{-3} mol/mol Ag of potassium thiocyanate, and 8.3×10^{-6} mol/mol Ag of selenourea were sequentially added to the emulsion, thereby optimally performing chemical sensitization.

The emulsions subjected to chemical sensitization as described above and protective layers in amounts as listed in Table 2 were coated on triacetylcellulose film supports having undercoating layers, thereby forming sample Nos. 9 to 14.

Table 2 Emulsion Coating Conditions

(1) Emulsion Layer	
Emulsion: Various types of emulsions	(silver 2.1 × 10^{-2} mol/m^2)
Coupler	(1.5 × 10^{-3} mol/m^2)
	
Tricresylphosphate	(1.10 g/m^2)
Gelatin	(2.30 g/m^2)
(2) Protective Layer	
2,4-dichlorotriazine-6-hydroxy-s-triazine sodium salt	(0.08 g/m^2)
Gelatin	(1.80 g/m^2)

These samples were left to stand at a temperature of 40° C and a relative humidity of 70% for 14 hours and exposed for 1/100 second through a gelatin filter SC50 available from Fuji Photo Film Co., Ltd. and a continuous wedge, and the following color development was performed.

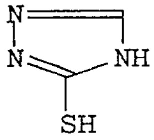
The densities of the developed samples were measured by using a green filter.

Step	Time	Temperature
Color development	2 min. 00 sec.	40°C
Bleach-fixing	3 min. 00 sec.	40°C
Washing (1)	20 sec.	35°C
Washing (2)	20 sec.	35°C
Stabilization	20 sec.	35°C
Drying	50 sec.	65°C

The processing solution compositions will be described below.

(Color Developing Solution)	(g)
Diethylenetriaminepentaacetic acid	2.0
1-hydroxyethylidene-1,1-diphosphonic acid	3.0
Sodium sulfite	4.0
Potassium carbonate	30.0
Potassium Bromide	1.4
Potassium Iodide	1.5 mg
Hydroxylamine sulfate	2.4
4-[N-ethyl-N-(β-hydroxyethyl)amino]-2-methylaniline sulfate	4.5
Water to make	1.0 ℓ
pH	10.05

(Bleach-Fixing Solution)	(g)
Ferric ammonium ethylenediaminetetraacetate (dihydrate)	90.0
Disodium ethylenediaminetetraacetate	5.0
Sodium sulfite	12.0
Ammonium thiosulfate aqueous solution (70%)	260.0 mℓ
Acetic acid (98%)	5.0 mℓ
Bleaching accelerator	0.01 mol



Water to make	1.0 ℓ
pH	6.0

(Washing Solution)

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & House Co.) and an OH type strongly basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/ℓ or less. Subsequently, 20 mg/ℓ of sodium isocyanuric acid dichloride and 1.5 g/ℓ of sodium sulfate were added. The pH fell within the range of 3.5 to 7.5.

(Stabilizing Solution)	(g)
Formalin (37%)	2.0 mℓ
Polyoxyethylene-p-monononyl-phenylether (average polymerization degree = 10)	0.3
Disodium ethylenediaminetetraacetate	0.05
Water to make	1.0 ℓ
pH	5.0 to 8.0

The sensitivity is represented by a relative value of a reciprocal of an exposure amount (lux•sec.) for giving a density of fog + 0.2.

In addition, the graininess of each sample was evaluated as follows.

Each sample was exposed to an amount of light for giving a density of fog + 0.5 and developed as described above, and an RMS graininess was measured by the method described in Macmillan Co., "The Theory of The Photographic Process, page 619.

The obtained results are summarized in Table 3.

Table 3

Sample No.	Emulsion	Aspect Ratio	Dislocation Lines	Chemical Sensitization	Relative Sensitivity	Fog	Relative Sensitivity
9 (Comparative Example)	E	6.0	~ 0	Gold·Sulfur	100	0.14	100
10 (Comparative Example)	E	6.0	~ 0	Gold·Selenium	62	0.68	91
11 (Comparative Example)	E	6.0	~ 0	Gold·Sulfur·Selenium	129	0.48	98
12 (Comparative Example)	F	5.4	20 or more	Gold·Sulfur·	123	0.14	97
13 (Comparative Example)	F	5.4	20 or more	Gold·Selenium	91	0.54	93
14 (Comparative Example)	F	5.4	20 or more	Gold·Sulfur·Selenium	162	0.15	97

As is apparent from Table 3, samples of emulsion of the present invention were low in fog and had high sensitivity.

EXAMPLE 3

(Preparation Method of Emulsion G)

1,000 mℓ of an aqueous solution containing 10.5 g of gelatin and 3 g of KBr were stirred at a temperature of 60°C, and an aqueous $AgNO_3$ solution (containing 8.2 g of $AgNO_3$) and an aqueous KBr solution (containing 5.7 g of KBr and 0.35 g of KI) were added to the solution by a double jet method. Gelatin was added to the resultant solution, and the temperature was increased to 75°C. After the silver potential was adjusted to be -40 mV, an aqueous $AgNO_3$ solution (containing 136.3 g of $AgNO_3$) and an aqueous KBr solution (containing 12.0 mol% of KI) were added by the double jet method. During this addition, the silver potential was maintained at -60 mV with respect to a saturated calomel electrode. The temperature was decreased to 40°C, and an aqueous silver nitrate solution (containing 3.2 g of $AgNO_3$) and an aqueous KI solution (containing 2.3 g of KI) were added over five minutes. After 7.0 x 10^{-7} mol/mol Ag of K_3IrCl_6 were added to the resultant solution, an aqueous silver nitrate solution (containing 22.3 g of $AgNO_3$) and an aqueous KBr solution were added by the double jet method over 5.35 minutes. During this addition, the silver potential was maintained at -100 mV with respect to the saturated calomel electrode.

After 20 mℓ of 0.1-N potassium thiocyanate were added, the resultant solution was desalted by a flocculation method, and gelatin was added. Thereafter, a pH and a pAg were adjusted to be 5.5 and 8.2, respectively, to prepare emulsion G. This emulsion G was a tabular grain emulsion having an average circle-equivalent diameter of 1.71 µm, an average thickness of 0.13 µm, and an average aspect ratio of 13.2. A variation coefficient of a circle-equivalent diameter of the emulsion was 42%.

(Preparation Method of Emulsion H)

1,000 mℓ of an aqueous solution containing 10.5 g of gelatin and 3 g of KBr were stirred at a temperature of 60°C, and an aqueous $AgNO_3$ solution (containing 8.2 g of $AgNO_3$) and an aqueous KBr solution (containing 5.7 g of KBr and 0.35 g of KI) were added to the solution by the double jet method. Gelatin was added to the resultant solution, and the temperature was increased to 75°C. After a potential was adjusted to be 0 mV, an aqueous $AgNO_3$ solution (containing 136.3 g of $AgNO_3$) and an aqueous KBr solution (containing 12.0 mol% of KI) were added by the double jet method. During this addition, the silver potential was maintained at 0 mv with respect to a saturated calomel electrode. After the silver potential was adjusted to be -60 mv, the temperature was decreased to 40°C, and an aqueous silver nitrate solution (containing 3.2 g of $AgNO_3$) and an aqueous KI solution (containing 2.3 g of KI) were added over five minutes. After 7.0 x 10^{-7} mol/mol Ag of K_3IrCl_6 were added to the resultant solution, an aqueous silver nitrate solution (containing 22.3 g of $AgNO_3$) and an aqueous KBr solution were added by the double jet method over 5.35 minutes. During this addition, the silver potential was maintained at -100 mv with respect to the saturated calomel electrode.

After 20 mℓ of 0.1-N potassium thiocyanate were added, the resultant solution was desalted by a flocculation method, and gelatin was added. Thereafter, a pH and a pAg were adjusted to be 5.5 and 8.2, respectively, to prepare emulsion H. This emulsion H was a tabular grain emulsion having an average circle-equivalent diameter of 1.42 µm, an average thickness of 0.21 µm, and an average aspect ratio of 6.8. A variation coefficient of a circle-equivalent diameter of the emulsion was 24%.

