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(71) Applicant: **KONICA CORPORATION**
26-2, Nishishinjuku 1-chome, Shinjuku-ku
Tokyo 160(JP)

(72) Inventor: **Suzuki, Katsuhiko, Konica Corporation**
1 Sakura-machi
Hino-shi, Tokyo(JP)
Inventor: **Hoshino, Hiroyuki, Konica Corporation**
1 Sakura-machi
Hino-shi, Tokyo(JP)

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

(54) Silver halide photographic emulsion.

(57) A silver halide photographic emulsion is disclosed. The emulsion comprises a silver bromide or iodobromide grain containing two or more kinds of multivalent metal compounds. At least one of the metal compounds, metal compound (1), is uniformly distributed in the grain and at least one of the metal compounds other than the metal compound (1), metal compound (2) is locally localized at interior and/or surface of the grain.

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FIELD OF THE INVENTION

The present invention relates to a silver halide photographic emulsion, more specifically to a silver halide photographic emulsion whose sensitivity, reciprocity law characteristics have been improved by metal doping.

BACKGROUND OF THE INVENTION

In recent years, the demand for a silver halide photographic light-sensitive material which provides high sensitivity and high image quality has been inceasing. To respond to such a demand, a technique which improves the photosensitive characteristics of the silver halide emulsion is needed, wherein the sensitivity is enhanced by controlling the charge carriers in the silver halide grains which take part in the latent image forming process.

Four main types of carriers are thought to be involved in the latent image forming process. They are interstitial silver ions and silver ion holes, i.e., Frenkel defect pair, and electrons and holes generated by light irradation.

In a dye-containing emulsion, electrons and holes generated in the dye, so that both of these two types of carriers are possibly injected into the silver halide grains. A method for optimizing the photosensitive characteristics of the silver halide grains must be able to control all the different types of carriers. That is, the method must at a time individual types of control for respective carriers in combination.

The carriers can be controlled by varying the halide composition in the individual silver halide grains. For example, silver iodobromide core shell grains that have an internally high AgI content with high iodide content, are frequently used in color films. This type of grain is known to have higher quantum yield than that of other types of grain with uniform silver halide composition. The sensitization mechanism of this internally iodide-rich grains is described in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 143331/1985; the mechanism can be attributable to charge separation of the holes and electrons caused by the distortion of band structure in individual grains which result from a difference in halide composition.

Nakayama and his colleagues proposed a charge separation model of electrons and dye holes caused by shallow electron trapping in the high iodide phase (Abstracts of lectures, 1987, Photographic Society of Japan, Annual Meeting, p. 49).

On page 246 of Fundamental of Photographic Science, Silver Photography (Corona Publishing Co., Ltd.) compiled by Photographic Society of Japan, it is stated that the iodide ions in the silver iodobromide emulsion promote the lattice defect or increase the number of interstitial silver ions and silver ion holes.

Although these methods can control the carriers by varying the halide composition in the individual grains, they cannot control each type of carrier independently. In addition, cannot necessarily be considered a method for optimally controlling the carriers without degrading various photographic properties because varying the halide composition of the grains not only affects photosensitive characteristics, but also the uniformity of grain growth, chemical sensitization, and developing property.

Unlike the silver chlorobromide emulsion in which mixed crystals are formed in arbitrary compound ratios, the silver iodobromide emulsion can only contain mixed crystals in limited compound ratios. For this reason, the controllability for carriers the silver iodobromide emulsion is limited compared to the silver chlorobromide emulsion because how much its halide composition can be varied is limited. In addition, it is known that the higher the amount of silver iodide in the silver iodobromide emulsion, the wider the composition and size distribution among grains [Fundamentals of Photographic Science, Silver Photography (Corona Publishing Co., Ltd.), compiled by Photographic Society of Japan, page 246].

Another effective means for controlling carriers is metal doping technique.

Metal doping refers to a technique of improving photographic characteristics by introducing primarily multivalent metal compounds into the silver halide grains.

Japanese Patent O.P.I. Publication Nos. 7042/1987 and 105940/1989, and other publications disclose a doping technique using iridium compounds; Japanese Patent O.P.I. Publication Nos. 183438/1988 and 245242/1989, and other publications disclose a technique of doping using rhodium compounds; and Japanese Patent O.P.I. Publication No. 121844/1989 disclose a technique of doping using iron compounds. Such doping techniques using a single metal compound are well known and researches are being made on various metals. Doping using a single compound, however, is not satisfactory a method for optimally controlling carriers.

