Method of manufacturing silver halide photographic emulsion.

In a method of manufacturing a silver halide photographic emulsion, a palladium compound is added in an amount of $5 \times 10^{-5}$ mol or more per mol of a silver halide after a grain formation step and before a desilverization step.
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The present invention relates to a method of manufacturing a silver halide photographic emulsion and, more particularly, to a stable method, i.e., a method having a good reproducibility, of manufacturing a silver halide photographic emulsion having a high sensitivity and a low fogging density. In particular, the present invention relates to a stable method, i.e., a method having a good reproducibility, of manufacturing a silver halide photographic emulsion which is subjected to reduction-sensitization in a grain formation step.

U.S. Patent 2,448,060 discloses that a sensitivity of an emulsion can be increased by adding a palladium compound and ascorbic acid to the emulsion after sulfur sensitization and before coating of the emulsion. U.S. Patent 2,568,079 discloses that especially a low-intensity sensitivity of an emulsion can be increased by adding a palladium compound to the emulsion after gold-plus-sulfur sensitization and before coating of the emulsion. U.S. Patents 2,472,627, 2,472,631, 2,566,245, and 2,566,263 disclose that a storage stability of a photosensitive material at high temperatures and high humidities can be improved by adding a palladium compound to the emulsion after chemical sensitization of the emulsion.

British Patent 1,351,309 discloses that a noble metal salt is added in an amount of $3 \times 10^{-7}$ to $3 \times 10^{-5}$ mol per mol of a silver halide during formation of silver halide grains (during conversion).

U.S. Patent 4,092,171 discloses that a high sensitivity can be obtained and a storage stability can be improved by adding an organic phosphonic acid complex of a palladium compound to an emulsion.

JP-A-61-67845 ("JP-A" means unexamined published Japanese patent application) discloses a method of manufacturing a silver halide emulsion, in which a monodisperse core/shell type silver halide grain having different silver iodide contents between portions near the surface and inside thereof is chemically ripened in the presence of at least one of a chalcogen sensitizer, a gold sensitizer, and a water-soluble palladium salt. JP-A-62-212641 discloses a method of manufacturing a silver halide emulsion, in which a silver halide grain having an (nnl) face is chemically sensitized in the presence of at least one of a chalcogen sensitizer, a gold sensitizer, and a compound of a Group VIII noble metal of the periodic table.

JP-A-48-87925 discloses that a sensitivity is increased while a gradation is reduced by adding a reducing agent in a process of forming silver halide grains. JP-B-58-1410 ("JP-B" means examined Japanese patent application) discloses that a sensitivity is increased without reducing a gradation by adding a reducing agent in a process of forming silver halide grains and then adding an oxidizing agent before the silver halide grain reaches its final size. When the present invention is applied to the above emulsion to which a reducing agent is added, an effect of the present invention is particularly significant.

It is an object of the present invention to provide a method of manufacturing a silver halide photographic emulsion with a high sensitivity and a low fogging density. It is another object of the present invention to provide a stable method of manufacturing the silver halide photographic emulsion and, more particularly, to provide a stable method of manufacturing a silver halide photographic emulsion which is subjected to reduction sensitization during a grain formation step.

The above objects of the present invention can be achieved by the following means. That is, the objects of the present invention can be achieved by a method of manufacturing a silver halide photographic emulsion, wherein a palladium compound is added in an amount of $5 \times 10^{-5}$ mol or more per mol of a silver halide after a grain formation step and before a desalting step. In particular, the objects of the present invention can be achieved by a method of manufacturing a silver halide photographic emulsion, wherein a palladium compound is added in an amount of $5 \times 10^{-5}$ mol or more per mol of a silver halide after a grain formation step of silver halide grains and before a desalting step, the silver halide grains having been subjected to reduction sensitization in the grain formation step.

The present invention will be described in detail below. A process of manufacturing a silver halide emulsion is roughly divided into grain formation, desalting, chemical sensitization, and coating steps. The grain formation step is further classified into e.g. nucleation, ripening, and precipitation. These steps are performed not in the above-mentioned order. For example, grain formation and chemical sensitization are simultaneously performed, or chemical sensitization is repeatedly performed. "To add a palladium compound after a grain formation step and before a desalting step" means that the palladium compound is added during a time interval from a timing at which addition of a silver salt solution is completed in grain formation step to a timing at which the desalting step is started. That is, the palladium compound can be added simultaneously with completion of addition of the silver salt solution or added at an arbitrary timing after completion of addition of the silver salt solution and before the desalting step. A total amount of the palladium compound can be added at once, can be divided and added several times, or can be continuously added over a predetermined time. The emulsion may be ripened after addition of the palladium compound and before the desalting step or left to stand at a high temperature for
a long time period after addition of the palladium compound and before the desalting step.

In the present invention, the palladium compound is added in an amount of $5 \times 10^{-5}$ mol or more, and preferably, $1 \times 10^{-3}$ mol or less per mol of a silver halide. Most preferably, the palladium compound is added in an amount of $1 \times 10^{-4}$ mol to $5 \times 10^{-4}$ mol per mol of the silver halide. If the amount is $1 \times 10^{-5}$ mol or less, the effect of the present invention cannot be obtained. If the amount is $1 \times 10^{-3}$ mol or more, another problem occurs.

In the present invention, the palladium compound means a divalent palladium salt or tetravalent palladium salt. The palladium compound is preferably represented by $R_2\text{PdX}_4$, wherein $R$ represents hydrogen, an alkali metal atom, or a ammonium group and $X$ represents halogen, e.g., chlorine, bromine, or iodine. More specifically, $K_2\text{PdCl}_4$, $(\text{NH}_4)_2\text{PdCl}_4$, $\text{Na}_2\text{PdCl}_4$, or $(\text{NH}_4)_2\text{PdCl}_4$ is preferable. Although $\text{PdCl}_2$, $\text{PdCl}_2\cdot 2\text{H}_2\text{O}$, $\text{Pd}(\text{NH}_3\text{(NO}_3\text{)})_2\cdot \text{Cl}_2$, $(\text{NH}_3)_2\text{PdCl}_2$, $\text{Pd(OH)}_2$, $\text{Pd(SO}_4\text{)}$, $\text{Pd(NO}_3\text{)}_2$, $\text{Na}_2\text{Pd}-$(NO$_3$)$_4$, or $(\text{NH}_3)_2\text{PdCl}_4$ can be used, a water-soluble palladium compound is preferable. Most preferably, these palladium compounds are used in combination with a thiocyanate ion in a molar amount five times that of the palladium compound.

Addition conditions of the palladium compound are arbitrary. That is, a temperature may be $30^\circ\text{C}$ to $80^\circ\text{C}$, and preferably, $40^\circ\text{C}$ to $70^\circ\text{C}$. A pH and a pAg may take arbitrary values. The pH is preferably 4 to 10.

In the present invention, the above palladium compound is most preferably added after grain formation of silver halide grains, which have been subjected to reduction sensitization in the grain formation step, and before the desalting step.

"Reduction sensitization is performed during the grain formation step of a silver halide emulsion" basically means that reduction sensitization is performed during nucleation, ripening, and precipitation. Reduction sensitization may be performed during nucleation or physical ripening in the initial stage of grain formation, or during precipitation. Most preferably, reduction sensitization is performed during precipitation of silver halide grains. The method of performing the reduction sensitization during precipitation includes a method in which reduction sensitization is performed while silver halide grains are grown by physical ripening or addition of a water-soluble silver salt and a water-soluble alkali halide and a method in which reduction sensitization is performed while precipitation is temporarily stopped and then grains are further precipitated.

In the present invention, reduction sensitization can be selected from a method in which a known reducing agent is added to a silver halide emulsion, a method called "silver ripening" in which precipitation or ripening is performed in a low-pAg atmosphere at a pAg of 1 to 7, and a method called "high-pH ripening" in which precipitation or ripening is performed in a high-pH atmosphere at a pH of 8 to 11. Alternatively, these methods can be performed in a combination of two or more thereof.

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

Known examples of the reduction sensitizer are a stannous salt, amines and polyamines, a hydrazine derivative, formamidinesulfonic acid, a silane compound, and a borane compound. In the present invention, these known compounds can be used singly or in a combination of two or more thereof. Compounds preferred as the reduction sensitizer are stannous chloride, thiourea dioxide, and dimethylamineborane. An addition amount of the reduction sensitizer must be properly selected since it depends on emulsion manufacturing conditions. The addition amount is preferably $10^{-4}$ to $10^{-3}$ mol per mol of a silver halide. Ascorbic acid or its salt can be preferably used as a reduction sensitizer. In this case, this reduction sensitizer is used in an amount of $5 \times 10^{-5}$ to $1 \times 10^{-4}$, preferably $5 \times 10^{-4}$ to $1 \times 10^{-3}$, and most preferably, $1 \times 10^{-3}$ to $1 \times 10^{-2}$ mol per mol of a silver halide.

The reduction sensitizer can be dissolved in water, alcohols, glycols, ketones, esters, and amides and then added during grain formation. Although the reduction sensitizer can be added in a reaction vessel beforehand, it is preferably added at an arbitrary timing during grain formation. Alternatively, the reduction sensitizer may be added to an aqueous solution of a water-soluble silver salt or water-soluble alkali halide, and grain formation may be performed by using these solutions. A method in which a solution of the reduction sensitizer is added several times or continuously added as grain formation progresses is also preferable.