(Preparation Method of Emulsion I)

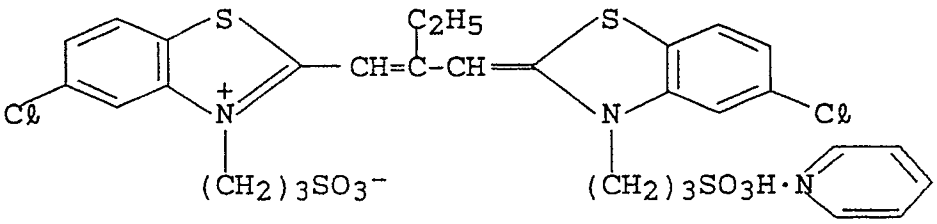
1,000 mℓ of an aqueous solution containing 10.5 g of gelatin and 3 g of KBr were stirred at a temperature of 60°C, and an aqueous AgNO3 solution (containing 8.2 g of $AgNO_3$)and an aqueous KBr solution (containing 5.7 g of KBr and 0.35 g of KI) were added to the solution by the double jet method. Gelatin was added to the resultant solution, and the temperature was increased to 75°C. After the silver potential was adjusted to be +20 mV, an aqueous $AgNO_3$ solution (containing 136.3 g of $AgNO_3$) and an aqueous KBr solution (containing 12.0 mol% of KI) were added by the double jet method. During this addition, a silver potential was maintained at +20 mV with respect to a saturated calomel electrode. After the silver potential was adjusted to be -60 mV, the temperature was decreased to 40°C, and an aqueous silver nitrate solution (containing 3.2 g of $AgNO_3$) and an aqueous KI solution (containing 2.3 g of KI) were added over five minutes. After 7.0 x 10^{-7} mol/mol Ag of K_3IrCl_6 were added to the resultant solution, an aqueous silver nitrate solution (containing 22.3 g of $AgNO_3$) and an aqueous KBr solution were added by the double jet method over 5.35 minutes. At this time, the silver potential was maintained at -100 mV with respect to the saturated calomel electrode.

After 20 mℓ of 0.1-N potassium thiocyanate were added, the resultant solution was desalted by a flocculation method, and gelatin was added. Thereafter, a pH and a pAg were adjusted to be 5.5 and 8.2, respectively, to prepare emulsion I. This emulsion I was a tabular grain emulsion having an average circle-equivalent diameter of 1.30 µm, an average thickness of 0.22 µm, and an average aspect ratio of 5.9. A variation coefficient of a circle-equivalent diameter of the emulsion was 23%.

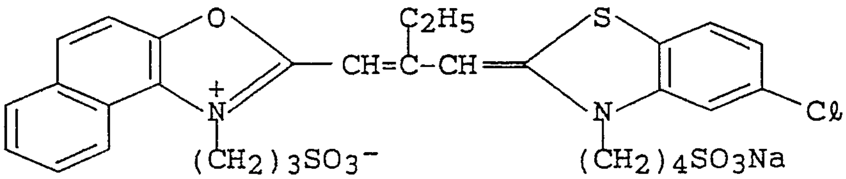
When the emulsions G, H, and I were observed at a liquid nitrogen temperature by a 200-kV transmission electron microscope, a large number of dislocation lines were found on the entire circumference of tabular grains in each emulsion.

The emulsions G, H, and I were subjected to gold-sulfur-selenium sensitization as follows. That is, each emulsion was heated up to 72°C, and 3.3 x 10^{-4}, 3.2 x 10^{-4}, and 1.7 x 10^{-5} mol/mol Ag of sensitizing dyes Dye-5, Dye-6, and Dye-7, respectively, 1 x 10^{-4} mol/mol Ag of the antifoggant V-8 shown in Table B, 3.2 × 10^{-5} mol/mol Ag of 5-benzylidene-3-ethylrhodanine, 9.2 × 10^{-6} mol/mol Ag of chloroauric acid, 3.0 × 10^{-3} mol/mol Ag of potassium thiocyanate, and 3 × 10^{-6} mol/mol Ag of selenourea were sequentially added to the emulsion, thereby optimally performing chemical sensitization. In this case, "optimal chemical sensitization" means chemical sensitization in which the highest sensitivity was obtained when exposure was performed for 1/100 second after the chemical sensitization.

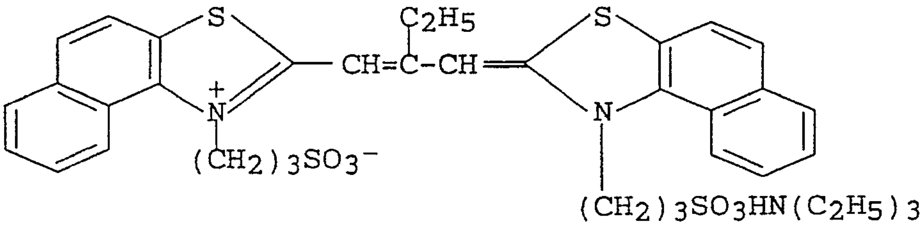
Dye-5



Dye-6



Dye-7



A plurality of layers having the following compositions were coated on undercoated triacetylcellulose film supports, thereby forming samples 301 to 303 as multilayered color light-sensitive materials. (Compositions of Light-Sensitive Layers)

Numerals corresponding to the respective components indicate coating amounts in units of g/m^2. The silver halide is represented by a silver coating amount. A coating amount of the sensitizing dye is represented in units of mols per mol of the silver halide in the same layer.

(Sample 301 to 303)

Layer 1: Antihalation Layer

Black colloidal silver	silver	0.18
Gelatin		1.40

Layer 2: Interlayer

2,5-di-t-pentadecylhydroquinone	0.18
EX-1	0.07
EX-3	0.02
EX-12	0.002
U-1	0.06
U-2	0.08
U-3	0.10
HBS-1	0.10
HBS-2	0.02
Gelatin	1.04

Layer 3: Donor Layer with Interlayer Effect on Red-Sensitive Layer

Emulsion 9	silver	1.2
Emulsion 10	silver	2.0
Sensitizing dye IV		4×10^{-4}
EX-10		0.10
HBS-1		0.10
HBS-2		0.10
Gelatin		2.82

Layer 4: Interlayer

EX-5	0.040

HBS-1		0.020
Gelatin		0.80
Layer 5: 1st Red-Sensitive Emulsion Layer		
Emulsion 1	silver	0.25
Emulsion 2	silver	0.25
Sensitizing dye I		1.5×10^{-4}
Sensitizing dye II		1.8×10^{-5}
Sensitizing dye III		2.5×10^{-4}
EX-2		0.335
EX-10		0.020
U-1		0.07
U-2		0.05
U-3		0.07
HBS-1		0.060
Gelatin		0.87
Layer 6: 2nd Red-Sensitive Emulsion Layer		
Emulsion 6	silver	1.0
Sensitizing dye I		1.0×10^{-4}
Sensitizing dye II		1.4×10^{-5}
Sensitizing dye III		2.0×10^{-4}
EX-2		0.400
EX-3		0.050
EX-10		0.015
U-1		0.07
U-2		0.05
U-3		0.07
Gelatin		1.30
Layer 7: 3rd Red-Sensitive Emulsion Layer		
Emulsion G, H, or I	silver	1.60
EX-3		0.010
EX-4		0.080
EX-2		0.097
EX-8		0.080
HBS-1		0.22
HBS-2		0.10
Gelatin		1.63

Layer 8: Interlayer

EX-5		0.040
HBS-1		0.020
Gelatin		0.80

Layer 9: 1st Green-Sensitive Emulsion Layer

Emulsion 1	silver	0.15
Emulsion 2	silver	0.15
Sensitizing dye V		3.0×10^{-5}
Sensitizing dye VI		1.0×10^{-4}
Sensitizing dye VII		3.8×10^{-4}
Sensitizing dye IV		5.0×10^{-5}
EX-6		0.260
EX-1		0.021
EX-7		0.030
EX-8		0.005
HBS-1		0.100
HBS-3		0.010
Gelatin		0.63

Layer 10: 2nd Green-Sensitive Emulsion Layer

Emulsion 3	silver	0.45
Sensitizing dye V		2.1×10^{-5}
Sensitizing dye VI		7.0×10^{-5}
Sensitizing dye VII		2.6×10^{-4}
Sensitizing dye IV		5.0×10^{-5}
EX-6		0.094
EX-22		0.018
EX-7		0.026
HBS-1		0.160
HBS-3		0.008
Gelatin		0.50

Layer 11: 3rd Green-Sensitive Emulsion Layer

Emulsion 4	silver	1.2
Sensitizing dye V		3.5×10^{-5}
Sensitizing dye VI		8.0×10^{-5}
Sensitizing dye VII		3.0×10^{-4}
Sensitizing dye IV		0.5×10^{-5}
EX-13		0.015

