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(54) **SILVER HALIDE EMULSION AND PROCESS FOR ITS PREPARATION.**

(57) A silver halide emulsion for photographic use and a process for its preparation. A monodisperse silver halide emulsion containing silver halide grains of octahedral or tetradecahedral crystals having a recess in the center of the (111) face suffers less fogging and has high sensitivity. This emulsion is prepared by treating a monodisperse silver halide emulsion containing silver halide grains of octahedral or tetradecahedral crystals with a solvent for silver halide.

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Specification

Silver halide emulsion and method for preparing the same

[Technical Field]

This invention relates to a light-sensitive silver halide emulsion for photography and more particularly to a light-sensitive silver halide emulsion of which the sensitivity, the antifogging property and the storability have been improved, and a method for preparing the same.

[Background of the technology]

Recently, requirement for a silver halide emulsion for photography have increasingly become severer and there have been made increasingly higher levels of requirement for photographic performances such as high sensitivity, excellent graininess, high sharpness, low fog density, sufficiently high optical density and so on.

Further, since exhaustion of silver resources is emphasized today, development of low-silver light-sensitive materials has strongly been desired. These requirements which seem to be different from each other at a first glance can mostly be satisfied by a manufacturing technique of producing a silver halide emulsion having a low fogging property and a high sensitivity and it is no exaggeration to say that a development of a silver halide emulsion having a low fogging property and a high sensitivity is the most important problem in the art. Moreover, in photographic materials having a poor storability a commercial value thereof is lowered and at the same time there is brought about a result that any satisfactory photograph cannot be obtained, and hence improvement in the storability as well as enhancement in the sensitivity is an important problem.

The most orthodox method for attaining photographic performances such as high sensitivity, low fogging property and so on is to enhance the quantum efficiency of a silver halide. For this purpose, knowledge of solid physics and the like have been positively taken into account. Studies in which the quantum efficiency has theoretically been calculated and an effect of the grain size distribution thereon has been investigated are described, for example, in a preliminary text for lectures at the symposium concerning the progress in photograph, Tokyo, 1980, "Interactions between light and materials for photographic applications", item 91. Accoording to this study, preparation of a monodispersed emulsion having a narrow grain size distribution is expected to be effective for enhancement of the quantum efficiency. Additionally, it is considered to be rational to infer that a monodispersed emulsion is advantageous not only for attainment of sensitization in a silver halide emulsion but also for an effective performance of high sensitivity with keeping a fogging property low in a step referred to as chemical sensitization which will be described in more detail below.

In an actual emulsion system, however, emulsions employing a monodispersed emulsion singly or in a mixture series are scarcely utilized and particularly with respect to a nega type high sensitivity emulsion, it can be said that they are never employed at all. This reason is that there has been widely known in this technical field that even if a monodispersed emulsion is prepared according to a generally known method and subjected to regular chemical sensitization, not only sensitization cannot be attained but also a result inferior to that given by generally used polydispersed emulsions is brought about.

For an industrial preparation of a monodispersed emulsion, there are required a control of the theoretically obtained rate at which silver ions and halogen ions are supplied to a reaction system, and a condition for sufficient stirring under a strict control of pAg and pH as described in Japanese Provisional Patent Publication No. 48521/1979. Silver halide emulsions prepared under such a condition as mentioned above comprise so called regular crystal grains which have any shape of cube, octahedron and tetradecahedron and have the face (100) and the face (111) at various proportions. The present inventors prepared monodispersed emulsions comprising octahedral or tetradecahedral grains and conducted the generally known chemical sensitization thereon, however, they could merely obtain results equivalent or rather inferior indeed to those given by polydispersed emulsions generally used in the art.

The reason why octahedral grains have not heretofore been employed for nega type high sensitivity light-sensitive materials, although octahedral grains are assumed to have a good relationship between the antifogging property and the sensitivity according to Japanese Patent Publication No. 23443/1973, is that from view point of enchancement of sensitivity they have disadvantages in that a large amount of light-sensitive nuclei are produced through chemical sensitization and a large amount of silver ions are present between crystal lattices during exposure and hence they are inferior to grains having other shapes.

Such characteristics of octahedral grains can be understood from reports in Journal of Photographic Science 14; 181-184 (1966); ibid, 16: 102-113 (1968); Photographiche Korrespondenz, 106: 149-160 (1970) and Journal of Japanese Photographic Society, 42; 112-121 (1979). Further, since the progress of the chemical sensitization of tetradecahedral grains is expected to be dominated by the face (111), tetradecahedral grains are considered to exhibit the same characteristic as that of octahedral grains and actually our studies have revealed that tetradecahedral grains have a property similar to that of octahedral grains.

On the other hand, it has been known in the art that a physical ripening (Ostwald Ripening) is advantageously conducted by addition of a solvent for a silver halide such as thiocyanates, thiourea derivatives, thioethers and the like to an emulsion. According to "Foundations of Photographic Engineering" -volume: Silver Salt Photograph, pages 242-244, published by Corona Co. (1969), the term physical ripening is defined as follows: a procedure in which grains with a large specific surface area are dissolved in a solvent to deposit or precipitate upon larger grains and thereby crystal growth are performed while reducing the number of grains. In physical ripening, it is thus a prerequisite to have grains grow by utilizing the difference in solubilities among grains having different grain sizes and therefore grain size distribution becomes generally broadened after physical ripening, so that it is considered to be not preferable as a method for preparing a monodispersed emulsion.

Moreover, though there has been known a technique for obtaining a high sensitivity in which a solvent for a silver halide such as thiourea derivatives, thioethers, thiocyanates and the like is added during a chemical ripening process, the resultant emulsion has defects in that the storability of products applied therewith is poor and hence is not practical.

[Disclosure of the invention]

An object of the present invention is to provide a light-sensitive silver halide emulsion having a low fogging property and a high sensitivity.

Another object of the present invention is to provide a light-sensitive silver halide emulsion having an excellent storability.

Still another object of the present invention is to provide a method for preparing such a light-sensitive silver halide emulsion as described above.