The present inventors have studied in detail an effect of an addition timing and an addition amount of a palladium compound on e.g., a sensitivity and a fogging density of a prepared emulsion, and have found that the best result can be obtained when a predetermined amount or more of a palladium compound is added before a desalting step. Although a preferable effect of a palladium compound can also be obtained when the palladium compound is added after the desalting step and before chemical sensitization, this effect is inferior to that obtained when the compound is added before the desalting step. More specifically,
a preferable effect is obtained by a silver halide photographic emulsion manufactured by performing reduction-sensitization in a grain formation step and chemical sensitization in the presence of a palladium compound in an amount of $1 \times 10^{-4}$ mol or more per mol of a silver halide. The reduction sensitization can be performed during any of nucleation and physical ripening in the initial stages of grain formation, and precipitation. Most preferably, reduction sensitization is performed during precipitation of silver halide grains. Note that the terms "during precipitation" and "reduction sensitization" are defined as described above. The silver halide emulsion subjected to a reduction-sensitization is desalted and then chemically sensitized in the presence of a palladium compound in an amount of $1 \times 10^{-4}$ mol or more per mol of a silver halide. More preferably, chemical sensitization is performed in the of $2 \times 10^{-4}$ mol or more of a palladium compound. In this case, the upper limit is $5 \times 10^{-3}$ mol. More preferably, chemical sensitization is performed in the presence of $1 \times 10^{-3}$ mol or less of a palladium compound. Most preferably, chemical sensitization is performed by using, together with a palladium compound, thiocyanate ions in an amount of mol five times or more that of the palladium compound. In this case, the expression "chemical sensitization in the presence of a palladium compound" means that a palladium compound is added and chemical sensitization at a high temperature is performed. Chemical sensitization is preferably performed at a temperature of 45°C or more, and more preferably, 50°C or more. Chemical sensitization is preferably performed for five minutes or more, and more preferably, 10 to 120 minutes. In this chemical sensitization, a sulfur sensitization method using an active gelatin or a compound containing sulfur capable of reacting with silver (e.g., thiosulfate, thioureas, mercapto compounds, and rhodanines); a reduction sensitization method using a reducing agent (e.g., stannous salt, amines, a hydrazine derivative, formamidine sulfonic acid and a silane compound); and a noble metal sensitization method using a noble metal compound (e.g., gold complex salt and complex salts of Group VII metals of the periodic table, e.g., Pt and Ir), can be used singly or in a combination of two or more thereof. The most preferable method is a combination of sulfur sensitization and gold sensitization (this is also called "gold-plus-sulfur sensitization") or a combination of sulfur sensitization, reduction sensitization, and gold sensitization. Chemical sensitization in the presence of a palladium compound is performed within pH and pAg ranges to be described later.

Generally, a silver halide photographic emulsion which is desalted and then chemically sensitized in the presence of a palladium compound in an amount of $1 \times 10^{-4}$ to $5 \times 10^{-3}$ mol per mol of a silver halide can achieve a higher sensitivity and a lower fogging density than those of an emulsion which is not added with a palladium compound. The sensitivity of this emulsion, however, tends to vary in accordance with sedimentation conditions in the desalting step. In addition, a resulted sensitivity of this emulsion is lower than that of an emulsion which is added with a palladium compound before the desalting step.

More preferably, at least one compound selected from compounds represented by formulas (I), (II), and (III) below is used in a process of manufacturing a silver halide emulsion subjected to reduction sensitization:

(I) $R-SO_2S-M$
(II) $R-SO_2S-R'$
(III) $RSO_2S-L_mSSO_2-R^2$ wherein $R$, $R'$, and $R^2$ may be the same or different and represent aliphatic, aromatic, or heterocyclic, $M$ represents a cation, $L$ represents a divalent bonding group, and $m$ represents 0 or 1.

A compound represented by formula (I), (II), or (III) may be a polymer containing a divalent group derived from a structure represented by formula (I), (II), or (III) as a repeating unit. If possible, $R$, $R'$, $R^2$, and $L$ may be bonded to form a ring.

Compounds represented by formulas (I), (II), and (III) will be described in more detail below. When each of $R$, $R'$, and $R^2$ is aliphatic, it is a saturated or unsaturated, straight-chain, branched, or cyclic aliphatic hydrocarbon group, and preferably, alkyl having 1 to 22 carbon atoms or alkenyl or alkynyl having 2 to 22 carbon atoms. These groups may have a substituent group. Examples of the alkyl are methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, 2-ethylhexyl, decyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, isopropyl, and t-butyl.

Examples of the alkenyl are allyl and butenyl.

Examples of the alkynyl group are propargyl and butynyl.

An aromatic group of $R$, $R'$, and $R^2$ is preferably a monocyclic or condensation ring aromatic group and preferably has 6 to 20 carbon atoms. Examples of such aromatic are phenyl and naphthyl. These groups can have a substituent group.

A heterocyclic group of $R$, $R'$, and $R^2$ is a 3- to 15-membered ring having at least one element of nitrogen, oxygen, sulfur, selenium, and tellurium, and at least one carbon atom. Examples of the heterocyclic group are pyrroldine, piperidine, pyridine, tetrahydrofuran, thiophene, oxazole, thiazole, imidazole, benzothiazole, benzoxazole, benzimidazole, selenazole, benzoselenazole, tellurazole, triazole, ben-
zotriazole, tetrazole, oxadiazole, and thiadiazole.

Examples of the substituent group on R, R¹, and R² are alkyl (e.g., methyl, ethyl, and hexyl), alkoxy (e.g., methoxy, ethoxy, and octyloxy), aryl (e.g., phenyl, naphthyl, and tolyl), hydroxy, halogen (e.g., fluorine, chlorine, bromine, and iodine), aryleoxy (phenoxy), alkylthio (methylthio and butylthio), arythio (phenylthio), acyl (acetyl, propionyl, butyryl, and valeryl), sulfonyl (methyl sulfonyl and phenylsulfonyl), acylamino (e.g., acetylamino and benzoylamino), sulfonylamino (e.g., methanesulfonylamino and benzenesulfonylamino), acyloxy (e.g., acetoxy and benzoxy), carboxyl, cyano, sulfo, amino, -SO₂SM, and -SO₂R¹.

Examples of the divalent bonding group represented by L are atom or atom group including at least one member selected from the group consisting of C, N, S, and O. More specifically, L is one or a combination of two or more of alkylene, alkenylene, alkinylene, arylene, -O-, -S-, -NH-, -CO-, and -SO₂-.

L is preferably a divalent aliphatic group or a divalent aromatic group. Examples of the divalent aliphatic group of L are \((-CH₂)\_n\) (n = 1 to 12), -CH₂-CH=CH-CH₂-, -CH₂C=CCH₂-, -CH₂-0-, and a xylylene group. Examples of the divalent aromatic group of L are phenylene and napthylene.

These substituent groups may further have the above-mentioned substituent groups.

M is preferably a metal ion or an organic cation. Examples of the metal ion are a lithium ion, a sodium ion, and a potassium ion. Examples of the organic cation are an ammonium ion (e.g., ammonium, tetramethylammonium, and tetraethylammonium), a phosphonium ion (e.g., tetraphenylphosphonium), and a guanidyl group.

When a compound represented by formula (I), (II), or (III) is a polymer, examples of its repeating unit are as follows.

\[
\begin{align*}
&\text{CH₃} \quad \text{SO₂SM} \\
&\text{CH₄} \quad \text{CO₂CH₂CH₂OCH₂CH₂SO₂SM} \\
&\text{CH₃} \quad \text{SO₂SM} \\
&\text{CH₄} \quad \text{CONH} \\
&\text{CH₄} \quad \text{CH₃} \\
&\text{CH₄} \quad \text{CH₂SO₂SM}
\end{align*}
\]

These polymers may be a homopolymer or a copolymer with another copolymerizable monomer.

Although examples of a compound represented by formula (I), (II), or (III) are listed in Table A, compounds are not limited to these examples.


A compound represented by formula (I), (II), or (III) is preferably added in an amount of 1 x 10⁻⁷ to 1 x 10⁻¹ mol per mol of a silver halide. The addition amount is more preferably 1 x 10⁻⁵ to 1 x 10⁻².
A compound represented by formula (I), (II), or (III) can be added at any timing in a manufacturing process, e.g., during grain formation of a silver halide emulsion or before or after chemical sensitization. The compound is preferably added before or during reduction sensitization. Reduction sensitization is preferably performed in the presence of the thiosulfonic acid compound during the silver halide grain formation step.

Although the compound can be added in a reaction vessel beforehand, it is preferably added at an arbitrary timing during grain formation. In addition, a compound represented by formula (I), (II), or (III) can be added in an aqueous solution of a water-soluble silver salt or water-soluble alkali halide to perform grain formation by using the aqueous solution. A method of adding a solution of a compound represented by formula (I), (II), or (III) several times or continuously adding it over a long time period during grain formation is also preferable.

A compound most preferable in the present invention is represented by formula (I).

A silver halide of any of silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide, and silver chloride can be used in a photographic emulsion layer of a photographic light-sensitive material used in the present invention. A preferable silver halide is silver iodobromide, or silver chlorobromide containing 30 mol% or less of silver iodide, or silver bromide, or silver bromochloride.

A silver halide grain to be used in the present invention can be selected from a regular crystal not including a twined crystal face and grains having a twinned crystal described in Japan Photographic Society ed., "Silver Salt Photographs, Basis of Photographic Industries", (Corona Co., P. 163) such as a single twinned crystal including one twinned crystal face, a parallel multiple twinned crystal including two or more parallel twinned crystal faces, and a non-parallel multiple twinned crystal including two or more non-parallel twinned crystal faces in accordance with its application. In the case of a regular crystal, a cubic grain having (100) faces, an octahedral grain having (111) faces, and a dodecahedral grain having (110) faces disclosed in JP-B-55 42737 and JP-A-60-222842 can be used. In addition, a grain having (hkl), e.g., (211) faces, a grain having (hkl), e.g., (331) faces, a grain having (hk0), e.g., (210) faces, and a grain having (hk1), e.g., (321) faces as reported in "Journal of Imaging Science", Vol. 30 P. 247, 1986 can be selectively used in accordance with an application although a preparation method must be improved. A grain including two or more types of faces, e.g., a tetradecahedral grain having both (100) and (111) faces, a grain having both (100) and (110) faces, and a grain having both (111) and (110) faces can be selectively used in accordance with an application.

The grain of a silver halide may be a fine grain having a grain size of 0.1 microns or less or a large grain having a projected surface area diameter of 10 microns. An emulsion may be a monodisperse emulsion having a narrow distribution or a polydisperse emulsion having a wide distribution.

A so-called monodisperse silver halide emulsion having a narrow size distribution, i.e., in which 80% or more (the number or weight of grains of all grains fall within the range of ±30% of an average grain size, can be used in the present invention. In order to satisfy target gradation of a light-sensitive material, two or more types of monodisperse silver halide emulsions having different grain sizes can be coated in a single layer or overlapped in different layers in emulsion layers having substantially the same color sensitivity. Alternatively, two or more types of polydisperse silver halide emulsions or a combination of monodisperse and polydisperse emulsions can be mixed or overlapped.