EX-11		0.100
EX-1		0.025
HBS-1		0.25
HBS-2		0.10
Gelatin		1.54
Layer 12: Yellow Filter Layer		
Yellow colloidal silver	silver	0.05
EX-5		0.08
HBS-1		0.03
Gelatin		0.95
Layer 13: 1st Blue-Sensitive Emulsion Layer		
Emulsion 1	silver	0.08
Emulsion 2	silver	0.07
Emulsion 5	silver	0.07
Sensitizing dye VIII		3.5×10^{-4}
EX-9		0.721
EX-8		0.042
HBS-1		0.28
Gelatin		1.10
Layer 14: 2nd Blue-Sensitive Emulsion Layer		
Emulsion 6	silver	0.45
Sensitizing dye VIII		2.1×10^{-4}
EX-9		0.154
EX-10		0.007
HBS-1		0.05
Gelatin		0.78
Layer 15: 3rd Blue-Sensitive Emulsion Layer		
Emulsion 7	silver	0.77
Sensitizing dye VIII		2.2×10^{-4}
EX-9		0.20
HBS-1		0.07
Gelatin		0.69
Layer 16: 1st Protective Layer		
Emulsion 8	silver	0.20
U-4		0.11
U-5		0.17
HBS-1		0.05

Gelatin	1.00
Layer 17: 2nd Protective Layer	
Polymethylacrylate grains (diameter = about 1.5 μm)	0.54
S-1	0.20
Gelatin	1.20

In addition to the above components, a gelatin hardener H-1, EX-14 to EX-21, and a surfactant were added to each layer. Emulsions 1-10 used in the samples were as follows.

Emulsion No.	Average AgI Content (%)	Average Grain Size (μm)	Variation Coefficient of Grain Size (%)	Diameter/ Thickness Ratio	Silver Amount Ratio (AgI content %)
Emulsion 1	4.0	0.45	27	1	Core/Shell=1/3(13/1), Double Structure Grain
" 2	8.9	0.70	14	1	Core/Shell=3/7(25/2), Double Structure Grain
" 3	10	0.75	30	2	Core/Shell=1/2(24/3), Double Structure Grain
" 4	10	1.05	35	3	Core/Shell=1/2(24/3), Double Structure Grain
" 5	4.0	0.25	28	1	Core/Shell=1/3(24/3), Double Structure Grain
" 6	14.0	0.75	25	2	Core/Shell=1/2(42/0), Double Structure Grain
" 7	14.5	1.30	25	3	Core/Shell=37/63(34/3), Double Structure Grain
" 8	1	0.07	15	1	Uniform Grain
" 9	5	0.90	30	2	Core/Shell=1/1(10/0), Double Structure Grain
" 10	7	1.50	25	2	Core/Shell=1/1(14/0), Double Structure Grain

Samples formed by using the emulsions G, H, and I in the layer are referred as sample 301, 302, and 303, respectively. Chemical stractures of the compounds used in the samples 301 to 303 are showed in the Table C.

The above color photographic light-sensitive materials 301 to 303 were exposed and processed by using an automatic developing machine (until an accumulated replenishing amount of a bleaching solution was increased to be three times a mother solution tank capacity), as follows.

Processing Method

Process	Time	Temperature	Replenishing Amount	Tank Volume
Color development	3 min. 15 sec.	38°C	15 mℓ	20 ℓ
Bleaching	6 min. 30 sec.	38°C	10 mℓ	40 ℓ
Washing	2 min. 10 sec.	35°C	10 mℓ	20 ℓ
Fixing	4 min. 20 sec.	38°C	20 mℓ	30 ℓ
Washing (1)	1 min. 05 sec.	35°C	Counter flow piping from (2) to (1)	10 ℓ
Washing (2)	1 min. 00 sec.	35°C	20 mℓ	10 ℓ
Stabilization	1 min. 05 sec.	38°C	10 mℓ	10 ℓ
Drying	4 min. 20 sec.	55°C		

The replenishing amount is represented by an amount per meter of a 35-mm wide sample

The compositions of the process solutions will be presented below.

Color Developing Solution:	Mother Solution (g)	Replenishment Solution (g)
Diethylenetriaminepentaacetate	1.0	1.1
1-hydroxyethylidene-1,1-diphosphonic acid	3.0	3.2
Sodium sulfite	4.0	4.9
Potassium carbonate	30.0	30.0
Potassium bromide	1.4	-
Potassium iodide	1.5 mg	-
Hydroxylamine sulfate	2.4	3.6

4-(N-ethyl-N-β-hydroxylethylamino)-2-methylaniline sulfate	4.5	7.2
Water to make	1.0 ℓ	1.0 ℓ
pH	10.05	10.10

Bleaching Solution:	Mother Solution (g)	Replenishment Solution (g)
Ferric sodium ethylenediamine-tetraacetate Trihydrate	100.0	140.0
Disodium ethylene-diaminetetraacetate	10.0	11.0
Ammonium bromide	140.0	180.0
Ammonium nitrate	30.0	40.0
Ammonia water (27%)	6.5 mℓ	2.5 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.0	5.5

Fixing Solution:	Mother Solution (g)	Replenishment Solution (g)
Disodium ethylene-diaminetetraacetate	0.5	1.0
Sodium sulfite	7.0	12.0
Sodium bisulfite	5.0	9.5
Ammonium thiosulfate aqueous solution (70%)	170.0 mℓ	240.0 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.7	6.6

Wash solution: Common for mother and replenishment solutions

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & House Co.) and an OH type strongly basic anion exchange resin (Amberlite IR-400) to set calcium and magnesium ion concentrations to be 3 mg/ℓ or less. Subsequently, 20 mg/ℓ of sodium isocyanuric acid dichloride and 1.5 g/ℓ of sodium sulfate were added. The pH of the solution fell within the range of 6.5 to 7.5.

Stabilizing Solution:	Mother Solution (g)	Replenishment Solution (g)
Formalin (37%)	2.0 mℓ	3.0 mℓ
Polyoxyethylene-p-monononylphenylether (average polymerization degree = 10)	0.3	0.45
Disodium ethylenediaminetetraacetate	0.05	0.08
Water to make	1.0	1.0
pH	5.0 - 8.0	5.0 - 8.0

The sensitivity is represented by a relative value of a reciprocal of an exposure amount for giving a fogging density and a density higher than the fogging density by 1.0, obtained by the characteristic curve of the cyan image. The obtained results are summarized in Table 4.

Table 4

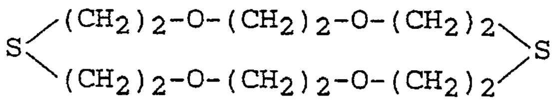
Sample No.	Emulsion	Aspect Ratio	Relative Sensitivity	Fog
301 (Present Invention)	G	13.2	100	0.18
302 (Present Invention)	H	6.8	132	0.16
303 (Present Invention)	I	5.9	141	0.14

As is apparent from Table 4, samples of emulsion of the present invention were low in fog and high in sensitivity.

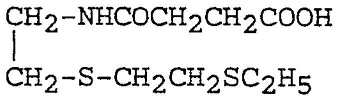
According to the present invention, an emulsion having higher sensitivity can be obtained. In addition, the present invention can provide a stable emulsion which is low in fog.

Table A

(a)

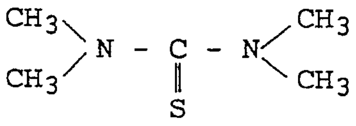


$HO-(CH_2)_2-S-(CH_2)_2-S-(CH_2)_2-OH$

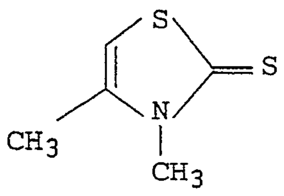


$CH_2-NHCOCH_2CH_2COOH$ / $CH_2-S-CH_2CH_2SC_2H_5$

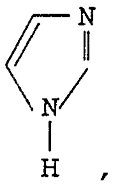
(b)



(c)



(d)



(e)

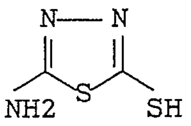
K_2SO_3 ,

(f)

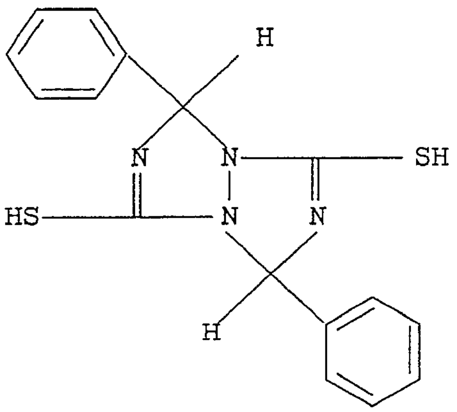
NH_4SCN ,
KSCN.