Japanese Patent O.P.I. Publication Nos. 184740/1988 and 125245/1990 disclose a doping technique using two dissimilar metal compounds. Also, Japanese Patent O.P.I. Publication Nos. 260137/1987 and

156239/1990 disclose a doping technique using two or more kinds of metal compounds as a mode of the invention. Merely adding two or more kinds of metal compounds is, however, not sufficient. A method for optimally controlling carriers must provide a concentration distribution suitable for the function of each dopant.

Japanese Patent O.P.I. Publication No. 183647/1989 discloses a technique of improving photosensitive characteristics by introducing localized silver bromide phase and iron ions into individual silver chlorobromide emulsion grains, giving an example of doping using two different metal ions with different distributions. However, this technique also based on halide composition difference as typified by localized silver bromide phase, and cannot be applied to silver iodobromide emulsions because it allows only limited control of carriers by varying halide composition.

Japanese Patent O.P.I. Publication No. 216136/1984 is related to a direct positive material and discloses a technique in which two different kinds of metal ions are used independently in respective doping processes. However, this technique is not intended for controlling carriers by use of multiple dopants because one kind of the metal ions is used for core formation to obtain a direct positive image forming emulsion.

To sum up, none of the proposed techniques feature doping using two or more metal compounds having different and optimum distributions so that the characteristics of the silver iodobromide emulsion or the silver bromide emulsion are improved by optimally controlling carriers.

SUMMARY OF THE INVENTION

The object of the invention is to provide a silver halide photographic emulsion whose sensitivity, reciprocity law characteristics, and other photographic properties have been improved by optimally controlling carriers by means of metal doping alone independent of the halide composition in the emulsion.

The above object of the invention is achieved by a silver halide photographic emulsion comprising a silver bromide or iodobromide grain containing two or more kinds of multivalent metal compounds. At least one of these metal compounds, metal compound (1), is uniformly distributed in the grain to satisfy the requirement that the volume of region in which the metal compound (1) is distributed in a concentration of not less than 1/2 of the maximum concentration of the metal compound (1) in the grain is at least 80% of the whole volume of the grain, and at least one of the metal compounds other than the metal compound (1), metal compound (2) is localized at interior and/or surface of the grain provided that the volume of region in which the metal compound (2) is distributed is not more than 50% of the whole volume of the grain.

DETAILED DESCRIPTION OF THE INVENTION

The silver halide photographic emulsion of the present invention comprises silver iodobromide grains or silver bromide grains. Though it is compatible with silver iodobromide grains having any composition distribution, it preferably in corporates silver iodobromide grains where intragrain halide-composition variation is small in order to maintain consistent emulsion characteristics such as grains is small. A small internal halide composition difference allows maximum use of uniform grain size distribution, crystal habit, chemical sensitization capability and developability. For silver iodobromide grains, it is preferable that the difference between highest and lowest iodide content phases is not more than 10 mol%, more preferably not more than 5 mol%. It is most preferable that the iodide content is uniform in the individual grains. Pure silver bromide grains are equally preferred alongside silver iodobromide grains having uniform iodide distribution.

The term "doping" or "to dope" means to incorporate a substance other than silver ions or halide ions into the silver halide grains.

The term "dopant" refers to compounds introduced into the silver halide grains by doping.

Preferable dopants are metal compounds such as those of Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Cd, Sn, Ba, Ce, Eu, W, Re, Os, Ir, Pt, Hg, Tl, Pb, and Bi. Among them, compounds of Fe(II), Fe(III), Ir(III), Ir(IV), Re(IV), Ru(III), Ru(IV), Os(III), Os(IV), Tl(III) and Pb(II) are particularly preferable.

The combination of two or more kinds of metal compounds according to the invention may be a combination of two or more compounds each comprises metal ion different from each other, in which the moieties of them other than the metal ions may be the same or different, or a combination of different compounds having the same metal ions.

It is preferable that the metal compound for doping are simple salts or metal complexes. Preferable metal complexes are those having a coordination number of 6, 5, 4, or 2. Greater preference is given to octahedral six-coordinated and planar four-coodinated metal complexes. The complexes may be one having mono- or polynuclear. Ligands which comprise complexes include CN^-, CO, NO_2^-, 1,10-phenanthroline, 2,2'-bipyridine, SO_3^-, ethylenediamene, NH_3, pyridine, H_2O, NCS, NCO, NO_3^-, SO_4^{2-}, OH^-, CO_3^{2-}, SSO_3^{2-}, N_3^-, S^{2-}, F^-, Cl^-, Br^-, and I^-. In the above, CN^- is particularly preferable as a ligand.