The photographic emulsions for use in the present invention can be prepared by methods described in, for example, P. Glafkides, "Chimie et Physique Photographique", Paul Montel, 1967; Duffin, "Photographic Emulsion Chemistry", Focal Press, 1986; and V.L. Zelikman et al., "Making and Coating Photographic Emulsion", Focal Press, 1984. That is, the photographic emulsion can be prepared by, e.g., an acid method, a neutralization method, and an ammonia method. Also, as a system for reacting a soluble silver salt and a soluble halide, a single mixing method, a double jet method, or a combination thereof can be used. Also, a so-called back mixing method for forming silver halide grains in the presence of excessive silver ions can be used. As one system of the double jet method, a so-called controlled double jet method wherein the pAg in the liquid phase generated by the silver halide is kept at a constant value can be used. According to this method, a silver halide emulsion having a regular crystal form and almost uniform grain sizes is obtained.
The silver halide emulsion containing the above-described regular silver halide grains can be obtained by controlling the pAg and pH during grain formation. More specifically, such a method is described in "Photographic Science and Engineering", Vol. 6, 159-165 (1962); "Journal of Photographic Science", Vol. 12, 242-251 (1964); U.S. Patent 3,655,394, and British Patent 1,413,748.

A tabular grain having an aspect ratio of 3 or more can also be used in the present invention. The tabular grain can be easily prepared by methods described in, for example, 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. When the tabular grain is used, covering power and a spectrally sensitizing efficiency of a sensitizing dye can be advantageously improved as described in detail in U.S. Patent 4,434,226.

The tabular grains are preferably used in the emulsion of the present invention. In particular, tabular grains in which grains having aspect ratios of 3 to 8 occupy 50% or more of a total projected surface area are preferable.

In the silver halide emulsion for use in the present invention a crystal structure may be uniform, may have different halogen compositions inside and outside 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 Patent 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-A-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 or sometimes different from that of the entire grain with a shell. More specifically, while the core portion is cubic, the grain with a shell is sometimes cubic or sometimes octahedral. On the contrary, while the core portion is octahedral, the grain with a shell is sometimes cubic or sometimes octahedral. In addition, while the core portion is a clear regular grain, the grain with a shell is sometimes slightly deformed or sometimes does not have any definite shape. Furthermore, 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-59-18254. A crystal to be bonded having a 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-0086772BI and EP-0064412B1 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 silver halide
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 are added therein, or they can be added in the reaction vessel together with one or more halides, a silver salt or a deflocculant. Alternatively, the ripening agents can be added in separate steps together with a halide and a silver salt.

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

After a grain formation step is performed (after precipitation or physical ripening) and a palladium compound is added, removal of soluble salts (a desalting step) is performed. For this purpose, a conventional nudel washing method of gelling gelatin or flocculation utilizing inorganic salts consisting of a multivalent anion such as sodium sulfate, an anionic surfactant, an anionic polymer (e.g., polyvinyl sulfate acid, or a gelatin derivative (e.g., aliphatic acylated gelatin, aromatic acylated gelatin, or aromatic carbamoylated gelatin) may be used.

An emulsion manufactured according to the manufacturing method of the present invention is subjected to chemical sensitization also after it is desalted. Chemical sensitization is preferably performed at 45°C or more, and more preferably, 50°C or more. Chemical sensitization is preferably performed for five minutes or more, and more preferably ten minutes or more. In this chemical sensitization, a sulfur sensitization method using active gelatin or a compound containing sulfur which can react with silver (e.g., thiosulfate, thioureas, mercapto compounds, and rhodanines); a selenium sensitization method; a reduction sensitization method using a gold complex salt, is preferably used singly or in a combination of two or more thereof.

The photographic emulsion for use in the present invention can contain various compounds in order to prevent fogging during the 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, e.g., benzothiazolium salts, nitrimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, aminotriazoles, benzotriazoles, mercaptotetrazoles, and mercaptocarbazoles (especially, 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptothiazines; a thioketo compound such as oxadrinthione; azaindines, e.g., triazaindines, tetrazaaindines (especially, 4-hydroxy-substituted-(1,3,3a,7)tetraazaindines), and pentaazaindines. Examples are described in U.S. Patents 3,954,474 and 3,982,947 and JP-B-52-28660.

In the present invention, the most preferable chemical sensitization is a combination of sulfur sensitization and gold sensitization (also called as gold-plus-sulfur sensitization). Chemical sensitization is performed at a pH of 4 or more, preferably, 5 or more, and most preferably 6 or 6.5 or more. The upper limit of the pH is 9 or less, and preferably, 8.5 or less.

The photographic emulsion for use in the present invention can be spectrally sensitized with, e.g., methine dyes. Examples of the dye are a cyanine dye, merocyanine dye, a complex cyanine dye, a complex merocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye, and hemioxonol dye. Most effective dyes are those belonging to a cyanine dye, a merocyanine dye, and a complex merocyanine dye. In these dyes, any nucleus normally used as a basic heterocyclic nucleus in cyanine dyes can be used. Examples of the nucleus are pyrrole nucleus, an oxazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, an oxazine nucleus, an imidazole nucleus, a tetrazole nucleus, and a pyridine nucleus; a nucleus obtained by condensing an alicyclic hydrocarbon ring to each of the above nuclei; and a nucleus obtained by condensing an aromatic hydrocarbon ring to each of the above nuclei, e.g., an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxadole nucleus, a naphthoxazolene nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoazalene nucleus, a benozimidazole nucleus, and a quinoline nucleus. These nuclei may be substituted on a carbon atom.

For a merocyanine dye or complex merocyanine dye, a 5- or 6-membered heterocyclic nucleus, e.g., a pyrazoline-5-one nucleus, a thiohydantoin nucleus, a 2-thiazazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus, and a thiobarbituric acid nucleus can be used as a nucleus having a ketomethylene structure.

These sensitizing dyes can be used singly or in a combination of two or more thereof. A combination of the sensitizing dyes is often used especially in order to perform supersensitization. Typical examples of the
The emulsion may contain, in addition to the sensitizing dye, a dye not having a spectral sensitizing effect or a substance substantially not absorbing visible light and having supersensitization.

The dye can be added in the emulsion at any timing conventionally known to be effective in emulsion preparation. Most ordinarily, the dye is added after completion of chemical sensitization and before coating. However, the dye can be added at the same time as a chemical sensitizer to simultaneously perform spectral sensitization and chemical sensitization as described in U.S. Patents 3,628,969 and 4,225,666, added before chemical sensitization as described in JP-A-58-113928, or added before completion of silver halide grain precipitation to start spectral sensitization. In addition, as described in U.S. Patent 4,225,666, the above compound can be separately added such that a portion of the compound is added before chemical sensitization and the remaining portion is added thereafter. That is, as described in U.S. Patent 4,183,756, the compound can be added at any timing during silver halide grain formation.

An addition amount may be $4 \times 10^{-6}$ to $1 \times 10^{-2}$ mol per mol of a silver halide. More preferably, when a silver halide grain size is 0.2 to 1.2 μm, an addition amount of about $5 \times 10^{-5}$ to $6 \times 10^{-3}$ mol is more effective.

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.

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

<table>
<thead>
<tr>
<th>Additives</th>
<th>RD No. 17643</th>
<th>RD No. 18716</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chemical sensitizers</td>
<td>page 23</td>
<td>page 648, right column</td>
</tr>
<tr>
<td>2. Sensitivity increasing agents</td>
<td>pages 23-24</td>
<td>page 648, right column to</td>
</tr>
<tr>
<td>3. Spectral sensitizers, super sensitizers</td>
<td>page 24</td>
<td>page 649, right column</td>
</tr>
<tr>
<td>4. Brighteners</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Antifoggants and stabilizers</td>
<td>pages 24-25</td>
<td>page 649, right column</td>
</tr>
<tr>
<td>6. Light absorbent, filter dye, ultraviolet absorbents</td>
<td>pages 25-26</td>
<td>page 649, right column to</td>
</tr>
<tr>
<td>7. Stain preventing agents</td>
<td>page 25, right column</td>
<td>page 650, left column</td>
</tr>
<tr>
<td>8. Dye image stabilizer</td>
<td>page 25</td>
<td>page 650, left to right columns</td>
</tr>
<tr>
<td>9. Hardening agents, column</td>
<td>page 26</td>
<td>page 651, left</td>
</tr>
<tr>
<td>10. Binder</td>
<td>page 26</td>
<td>do</td>
</tr>
<tr>
<td>11. Plasticizers, lubricants</td>
<td>page 27</td>
<td>page 650, right column</td>
</tr>
<tr>
<td>12. Coating aids, surface active agents</td>
<td>pages 28-27</td>
<td>do</td>
</tr>
<tr>
<td>13. Antistatic agents</td>
<td>page 27</td>
<td>do</td>
</tr>
</tbody>
</table>

In this invention, various color couplers can be used in the light-sensitive material. Specific examples of these couplers are described in above-described Research Disclosure, 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, 4,022,820, 30 4,326,024, and 4,401,752, JP-B-58 10739, and British Patents 1,425,020 and 1,476,760.


Examples of a cyan coupler are phenol and naphthol couplers, and preferably, those described in, e.g.,


Typical examples of a polymerized dye-forming coupler are described in U.S. patents 3,451,820, 4,080,211, and 4,367,282, and British Patent 2,102,173.


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, 4,333,483, and 4,310,618; DIR redox compound or DIR coupler releasing couplers 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; bleaching accelerator releasing couplers described in, e.g., RD. Nos. 11449 and 24241 and JP-A-61-201247; and a legand releasing coupler described in, e.g., U.S. Patent 4,553,477.

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

Examples of a high-boiling solvent used in an oil-in-water dispersion method are described in, e.g., U.S. Patent 2,322,027.

Examples of a high-boiling organic solvent to be used in the oil-in-water dispersion method and having a boiling point of 175°C or more at normal pressure are phthalic esters (e.g., dibutylphthalate, dicyclohexylphthalate, di-2-ethylhexylphthalate, decylphthalate, bis(2,4-di-t-amylphenyl)phthalate, bis(2,4-di-t-amylphenyl)isophthalate, and bis((1,1-diethylpropyl)phthalate), phosphates or phosphonates (e.g., triphenylphosphate, tricyclohexylphosphate, 2-ethylhexylphosphonate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphosphate, tributoxyethylphosphate, trichloropropylphosphate, and di-2-ethylhexylphosphonate), benzoates (e.g., 2-ethylhexylbenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethylacetamido, N,N-diethyllauriamide, and N-tetracyclopyrrolidone), alcohols or phenols (e.g., isostearyl alcohol and 2,4-di-t-tert-amylphenol), aliphatic carboxylates (e.g., bis(2-ethylhexyl)sebacate, diocylsebacate, glyceroltrihexacontylicate, and triocylfumarate), and hydrocarbons (e.g., paraffin, dodecylbenzene, and disopropylphthalate). An organic solvent having a boiling point of about 30°C or more, and preferably, 50°C to about 160°C can be used as a co-solvent. Typical examples of the co-solvent are ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethylacetate, and dimethylformamide.