Table B

V-1



V-2



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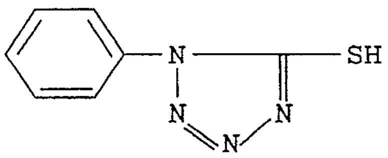
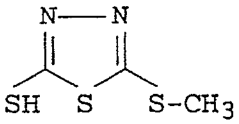
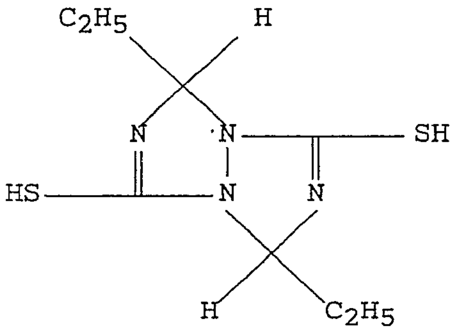


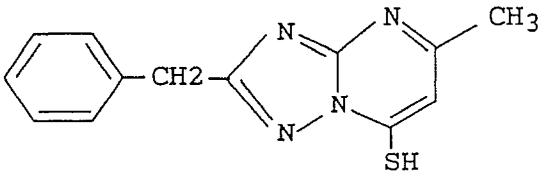
V-4



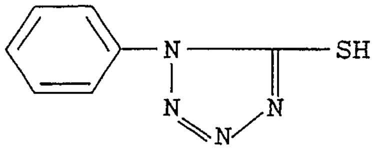
V-5



V-6



V-7



V-8

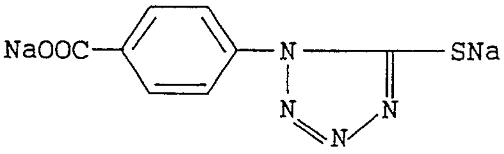
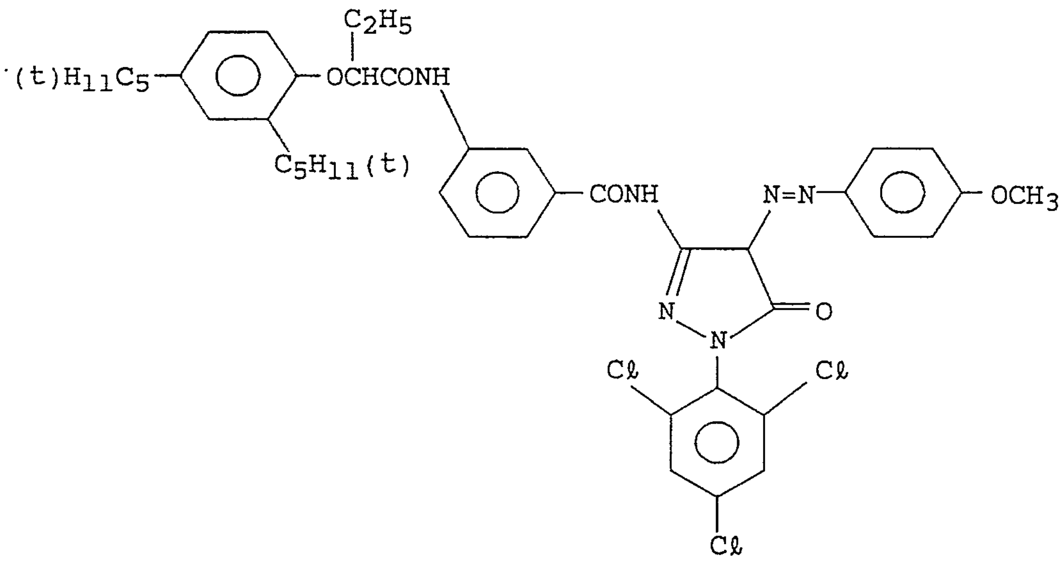
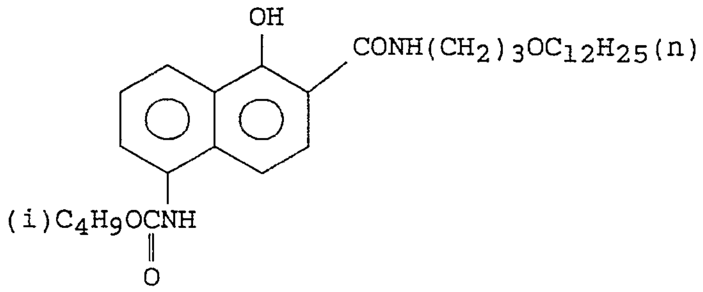