Metal complexes particularly useful are potassium salt complexes such as $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, K_2IrCl_6, K_2IrBr_6, K_2ReCl_6, K_2RuCl_6, $K_2Ru(CN)_6$, $K_2Os(CN)_6$, K_3TlCl_6 or an ammonium salt, sodium salt, or cesium salt each having any of the above complexes as a substituent.

Simple salts which are preferably used include halides, nitrates, sulfates, and perchlorates of the above metals. They are typically $FeCl_2$, $FeCl_3$, $Pb(NO_3)_2$, and $IrCl_3$, the halides and nitrates of Fe^{2+}, Fe^{3+}, Pb^{2+}, Ir^{3+}, and Ir^{4+} are particularly preferred.

A dopant may be able to control more than one type of carrier. It is believed that most of the multivalent metal ions affect the silver ions interstitial sites, of which some have hole trap-or electron trap-capability.

Dopants can be classified into three main types according to whether they are primarily capable of trapping electrons, holes, or controlling interstitial silver ions.

For example, Leubner disclosed in The Journal of Photographic Science Vol. 31, 93 (1983) that iridium complexes used for doping principally have electron trap capability. Japanese Patent O.P.I. Pub. No. 121844/1989 discloses a method in which ferrous ions are used to trap holes.

It is preferable that dopants to be locally distributed are capable of controlling electrons and/or holes by trapping them.

It is preferable that dopants to be uniformly distributed are capable of controlling interstitial silver ions and silver ion holes (Frenkel defect pair) or are capable of controlling holes by trapping them.

In the present invention, "uniformly distributed" means that the portion which have a concentration of dopant of not less than 1/2 of the maximum concentration of dopant, occupies at least 80% of the individual grain volume. It is preferable portion having a dopant concentration not less than 1/2 of the maximum dopant concentration occupies at least 85%, more preferably at least 90%, and most preferably 100% of the individual grain volume. In addition, it is preferable that the minimum and maximum concentration ratio of the uniformly distributed dopant in the minimum concentrarion portion to that in the mximum concentration portion is at least 3 to 2, more preferably at least 4 to 3. Further, it is preferable that the concentration of the uniformly distributed dopant is 10^{-9} to 10^{-3} mole, more preferably 5×10^{-7} to 10^{-5} mole per mole of silver. As metal compounds to be uniformly distributed in the grain, compounds of Fe(II), Fe(III), Ru(III), Ru(IV), Os(III), Os(IV) and Pb(II) are preferable.

In the present invention "locally distributed" or "localized" means that 80 mol% or more, more preferably 90 mol% or more, of the dopant contained in a grain is distributed over not more than 50% of the grain volume. As metal compounds to be locally distributed in the grain, compounds of Ir(III), Ir(IV), Re(IV), Tl(III), Fe(II), Fe(III), Ru(III), Ru(IV), Os(III), Os(IV) and Pb(II) are preferable. The preferable distribution mode of the localized dopant depends on the type of metal ion because each metal ion has a particular electron or hole trap capability. In the case of Ir(III), Ir(IV), Re(IV) and Tl(III) compounds, the preferable concentration is 10^{-5} to 10^{-8} mole per mole of the total amount of silver and the preferable distribution region is 0.1% to 10% of the grain volume. In the case of Fe(II), Fe(III), Ru(IV), Ru(III), Ru(IV), Os(III), Os(IV) and Pb(II), the preferable Fe concentration is 10^{-3} to 10^{-7} mole per mole of the total amount of silver and the preferable distribution region is 45% to 15% of the grain volume.

In the present invention, kinds of metal compound to be uniformly distributed and to be locally distributed each may be 2 or more. It is particularly preferable that kinds of metal compound contained in the grain are three or more in total.

It is preferable to use a monodispersed silver halide emulsion for the silver halide photographic emulsion of the invention. In a monodispersed silver halide emulsion, the silver halide grains whose sizes fall within ±20% of average grain sized account for at least 70wt%, preferably at least 80wt%, and more preferably at least 90wt% of the total silver halide.

A monodispersed emulsion has a distribution coefficient, which is defined by 100 times [standard grain size deviation divided by average grain size], of not more than 20%, preferably not more than 15%. Grain size in the invention is the length of one edge of a cube having the same volume as the grain.

The silver halide emulsion of the present invention contains grains having an average size of preferably 0.1 to 10 µm, more preferably 0.1 to 5.0 µm, and even more preferably 0.3 to 1.4 µm.