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

Preferably, in a silver halide color light-sensitive material which comprises at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler, and at least one red-sensitive silver halide emulsion layer containing a cyan coupler on a support, at least one of the emulsion layers contains a silver halide photographic emulsion manufactured by performing addition of palladium compound in amount of not less than 5 x 10^-5 mol per mol of a silver halide after a grain formation step and before a desalting step.

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

When the present invention is used as a material for color photographing, the present invention can be applied to light-sensitive materials having various structures and to light-sensitive materials having combinations of layer structures and special color materials.

Examples of a support suitable for use in this invention are described in the above-mentioned RD. No. 17643, page 28 and ibid., No. 18716, page 647, right column to page 648, left column.

The photographic light-sensitive materials of this invention can be processed by the ordinary processes as described, for example, in the above-described Research Disclosure, No. 17643, pages 28 to 29 and ibid., No. 18716, page 651, left to right columns.

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

In general, the color developer contains a pH buffering agent such as a carbonate, a borate or a phosphate of an alkali metal, and a development restrainer or antifoggant such as a bromide, an iodide, a benzimidazole, a benzothiazole or a mercaptro compound. If necessary, the color developer may also contain a preservative such as hydroxylamine, diethyldihydroxylamine, a hydrazine sulfite, a phenylenediamine, triethanolamine, a catechol sulfonic acid or a triethylenediamine(1,4-diazabicyclo[2,2,2]octane); an organic solvent such as ethylene glycol or diethylene glycol; a development accelerator such as benzyl alcohol, polyoxyethylene glycol, a quaternaruy ammonium salt or an amine; a dye forming coupler; a competing coupler; a fogging agent such as sodium boron hydride; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a viscosity imparting agent; and a chelating agent such as an aminopolycarboxylic acid, an aminopolysulfonic acid, an alkylphosphonic acid or a phosphonocarboxylic acid. Examples of the chelating agent are ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediamente-betaacetic acid, hydroxyethylyiminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrito-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N'-tetramethylenephosphonic acid and ethylenediamine-di(p-hydroxyphenyl)acetic acid, and salts thereof.

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

The pH of the color and black-and-white developers is generally 9 to 12. Although a replenishment amount of the developer depends on a color photographic light-sensitive material to be processed, it is generally 3 liters or less per m² of the light-sensitive material. The replenishment amount can be decreased to be 500 ml less by decreasing a bromide ion concentration in a replenishing solution. In order to decrease the replenishment amount, a contact area of a processing tank with air is preferably decreased to prevent evaporation and oxidation of the solution upon contact with air. The replenishment amount can be decreased by using a means capable of suppressing an accumulation amount of bromide ions in the developer.

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

The photographic emulsion layer is generally subjected to bleaching after color development. The bleaching may be performed either simultaneously with fixing (bleach-fixing) or independently thereof. In addition, in order to increase a processing speed, bleach-fixing may be performed after bleaching. Also, processing may be performed in a bleach-fixing bath having two continuous tanks, fixing may be performed before bleach-fixing, or bleaching may be performed after bleach-fixing, in accordance with applications. Examples of the bleaching agent are a compound of a multivalent metal such as iron (III), cobalt (III), chromium (VI) and copper (II); a peroxide; a quinone; and a nitro compound. Typical examples of the
bleaching agent are a ferricyanide; a dichromate; an organic complex salt of iron (III) or cobalt (II), e.g., a complex salt of an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediennetetraacetic acid, methyliminodiacetic acid, and 1,3-diaminopropanetetraacetic acid, and glycochelatrimininetetraacetic acid, or a complex salt of citric acid, tartaric acid or malic acid; a persulfate; a bromate; a permanganate; and a nitrobenzene. Of these compounds, an iron (III) complex salt of aminopolycarboxylic acid such as an iron (III) complex salt of ethylenediaminetetraacetic acid, and a persulfate are preferred because they can increase a processing speed and prevent an environmental contamination. The iron (III) complex salt of aminopolycarboxylic acid is effective in both the bleaching and bleach-fixing solutions. The pH of the bleaching or bleach-fixing solution using the iron (III) complex salt of aminopolycarboxylic acid is normally 5.5 to 8. In order to increase the processing speed, however, processing can be performed at a lower pH.


These bleaching accelerators may be added in the light-sensitive material. These bleaching accelerators are effective especially in bleach-fixing of a photographic color light-sensitive material.

Examples of the fixing agent are a thiosulfate, a thiocyanate, a thioether-based compound, a thiourea and a large amount of an iodide. Of these compounds, a thiosulfate, especially, ammonium thiosulfate can be used in a widest range of applications. As a preservative of the bleach-fixing solution, a sulfite, a bisulfite or a carbonyl bisulfite adduct is preferred.

The photographic light-sensitive material of the present invention is normally subjected to washing and/or stabilizing steps after delversing. 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 an used material such as 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 Engineers", 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-61-131632. In addition, a germicide such as an isothiazolone compound and cyanoazole 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", Eiseiigijutsu-Kai ed., "Sterilization, Antibacterial, and Antifungal Techniques for Microorganisms", and Nippon Bokin Bokabi Gakkai ed., "Cyclopedia 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. Normally, the washing time is 20 seconds to 10 minutes at a temperature of 15° C to 45° C, and preferably, 30 seconds to 5 minutes at 25° C to 40° C. The light-sensitive material of the present invention can be processed directly by a stabilizing solution 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, further, subsequently to said washing. An example is a stabilizing bath containing formalin and a surface-active agent to be used as a final bath of the photographic color light-sensitive material. Various chelating agents or antifungal agents can be added also in the stabilizing
An overflow solution produced upon washing and/or replenishment of the stabilizing solution can be reused in another step such as a desilvering step.

The silver halide light-sensitive material of the present invention may contain a color developing agent in order to simplify processing and increase a processing speed. For this purpose, various precursors of a color developing agent are preferably used. Examples of the precursor are an indoaniline-based compound described in U.S. Patent 3,342,597, Schiff base type compounds described in U.S. Patent 3,342,599, and Research Disclosure Nos. 14,850 and 15,159, an aldol compound described in RD No. 13,924, a metal salt complex described in U.S. Patent 3,718,462, and a urethane-based compound described in JP-A-53-135628.


Each processing solution in the present invention is used at a temperature of 10°C to 50°C. Although a normal processing temperature is 33°C to 38°C, processing may be accelerated at a high temperature to shorten a processing time, or image quality or stability of a processing solution may be improved at a lower temperature. In order to save silver for the light-sensitive material, processing using cobalt intensification or hydrogen peroxide intensification described in West German Patent No. 2,226,770 or U.S. Patent 3,674,499 may be performed.


The present invention will be described in detail below by way of its examples. The present invention, however, is not limited to those examples.

**EXAMPLE 1**

The present invention will be described below by comparing it with comparative examples.

**Preparation Method of Em-A**

1,000 mL of an aqueous solution containing 40 g of gelatin and 0.2 g of KBr were strongly stirred at 75°C. 208 mL of an aqueous silver nitrate solution (containing 1.46 g of AgNO₃) and 208 mL of an aqueous KBr solution (containing 1.1 g of KBr) were simultaneously added to the resultant solution over 17 minutes. A silver potential of the resultant solution was adjusted to -25 mV with respect to a saturated calomel electrode, and 0.6 mg of thiourea dioxide were added in the form of an aqueous solution. Thereafter, 471 mL of an aqueous silver nitrate solution (containing 94.2 g of AgNO₃) and an aqueous KBr solution (KBr = 14.6 wt%) were simultaneously added to the resultant solution over 33 minutes. In this addition, the flow rates of the aqueous silver nitrate solution were adjusted to 1 mL/min and 19 mL/min at the initial and final stages, respectively, maintaining the silver potential of the reaction solution at -25 mV. After addition, the resultant solution was ripened for 10 minutes and then desalted by a flocculation method. 43 g of gelatin were added, a pH was adjusted to 6.9 and pAg was adjusted to 8.0 at 40°C, thereby obtaining a yield of 700 g. 3.0 x 10⁻³ mol/molAg of potassium thiocyanate, 3.0 x 10⁻⁵ mol/molAg of sodium thiosulfate, and 1.2 x 10⁻⁴ mol/molAg of potassium chloroaurate were added and the mixture was stirred at 60°C for 40 minutes to perform chemical sensitization, thereby preparing Em-A. The prepared emulsion consisted of monodisperse octahedral grains having an average circle-equivalent diameter of 0.80 μm and a variation coefficient of a circle-equivalent diameter of 9%.

**Preparation Method of Em-B**

Em-B was prepared following the same procedures as for Em-A except that 4 x 10⁻⁴ mol/molAg of (NH₄)₂PdCl₄, and 2 x 10⁻³ mol/molAg of potassium thiocyanate were added over three minutes from 20 minutes after addition of the aqueous silver nitrate solution at the second stage was started to 10 minutes before it was finished.
Preparation Method of Em-C

Em-C was prepared following the same procedures as for Em-A except that \( 4 \times 10^{-4} \) mol/molAg of \((NH_4)_2PdCl_4\) and \(2 \times 10^{-3}\) mol/molAg of potassium thiocyanate were added 10 minutes before a chemical sensitizer was added in chemical sensitization.

Preparation Method of Em-D

Em-A was dissolved at 40° C, and \(4 \times 10^{-4}\) mol/molAg of \((NH_4)_2PdCl_4\) and \(2 \times 10^{-3}\) mol/molAg of potassium thiocyanate were added to the solution. The resultant mixture was stirred for 30 minutes to prepare Em-D.

Preparation Method of Em-E

Em-E was prepared following the same procedures as for Em-A except that \(4 \times 10^{-4}\) mol/molAg of \((NH_4)_2PdCl_4\) and \(2 \times 10^{-3}\) mol/molAg of potassium thiocyanate were added two minutes after addition of the aqueous silver nitrate solution at the second stage was finished and stirred for eight minutes, and then the solution mixture was desalted by a flocculation method.

Preparation Method of Em-F

Em-F was prepared following the same procedures as for Em-A except that \(4 \times 10^{-4}\) mol/molAg of \((NH_4)_2PdCl_4\) and \(2 \times 10^{-3}\) mol/molAg of potassium thiocyanate were added immediately before desalted was performed by the flocculation method.