Table C

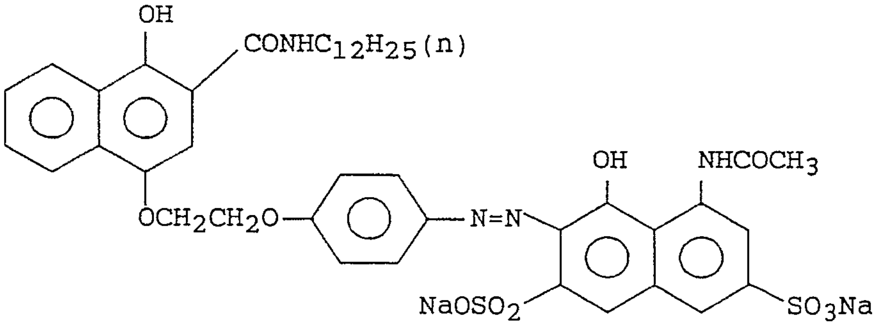
EX-1



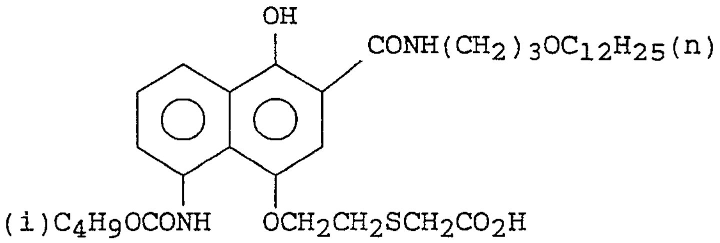
EX-2



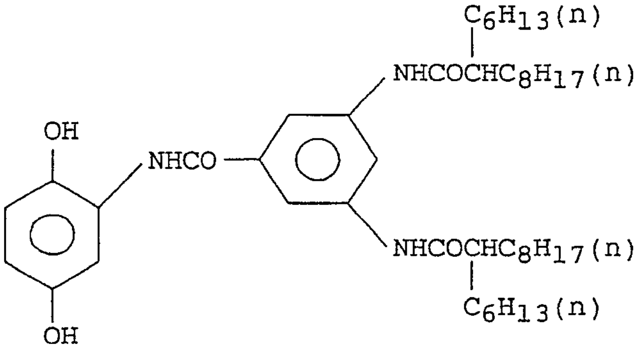
EX-3



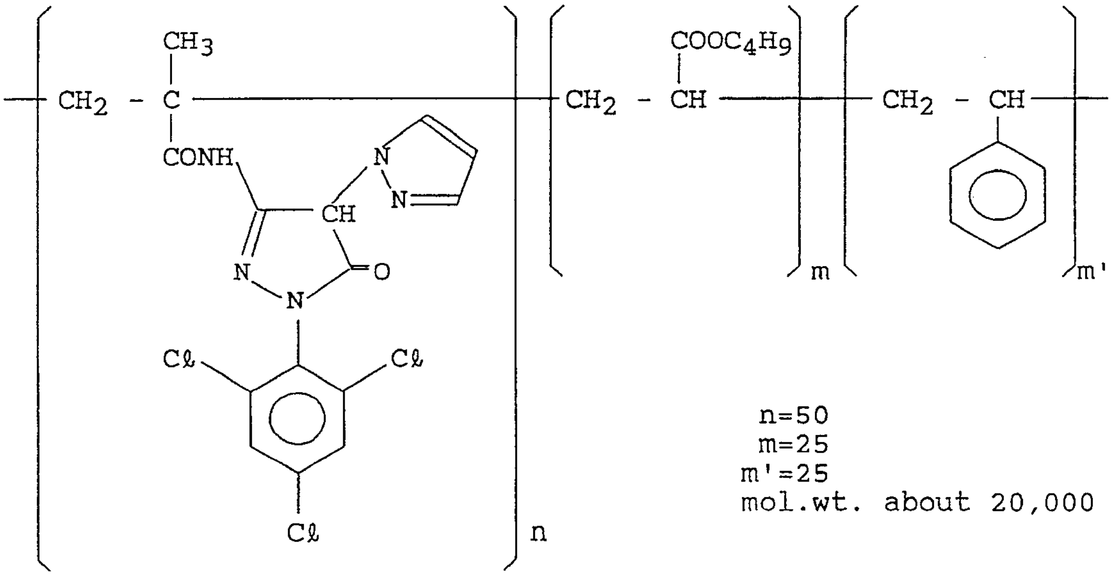
EX-4



EX-5

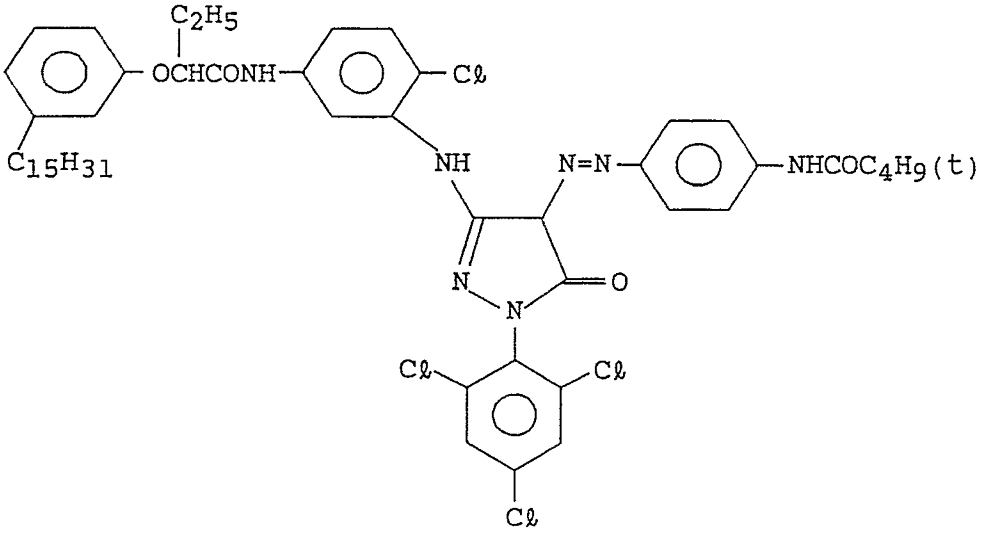


EX-6

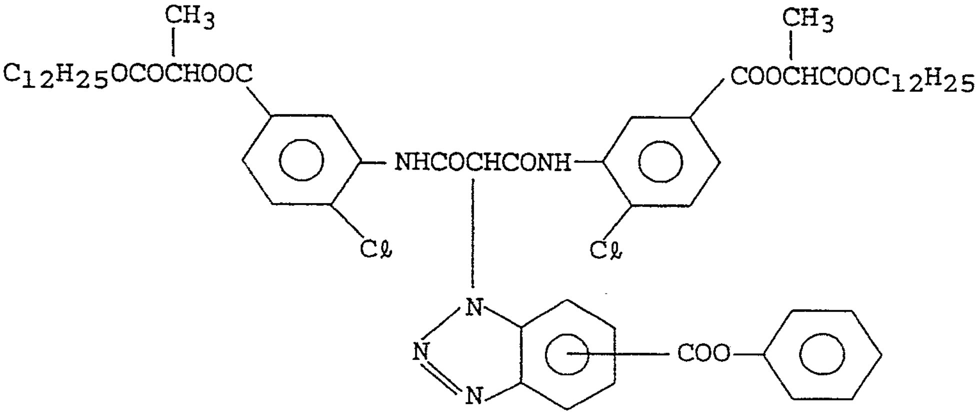


n=50
m=25
m'=25
mol.wt. about 20,000

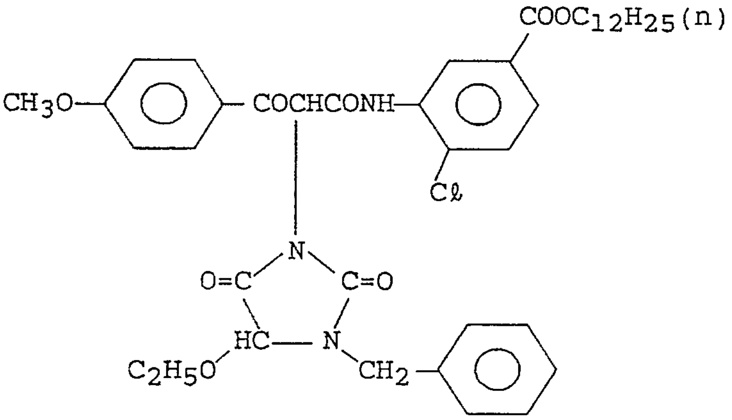
EX-7


C2H5
OCHCONH
Cℓ
C15H31
NH
N=N
NHCOC4H9(t)
N
N
O
Cℓ
Cℓ
Cℓ

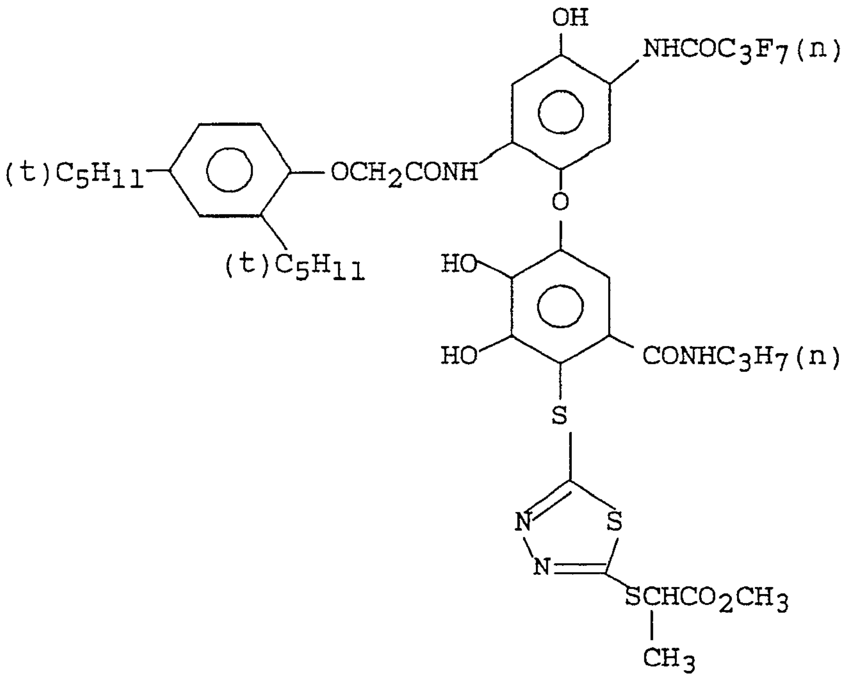
EX-8


CH3
C12H25OCOCHOOC
CH3
COOCHCOOC12H25
NHCOCHCONH
Cℓ
Cℓ
N
N
N
COO

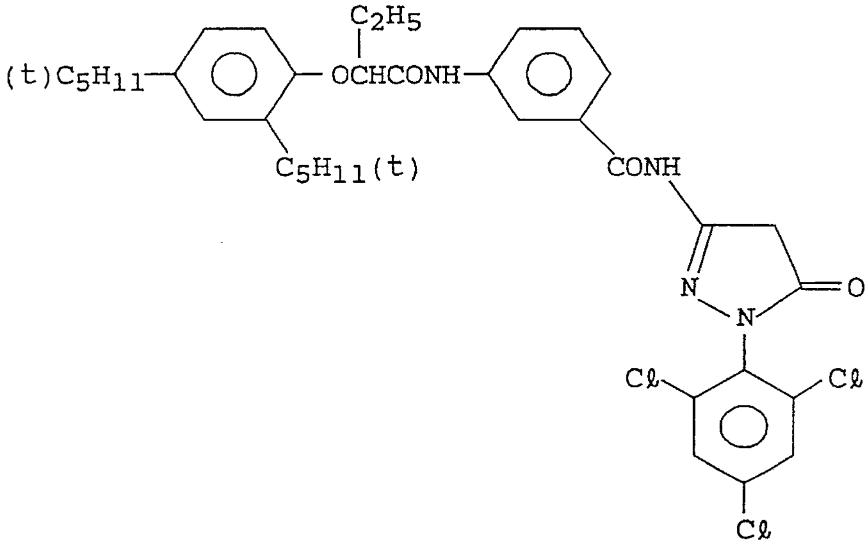
EX-9


COOC12H25(n)
CH3O
COCHCONH
Cℓ