We have made intensive studies to obtain a high sensitivity in a monodispersed emulsion, from which no expected results had hereinfore been derived in spite of the presence of a theoretical expectation and as a result, the present inventors have found that the objects of the present invention can be accomplished by a monodispersed silver halide emulsion comprising silver halide grains having a recess at the central part of the face (111) of octahedral crystals or tetradecahedral crystals; and a method for preparing a silver halide emulsion in which a monodispersed silver halide emulsion containing silver halide grains comprising octahedral crystals or tetradecahedral crystals is subjected, after formationof said silver halide grains, to treatment with a solvent for the silver halide to the degree that the recess is formed at the central part of the face (111) of crystals described above, followed by desalting.

In the present invention, a recess which is positioned at the central part of the case (111) of octahedral crystals or tetradecahedral crystals is a recess of which the depth is 0.20 ℓ to 0.05 ℓ at the deepest point thereof, wherein ℓ is a diameter of the circumsphere for the silver halide grain having said recess (octahedral or tetradecahedral crystals having such a recess are hereinafter referred to also as the "skeleton crystal of the present invention"). The silver halide emulsion according to the present invention includes emulsions in which a part or all of silver halide grain groups comprising octahedral or tetradecahedral crystals contained therein are grains having such a recess as described above, however, an emulsion in which 1 % or more (in terms of the number of grains) of said grain groups are grains having such a recess, and silver halide grain groups contained in said emulsion consist essentially of silver halide grains comprising octahedral crystals or tetradecahedral crystals is preferable, and also as to the degree to which the grains are subjected to treatment with a solvent for the silver halide (whereinafter referred to as "solvent treatment") in the manufacturing method of the present invention, such an emulsion as mentioned above is similarly preferable.

Even if silver halide grains comprising octahedral crystals or tetradecahedral crystalsare subjected to solvent treatment, the emulsion which has been subjected to the solvent treatment of the present invention has a lower fogging property and a higher sensitivity after chemical ripening as compared with an emulsion which has been subjected to solvent treatment so that the shapes of grainsbecome spherical forms, confetto-like forms (defined as such, when the depth of the recess as described above exceeds 0.20 ℓ) or a potato-like forms (defined as such, when the outer crystal habit is indefinite and irregular, and the grains having the spherical form are indefinite also in the outer crystal habit but different from the potato-like form in the point that grain shapes are uniform).

When the silver halide emulsion according to the present invention is coated and oriented on a support to obtain its X-ray diffraction by the powder method, the intensity of the diffracted ray for the face (220) is preferably less than 15 % of that for the face (111) and more preferably less than 8 %.

Silver halide grains contained in the monodispersed silver halide emulsion according to the present invention has such a level of monodispersion that the breadth for grain size distribution is preferably 19 % or less in terms of CV, wherein CV designates the coefficient of variation represented by an equation: (Standard deviation/average grain size) x 100 = CV %; and more preferably 13 % or less. Be noted here that the grain size is expressed by the diameter of the circumcircle in an electron microscopic photograph of the silver halide grain.

In the method of the present invention, the monodispersed silver halide emulsion to be treated with a solvent may preferably such that the silver halide grains contained therein comprise essentially of octahedral or tetradecahedral silver halide crystals. Further, breadth of the grain size distribution of the silver halide grains contained in the monodispersed silver halide emulsion to be treated with a solvent is 15 % or less in terms of CV and more preferably 10 % or less.

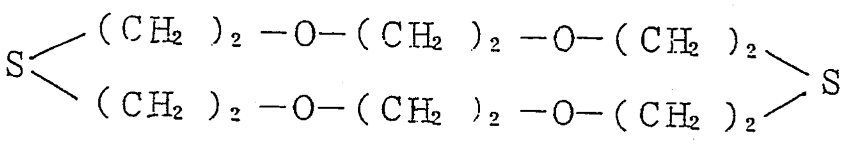
In the method of the present invention, solvent treatment may be conducted merely by adding a solvent for a silver halide (AgX) to a silver halide emulsion in which silver halide grains have been formed into the final size and shape through completion of a mixing or a mixing followed by a physical ripening procedure; and subsequently by mixing uniformly to act said solvent onto the surface of the silver halide grain. Therefore, there may be employed a procedure similar to a procedure for the conventional chemical ripening in which a solvent is used in place of a chemical sensitizer. Moreover, after formation of silver halide grains, there may be conducted desalting (including washing with water) prior to the solvent treatment.

As the solvent for a silver halide used in the manufacturing method of the present invention, there may be employed any solvent capable of forming a recess at the central part of the face (111) of said grain surfaces when the solvent acts on the surface of said silver halide grains comprising octahedral or tetradecahedral crystals. Further, it is preferable that said solvent is not a compound capable of reacting with a silver halide to form silver sulfide.

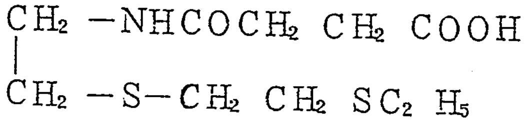
Solvents for a silver halide employed in the present invention include (a) organic thioethers as described in U.S. Patent Nos. 3,271,157, 3,531,289 and 3,574,628, Japanese Provisional Patent Publication Nos. 1019/1979 and 158917/1979; (b) thiourea derivatives as described in Japanese Provisional Patent Publication Nos. 82408/1978, 77737/1980 and 2982/1980, (c) solvents for a silver halide having a thiocarbonyl group sandwiched between an oxygen atom or a sulfur atom and a nitrogen atom as discribed in Japanese Provisional Patent Publication No. 144319/1978 (d) imidazoles as described in Japanese Provisional Patent Publication No. 100717/1979, (e) sulfites, (f) thiocyanates and the like.