Emulsion layer of Em-A to Em-F and protective layer were coated in amounts as listed in Table 1 on triacetylcellulose film supports having undercoating layers, thereby preparing samples.
Table 1  Emulsion Coating Conditions

(1) Emulsion Layer

Emulsion...Em-A to Em-F  
(silver 2.1 × 10^{-2} \text{ mol/m}^2)

Coupler  
(1.5 × 10^{-3} \text{ mol/m}^2)

\[ \text{tC}_{5}\text{H}_{11} \quad \text{OCHCONH} \quad \text{tC}_{5}\text{H}_{11} \]

\[ \text{CONH} \quad \text{N} \quad \text{O} \quad \text{N} \quad \text{C} \quad \text{C} \quad \text{C} \]

Tricresylphosphate  
(1.10 g/m^2)

Gelatin  
(2.30 g/m^2)

(2) Protective Layer

2,4-dichloro-6-hydroxy-s-triazine sodium salt  
(0.08 g/m^2)

Gelatin  
(1.80 g/m^2)

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 seconds through a continuous wedge, thereby performing the following color development.

Densities of the developed samples were measured using a green filter.

<table>
<thead>
<tr>
<th>Processing Method</th>
<th>Process Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color Development</td>
<td>2 min 00 sec</td>
<td>40°C</td>
</tr>
<tr>
<td>Bleach-Fixing</td>
<td>3 min 00 sec</td>
<td>40°C</td>
</tr>
<tr>
<td>Washing (1)</td>
<td>20 sec</td>
<td>35°C</td>
</tr>
<tr>
<td>Washing (2)</td>
<td>20 sec</td>
<td>35°C</td>
</tr>
<tr>
<td>Stabilizing</td>
<td>20 sec</td>
<td>35°C</td>
</tr>
<tr>
<td>Dry</td>
<td>50 sec</td>
<td>65°C</td>
</tr>
</tbody>
</table>

The processing solution compositions will be described below.
**Color Developing Solution:**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylenetriaminepentacetic Acid</td>
<td>2.0</td>
</tr>
<tr>
<td>1-hydroxyethylidene-1,1-diphosphonic Acid</td>
<td>3.0</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>4.0</td>
</tr>
<tr>
<td>Potassium Carbonate</td>
<td>30.0</td>
</tr>
<tr>
<td>Potassium Bromide</td>
<td>1.4</td>
</tr>
<tr>
<td>Potassium Iodide</td>
<td>1.5 mg</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>2.4</td>
</tr>
<tr>
<td>4-(N-ethyl-N-$\beta$-hydroxyethylamino)-2-methylaniline Sulfate</td>
<td>4.5</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 l</td>
</tr>
<tr>
<td>pH</td>
<td>10.05</td>
</tr>
</tbody>
</table>

**Bleach-Fixing Solution:**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric Ammonium Ethylenediaminetetraacetate Dihydrate</td>
<td>90.0</td>
</tr>
<tr>
<td>Disodium Ethylenediaminetetraacetate</td>
<td>5.0</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>12.0</td>
</tr>
<tr>
<td>Ammonium Thiosulfate Aqueous Solution (70%)</td>
<td>260.0 ml</td>
</tr>
<tr>
<td>Acetic Acid (98%)</td>
<td>5.0 ml</td>
</tr>
<tr>
<td>Bleach Accelerator</td>
<td>0.01 mol</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 l</td>
</tr>
<tr>
<td>pH</td>
<td>6.0</td>
</tr>
</tbody>
</table>

**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 & Haas Co.) and an OH type 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 dichloroisocyanurate 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:**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formalin (37%)</td>
<td>2.0 ml</td>
</tr>
<tr>
<td>Polyoxyethylene-p-monononylphenylether (average polymerization degree = 10)</td>
<td>0.3</td>
</tr>
<tr>
<td>Disodium Ethylenediaminetetraacetate</td>
<td>0.05</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 l</td>
</tr>
<tr>
<td>pH</td>
<td>5.0 to 8.0</td>
</tr>
</tbody>
</table>

The sensitivity is represented by a relative value of a reciprocal of an exposure amount in units of
luc/sec. at a fogging density of 0.2.

The results are summarized in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Emulsion No.</th>
<th>Remarks</th>
<th>Addition Timing of Palladium Compound</th>
<th>Relative Sensitivity</th>
<th>Fogging Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Em-A</td>
<td>Comparative Example</td>
<td>---</td>
<td>100</td>
<td>0.64</td>
</tr>
<tr>
<td>Em-B</td>
<td>Comparative Example</td>
<td>During Grain Formation</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Em-C</td>
<td>Comparative Example</td>
<td>Before Chemical Sensitization</td>
<td>126</td>
<td>0.36</td>
</tr>
<tr>
<td>Em-D</td>
<td>Comparative Example</td>
<td>After Chemical Sensitization and Before Coating</td>
<td>74</td>
<td>0.55</td>
</tr>
<tr>
<td>Em-E</td>
<td>Present Invention</td>
<td>After Grain Formation and Before Desilverization</td>
<td>135</td>
<td>0.18</td>
</tr>
<tr>
<td>Em-F</td>
<td>Present Invention</td>
<td>After Grain Formation and Before Desilverization</td>
<td>129</td>
<td>0.24</td>
</tr>
</tbody>
</table>

As is apparent from Table 2, a high sensitivity was realized at a low fogging density only when a palladium compound was added after the grain formation step and before the desalting step in accordance with the present invention. When the palladium compound was added during grain formation (Em-B), no image could be obtained.

Processes for preparing Em-A and Em-E were repeated three times to prepare Em-A1, Em-A2, and Em-A3 and Em-E1, Em-E2, and Em-E3, respectively. These emulsions were coated, exposed, and developed following the same procedures as described above, thereby obtaining the results shown in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Emulsion No.</th>
<th>Relative Sensitivity</th>
<th>Fogging Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Em-A1</td>
<td>105</td>
<td>0.58</td>
</tr>
<tr>
<td>Em-A2</td>
<td>112</td>
<td>0.52</td>
</tr>
<tr>
<td>Em-A3</td>
<td>95</td>
<td>0.82</td>
</tr>
<tr>
<td>Em-E1</td>
<td>135</td>
<td>0.18</td>
</tr>
<tr>
<td>Em-E2</td>
<td>135</td>
<td>0.20</td>
</tr>
<tr>
<td>Em-E3</td>
<td>141</td>
<td>0.18</td>
</tr>
</tbody>
</table>

As is apparent from Table 3, the repeating reproducibility of an emulsion was significantly improved when the palladium compound was added after the grain formation step and before the desalting step in accordance with the present invention. That is, the manufacture of the silver halide photographic emulsion was stabilized.

Em-C1, Em-C2, Em-E4, and Em-E5 were prepared following the same procedures as for Em-C and Em-E, respectively, except that a time required for flocculation was changed. These emulsions were coated, exposed, and developed following the same procedures as described above, thereby obtaining the results shown in Table 4.
As is apparent from Table 4, the reproducibility of an emulsion was significantly improved regardless of a flocculation time when the palladium compound was added after the grain formation step and before the desalting step in accordance with the present invention. That is, a stable method of manufacturing a silver halide photographic emulsion was achieved.

EXAMPLE 2

A palladium compound addition amount dependency of emulsion will be described below.

Preparation Method of Em-G

An aqueous solution containing gelatin and KBr was maintained at 40 °C, and an aqueous silver nitrate solution (containing 32.7 g of AgNO₃) and a halogen solution (containing 24.9 g of KBr and 1.3 g of KI) were added to the solution over four minutes under constant stirring. After an aqueous solution containing KBr and gelatin was added, the resultant mixture was heated up to 70 °C, and an aqueous solution containing 6 mg of dimethylamineborane and an aqueous solution containing 100 mg of a compound 1-2 listed in Table A were simultaneously added. Thereafter, an aqueous silver nitrate solution (containing 152.3 g of AgNO₃) and an aqueous halogen solution (containing 5.3 wt% of KI with respect to KBr) were added over 32.1 minutes. In this addition, a silver potential of the reaction solution was maintained at 0 mV with respect to a saturated calomel electrode. Thereafter, an aqueous silver nitrate solution (containing 7.2 g AgNO₃) and an aqueous NaCl solution (containing 6.7 g of NaCl) were added over 1.5 minutes. The resultant mixture was desalted by a flocculation method five minutes after the addition was finished. Gelatin was added and a pH was adjusted to 6.8 and a pAg was adjusted to 8.0 at 40 °C. This emulsion consisted of tabular grains having an average thickness of 0.13 μm, an average circle-equivalent diameter of 0.68 μm, a variation coefficient of a circle-equivalent diameter of 28%, and an aspect ratio of 5.2.

1.40 x 10⁻³ mol/molAg of a sensitizing dye A below were added to the above emulsion:

Sensitizing Dye A

Thereafter, 3.0 x 10⁻³ mol/molAg of potassium thiocyanate, 4.8 x 10⁻⁵ mol/molAg of sodium...
thiosulfate, and \(1.0 \times 10^{-6}\) mol/molAg of potassium chloroaurate were added at 64°C and stirred for 40 minutes. \(5 \times 10^{-4}\) mol/molAg of an antifoggant A below were added, and the resultant mixture was cooled, thereby preparing Em-G:

\[
\text{NaOC} - \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array} - \text{SNa}
\]

Preparation Method of Em-H

Em-H was prepared following the same procedures as for Em-G except that \(1 \times 10^{-5}\) mol/molAg of \((\text{NH}_4)_2\text{PdCl}_4\) and \(5 \times 10^{-5}\) mol/molAg of potassium thiocyanate were added 30 seconds after addition of silver nitrate was finished, and the resultant mixture was stirred for five minutes and desalted by the flocculation method.

Preparation Method of Em-I

Em-I was prepared following the same procedures as for Em-G except that \(5 \times 10^{-5}\) mol/molAg of \((\text{NH}_4)_2\text{PdCl}_4\) and \(2.5 \times 10^{-4}\) mol/molAg of potassium thiocyanate were added 30 seconds after addition of silver nitrate was finished, and the resultant mixture was stirred for five minutes and desalted by the flocculation method.