The monodispersed emulsion of the invention may comprise normal crystals such as a cubic, tetradecahedral, or octodecahedral crystal, or twin crystals such as a tabular crystal, or both normal and twin crystals.

With tabular twin crystal grains, those having a diameter- (of a disk having an area equal to the projected area of grain) to-thickness ratio of 1 to 20, more preferably between 1.2 to 8.0, and most preferably between 1.5 to 5.0, preferably occupy at least 60% of the projected area of the grains.

The monodispersed normal crystal grain emulsion can be manufactured using the methods disclosed in Japanese Patent O.P.I Publication Nos. 177535/1984, 138538/1985, 52238/1984, 143331/1985, 35726/1985, 258536/1985, and 14636/1986.

The monodispersed twinned crystal grain emulsion can be prepared by the method which consists in growing spherical seed emulsion disclosed in, for example, Japanese Patent O.P.I. Publication No. 14636/1986.

When growing the silver halide grains in the silver halide emulsion of the present invention, the device disclosed in Japanese Patent O.P.I. Publication No. 160128/1987 is preferably used.

In order to grow the silver halide grains in the emulsion, it is preferable to add aqueous silver nitrate solution and aqueous halide solution by the double-jet method. Note that silver iodide can be used to supply iodide to the system. It is preferable to add the solutions at such a rate as not to allow new nuclei formation nor spreading in size distribution caused by Ostwald ripening, that is at 30 to 100% the rate at which new nuclei are formed.

Another way to grow grains is to add fine silver halide grains in the emulsion, dissolve them, and to recrystallize them Abstract of lectures, Photographic Society of Japan, 1983, Annual Meeting, p. 88.

The preferable conditions for growing silver halide grains in the emulsion are a pAg of 5 to 11, a temperature of 40 to 85 °C, and a pH of 1.5 to 12.

The following dopant addition methods suitable for obtaining the silver halide emulsion of the invention are preferably used.

(1) When preparing grains, a dopant is added to the mother liquor before adding aqueous silver nitrate solution and other solutions.

(2) When preparing grains, a dopant is previously added to aqueous silver nitrate solution, aqueous halide solution, the fine grain emulsion or to other solutions being added.

(3) During grain formation, a dopant is dissolved in a suitable solvent or dispersed in a suitable dispersing medium, and then added.

For uniform distribution of dopant, method (2) is particularly preferred. For localized distribution of dopant, any method (1), (2), or (3) may be preferably used according to the requirements.

The finished silver halide photographic emulsion of the present invention containing grains possessing the intended characteristics are preferably desalinized by a known method. The useful method include a method using a gelatin flocculant, or the noodle-washing method in which gelatin is gelated may be used as well as a flocculation method using inorganic salts containing multivalent anions such as sodium sulfate, anionic sufactants, or anionic polymers such as polystyrenesulfonic acid, or the precipitation method which uses gelatin derivatives such as acylated gelatin and carbamoylated gelatin.

The so-desalinized silver halide grains are redispersed in the gelatin solution, so that a silver halide emulsion is prepared.

The silver halide photographic emulsion of the present invention can be preferably used for silver halide color photographic light-sensitive materials.

The silver halide photographic emulsion of the present invention is physically and chemically ripened, and spectrally sensitized before preparing a color photographic light-sensitive material. The additives used in the above processes are described in Research Disclosure Nos. 17643, 18716, and 308119 (hereinafter referred to as RD17463, RD18716, and RD308119 respectively). The additives are found in the pages and sections in the following table.

Item	RD308119	RD17643	RD18716
Chemical sensitizer	p. 996, Sec. III-A	p. 23	p. 648
Spectral sensitizer	p. 996, Sec. IV-A-A, B, C, H, I, J	pp. 23~24	pp. 648~649
Supersensitizer	p. 996, Sec. IV-A-3, J	pp. 23~24	pp. 648~649
Antifogging agent	p. 998, Sec. VI	pp. 24~25	p. 649
Stabilizer	p. 998, Sec. VI	pp. 24~25	p. 649

Known photographic additives used for the silver halide photographic emulsion of the invention in order to prepare a color photographic light-sensitive material are also listed in the above Research Disclosures.

Related items are found in the pages and sections in the table below.