Specific compounds will be given below:

(a)

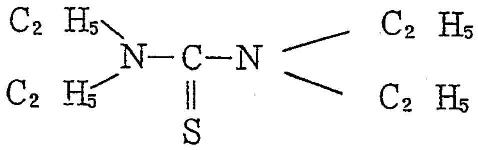


$HO-(CH_2)_2-S-(CH_2)_2-S-(CH_2)_2-OH$

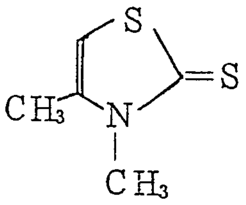


$$\begin{array}{l} CH_2-NHCOCH_2CH_2COOH \\ | \\ CH_2-S-CH_2CH_2SC_2H_5 \end{array}$$

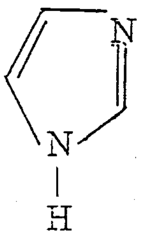
(b)



(c)



(d)



(e) K_2SO_3

(f) NH_4SCN

$KSCN$

As particularly preferred solvents, there may be mentioned thiocyanates and sulfites.

Amount of the solvent used in the present invention may be, for example, in case of thiocyanate, preferably in the range of 0.5 to 5 g/mole AgX, though it is variable depending on the kind of a solvent and so on. In cases the amount is less than this range, substantial change in grain shape after solvent treatment is not observed, and in cases the amount exceeds this range, the progress of the physical ripening becomes remarkable and grain size distribution is liable to be broadened.

Further, with respect to the vertex of crystal faces on the surface of silver halide grains comprising octahedral or tetradecahedral crystals contained in the silver halide of the present invention; for octahedral crystals it is preferable that the radius of curvature of roundness at said vertex is less than 1/6 r, wherein r is a length of one side of a triangle supposedly formed by extending sides of an arbitrary triangle constituting the outer surface thereof; and for tetradecehedral crystals, when a polygon having the largest area selected from triangles, squares, hexagons and octagons which constitute the outer surface is noted, it is preferable that the radius of curvature of roundness at the vertex of said polygon is less than 1/6 r, wherein r is a length of one side of a polygon which is supposedly formed by extending sides thereof or r is a length of the longest side in case not a regular polygon.

Further, in the preferred embodiment in the manufacturing method of the present invention, it is desirable that there are essentially no differences in the average grain size and in the grain size distribution of the silver halide grains contained in the silver halide emulsion of the present invention between those before and after solvent treatment, respectively.

By the description that there are essentially no differences in the average grain size and the grain size distribution is meant that rates of changes, $\Delta\bar{r}/\bar{r}$ and $\Delta s/s$ for average grain size $\bar{r}$ and for the grain size distribution s which are defined by the following equations, respectively,

$$\bar{r} = \frac{\Sigma ri}{n}$$

$$S = \sqrt{\frac{\Sigma(ri-\bar{r})^2}{n-1}} \times 100\ (\%)$$

are within 5 % and 0 - 20 %, respectively.

In the above definition, "n" referred to here designates the number of measured grains and "ri" designates the grain size of a grain measured in order of i.

When the differences in grain size distributions between those before and after solvent treatment fall within the range described above, the effect of the method of the present invention is remarkably large as compared with the effect in case out of this range. It is inferred that this is attributable to the fact that the degree of the physical ripening becomes remarkable in case said difference is out of this range. If grain size distribution of the silver halide emulsion to be subjected to solvent treatment ranges within the value of CV described above, physical ripening is hard to occur and thereby the effect of the present invention can be sufficiently exhibited, with a result that the difference between grain size distributions before and after solvent treatment falls approximately within the range described above.

The silver halide emulsion of the present invention includes, as one of the embodiments, an emulsion comprising two or more kinds of the monodispersed emulsions according to the present invention having different average grain sizes in admixture with each other. In the method for preparing such an emulsion described above, it is preferable to subject each emulsion individually to the solvent treatment and chemical ripening of the present invention prior to mixing of the emulsions.

In the present invention the grain groups containing the skelton crystals of the present invention or, the silver halide grain groups to be treated with a solvent comprise substantially grains which are octahedral crystals or tetradecahedral crystals and an effect given by grains having these crystal habits is unexpectedly large and remarkable as compared with that given by grains having other crystal habits than said habits.

As silver halide grains comprising tetradecahedral crystals contained in the silver halide emulsion of the present invention, tetradecahedral crystals constituted mainly of the face (111) (grains giving the external appearance of hexagon and square and grains giving the external appearance of square and triangle) is particularly preferable. Tetradecahedral crystals constituted mainly of the face (100) (grains giving the external appearance of octagon and triangle) is liable to become spherical when treated with a solvent.

The manufacturing method of the present invention is characterized in that after formation of silver halide grains, the grains are treated with a solvent for a silver halide to a specifically determined degree, before desalting and hence it is different from a technique in which a solvent for a silver halide, for example, ammonia is present at the time of formation of silver halide grains.

As a preferred embodiment in the manufacturing method of the present invention, a monodispersed emulsion having silver halide grains comprising octahedral crystals or tetradecahedral crystals are preferably ones prepared according to the ammonia method.

This invention exhibits particularly large effect when it is applied to a silver halide emulsion for color development. In this case, the sensitivity in an emulsion of the present invention reaches about six times the sensitivity given by an emulsion prepared without such solvent treatment of the present invention and further increase in fogging is scarecely observed even at such a high sensitivity.

Silver halide grains according to the present invention may coexist with a cadmium salt, a zinc salt, a lead salt, a thallium salt, a iridium salt or complex salts thereof, a rhodium salt or a complex salt thereof, or an ion complex salt and the like in the course of formation of grains, treatment with a solvent and so on.

Further, for the silver halide emulsion according to the present invention there may be used, for example, silver bromide, silver iodide, silver chloride, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide and the like. The preferred silver halide emulsion comprises silver halobromide containing at least 50 mole % of silver bromide and the most preferred emulsion comprises silver iodobromide, particularly containing 10 mole % or less of silver iodide.

Silver halide grains of the present invention may be different in phases between inner portion and surface layer thereof or may comprise a uniform phase. Regardless of the distribution in composition of halogen within silver halide grains described above, reduction sensitization may be conducted at any stage before completion of grain growth and treatment with a solvent.

Silver halide grains according to the present invention have preferably an average grain size of 0.1 - 4 µm and more preferably of 0.2 - 2 µm.