N
O=C
C=O
HC
N
C2H5O
CH2

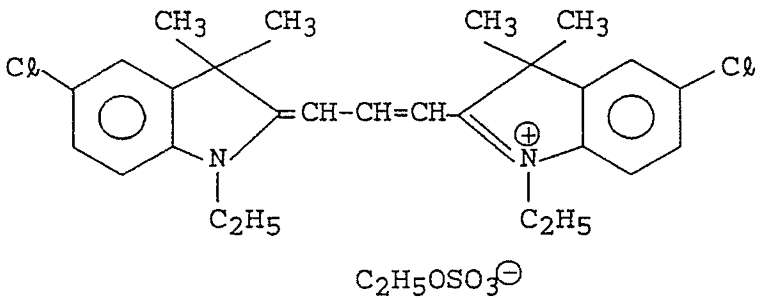
EX-10


OH
NHCOC3F7(n)
(t)C5H11
OCH2CONH
(t)C5H11
O
HO
HO
CONHC3H7(n)
S
N
S
N
SCHCO2CH3
CH3

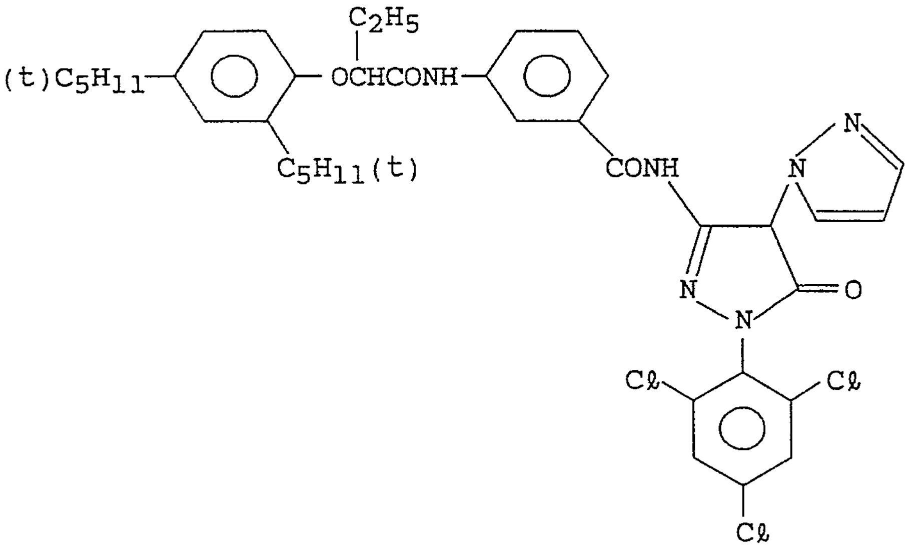
EX-11


C2H5
(t)C5H11
OCHCONH
C5H11(t)
CONH
N
N
O
Cℓ
Cℓ
Cℓ

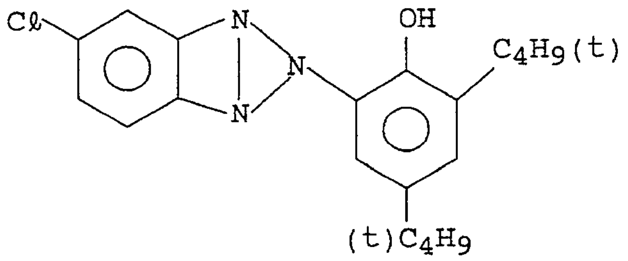
EX-12


CH3
CH3
CH3
CH3
Cl
Cl
CH-CH=CH
N
N
C2H5
C2H5
C2H5OSO3

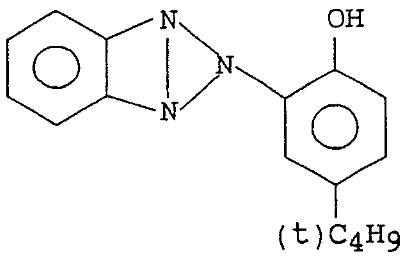
EX-13


(t)C5H11
C2H5
OCHCONH
C5H11(t)
CONH
N
N
N
N
O
Cl
Cl
Cl

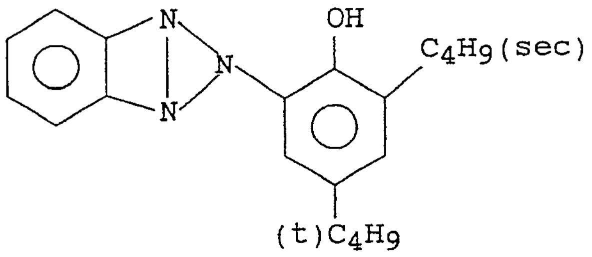
U-1



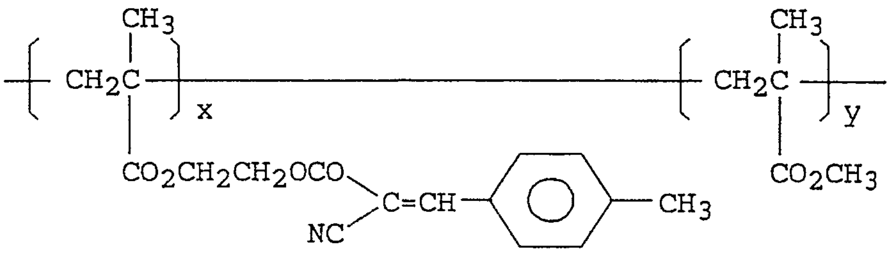
U-2



U-3

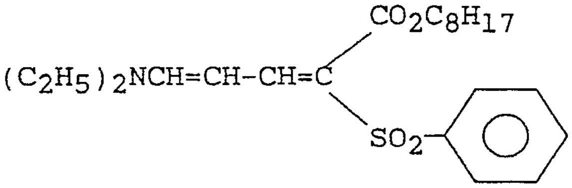


U-4



x:y = 70:30 (wt%)