Items	RD308119	RD17643	RD18716
Anticoloring mixing agent	p. 1002, Sec. VII-I	p. 25	p. 650
Dye image stabilizer	p. 1001, Sec. VII-J	p. 25	
Brightening agent	p. 998, Sec. V	p. 24	
UV ray absorber	p. 1003, Sec. VIII-C, XIIIC	pp. 25~26	
Light absorber	p. 1003, Sec. VIII	pp. 25~26	
Light scattering agent	p. 1003, Sec. VIII		
Filter dye	p. 1003, Sec. VIII	pp. 25~26	
Binder	p. 1003, Sec. IX	p. 26	p. 651
Antistatic agent	p. 1006, Sec. XIII	p. 27	p. 650
Hardener	p. 1004, Sec. X	p. 26	p. 651
Plasticizer	p. 1006, Sec. XII	p. 27	p. 650
Lubricant	p. 1006, Sec. XII	p. 27	p. 650
Activator, coating aid	p. 1005, Sec. XI	pp. 26~27	p. 650
Matting agent	p. 1007, Sec. XVI		
Developing agent (contained in light-sensitive material)	p. 1011, Sec. XXB		

Various couplers can be used when using the silver halide photographic emulsion of the invention in order to prepare a color photographic light-sensitive material. Specific examples are given in the Research Disclosures above. Related items are listed in the pages and sections given in the following table.

Item	RD308119	RD17643
Yellow coupler	p. 1001, Sec. VII-D	Sec. VII-C~G
Magenta coupler	p. 1001, Sec. VII-D	Sec. VII-C~G
Cyan coupler	p. 1001, Sec. VII-D	Sec. VII-C~G
Colored coupler	p. 1002, Sec. VII-G	Sec. VII-G
DIR coupler	p. 1001, Sec. VII-F	Sec. VII-F
BAR coupler	p. 1002, Sec. VII-F	
Other couplers which release a useful residue	p. 1001, Sec. VII-F	
Alkali-soluble coupler	1001, Sec. VII-E	

Additives used for the silver halide emulsion of the invention in order to prepare a color photographic light-sensitive material can be added by the dispersion method described in RD308119, section XIV.

When using the silver halide photographic emulsion of the invention in order to prepare a color photographic light-sensitive material, supports described on page 28 of RD17643, pages 647 and 648 of RD18716, and section XVII of RD308119 above can be used.

The color photographic light-sensitive material comprising the silver halide emulsion of the invention may have auxilary layers such as a filter layer and intermediate layer described in section XVII-K of the foregoing RD308119.

The color photographic light-sensitive material containing the silver halide emulsion of the invention may have various layer configurations. It may have a conventional layer order, inverted layer order or unit layer structure described in section VII-K of the aforementioned RD308119.

The silver halide emulsion of the invention can be preferably used for various color light-sensitive materials. Representative examples are color negative films for general use and for movie-making, color reversal films for slides and T.V., color paper, color positive films, and color reversal paper.

The color photographic light-sensitive material comprising the silver halide photographic emulsion of the invention can be developed using the usual methods disclosed in the aforementioned RD17643 (pp. 28 to 29), RD18716 (p. 615), and RD308119 (Sec. XIX).

EXAMPLES

The invention is hereunder described in detail using the following examples. However, the scope of the invention is not limited to these examples.

Examples

(Preparation of comparative emulsion Em-1)

With the temperature of solution A kept at 40 °C, and while it was thoroughly stirred, solutions B, C_1, and C_2 were added at rates shown in Table 1 using the double-jet method. During addition, solutions D and E were used to control pH and pAg as shown in Table 1. The obtained emulsion was washed and dispersed using a usual method and the resulting emulsion was named Em-1. Electron microscopic observation revealed that the emulsion grains were regular octahedral grains having an average size of 1.00 μm.

(Preparation of comparative emulsion Em-2)

Em-2 was prepared in the same way as Em-1, except that 93.7 mg and 187.0 mg of lead nitrate were added to solutions C_1 and C_2 respectively.

(Preparation of comparative emulsion Em-3)

Em-3 was prepared in the same way as Em-1, except that 15.0 mg and 29.8 mg of potassium ferrocyanide trihydrate were added to solutions C_1 and C_2 respectively.

(Preparation of comparative emulsion Em-4)

Em-4 was prepared in the same way as Em-1, except that 151.2 mg and 301.8 mg of potassium hexachlorothallate (III) were added to solutions C_1 and C_2 respectively.

(Preparation of comparative emulsion Em-5)

Em-5 was prepared in the same way as Em-1, except that 16.6 mg and 33.0 mg of potassium hexacyanorhuthenate (II) trihydrate were added to solutions C_1 and C_2 respectively.