Preparation Method of Em-J

Em-J was prepared following the same procedures as for Em-G except that \(1 \times 10^{-4}\) mol/molAg of \((\text{NH}_4)_2\text{PdCl}_4\) and \(5 \times 10^{-4}\) mol/molAg of potassium thiocyanate were added 30 seconds after addition of silver nitrate was finished, and the resultant mixture was stirred for five minutes and desalted by the flocculation method.

Preparation Method of Em-K

Em-K was prepared following the same procedures as for Em-G except that \(4 \times 10^{-4}\) mol/molAg of \((\text{NH}_4)_2\text{PdCl}_4\) and \(2 \times 10^{-3}\) mol/molAg of potassium thiocyanate were added 30 seconds after addition of silver nitrate was finished, and the resultant mixture was stirred for five minutes and desalted by the flocculation method.

Preparation Method of Em-L

Em-L was prepared following the same procedures as for Em-I except that \(5 \times 10^{-4}\) mol/molAg of \((\text{NH}_4)_2\text{PdCl}_4\) and \(2.5 \times 10^{-3}\) mol/molAg of potassium thiocyanate were added ten minutes before the chemical sensitizer was added in chemical sensitization.

A coating aid and a hardener were added to Em-G to Em-L and the resultants were coated on cellulose film bases in a Ag coating amount of 2 g/m². Each coated emulsion was exposed for one second through a continuous wedge to a tungsten electric lamp (color temperature = 2,854 K). The exposed coated emulsion was developed at 20°C for ten minutes by using the following surface developer (MAA-1).
The sensitivity of an obtained emulsion is represented by a relative value of a reciprocal of an exposure amount required to obtain an optical density of a fogging density plus 0.1.

The obtained results are summarized in Table 5.

Table 5

<table>
<thead>
<tr>
<th>Emulsion No.</th>
<th>Remarks</th>
<th>Addition Amount of Palladium Compound (mol/molAg)</th>
<th>Relative Sensitivity</th>
<th>Fogging Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Em-G</td>
<td>Comparative Example</td>
<td>0</td>
<td>100</td>
<td>0.18</td>
</tr>
<tr>
<td>Em-H</td>
<td>Comparative Example</td>
<td>$1 \times 10^{-5}$</td>
<td>105</td>
<td>0.16</td>
</tr>
<tr>
<td>Em-I</td>
<td>Present Invention</td>
<td>$5 \times 10^{-5}$</td>
<td>115</td>
<td>0.10</td>
</tr>
<tr>
<td>Em-J</td>
<td>Present Invention</td>
<td>$1 \times 10^{-4}$</td>
<td>117</td>
<td>0.06</td>
</tr>
<tr>
<td>Em-K</td>
<td>Present Invention</td>
<td>$4 \times 10^{-4}$</td>
<td>132</td>
<td>0.03</td>
</tr>
<tr>
<td>Em-L</td>
<td>Present Invention</td>
<td>$5 \times 10^{-5}$ and $5 \times 10^{-4}$ upon Chemical Sensitization</td>
<td>120</td>
<td>0.06</td>
</tr>
</tbody>
</table>

As is apparent from Table 5, a high sensitivity was obtained at a low fogging density when a palladium compound was added in an amount of $5 \times 10^{-5}$ mol or more per mol of a silver halide after the grain formation step and before the desalting step.

**EXAMPLE 3**

Effects of an emulsion of the present invention in a multilayered color light-sensitive material will be described below.

Layers having the following compositions were formed on an undercoated triacetylcellulose film support, thereby preparing a sample as a multilayered color light-sensitive material.

(Compositions of Light-Sensitive Layers)

The coating amount of a silver halide and colloid silver are represented in units of g/m² of silver, that of couplers, additives, and gelatin is represented in units of g/m², and that of a sensitizing dye is represented by the number of mol per mol of the silver halide in the same layer. Symbols representing additives have the following meanings. Note that if an additive has a plurality of effects, only one of the effects is shown.

UV; ultraviolet absorbent, Solv; high-boiling organic solvent, EXF; dye, EXS; sensitizing dye, EXC; cyan coupler, EXM; magenta coupler, EXY; yellow coupler, and Cpd; additive

20
Layer 1: Antihalation Layer

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Colloid Silver</td>
<td>0.15</td>
</tr>
<tr>
<td>Gelatin</td>
<td>2.9</td>
</tr>
<tr>
<td>UV-1</td>
<td>0.03</td>
</tr>
<tr>
<td>UV-2</td>
<td>0.06</td>
</tr>
<tr>
<td>UV-3</td>
<td>0.07</td>
</tr>
<tr>
<td>Solv-2</td>
<td>0.08</td>
</tr>
<tr>
<td>ExF-1</td>
<td>0.01</td>
</tr>
<tr>
<td>ExF-2</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Layer 2: Low-Speed Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 4 mol%, homogeneous AgI type, circle-equivalent diameter = 0.8 μm, thickness = 0.2 μm, variation coefficient of circle-equivalent diameter = 37%, tabular grain diameter/thickness ratio = 3.0)

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelatin</td>
<td>0.8</td>
</tr>
<tr>
<td>ExS-1</td>
<td>6.9 x 10^{-4}</td>
</tr>
<tr>
<td>ExS-2</td>
<td>5.2 x 10^{-4}</td>
</tr>
<tr>
<td>ExS-5</td>
<td>6.9 x 10^{-4}</td>
</tr>
<tr>
<td>ExS-7</td>
<td>2.4 x 10^{-5}</td>
</tr>
<tr>
<td>ExC-1</td>
<td>0.17</td>
</tr>
<tr>
<td>ExC-2</td>
<td>0.03</td>
</tr>
<tr>
<td>ExC-3</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Layer 3: Medium-Speed Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 6 mol%, internally high AgI type having core/shell ratio of 2 : 1, sphere-equivalent diameter = 0.65 μm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 2.0)
coating silver amount 0.65

Silver Iodobromide Emulsion (AgI = 4 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.4 μm, variation coefficient of sphere-equivalent diameter = 37%, tabular grain, diameter/thickness ratio = 2.0)
coating silver amount 0.1

Gelatin 1.0
ExS-1 2 × 10⁻⁴
ExS-2 1.2 × 10⁻⁴
ExS-5 2 × 10⁻⁴
ExS-7 7 × 10⁻⁶
ExC-1 0.31
ExC-2 0.01
ExC-3 0.06

Layer 4: High-Speed Red-Sensitivity Emulsion Layer

Silver Iodobromide Emulsion I (internally high AgI type having core/shell ratio of 2 : 1, sphere-equivalent diameter = 0.7 μm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 2.5)
coating silver amount 0.9

Gelatin 0.8
ExS-1 1.6 × 10⁻⁴
ExS-2 1.6 × 10⁻⁴
ExS-5 1.6 × 10⁻⁴
ExS-7 6 × 10⁻⁴
ExC-1 0.07
ExC-4 0.05
Solv-1 0.07
Solv-2 0.20
Cpd-7 4.6 × 10⁻⁴

Layer 5: Interlayer

Gelatin 0.6
UV-4 0.03
UV-5 0.04
Cpd-1 0.1
Polyethylacrylate Latex 0.08
Solv-1 0.05

Layer 6: Low-Speed Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 4 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.4 μm, variation coefficient of sphere equivalent diameter = 37%, tabular grain, diameter/thickness ratio = 2.0)

coating silver amount 0.18

Gelatin
ExS-3 2 x 10^{-4}
ExS-4 7 x 10^{-4}
ExS-5 1 x 10^{-4}
ExM-5 0.11
ExM-7 0.03
ExY-8 0.01
Solv-1 0.09
Solv-4 0.01

Layer 7: Medium-Speed Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 4 mol%, surface high AgI type having core/shell ratio of 1 : 1, circle-equivalent diameter = 1.0 μm, thickness = 0.2 μm, variation coefficient of circle-equivalent diameter = 15%, tabular grain, diameter/thickness ratio = 5.0)

coating silver amount 0.27

Gelatin
ExS-3 4 x 10^{-4}
ExS-4 1.4 x 10^{-3}
ExS-5 2 x 10^{-4}
ExM-5 0.17
ExM-7 0.04
ExY-8 0.02
Solv-1 0.14
Solv-4 0.02
Layer 8: High-Speed Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 8.7 mol%, multilayered structure grain having silver ratio of 3 : 4 : 2 from inside, AgI contents = 24, 0, and 3 mol% from inside, sphere-equivalent diameter = 0.7 μm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 1.6)

coating silver amount 0.7

Gelatin 0.8
ExS-4 $5.2 \times 10^{-4}$
ExS-5 $1 \times 10^{-4}$
ExS-8 $0.3 \times 10^{-4}$
ExM-5 0.1
ExM-6 0.03
ExY-8 0.02
ExC-1 0.02
ExC-4 0.01
Solv-1 0.25
Solv-2 0.06
Solv-4 0.01
Cpd-7 $1 \times 10^{-4}$

Layer 9: Interlayer

Gelatin 0.6
Cpd-1 0.04
Polyethylacrylate Latex 0.12
Solv-1 0.02
Layer 10: Donor Layer having Interlayer Effect on Red-Sensitive Layer

Silver Iodobromide Emulsion (AgI = 6 mol%, internally high AgI type having core/shell ratio of 2:1, sphere-equivalent diameter = 0.7 μm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 2.0)
coating silver amount 0.68

Silver Iodobromide Emulsion (AgI = 4 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.4 μm, variation coefficient of sphere-equivalent diameter = 37%, tabular grain, diameter/thickness ratio = 2.5)
coating silver amount 0.19

Gelatin 1.0
ExS-3 $6 \times 10^{-4}$
ExM-10 0.19
Solv-1 0.20

Layer 11: Yellow Filter Layer

Yellow Colloid Silver 0.06
Gelatin 0.8
Cpd-2 0.13
Solv-1 0.13
Cpd-1 0.07
Cpd-6 0.002
H-1 0.13

Layer 12: Low-Speed Blue-Sensitive Emulsion Layer

Em-G to Em-L coating silver amount 0.45

Gelatin 1.8
ExC-1 0.06
ExC-4 0.03
ExY-9 0.14
ExY-11 0.89
Solv-1 0.42
Layer 13: Interlayer

Gelatin 0.7
ExY-12 0.20
Solv-1 0.34

Layer 14: High-Speed Blue-Sensitive Emulsion Layer

Silver Chloroiodobromide Emulsion (AgI = 10 mol%, internally high AgI type, AgCl = 7 mol%, inner shell AgCl type, circle-equivalent diameter = 2.0 μm, thickness = 0.3 μm, variation coefficient of circle-equivalent diameter = 30%, tabular grain, diameter/thickness ratio = 7.0) coating silver amount 0.5

Gelatin 0.5
ExS-6 7 x 10^-4
ExY-9 0.01
ExY-11 0.20
ExC-1 0.02
Solv-1 0.10

Layer 15: 1st Protective Layer

Fine Grain Silver Bromide Emulsion (AgI = 2 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.07 μm) coating silver amount 0.12

Gelatin 0.9
UV-4 0.11
UV-5 0.16
Solv-5 0.02
H-1 0.13
Cpd-5 0.10
Polyethylacrylate Latex 0.09
Layer 16: 2nd Protective Layer

Fine Grain Silver Iodobromide Emulsion
(Agl = 2 mol%, homogeneous AgI type,
sphere-equivalent diameter = 0.07 μm)
coating silver amount: 0.36

Gelatin: 0.55

Polymethylmethacrylate Grain
(diameter = 1.5 μm): 0.2

H-1: 0.17

In addition to the above components, a stabilizer for emulsion Cpd-3 (0.07 g/m²) and a surfactant Cpd-4 (0.03 g/m²) were added as coating aids to each layer.