Further, in the method for preparing the emulsion of the present invention, there may be suitably employed, as means for desalting, the Nudel rinsing, dialysis or a coagulation technique, which is commonly employed in a general emulsion manufacture.

To the emulsion of the present invention there may be applied various kinds of chemical sentization which is applicable to a general emulsion. Namely, chemical ripening may be conducted by use in single or in combination of chemical sensitizers such as noble metal sensitizers, including water-solbule gold salts, water-soluble platinum salts, water-soluble palladium salts, water-soluble rhodium salts, water-soluble iridium salts and the like; a sulfur sensitizer; a selenium sensitizer; and reduction sensitizers including polyamine, stannous chloride and the like.

In the manufacturing method of the present invention, an embodiment in which any solvent for a silver halide is not added during the chemical ripening may preferably be mentioned.

The silver halide emulsion of the present invention can optically be sensitized to a desired wave length region. A spectral sensitization method for the emulsion of the present invention is not particularly critical and can be accomplished, for example, by use in single or in combination (e.g., supersensitization) of spectral sensitizers such as cyanine dyes or merocyanine dyes including a zeromethine dye, a monomethine dye, a dimethine dye, a trimethine dye and the like.

These sensitization techniques mentioned above, are described in U. S. Patent Nos. 2,688,545, 2,912,329, 3,397,060, 3,615,635 and 3,628,964; British Patent Nos. 1,195,302, 1,242,588 and 1,293,862; Offenlegungsschrift (OLS) Nos. 2,030,325 and 2,121,780; Japanese Patent Publication Nos. 4936/1968, 14030/1969 and the like. The selection may be optionally made depending on the application or purpose of light-sensitive materials, such as a desired wave length region to be sensitized or a desired sensitivity.

The monodispersed silver halide emulsion of the present invention may be put to use keeping its grain size distribution intact or may be put to use in combination with two or more monodispersed emulsions having different average grain sizes by blending these emulsions at an arbitrary stage so as to obtain a disired gradation. The emulsion of the present invention, however, may include an emulsion containing silver halide grains other than those of the present invention to such an extent that the effectiveness of the present invention is not thereby impaired.

The emulsion of the present invention may include generally usable various additives depending on the purpose thereof. As additives described above, there are mentioned, for example, stabilizers and antifogging agents such as azaindenes, triazoles, tetrazoles, imidazolium salts, tetrazolium salts, polyhydroxy compounds and the like; hardener such as aldehyde series, aziridine series, isoxazole series, vinylsulfonic series, acryloyl series, carbodiimide series, maleimide series, methanesulfonic ester series, triazine series and the like; development accelerators such as benzyl alcohol, polyoxyethylene series compounds and the like; image stabilizers such as chroman series, coumaran series, bisphenol series and phosphorous ester series; lubricants such as waxes, glycerides of higher fatty acids, higher esters of higher fatty acids and the like. Further, as a coating agent, improvers for permeability of a treatment solution, defoaming agents and agents for controlling various physical properties of light-sensitive materials, there may be used a various type of surfactants such as those of anionic type, cationic type, nonionic type or amphoteric type. As antistatic agents, diacetylcellulose, styrene perfluoroalkyllithium maleate copolymer, an alkali salt of a reaction product between styrene maleic anhydride copolymer and p-aminobenzenesulfonic acid and the like are effective. As matting agents, there may be mentioned methyl polymethacrylate, polystyrene, alkali-soluble polymers and the like. Further, it is also possible to use a colloidal silica. As latexes which are added to improve the physical properties of the coated film, there may be mentioned acrylic esters, vinyl esters and the like and their copolymers with the other monomers having an ethylic group. As gelatin plasticizers there may be mentioned glycerin and glycol series compounds, and as thickening agents there may be mentioned styrene-sodium maleate copolymer, alkyl vinyl ether maleate copolymer and the like.

As supports for the light-sensitive material manufactured by the use of the emulsion of the present invention which is prepared in the above-mentioned manner, there may be mentioned, for example, baryta paper, polyethylene-coated paper, polypropylene synthetic paper, glass paper, cellulose acetate, cellulose nitrate, polyvinyl acetal, polypropylene, a polyester film, for example, polyethyleneterephthalate and the like, polystyrene and so on. The support is suitably selected from them depending upon the use and the purpose of the silver halide light-sensitive photographic material, respectively.

Supports may be provided with undercoating if desired.

The emulsion of the present invention may be effectively used for a variety of light-sensitive materials for general black and white photography, X-ray photography, color photography, infrared photography, microphotography, silver dye bleach process, reversal development, diffusion transfer process and the like.

Further, when the emulsion of the present invention is applied to a light-sensitive material for color photography, techniques and materials which are commonly used for light-sensitive color photographic materials may be used, for instance, by incorporating cyan, magenta and yellow couplers in a combination into the emulsion of the present invention which has previously been adjusted for red-sensitivity, green-sensitivity and blue-sensitivity. As yellow couplers, there may be used open-chain ketomethylene series couplers known to the art, among which benzoylacetanilide series and pivaloylacetanilide series compounds are useful.

As magenta couplers, there may be used pyrazolone series compounds, indazolone series compounds and cyanoacetyl compounds and as cyan couplers, phenol series compounds, naphthol series compounds and the like.

The light-sensitive material prepared by the use of the emulsion of the present invention may be developed by a known method commonly used after exposure.

The black and white developer is an alkaline solution containing developing agents such as hydroxy benzenes, aminophenols, or aminobenzenes, and it may further contain alkali metal salts such as a sulfite, a carbonate, a bisulfite, a bromide and an iodide. When the light-sensitive material is for color photography, it may be developed by a color developing process which is commonly used. In a reversal process, it is firstly developed by a developer for a black and white negative and then subjected to white color exposure, or subjected to treatment in a bath containing an antifogging agent, and further developed for color development in an alkaline developing solution containing color developing agents. There is no particular restriction to the method for treatment, and any method may be applied. As a typical example, however, there may be mentioned, a system in which bleach-fix treatment is conducted after the color development and further washing and stabilizing treatments are carried out as the case requires, or a system in which the bleaching and the fixing are separately carried out after the color development, and further washing and stabilizing treatments are carried out as the case requires.