(Preparation of comparative emulsion Em-6)

Em-6 was prepared in the same way as Em-1, except that 44.8 mg of potassium ferrocyanide trihydrate was added to solution C_1.

(Preparation of comparative emulsion Em-7)

Em-7 was prepared in the same way as Em-1, except that when the remaining amount of solution B was 440.7 ml its addition was stopped temporarily and restarted 5 minutes after the addition of 1.06 ml of a 2.0×10^{-3} M aqueous solution of potassium hexachloroiridate (IV). Note that the aqueous potassium hexachloroiridate solution was added immediately after it was prepared.

(Preparation of comparative emulsion Em-8)

Em-8 was prepared in the same way as Em-1, except that when the remaining amount of solution B was 44.8 ml, its addition was stopped temporarily, and restarted 5 minutes after the addition of 1.06 ml of a

2×10^{-3} M aqueous solution of potassium hexachlororuthenate (IV). Note that the aqueous potassium hexachlororuthenate (IV) solution was added immediately after it was prepared.

(Preparation of comparative emulsion Em-9)

Em-9 was prepared in the same way as Em-7, except that 280.7 mg of lead nitrate was added to solution C_2.

(Preparation of comparative emulsion Em-10)

Em-10 was prepared in the same way as Em-7, except that 44.8 mg of potassium ferrocyanide trihydrate was added to solution C_1.

(Preparation of comparative emulsion Em-11)

Em-11 was prepared in the same way as Em-1, except that 93.7 mg of lead nitrate and 15.0 mg of potassium ferrocyanide were added to solution C_1, and 187.0 mg of lead nitrate and 29.8 mg of potassium ferrocyanide were added to solutions C_1.

(Preparation of inventive emulsion Em-12)

Em-12 was prepared in the same way as Em-1, except that 93.7 mg of lead nitrate and 44.8 mg of potassium ferrocyanide were added to solution C_1, and 187.0 mg of lead nitrate were added to solution C_2.

(Preparation of inventive emulsion Em-13)

Em-13 was prepared in the same way as Em-7, except that 93.7 mg and 187.0 mg of lead nitrate were added to solutions C_1 and C_2, respectively.

(Preparation of inventive emulsion Em-14)

Em-14 was prepared in the same way as Em-7, except that 151.2 mg and 301.8 mg of potassium hexachlorothallate (III) were added to solution C_1 and C_2, respectively.

(Preparation of inventive emulsion Em-15)

Em-15 was prepared in the same way as Em-7, except that 15.0 mg and 29.8 mg of potassium ferrocyanide were added to solutions C_1 and C_2, respectively.

(Preparation of inventive emulsion Em-16)

Em-16 was prepared in the same way as Em-8, except that 93.7 mg and 187.0 mg of lead nitrate were added to solutions C_1 and C_2, respectively.

(Preparation of inventive emulsion Em-17)

Em-17 was prepared in the same way as Em-8, except that 15.0 mg and 29.8 mg of potassium ferrocyanide trihydrate were added to solutions C_1 and C_2, respectively.

Em-18 was prepared in the same way as Em-8, except that 16.6 mg and 33.0 mg of potassium hexacyanorhuthenate (III) trihydrate were added to solutions C_1 and C_2, respectively.

(Preparation of inventive emulsion Em-19)

Em-19 was prepared in the same way as Em-8, except that 16.6 mg of potassium hexacyanoruthenate (III) trihydrate and 93.7 mg of lead nitrate were added to solution C_1, and 33.0 mg of potassium hexacyanoruthenate and 187.0 mg of lead nitrate were added to solution C_2.

(Preparation of inventive emulsion Em-20)

Em-20 was prepared in the same way as Em-7, except that 93.7 mg of lead nitrate and 44.8 mg of potassium ferrocyanide were added to solution C_1, and 187.0 mg of lead nitrate were added to solution C_2.

Electron microscope observation of the grains on the aforementioned Em-2 to Em-20 revealed that they were about the same size and had similar crystal habits.

Solution A	
Ossein gelatin Sodium polyisopropylene-polyethyleneoxy-disuccinate (10% methanol solution) Acetic acid (56%) Ammonia (28%) Silver bromide seed emulsion (average grain size 0.240 μ)	101.7 g 30.0 ml 93.3 ml 155.4 ml 0.1465 mole equivalent
Pure water was added to 10593.0 ml.	

Solution B	
Silver nitrate	1775.1 g
Ammonia (28%)	1448.0 ml
Pure water was added to 4975.5 ml.	