In addition, SPC-1 and SPC-2 were added in order to stabilize processing properties and film physical properties. Formulas of the used compounds are listed in Table B.

Samples in which Em-G, Em-H, Em-I, Em-J, Em-K, and Em-L prepared in Example 2 were used in the layer 12, are designated samples 301, 302, 303, 304, 305, and 306, respectively.

The samples of color photographic light-sensitive materials 301 to 306 as described above were exposed and processed (until an accumulated replenishing amount of a breaching solution became three times a capacity of a mother solution tank) by using an automatic developing machine in accordance with the following method.

<table>
<thead>
<tr>
<th>Process</th>
<th>Time</th>
<th>Temperature</th>
<th>Replenishing Amount*</th>
<th>Tank Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color Development</td>
<td>3 min. 15 sec.</td>
<td>38°C</td>
<td>15 ml</td>
<td>20 l</td>
</tr>
<tr>
<td>Bleaching</td>
<td>6 min. 30 sec.</td>
<td>38°C</td>
<td>10 ml</td>
<td>40 l</td>
</tr>
<tr>
<td>Washing</td>
<td>2 min. 10 sec.</td>
<td>35°C</td>
<td>10 ml</td>
<td>20 l</td>
</tr>
<tr>
<td>Fixing</td>
<td>4 min. 20 sec.</td>
<td>38°C</td>
<td>20 ml</td>
<td>30 l</td>
</tr>
<tr>
<td>Washing (1)</td>
<td>1 min. 05 sec.</td>
<td>38°C</td>
<td>Counter flow piping from (2) to (1)</td>
<td>10 l</td>
</tr>
<tr>
<td>Washing (2)</td>
<td>1 min. 00 sec.</td>
<td>38°C</td>
<td>20 ml</td>
<td>10 l</td>
</tr>
<tr>
<td>Stabilization</td>
<td>1 min. 05 sec.</td>
<td>38°C</td>
<td>10 ml</td>
<td>10 l</td>
</tr>
<tr>
<td>Drying</td>
<td>4 min. 20 sec.</td>
<td>55°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*) A replenishing amount per meter of a 35-mm wide sample.

The compositions of the process solutions will be presented below.

Color Developing Solution:

<table>
<thead>
<tr>
<th></th>
<th>Mother Solution (g)</th>
<th>Replenishment Solution (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylenetriaminepentaacetae</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>1-hydroxyethylidene-1,1-diphosphonic Acid</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>4.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Potassium Carbonate</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Potassium Bromide</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>Potassium Iodide</td>
<td>1.5 mg</td>
<td>-</td>
</tr>
<tr>
<td>Hydroxylamine Sulfate</td>
<td>2.4</td>
<td>3.6</td>
</tr>
<tr>
<td>4-(N-ethyl-N-β-hydroxyethylamino)-2-methylamine Sulfate</td>
<td>4.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 l</td>
<td>1.0 l</td>
</tr>
<tr>
<td>pH</td>
<td>10.05</td>
<td>10.10</td>
</tr>
</tbody>
</table>
**Bleaching Solution:**

<table>
<thead>
<tr>
<th></th>
<th>Mother Solution (g)</th>
<th>Replenishment Solution (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric Sodium Ethylenediaminetetraacetate Trihydrate</td>
<td>100.0</td>
<td>140.0</td>
</tr>
<tr>
<td>Disodium Ethylenediaminetetraacetate</td>
<td>10.0</td>
<td>11.0</td>
</tr>
<tr>
<td>Ammonium Bromide</td>
<td>140.0</td>
<td>180.0</td>
</tr>
<tr>
<td>Ammonium Nitrate</td>
<td>30.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Ammonia Water (27%)</td>
<td>6.5 ml</td>
<td>2.5 ml</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 l</td>
<td>1.0 l</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

**Fixing Solution:**

<table>
<thead>
<tr>
<th></th>
<th>Mother Solution (g)</th>
<th>Replenishment Solution (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disodium Ethylenediaminetetraacetate</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>7.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Sodium Bisulfite</td>
<td>5.0</td>
<td>9.5</td>
</tr>
<tr>
<td>Ammonium Thiosulfite Aqueous Solution (70%)</td>
<td>170.0 ml</td>
<td>240.0 ml</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 l</td>
<td>1.0 l</td>
</tr>
<tr>
<td>pH</td>
<td>6.7</td>
<td>6.6</td>
</tr>
</tbody>
</table>

**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 & Haas 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 dichloroisocyanurate 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.
<table>
<thead>
<tr>
<th>Stabilizing Solution:</th>
<th>Mother Solution (g)</th>
<th>Replenishment Solution (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formalin (37%)</td>
<td>2.0 mč</td>
<td>3.0 mč</td>
</tr>
<tr>
<td>Polyoxymethylene-p-monomonylphenylether (average polymerization degree = 10)</td>
<td>0.3</td>
<td>0.45</td>
</tr>
<tr>
<td>Disodium Ethylenediaminetetraacetate</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>Water to make</td>
<td>1.0 1</td>
<td>1.0 1</td>
</tr>
<tr>
<td>pH</td>
<td>5.0 - 8.0</td>
<td>5.0 - 8.0</td>
</tr>
</tbody>
</table>
The sensitivity is represented by a relative value of a reciprocal of an exposure amount for giving a density higher than a fogging density by 1.0 with respect to a characteristic curve of a yellow image. The results are summarized in Table 6.

Table 6

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Emulsion No.</th>
<th>Remarks</th>
<th>Relative Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>Em-G</td>
<td>Comparative Example</td>
<td>100</td>
</tr>
<tr>
<td>302</td>
<td>Em-H</td>
<td>Comparative Example</td>
<td>107</td>
</tr>
<tr>
<td>303</td>
<td>Em-I</td>
<td>Present Invention</td>
<td>135</td>
</tr>
<tr>
<td>304</td>
<td>Em-J</td>
<td>Present Invention</td>
<td>158</td>
</tr>
<tr>
<td>305</td>
<td>Em-K</td>
<td>Present Invention</td>
<td>178</td>
</tr>
<tr>
<td>306</td>
<td>Em-L</td>
<td>Present Invention</td>
<td>151</td>
</tr>
</tbody>
</table>

As is apparent from Table 6, a high sensitivity was obtained when a palladium compound was added in an amount of $5 \times 10^{-5}$ mol or more per mol of a silver halide after the grain formation step and before the desalting step.

According to the present invention, a stable method of manufacturing a silver halide photographic emulsion can be achieved. In particular, a stabilized method of manufacturing a silver halide photographic emulsion subjected to reduction sensitization in grain formation step can be achieved.

Table A

(1-1) CH$_3$SO$_3$SNa
(1-2) C$_2$H$_5$SO$_2$SNa
(1-3) C$_3$H$_7$SO$_2$SK
(1-4) C$_4$H$_9$SO$_2$SLi
(1-5) C$_6$H$_{13}$SO$_2$Sna
(1-6) C$_8$H$_{17}$SO$_2$SNa

\[ (1-7) \text{CH}_3(\text{CH}_2)_3\text{CHCH}_2\text{SO}_2\text{S} \cdot \text{NH}_4 \]
\[ \text{C}_2\text{H}_5 \]

(1-8) C$_{10}$H$_{21}$SO$_2$SNa
(1-9) C$_{12}$H$_{25}$SO$_2$SNa
(1-10) C$_{16}$H$_{33}$SO$_2$SNa

\[ (1-11) \text{CH}_3 \searrow \text{CH-SO}_2\text{SK} \]
\[ \text{CH}_3 \swarrow \text{CH-SO}_2\text{SK} \]

(1-12) t-C$_4$H$_9$SO$_2$SNa
(1-13) CH$_3$OCH$_2$CH$_2$SO$_2$SNa
(1-14) $\text{CH}_2\text{SO}_2\text{SK}$

(1-15) $\text{CH}_2 = \text{CHCH}_2\text{SO}_2\text{Na}$

(1-16) $\text{SO}_2\text{SNa}$

(1-17) $\text{Cl} - \text{SO}_2\text{SNa}$

(1-18) $\text{CH}_3\text{CONH} - \text{SO}_2\text{SNa}$

(1-19) $\text{CH}_3\text{O} - \text{SO}_2\text{SNa}$

(1-20) $\text{H}_2\text{N} - \text{SO}_2\text{SNa}$

(1-21) $\text{CH}_3 - \text{SO}_2\text{SNa}$

(1-22) $\text{HO}_2\text{C} - \text{SO}_2\text{SK}$

(1-23) $\text{COOH}$

(1-24) $\text{HO} - \text{CH}_3 - \text{SO}_2\text{SNa}$
(1-25) \[
\begin{array}{c}
\textbf{N} \\
\textbf{S}O_2 \textbf{SNa}
\end{array}
\]

(1-26) \[
\begin{array}{c}
\textbf{C}H_3 \\
\textbf{N} \quad \textbf{O} \\
\textbf{S}O_2 \textbf{SNa}
\end{array}
\]

(1-27) \[
\begin{array}{c}
\textbf{S}O_2 \textbf{SK}
\end{array}
\]

(1-28) \[
\begin{array}{c}
\textbf{O} \\
\textbf{N}-(\textbf{CH}_2)_3 \textbf{S}O_2 \textbf{SNa}
\end{array}
\]

(1-29) \[
\textbf{K}SSO_2(\textbf{CH}_2)_2 \textbf{S}O_2 \textbf{SK}
\]