[Best mode for effecting the invention]

The present invention is illustrated referring to the following Examples, however, it is not limited to these specific Examples.

Example 1

According to the method as disclosed in Japanese Provisional Patent Publication No. 48521/1979, there was prepared a monodispersed octahedron series emulsion having an average grain size of 0.65 µm and a grain size distribution s of 8 % comprising silver iodobromide containing 2 mole% of silver iodide.

The obtained emulsion was divided to each of which, ammonium rhodanide or tetramethylthiourea was added to conduct ripening at 50 °C, followed by desalting and washing with water according to the ordinary method and then pAg value was adjusted to 8.2 at 40 °C. There are shown in Table 1 added amounts of ammonium rhodanide and tetramethylthiourea and results with respect to grain shapes after treatment obtained by observation through an electron microscope. These emulsions were designated as Em - 1 to Em - 5.

Em - 1 is an emulsion for comparison, which has not been subjected to treatment.

Table 1

Emulsion No.	Added amount of ammonium rhodanide mg/mole AgX	Added amount of tetramethyl-thiourea mg/mole AgX	Shape of grain after solvent treatment	Grain size distribution after treatment with a solvent (%)	Period of time for solvemt treatment (minute)
Em - 1	-	-	octahedral	8	60
Em - 2	600	-	comprising mainly octahedral crystals with containing 2 % of the skeleton crystals of the present invention	9	60
Em - 3	6000	-	comprising mainly octahedral crystals with containing 2 % of the skeleton crystals of the present invention and 3 % of twinned crystals	17	60
Em - 4	-	120	comprising spherical grains	9	60
Em - 5	-	25	comprising mainly spherical grains with containing 10 % of confetto-shaped grains	8	30

To the resultant emulsions Em - 1 to Em - 5, 0.45 ml of a 0.2 % by weight aqueous solution of chloroauric acid tetrahydrate and 1.5 ml of a 0.25 % by weight aqueous solution of sodium thiosulfate dihydrate based on one mole of AgX were added and subjected to chemical ripening at 46 °C. After completion of the ripening, to these emulsions 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and phenylmercaptotetra-zole were added. Then, as couplers, 15 g of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amylphenoxyacetamido)benz-amide-5-pyrozolone dissolved in 30 ml of ethyl acetate and 15 ml of butyl phthalate was mixed with 20 ml of a 10 % by weight aqueous alkanole B (alkylnaphthalenesulfonate, manufactured by Du'Pont Co) solution and 200 ml of a 5 % by weight aqueous gelatin solution, followed by emulsification and dispersion in a colloid mill. To 1 kg of said emulsions, thus obtained dispersion was added, applied on a triacetate film support so that the amount of Ag thereon may be 20 mg/dm^2, followed by drying to prepare Samples No. 1 to 10. Particulars of samples are shown in Table 2.

Table 2

Applied sample No.	Emulsion No.	Period of time for chemical ripening (minute)
1	Em - 1	120
2	Em - 1	140
3	Em - 2	70
4	Em - 2	90
5	Em - 3	60
6	Em - 3	80
7	Em - 4	40
8	Em - 4	60
9	Em - 5	40
10	Em - 5	60

Ten Samples described above were exposed through an optical wedge (1/50 sec.), color developed at 38 °C for 2 minutes by the use of a color developing solution having the following composition, followed by washing with water after bleaching and fixing and the sensitivity and the antifogging property were evaluated. The results are shown in Table 3.

(Composition of color developer)

4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine half-sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g

Made up to 1 liter with water and adjusted to pH 10.0 with potassium hydroxide.

Table 3

Sample No.	Emulsion No.	Sensitivity*	Fog
1 (Standard)	Em - 1	100	0.04
2 (")	Em - 1	120	0.05
3 (The present invention)	Em - 2	400	0.04
4 (")	Em - 2	600	0.05
5 (")	Em - 3	200	0.04
6 (")	Em - 3	280	0.08
7 (Comparative example)	Em - 4	180	0.04
8 (")	Em - 4	220	0.11
9 (")	Em - 5	180	0.04
10 (")	Em - 5	220	0.11

* The sensitivity was expressed by an exposure amount which gives a fog density of plus 0.1, in terms of its relative value.

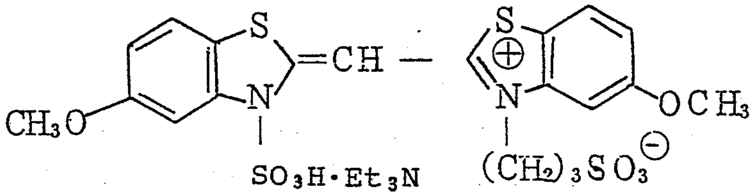
As apparent from Table 3, in the emulsion of the present invention, it was found that, it has a remarkably enhanced sensitivity as compared with a similar emulsion free from the skeleton crystals of the present invention and also is able to reach a higher level of sensitivity as compared with Em - 3 with a broadened grain size distribution and Em - 5 containing confetto-like grains or Em - 4 comprising spherical grains, and further, increase in fogging generated by chemical ripening is mild, giving thereby the improved anti-progress of fogging.

Example 2

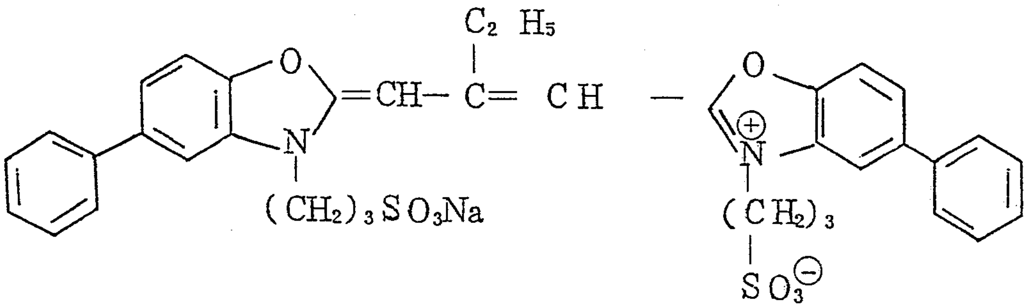
To Em - 1 to Em - 5 in Example 1, 0.45 ml of a 0.2 % by weight aqueous chloroauric acid tetrahydrate solution and 1.5 ml of a 0.25 % by weight aqueous sodium thiosulfate dihydrate solution based on one mole of AgX were added respectively and the thus obtained emulsions were subjected to chemical ripening at 46 °C for 110, 60, 50, 30 and 30 minutes, respectively and divided into three portions.