UV-5



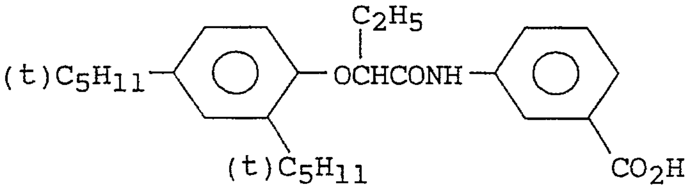
HBS-1

tricresylphosphate

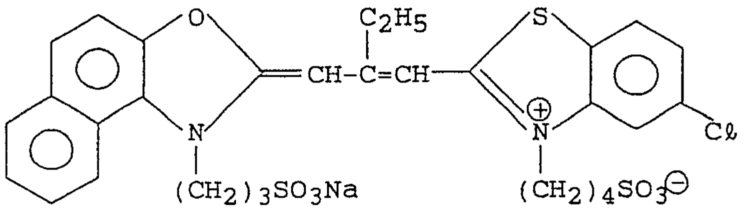
HBS-2

di-n-butylphthalate

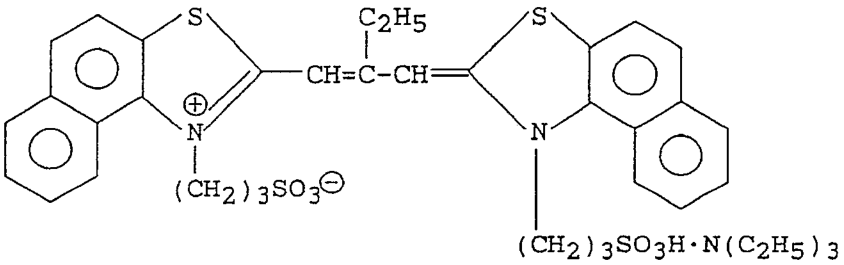
HBS-3



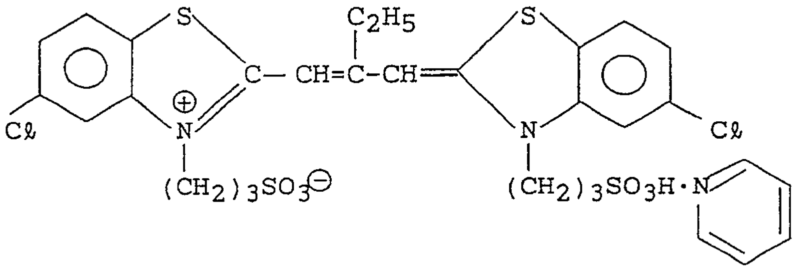
Sensitizing dye I



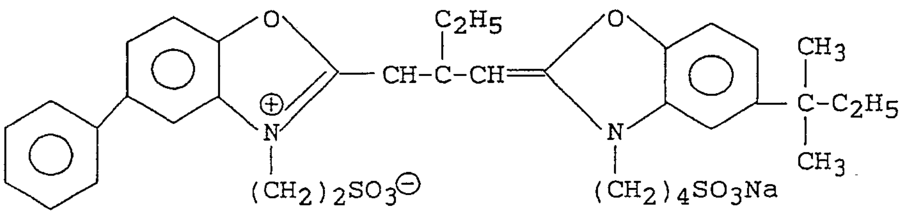
Sensitizing dye II



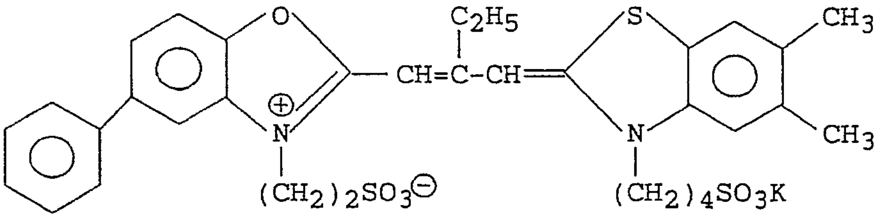
Sensitizing dye III



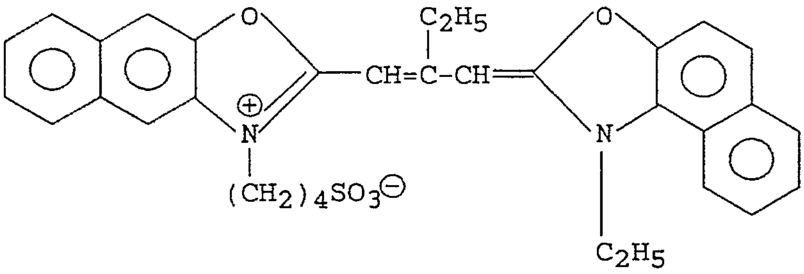
Sensitizing dye IV



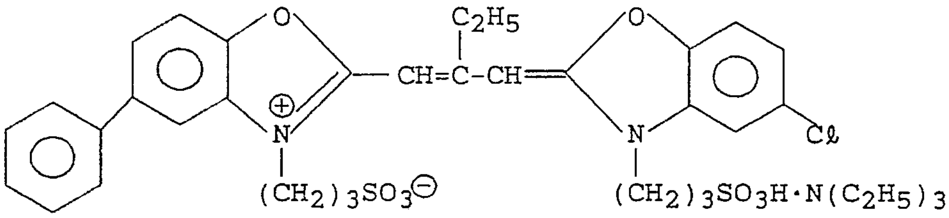
Sensitizing dye V



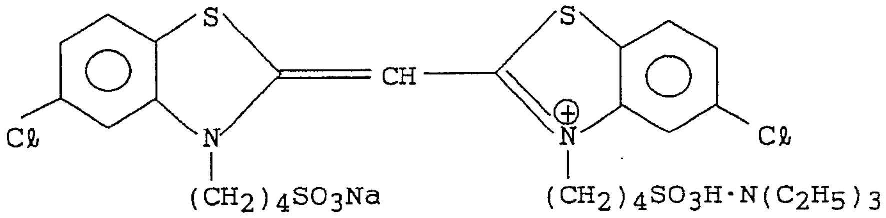
Sensitizing dye VI



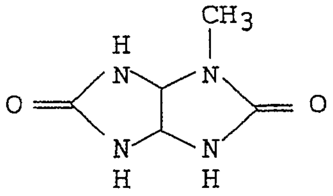
Sensitizing dye VII



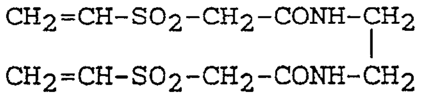
Sensitizing dye VIII



S-1

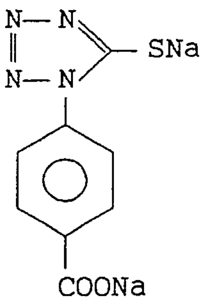


H-1

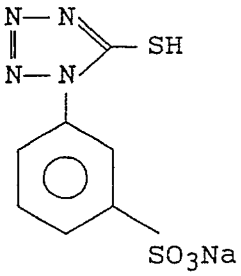


$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \end{array}$$

Ex-14



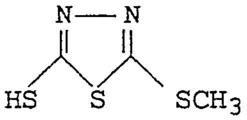
Ex-15



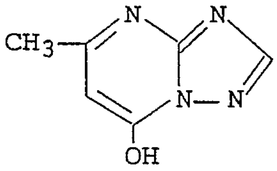
Ex-16

copolymer of polyvinilpyrrolidone and polyvinylalchol

Ex-17



Ex-18



Ex-19

1,2-benzisothiazoline-3-one

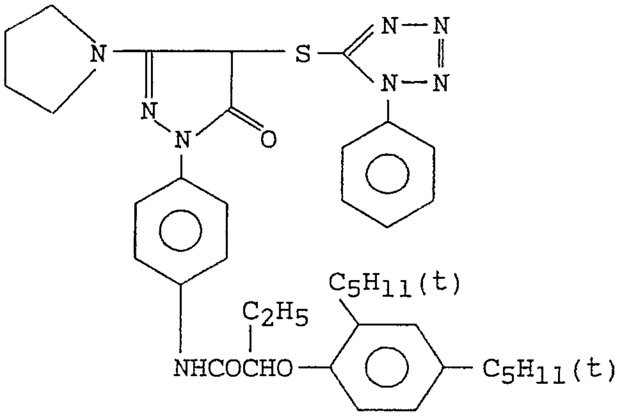
Ex-20

n-butyl-p-hydroxybenzoate

Ex-21

2-phenoxyethanol

Ex-22



Claims

1. A silver halide photographic emulsion containing tabular silver halide grains consisting of silver chloroiodobromide, silver iodobromide, silver chlorobromide, or silver bromide, having an aspect ratio of 3 or more, having at least one dislocation line per grain, and having been subjected to chemical

sensitization by at least one selenium sensitizer, at least one gold sensitizer, and at least one sulfur sensitizer.

2. The silver halide photographic emulsion according to claim 1, characterized in that said tabular silver halide grains have 10 or more of dislocation lines per grain.

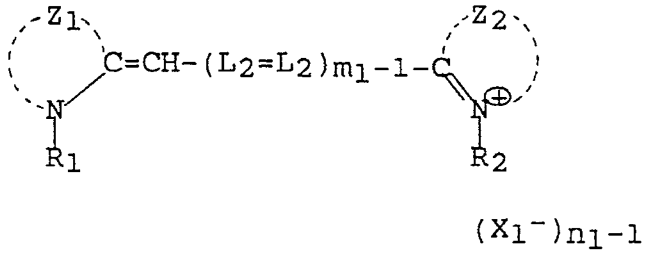
3. A photographic light-sensitive material comprising at least one silver halide emulsion layer on a support, characterized in that tabular silver halide grains according to claim 1 account for at least 50% of a total projected area of silver halide grains in said silver halide emulsion layer.

4. The photographic material according to claim 3, characterized in that said silver halide grains occupying at least 50% of the total projected area of the silver halide grains in said silver halide emulsion layer are tabular silver halide grains according to claim 1 having an average aspect ratio of 3 or more and less than 8.

5. The silver halide photographic emulsion according to claim 1, characterized in that a sensitizing dye is added during or before the chemical sensitization.