C_1	
Ossein gelatin	33.2 g
Potassium bromide	406.8 g
Potassium iodide	11.58 g
Pure water was added to 1660.8 ml.	

Solution C_2	
Ossein gelatin	66.3 g
Potassium bromide	811.9 g
Potassium iodide	23.11 g
Pure water was added to 3314.7 ml.	

Solution D	
Acetic acid (56%)	3000.0 ml

Solution E	
Potassium bromide	208.0 g
Pure water was added to 500.0 ml.	

Table 1

Time	Addition rate of solution B (ml/min.)	Addition rate of solution C_1 (ml/min.)	Addition rate of solution C_2 (ml/min.)	pH	pAg
0′00″	3.38	3.38		9.00	9.70
11′38″	5.43	5.43		9.00	9.70
19′48″	7.24	7.24		9.00	9.70
26′05″	9.10	9.10		9.00	9.70
31′10″	11.10	11.10		9.00	9.70
35′24″	12.98	12.98		9.00	9.70
42′09″	17.12	17.12		9.00	9.70
49′37″	23.52	23.52		9.00	9.70
60′20″	32.47	32.47		8.93	9.80
74′54″	42.25	42.25		8.81	10.00
81′52″	44.22	44.22		8.74	10.10
81′53″	44.22		44.22	8.74	10.10
85′10″	44.92		44.92	8.71	10.16
100′56″	43.16		43.16	8.56	10.40
111′04″	45.40		45.40	8.46	10.42
121′58″	46.08		46.08	8.34	10.44
155′50″	41.49		41.49	8.01	10.50
157′02″	41.49		41.49	8.00	10.50

(Sensitivity Evaluation)

After subjecting Em-1 to Em-7 to optimum chemical sensitization using sodium thiosulfate, appropriate amounts of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, polyvinylpyrolidone, dioctylsodium sulfosuccinate as coating aid, 1,2-bis(vinylsufonyl)ethane as hardener were added to each emulsion. Then, each resulting emulsion was applied to a triacetylcellulose (TAC) base to obtain samples for sensitometry.

Each sample was exposed through an optical wedge and filter at 32 CMS in each of different exposure times, 1/100 second and 8 seconds, and then processed according to the following conditions.

Processing steps (processing temperature 20 ° C)	Processing time
Developing	10 min.
Stopping	2 min.
Fixing	5 min.
Washing	10 min.

(Processing solution)

Metol	2.5 g
L-ascorbic acid	10.0 g
Sodium metaborate tetrahydrate	35.0 g
Potassium bromide	1.0 g
Pure water was added to 1000.0 ml.	

(Stopping solution)

Acetic acid (3%)

(Fixing solution)

Konica Fix (Konica Corp.)

The density of each processed sample was determined using an optical densitometer in order to evaluate the sensitivity of each sample. The sensitivity was obtained as a reciprocal of the exposure value (true value) which gives a density equal to the minimum optical density + 0.1 and was expressed as a value relative to emulsion Em-1 set at 100. The evaluation results are summarized in Table 2.

Table 2

Emulsion No.	Uniform doping	Localized doping	Sensitivity (1/100″)	Sensitivity (8″)	
Em-1	-	-	100	100	Comparative Example
Em-2	$Pb(NO_3)_2$	-	126	125	Comparative Example
Em-3	$[FeCl_6]^{-4}$	-	122	129	Comparative Example
Em-4	$[TlCl_6]^{-3}$	-	98	111	Comparative Example
Em-5	$[Ru(CN)_6]^{-4}$	-	119	127	Comparative Example
Em-6	-	$[Fe(CN)_6]^{-4}$	120	131	Comparative Example
Em-7	-	$[IrCl_6]^{-2}$	112	115	Comparative Example
Em-8	-	$[RuCl_6]^{-2}$	97	99	Comparative Example
Em-9	-	$Pb(NO_3)_2$, $[IrCl_6]^{-2}$	111	110	Comparative Example
Em-10	-	$[Fe(CN)_6]^{-4}$, $[IrCl_6]^{-2}$	130	133	Comparative Example
Em-11	$Pb(NO_3)_2$	-	128	135	Comparative Example
Em-12	$Pb(NO_3)_2$	$[Fe(CN)_6]^{-4}$	152	166	Invention
Em-13	$Pb(NO_3)_2$	$[IrCl_6]^{-2}$	158	173	Invention
Em-14	$[TlCl_6]^{-3}$	$[IrCl_6]^{-2}$	143	157	Invention
Em-15	$[Fe(CN)_6]^{-4}$	$[IrCl_6]^{-2}$	151	170	Invention
Em-16	$Pb(NO_3)_2$	$[RuCl_6]^{-2}$	141	152	Invention
Em-17	$[Fe(CN)_6]^{-4}$	$[RuCl_6]^{-2}$	137	146	Invention
Em-18	$[Ru(CN)_6]^{-3}$	$[RuCl_6]^{-2}$	132	142	Invention
Em-19	$Pb(NO_3)_2$, $[Ru(CN)_6]^{-3}$	$[RuCl_6]^{-2}$	182	199	Invention
Em-20	$Pb(NO_3)_2$	$[Fe(CN)_6]^{-4}$, $[IrCl_6]^{-2}$	191	222	Invention