Thereafter to the resultant emulsions spectral sensitizing dyes (1) to (3) as shown below were added in a amount so as to be 150 mg based on one mole of AgX in the form of a methanolic solution and stirred for 10 minutes.

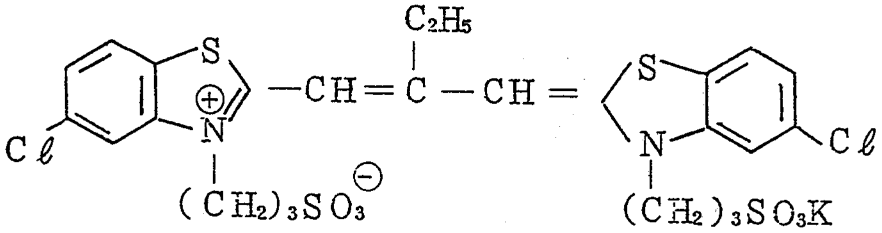
(1)



(2)



(3)



Then, in quite the same manner as in Example 1, the additives were added to the obtained emulsion, and coating and drying were conducted to prepare Sample Nos. 11 to 25.

In Table 5 are shown emulsion No., period of time for chemical ripening and a kind of sensitizing dye corresponding to each samples.

Table 5

Sample No.	Emulsion No.	Period of time for chemical ripening (minute)	Sensitizing dye
11	Em - 1	110	(1)
12	Em - 1	110	(2)
13	Em - 1	110	(3)
14	Em - 2	60	(1)
15	Em - 2	60	(2)
16	Em - 2	60	(3)
17	Em - 3	50	(1)
18	Em - 3	50	(2)
19	Em - 3	50	(3)
20	Em - 4	30	(1)
21	Em - 4	30	(2)
22	Em - 4	30	(3)
23	Em - 5	30	(1)
24	Em - 5	30	(2)
25	Em - 5	30	(3)

Fifteen Samples described above were exposed through an optical wedge, developed at 38 °C for 2 minutes by the use of the same color developing solution as in Example 1 and washed with water after bleaching and fixing to be subjected to evaluation of the sensitivity and the antifogging property. Sample Nos. 12, 13, 15, 16, 18, 19, 21, 22, 24 and 25 were, however, exposed through a glass filter Y-48 (manufactured by Toshiba Glass Co., Ltd.). Results in sensitometry are shown in Table 6.

Table 6

Sample No.	Fog	Sensitivity*	Sample No.	Fog	Sensitivity*
11	0.04	100	19	0.04	200
12	0.04	100	20	0.04	180
13	0.04	100	21	0.04	180
14	0.04	400	22	0.04	160
15	0.04	380	23	0.04	170
16	0.04	380	24	0.04	180
17	0.04	180	25	0.04	180
18	0.04	200			

* The sensitivity was expressed by an exposure amount which gives a fog density of plus 0.1 for each dye, in terms of its relative value, assuming the sensitivity of the Standard Sample Nos. 11 to 13 as 100.

As apparent from Table 6, the effectiveness of the present invention could be also recognized in case where a spectral sensitizing dye was added.

Example 3

To monodispersed octahedral series emulsion which was prepared in the same manner as in Comparative emulsion Em - 1 in Example 1, and followed by desalting and washing with water without treatment with a solvent, 0.45 ml of a 0.2 % by weight aqueous chloroauric acid tetrahydrate solution and 1.5 ml of a 0.25 % by weight aqueous sodium thiosulfate dihydrate solution and 60 ml of a 1 % by weight aqueous ammonium rhodanide solution based on one mole of AgX each were added and the resultant emulsions were subjected to chemical ripening at 46 °C for 80 minutes. Subsequently, the additives were added in the same manner as in Example 1, followed by coating and drying. This samples is designated as Sample No. 26. After completion of heat treatment of Sample No. 26 together with Sample Nos. 1 and 3 at 55 °C under a relative humidity (R.H.) of 80 % for 72 hours, the same sensitometry as in Example 1 was conducted to compare with samples prepared without heat treatment. The results were shown in Table 7.

Table 7

Sample No.	Developed immediately before coating		Developed after heat-treatment	
	Sensitivity*	Fog	Sensitivity*	Fog
1 (Standard)	100	0.04	80	0.07
3 (The present invention)	400	0.04	380	0.05
26 (Comparative example)	220	0.04	120	0.11

* The sensitivity was expressed by its relative sensitivity, assuming the sensitivity of Sample No. 1 immediately after coating as 100.

From the results in Table 7, it was found that, in cases where a solvent for a silver halide is added during chemical ripening, Sample No. 26 exhibited lower level of sensitization as compared with those of the present invention though larger sensitization was recognized as compared with the Standard Sample No. 1 (without solvent treatment) and are inferior to those of the present invention in desensitization and induction of fog due to heat treatment.

Example 4

According to the method as disclosed in U.S. Patent No. 3,773.516, there was prepared a polydispersed octahedral series silver iodobromide emulsion containing 2 mole% of silver iodide. The average grain size and the grain size distribution of this emulsion were 0.8 μm and 34 %, respectively. This emulsion was designated as Em - 6. In the same manner as in Example 1, this emulsion was subjected to solvent treatment with 600 mg/mole AgX of ammonium rhodanide at 50 °C for 60 minutes and washed with water. The average grain size and the distribution of Em - 6 after solvent treatment were 0.85 μm and 42 %, respectively. Thereafter, there were conducted chemical ripening with chloroauric acid and sodium thiosulfate, addition of additives, coating and drying to prepare Sample No. 27.