6. The silver halide photographic emulsion according to claim 5, characterized in that the sensitizing dye is a dye represented by a formula (I):

Formula (I)



wherein Z_1 and Z_2 each represent an atom group required to form a heterocyclic nucleus,
L_1 or L_2 represents a methine group and a methine group having a substituent group,
R_1 and R_2 each represent alkyl or alkyl having substituent group,
m_1 represents 1, 2, or 3,
$x_1^{\ominus}$ represents an acid anion group, and
n_1 represents 1 or 2.

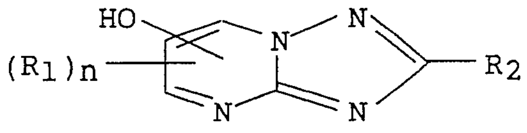
7. The silver halide photographic emulsion according to claim 1, characterized in that said tabular silver halide grains are monodisperse.

8. The silver halide photographic emulsion according to claim 1, characterized in that a labile selenium compound is used as the selenium sensitizer.

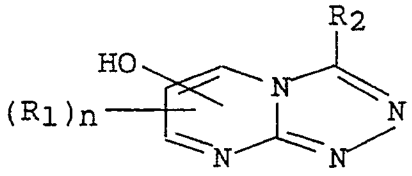
9. The silver halide photographic emulsion according to claim 1, characterized in that said tabular silver halide grains have been subjected to reduction sensitization during grain formation.

10. The silver halide photographic emulsion according to claim 5, characterized in that a compound represented by formula (II), (III) or (IV) has been added to the silver halide emulsion:

Formula (II)

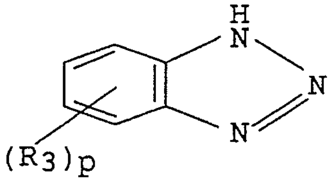


Formula (III)



wherein R_1 and R_2 each represent hydrogen or aromatic moiety, and n represents 1 or 2;

Formula (IV)



wherein p represents 0 or an integer of 1 to 4, and R_3 represents halogen, aliphatic group or aryl.

11. The silver halide photographic emulsion according to claim 5, characterized in that a nitrogen-containing heterocyclic compound having a mercapto group, has been added to the silver halide emulsion.

FIG. 1 (EMULSION A)

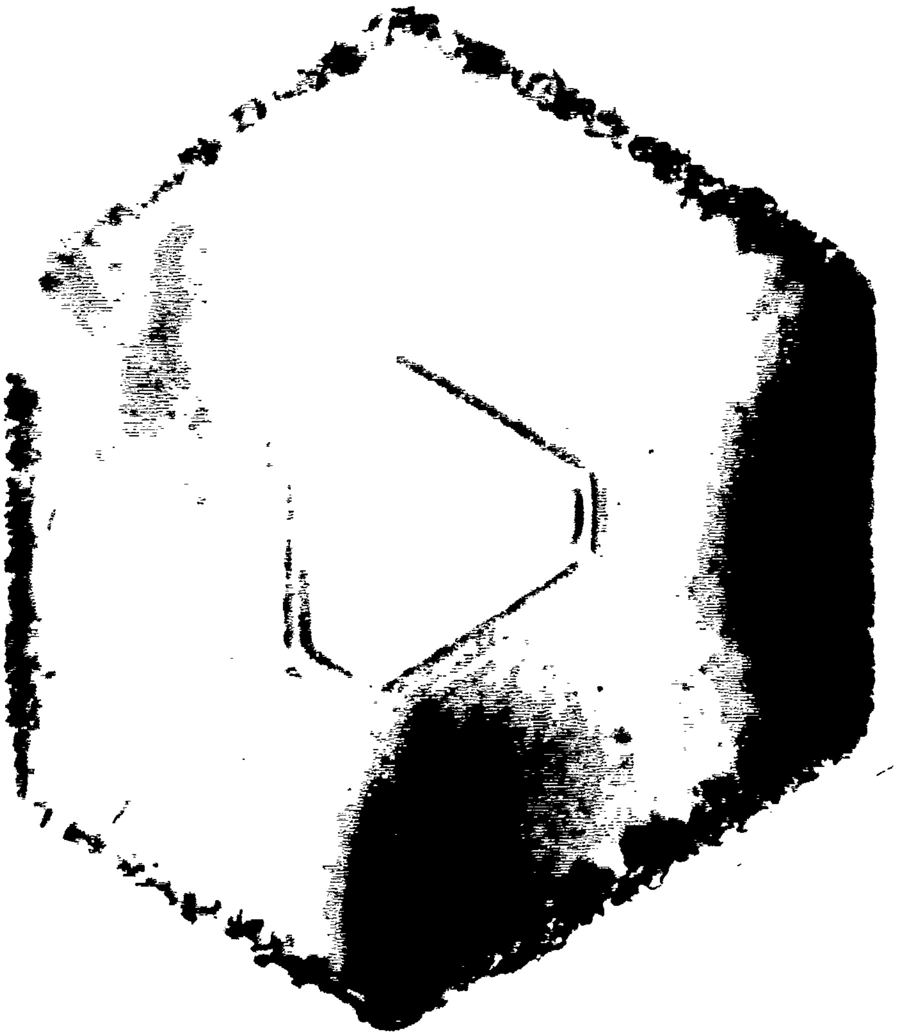
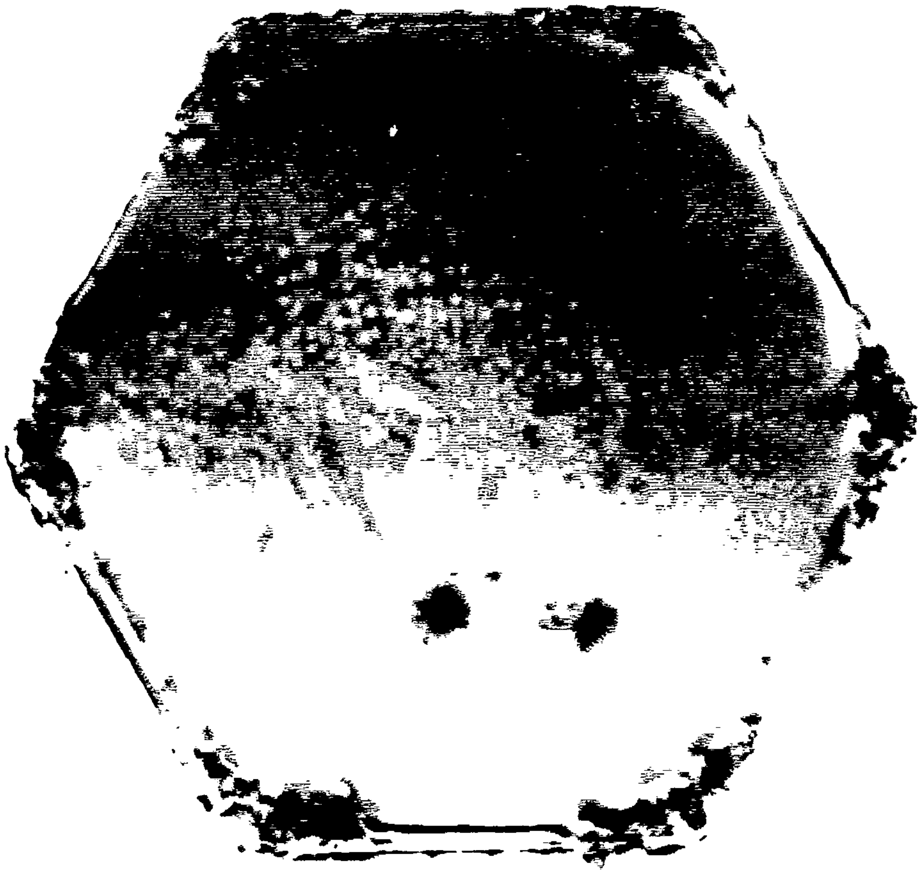


FIG. 2 (EMULSION C)



F I G. 3 (EMULSION D)

FIG. 4 (EMULSION E)

FIG. 5 (EMULSION F)

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 2158

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y,D	EP-A-0 282 896 (FUJI PHOTO FILM COMPANY LIMITED) * the whole docum& JP-A-63-220238 * – – –	1-11	G 03 C 1/09 G 03 C 1/035
Y,D	DE-A-1 472 836 (EASTMAN KODAK COMPANY) * the whole document & JP-A-4313489 * – – – – –	1-11	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	03 June 91	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document