As apparent from Table 2, silver halide emulsions Em-12 to Em-20 of the invention, which were subjected to doping two or more multivalent metallic compounds, have increased sensitivity and good reciprocity law characteristics.

The two or more multivalent metallic compounds used in the invention may consist of the same or dissimilar metal types. The combination of compounds deriving from the same metal preferably contain a simple salt in conjunction with a complex; complexes having different ligand combinations; or complexes in which the central metals have different oxidation numbers; as well as stereoisomers such as geometric isomers. It is further desirable to use metals having different valencies in conjunction, wherein preferable metal is iridium.

Claims

1. A silver halide photographic emulsion comprising a silver bromide or iodobromide grain containing two or more kinds of multivalent metal compounds, wherein at least one of said metal compounds, metal compound (1), is uniformly distributed in said grain provided that the volume of region in which said metal compound (1) is distributed in a concentration of not less than 1/2 of the maximum concentration of said metal compound (1) in said grain is at least 80% of the whole volume of said grain, and at least one of said metal compounds other than said metal compound (1), metal compound (2), is localized at interior and/or surface of said grain provided that the volume of region in which said metal compound (2) is distributed is not more than 50% of the whole volume of said grain.

2. The emulsion of claim 1, wherein said silver halide grain substantially comprises silver bromide.

3. The emulsion of claim 1, wherein said silver halide grain substantially comprises silver iodobromide in which silver iodide is uniformly distributed in said grain.

4. The emulsion of claim 1, 2 or 3, wherein the volume of region in which said metal compound (1) is distributed in a concentration of not less than 1/2 of the maximum concentration of said metal compound (1) in said grain is 100% of the volume of said grain.

5. The emulsion of claims 1 or 2 to 4, wherein the ratio of the minimum concentration of said metal compound (1) to the maximum concentration of said metal compound (1) in said grain is 3 : 4.

6. The emulsion of claims 1 or 2 to 5, wherein at least one of said metal compounds (1) and (2) is a cyano complex.

7. The emulsion of claims 1 or 2 to 6, wherein said metal compounds (1) and (2) are selected from the group consisting of compounds of Fe(II), Fe(III), Ir(III), Ir(IV), Re(IV), Ru(III), Ru(IV), Os(III), Os(IV), Tl(III) and Pb(II).

8. The emulsion of claim 7, wherein said metal compound (1) is a salt of Pb(II), $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{2-}$ or $[Os(CN)_6]^{2-}$ and metal compound (2) is a salt of $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{2-}$, $[Os(CN)_6]^{2-}$, $[IrCl_6]^{2-}$ or $[IrBr_6]^{2-}$.

9. The emulsion of claim 7, wherein said compound (1) is a compound of Fe(II), Fe(III), Ru(III), Ru(IV), Os(III), Os(IV) or Pb(II).

10. The emulsion of claim 7, wherein said compound (2) is a compound of Fe(II), Fe(III), Ru(III), Ru(IV), Os(III), Os(IV) or Pb(II) and content thereof in said silver halide grain is 10^{-7} moles to 10^{-3} moles per mole of silver halide, and said compound is localized in a volume of 15% to 45% of whole volume of said silver halide grain..

11. The emulsion of claim 9, wherein said compound of Ir(III), Ir(IV), Re(IV) or Tl(III) is contained in said silver halide grain in an amount of 10^{-7} moles to 10^{-3} moles per mole of silver halide and is localized in a volume of 0.1% to 10% of whole volume of said silver halide grain.

12. The emulsion of claims 1 or 2 to 11, wherein the content of said metal compound (1) in said silver halide grain is within the range of from 1×10^{-8} mol to 5×10^{-5} mol per mol of silver halide.

13. The emulsion of claims 1 or 2 to 12, wherein said silver halide grain contains three or more kinds of mutivalent metal compound.