On the other hand, an emulsion having the same value of latitude as in the thus obtained emulsion was prepared according to the following method. At first, there were prepared two kinds of monodispersed octahedral series silver iodobromide emulsions Em - 7 and Em - 8, which have an average grain size of 1.0 μm and 0.5 μm, respectively, and contain 2 mole % of silver iodide, and the resultant emulsions were subjected to solvent treatment with 600 mg/

mole AgX of ammonium rhodanide at 50 °C for 60 minutes, followed by washing with water and then further subjected to the optimum sensitization with chloroauric acid and sodium thiosulfate, respectively.

To an emulsion prepared by mixing Em - 7 and Em - 8 at a proportion defined by an equation, Em - 7 : Em - 8 = 7 : 3 in terms of the ratio between weights of silver halide in Em - 7 and Em - 8, additives were added in the same manner as discribed in Example 1, and the mixture was coated to obtain Sample No. 28.

The thus obtained emulsion was subjected to sensitometry and development treatment in the same manner as in Example 1. The results are shown in Table 8.

Further, observation of silver halide grains in Sample Nos. 27 and 28 by the use of an electron microscopic photography revealed that Sample No. 27 has potato-shaped grains and Sample No. 28 has octahedral grains containing 1 % of skeleton crystals of the present invention.

Table 8

Sample No.	Emulsion No.	Sensi- * tivity	Fog	r
27	Em - 6	75	0.05	1.52
28	Em - 7 + Em - 8 (7 : 3) (The present invention)	100	0.03	1.56

* The sensitivity was expressed in terms of its relative sensitivity, assuming the sensitivity of Sample No. 28 as 100.

As apparent from Table 8, an emulsion prepared by blending monodispersed emulsions according to the present invention was superior to a polydispersed emulsion treated with a solvent, in the antifogging property and the sensitivity.

Example 5

According to Japanese Provisional Patent Publication No. 48521/1979, a monodispersed tetradecahedral series emulsion (giving appearances of hexagon and square) which comprises silver iodobromide containing 2 mole% of silver iodide and has an average grain size of 0.70 μm and a grain size distribution s of 8 % was prepared. This emulsion was divided and to each emulsion ammonium rhodanide or tetramethylthiourea was added and the resultant emulsions were subjected to ripening at 50 °C for 60 minutes and adjusted to pAg 8.2 at 40 °C after desalting and washing with water according to the ordinary method. These emulsions were designated as Em - 9 to Em - 12. Added amounts of ammonium rhodanide and tetramethylthiourea and results of observation on grain shapes after solvent treatment obtained through an electron microscope are shown in Table 9.

Table 9

Emulsion No.	Added amount of ammonium rhodanide mg/mole AgX	Added amount of tetramethylthiourea mg/mole AgX	Shape of grain after solvent treatment	Grain size distribution after solvent treatment (%)
Em - 9	-	-	tetradecahedral	8
Em - 10	600	-	comprising mainly tetradecahedral crystals with containing 2 % of skeleton crystals of the present invention	9
Em - 11	6000	-	rounded at the vertex of crystals and approximately spherical with leaving tetradecahedral shapes	11
Em - 12	-	120	comprising spherical grains	9

With respect to Em - 9 to 12, there were conducted chemical ripening, addition of additives, coating and drying in the same manner as in Example 1 except that two time amount of sodium thiosulfate were added and chemical ripening was conducted for a period of time as shown in Table 10 to prepare Sample Nos. 29 to 36. With respect to samples thus obtained, sensitometry was conducted in the same manner as in Example 1. There are shown particulars of samples in Table 10 and results obtained by sensitometry in Table 11.

Table 10

Applied sample No.	Emulsion No.	Period of time for chemical ripening (minute)
29	Em - 9	120
30	Em - 9	140
31	Em - 10	80
32	Em - 10	100
33	Em - 11	50
34	Em - 11	70
35	Em - 12	40
36	Em - 12	60

Table 11

Sample No.	Emulsion No.	Sensitivity*	Fog
29 (Standard)	Em - 9	100	0.04
30 (")	Em - 9	110	0.05
31 (The present invention)	Em - 10	350	0.04
32 (")	Em - 10	560	0.05
33 (Comparative example)	Em - 11	180	0.04
34 (")	Em - 11	220	0.09
35 (")	Em - 12	160	0.04
36 (")	Em - 12	200	0.11

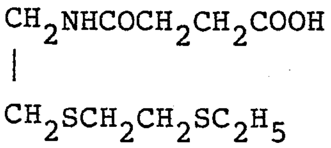
* The sensitivity was expressed by an exposure amount which gives a fog density of plus 0.1 in terms of its relative value.

As apparent from Table 11, the silver halide emulsion according to the present invention exhibits a remarkably higher sensitivity as compared with an emulsion having ordinary tetradecahedral crystal grains, though only a slight change in grain shapes was observed, and further is able to reach a higher level of sensitivity and gives a mild increase in fogging generated by chemical ripening as compared with Em - 11 in which crystals are formed into approximately shperical shapes by solvent treatment with increased amount of solvent and Em - 12 comprising perfectly spherical grains, and thereby the degree of progres for fogging was decreased.

Comparative example 1

According to the same method as disclosed in Japanese Provisional Patent Publication No. 48521/1979, there was prepared a monodispersed cubic series emulsion which comprises silver iodobromide containing 2 mole % of silver iodide and has an average grain size of 1.0 µm. This emulsion was divided into four portions and to each of portions ammonium rhodanide, tetramethylthiourea or thioether represented by the formula [I] below was added and the resultant emulsions were subjected to ripening at 50 °C for 60 minutes and adjusted to pAg 8.2 at 40 °C after desalting and washing with water according to the ordinary method. Emulsions thus obtained were designated as Em - 13 to Em - 16. In Table 12 are shown added amounts of solvents and result of observation on grain shapes after treatment obtained through an electron microscope.