(1-30) \[
\textbf{N}aSSO_2(\textbf{CH}_2)_4 \textbf{S}O_2 \textbf{SNa}
\]

(1-31) \[
\textbf{N}aSSO_2(\textbf{CH}_2)_4 \textbf{S}(\textbf{CH}_2)_4 \textbf{S}O_2 \textbf{SNa}
\]

(1-32) \[
\begin{array}{c}
\textbf{S}O_2 \textbf{SNa}
\end{array}
\]

32
(1-33) \( \begin{array}{c}
\text{CONH} \\
\text{CO}_2\text{CH}_3 \\
\text{SO}_2\text{SNa}
\end{array} \)
\( \quad x : y = 1/1 \) (mole ratio)

(2-1) \( \text{C}_2\text{H}_5\text{SO}_2\text{SCH}_3 \)

(2-2) \( \text{C}_8\text{H}_{17}\text{SO}_2\text{SCH}_2\text{CH}_3 \)

(2-3) \( \text{SO}_2\text{S} \)

(2-4) \( \text{CH}_3\text{SO}_2\text{S} \)

(2-5) \( \text{C}_2\text{H}_5\text{SO}_2\text{SCH}_2\text{CN} \)

(2-6) \( \text{SO}_2\text{SCH}_2\text{CH}_3\text{CCH}_3 \)

(2-7) \( \text{CH}_3\text{C}_4\text{H}_9\text{SO}_2\text{SCH}_2\text{CN} \)

(2-8) \( \text{C}_6\text{H}_{13}\text{SO}_2\text{SCH}_2\text{CN} \)
(2-15) \[ \text{C}_2\text{H}_5\text{SO}_2\text{SCH}_2\text{N} \]

(2-16) \[ \text{C}_8\text{H}_{17}\text{SO}_2\text{SCH}_2\text{CH}_2\text{SO}_2 - \text{CH}_3 \]

(2-17) \[ \text{C}_2\text{H}_5\text{SO}_2\text{SCH}_2\text{N} - \text{CH}_2\text{CH}_2\text{OH} \]

(2-18) \[ \text{C}_2\text{H}_5\text{SO}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \]

(2-19) \[ \text{C}_2\text{H}_5\text{SO}_2\text{S} - \text{O} - \text{C}  \]

(2-20) \[ \text{CH}_3\text{O} - \text{SO}_2\text{SCH} = \text{CH} - \text{N} \]

(2-21) \[ \text{CH}_3\text{SSO}_2(\text{CH}_2)_4\text{SO}_2\text{SCH}_3 \]

(2-22) \[ \text{CH}_3\text{SSO}_2(\text{CH}_2)_2\text{SO}_2\text{SCH}_3 \]
(2-23) \[(\text{CH}-\text{CH}_2)\n\]
\[
\begin{array}{c}
\text{CH}_2\text{SSO}_2\text{C}_2\text{H}_5
\end{array}
\]

(2-24) \[(\text{CH}-\text{CH}_2)^x(\text{CH}-\text{CH}_2)^y\]
\[
\begin{array}{c}
\text{CO}_2\text{C}_2\text{H}_5
\end{array}
\]
\[
x : y = 2 : 1
\]
\[
\text{(mole ratio)}
\]

(2-25) \[(\text{CH}_2)^4\]
\[
\begin{array}{c}
\text{SO}_2\text{S}
\end{array}
\]

(3-1) \[
\begin{array}{c}
\text{CH}_3
\end{array}
\]
\[
\begin{array}{c}
\text{SO}_2\text{S(}\text{CH}_2\text{)}_2\text{SSO}_2
\end{array}
\]
\[
\begin{array}{c}
\text{CH}_3
\end{array}
\]

(3-2) \[
\text{C}_2\text{H}_5\text{SO}_2\text{SCH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{SSO}_2\text{C}_2\text{H}_5
\]

(3-3) \[
\text{C}_8\text{H}_{17}\text{SO}_2\text{SCH}_2
\]
\[
\begin{array}{c}
\text{CH}_2\text{SSO}_2\text{C}_8\text{H}_{17}
\end{array}
\]

(3-4) \[
\text{C}_2\text{H}_5\text{SO}_2\text{SCH}_2\text{N(}\text{CH}_2\text{CH}_2\text{)}\text{NCH}_2\text{SSO}_2\text{C}_2\text{H}_5
\]
\[
\begin{array}{c}
\text{CH}_2\text{CH}_2\text{OH}
\end{array}
\]
\[
\begin{array}{c}
\text{CH}_2\text{CH}_2\text{OH}
\end{array}
\]
(3-5) \[ \text{structure 1} \]

(3-6) \[ \text{structure 2} \]

(3-7) \[ \text{C}_2\text{H}_5\text{SO}_2\text{SSSO}_2\text{C}_2\text{H}_5 \]

(3-8) \[ (n)\text{C}_3\text{H}_7\text{SO}_2\text{SSSO}_2\text{C}_3\text{H}_7(n) \]

(3-9) \[ \text{structure 3} \]
Table B

UV-1

UV-2

UV-3
UV-4

(x/y = 7/3, weight ratio)

UV-5

Solv-1

tricresyl phosphate

Solv-2
Solv-4

\[ \text{(t)C}_5\text{H}_n \quad \overset{\text{O-CH-C-NH}}{\text{O}} \quad \text{(t)C}_5\text{H}_n \]

Solv-5
trihexyl phosphate

ExF-1

\[ \text{CO-NH-(CH}_3^3\text{O-CH}_r\text{C}_5\text{H}_n(t) \quad \text{CH}_3 \quad \text{H}_5\text{C}_2, \text{C}_2\text{H}_5} \]
ExF-2

(t)H₅C₅

C₆H₁₃

O-CH-CO-NH

ExS-1

O

C₂H₅

N

(\text{CH}_2\text{S}O_3^-)

ExS-2

N

C₂H₅

(\text{CH}_2\text{S}O_3^-)

(\text{CH}_2\text{S}O_3\text{Na})
ExC-3

ExC-4
ExM-5

\[(\text{CH}_2-\text{C})_x \text{CH}_3\]

\[\text{CO-NH} \]

\[\text{CO-O-C}_4\text{H}_9\]

\[x = 50\]
\[y = 25\]
\[z = 25\]

weight ratio

mol. wt. about 20,000

ExM-6

\[(t)\text{C}_5\text{H}_{11}\]

\[\text{O} \]

\[\text{C}_2\text{H}_5\]

\[\text{Cl}\]

\[\text{Cl}\]

\[\text{O-CH}_3\]

\[\text{Cl}\]

\[\text{Cl}\]
1. A method of manufacturing a silver halide photographic emulsion, wherein a palladium compound is added in an amount of not less than $5 \times 10^{-5}$ mol per mol of a silver halide after a grain formation step and before a desalting step.

2. The method according to claim 1, characterized in that silver halide grains are subjected to reduction sensitization in the grain formation step.

3. The method according to claim 1, characterized in that said palladium compound is added in an amount of $5 \times 10^{-5}$ to $1 \times 10^{-3}$ mol per mol of a silver halide.

4. The method according to claim 1, characterized in that said palladium compound is added in an amount of $1 \times 10^{-4}$ to $5 \times 10^{-4}$ mol per mol of a silver halide.

5. The method according to claim 1, characterized in that said palladium compound is represented by $R_2PdX_6$ or $R_2PdX_4$ wherein R represents a hydrogen atom, an alkaline metal atom, or an ammonium group, and X represents a halogen atom.

6. The method according to claim 5, characterized in that said palladium compound is used together with thiocyanate ions in a molar amount not less than five times that of said palladium compound.

7. The method according to claim 1, characterized in that at least one compound selected from a group consisting of compounds represented by following formulas (I), (II), and (III) is used in a process of manufacturing a reduction-sensitized silver halide emulsion:

(I) $R$-$SO_2S$-$M$

(II) $R$-$SO_2S$-$R_1$

(III) $RSO_2S$-$L_m$-$SSO_2$-$R_2$

wherein $R$, $R_1$, and $R_2$ may be the same or different and represent an aliphatic group, an aromatic group, or a heterocyclic group, $M$ represents a cation, $L$ represents a divalent bonding group, $m$ represents 0 or 1, compounds represented by formulas (I) to (III) may be polymers containing divalent groups derived from structures represented by formulas (I) to (III) as a repeating unit, and if possible, $R$, $R_1$, $R_2$, and $L$ may be bonded with each other to form a ring.

8. The method according to claim 7, characterized in that a compound represented by formula (I) is used.

9. The method according to claim 7, characterized in that $1 \times 10^{-5}$ to $1 \times 10^{-2}$ mol/molAg of compounds represented by formulas (I), (II), and (III) are used.

10. The method according to claim 1, characterized in that said silver halide emulsion comprises regular silver halide grains.

11. The method according to claim 1, characterized in that said silver halide emulsion is a monodisperse silver halide emulsion having a grain size distribution in which not less than 80% of all grains fall within a range of ±30% of an average grain size, the percent being represented by the number or weight of grains.

12. The method according to claim 1, characterized in that said silver halide emulsion comprises tabular silver halide grains having an aspect ratio of not less than 3.

13. The method according to claim 1, characterized in that not less than 50% of a total projected area of the silver halide emulsion are occupied by tabular grains having aspect ratios of 3 to 8.

14. A silver halide color light-sensitive material which comprises at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler, and at least one red-sensitive silver halide emulsion layer containing a cyan coupler on a support, wherein at least one of said emulsion layers contains a silver halide photographic emulsion manufactured by performing addition of palladium compound in amount of not less than $5 \times 10^{-5}$ mol per mol of a silver halide after a grain formation step and before a desalting step.
### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. ClS)</th>
</tr>
</thead>
</table>
* page 308, left-hand column, line 12 - page 308, left-hand column, line 18  
* page 310, right-hand column, line 8 - page 310, right-hand column, line 27 | 1-5 | G03C1/09 |
* page 69, right-hand column, line 1 - page 69, right-hand column, line 3 | 1-5 | |
--- | 1-5 | |
* the whole document | --- | |
*table 4* | 1-5 | |
| X        | DE-A-2824082 (FUJI PHOTO FILM) *claims*  
--- | 7-0 | |

The present search report has been drawn up for all claims.

**Place of search:** THE HAGUE  
**Date of completion of the search:** 26 FEBRUARY 1990  
**Examiner:** BUSCH A.J.

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<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
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