[I]



$$\begin{array}{l} CH_2NHCOCH_2CH_2COOH \\ | \\ CH_2SCH_2CH_2SC_2H_5 \end{array}$$

Table 12

Emulsion No.	Added amount nf ammonium rhodanide mg/mole AgX	Added amount of tetra-methylthio-urea mg/mole AgX	Added amount of thioether [I] mg/mole AgX	Shape of grain after solvent treatment	Grain size distribution after solvent treatment (%)
Em - 13	-	-	-	cubic	8
Em - 14	600	-	-	spherical	10
Em - 15	-	50	-	slightly rounded at the vertex of crystals	9
Em - 16	-	-	70	slightly rounded at the vertex of crystals	9

To Em - 13 to Em - 16, 0.3 ml of a 0.2 % by weight aqueous chloroauric acid tetrahydrate solution and 10.8 ml of a 0.25 % by weight aqueous sodium thiosulfate dihydrate solution based on 1 mole AgX were added and the resultant emulsions were subjected to chemical ripening at 51 °C. Thereafter, addition of additives, coating, drying, development and sensitometry were conducted in the same manner as in Example 1. Samples thus obtained were designated as Sample Nos. 37 to 44. There are shown particulars of samples in Table 13 and results obtained by sensitometry in Table 14.

Table 13

Sample No.	Emulsion No.	Period of time for chemical ripening (minute)
37	Em - 13	20
38	Em - 13	30
39	Em - 14	10
40	Em - 14	20
41	Em - 15	5
42	Em - 15	10
43	Em - 16	20
44	Em - 16	30

Table 14

Sample No.	Emulsion No.	Sensitivity*	Fog
37	Em - 13	100	0.04
38	Em - 13	130	0.06
39	Em - 14	120	0.04
40	Em - 14	200	0.10
41	Em - 15	100	0.04
42	Em - 15	120	0.12
43	Em - 16	110	0.04
44	Em - 16	150	0.09

* The sensitivity was expressed by an exposure amount which gives a fog density of plus 0.1 in terms of its relative value.

As apparent from the aforesaid, in case of an cubic series emulsion, a recess is not formed even if the treatment according to the present invention is conducted and further the emulsion accelerates fogging which is liable to be induced during chemical sensitization.

Claims:

1. A monodispersed silver halide emulsion which comprises silver halide grains having a recess at the central part of the face (111) of octahedral crystals or tetradecahedral crystals.

2. The silver halide emulsion according to claim 1, wherein said silver halide is silver iodobromide containing 50 % or less of silver iodide.

3. The silver halide emulsion according to claim 2, wherein said silver halide is silver iodobromide containing 10 % or less of silver iodide.

4. The silver halide emulsion according to claim 1, wherein said recess has a depth of 0.20 to 0.05 ℓ at the deepest point thereof, in which ℓ is a diameter of the circumsphere for the silver halide grain.

5. The silver halide emulsion according to claim 1, wherein 1 % or more of total number of said silver halide grains have said recess.

6. The silver halide emulsion according to claim 1, wherein grain size distribution of said silver halide grains has a breadth of 19 % or less in terms of the coefficient of variation.

7. The silver halide emulsion according to claim 6, wherein grain size distribution of said silver halide grains has a breadth of 13 % or less in terms of the coefficient of variation.

8. The silver halide emulsion according to claim 1, wherein the intensity of the diffracted ray for the face (220) is less than 15 % of that for the face (111) in X-ray diffraction by the powder method of said emulsion which is oriented and coated on a support.

9. A manufacturing method for a silver halide emulsion characterized in that a monodispersed silver halide emulsion containning silver halide grains comprising octahedral crystals or tetradecahedral crystals, is subjected, after formation of said silver halide grains, to treatment with a solvent for the silver halide to the degree that a recess is formed at the central part of the face (111) of said crystal; followed by desalting.

10. The manufacturing method according to claim 9, wherein the silver halide grains of the emulsion to be treated with a solvent are silver iodobromide containing 50 % or less of silver iodide.

11. The manufacturing method according to claim 10, wherein the silver halide grains of the emulsion to be treated with a solvent are silver iodobromide containing 10 % or less of silver iodide.

12. The manufacturing method according to claim 9, wherein the monodispersed silver halide emulsion to be treated with a solvent is an emulsion prepared by the Ammonium method.

13. The manufacturing method according to claim 9, wherein average grain size of the silver halide grains of the emulsion to be treated with a solvent is 0.1 to 4 μm.

14. The manufacturing method according to claim 13, wherein average grain size of the silver halide grains of the emulsion to be treated with a solvent is 0.2 to 2 μm.

15. The manufacturing method according to claim 9, wherein the grain size distribution of silver halide grains of the emulsion to be treated with a solvent has a breadth of 15 % or less in terms of the coefficient of variation.

16. The manufacturing method according to claim 15, wherein the grain size distribution of silver halide grains of the emulsion to be treated with a solvent has a breadth of 10 % or less in terms of the coefficient of variation.

17. The manufacturing method according to claim 9, wherein the solvent is at least one kind of compound selected from the group consisting of organic thioethers, thiourea derivatives, solvents for a silver halide having a thiocarbonyl group sandwiched between an oxygen atom or a sulfur atom and a nitrogen atom, imidazoles, sulfites and thiocyanates.

18. The manufacturing method according to claim 9, wherein the solvent is thioethers or thiourea derivatives.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP82/00470

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.^{3} G03C 1/02

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
I P C	G03C 1/00-1/02, 1/06-1/10

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	JP,A, 49-114418 (Agfa-Gevaert A.G.) 31. October. 1979 (31.10.79) & DE,A, 2,306,447 & US,A, 3,966,476	1 - 8
E	JP,A, 57-182730 (Konishiroku Photo Industry Co., Ltd.), 10. November. 1982 (10.11.82)	9 - 18

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] March 14, 1983 (14.03.83)	Date of Mailing of this International Search Report [2] March 28, 1983 (28.03.83)
International Searching Authority [1] Japanese Patent Office	Signature of Authorized Officer [20]