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

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EP 0 096 727 B1

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Description

This invention relates to light-sensitive silver halide emulsion for photography and more particularly to a silver iodobromide type 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.

Recently, requirement for a silver iodobromide type 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 not 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 application", item 91. According 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 negative 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 negative type high sensitivity light-sensitive materials, although octahedral grains are assumed to have a good relationship between the anti-fogging property and the sensitivity according to Japanese Patent Publication No. 23443/1973, is that from view point of enhancement 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); *Photographic 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 high sensitivity grains can be obtained in a short period if a physical ripening (Ostwald Ripening) is conducted after 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 preferably 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 therein is poor and hence is not practical.

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 having silver halide grains which have octahedral crystals or tetradecahedral crystals primarily constituted of the face (111) and comprise substantially iodobromide grains, the grains having the characteristic features that they exhibit roundness at the vertices of the crystal faces the radius of curvature of said roundness being, for octahedral crystals, 1/10 r—1/6 r with respect to the angle of the vertex, wherein r is a length of one side in a triangle supposedly formed by extending sides of one arbitrary outer surface of a crystal and, for tetradecahedral crystals, 1/10 r—1/6 r with respect to the angle, wherein r is a length of the longest side in a polygon having the largest area selected from polygons which are supposedly formed by extending sides of each outer surface in crystal.

The invention also relates to a manufacturing method for a silver halide emulsion characterized in that a monodispersed silver halide emulsion having monodispersed silver grain which comprise octahedral crystals or tetradecahedral crystals constituted mainly of the face (111) and which substantially comprise silver iodobromide grains is subjected, after formation of said silver halide grains, to treatment with a thioether or thiourea solvent until the radius of curvature of roundness at the vertices of the crystal faces of said silver halide grains is, for octahedral crystals, 1/10 r—1/6 r with respect to the angle of the vertex, wherein r is a length of one side in a triangle supposedly formed by extending sides of one arbitrary outer surface of the crystal, and for tetradecahedral crystals, 1/10 r—1/6 r with respect to the angle, wherein r is a length of the longest side in a polygon having the largest area selected from polygons which are supposedly formed by extending sides of each outer surface in crystals; followed by desalting and chemical ripening.

In the present invention, silver halide grains which are tetradecahedral crystals comprise crystals primarily constituted of the face (111), namely, comprise grains giving the external appearance of hexagon and square and grains giving the external appearance of square and triangle, 30% or more of total surface area in the grains having been occupied by the area of said face (111). Grains comprising crystals primarily constituted of the face (100) and giving the external appearance of octagon and triangle are not preferable for the objects of the present invention.

As the silver halide emulsion according to the present invention, an emulsion in which 20% or more (in terms of number of the grains) of total silver halide grains contained therein consist of silver halide grains having such a roundness as described above is preferable and also as to the degree to which the grains are subjected to treatment with a solvent for a silver halide (hereinafter referred to as "solvent treatment") in the manufacturing method, it is similarly preferable.

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 power method, the intensity of the diffracted ray for the face (220) is preferably less than 8% of that for the face (111).

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) $\times$ 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.

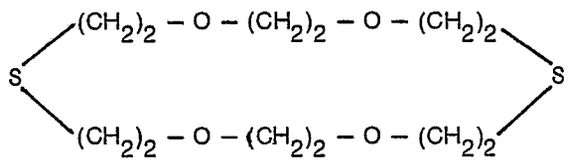
In the method for preparing the emulsion of the present invention, the monodispersed silver halide emulsion to be treated with the solvent is such that the silver halide grains contained therein consist essentially of octahedral or tetradecahedral silver halide crystals. Further, breadth of the grain 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.

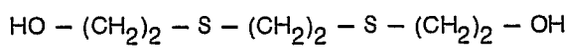
In the method for preparing the emulsion of the present invention, solvent treatment may be conducted merely by adding the thioether or thiourea solvent for a silver halide (AgX) to a silver halide emulsion in which silver halide grains have been formed into the final size and shape through completion of a mixing or a mixing followed by a physical ripening procedure; and subsequently by mixing uniformly

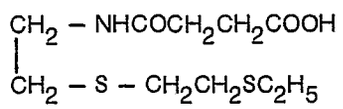
to act said solvent onto the surface of the silver halide grain. Therefore, there may be employed a procedure similar to a procedure for the conventional chemical ripening in which a solvent is used in place of a chemical sensitizer. Moreover, after formation of silver halide grains, there may be conducted desalting (including washing with water) prior to the solvent treatment. The solvent treatment is itself followed by desalting and chemical ripening.

The solvents for silver halide employed in the present invention are (a) organic thioethers as described in the specifications of US—A—3271157, 3531289 and 3574628; JO—A—1019/1979 and —158917/1979; or (b) thiourea derivatives as described in JP—A—82408/1978, —77737/1980 and —2982/1980.

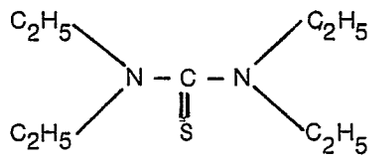
(a)







(b)



The silver halide emulsion of the present invention has a lower fogging property and a higher sensitivity as compared with an emulsion which comprises grains consisting of octahedral crystals or tetradecahedral crystals which have been subjected to solvent treatment to be shaped into a spherical form, a confetto-like form (defined as such, when a recess at a central part of the face (111) of the grain has a depth of 0.20 l or more, wherein l represents a diameter of the circumsphere for the grain) or a potato-like form (defined as such, when an outer crystal habit of the grain is indefinite and irregular).

Further, in the manufacturing method for the silver halide emulsion 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 emulsion 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, $\triangle\bar{r}/\bar{r}$ and $\triangle s/s$ 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, the 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 manufacturing method of the present invention, the silver halide grains to be treated with a solvent are octahedral crystals or tetradecahedral crystals described above 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.

The manufacturing method of the present invention is characterized in that after formation of silver halide grains, the grains are treated with the specific 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 an embodiment of the present invention, the monodispersed emulsion having silver halide grains comprising octahedral crystals or tetradecahedral crystals is preferably one 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 subjected to solvent treatment of the present invention reaches about five times the sensitivity given by an emulsion prepared without such solvent treatment of the present invention and further increase in fogging is scarcely 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 in the course of formation of grains or treatment with the solvent.

Silver iodobromide grains of the present invention preferably contain silver iodide at proportion of 0.5 to 15 mole% and more preferably 10 mole% or less.

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.

The light-sensitive silver halide emulsion according to the present invention may be subjected to doping treatment using various kinds of metallic salts or metallic complex salts during formation of silver halide precipitates, during or after grain growth. There may be applied, for example, metallic salts and complex salts of gold, platinum, palladium, iridium, rhodium, bismuth, cadmium, copper, and combinations of these salts.

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 and to the chemical ripening in the method of the present invention, there may be applied various kinds of chemical sensitization which is applicable to a general emulsion. Namely, chemical ripening may be conducted by use, singly or in combination, of chemical sensitizers such as noble metal sensitizers, including water-soluble gold salts, water-soluble platinum salts, water-soluble palladium salts, water-soluble rhodium salts or water-soluble iridium salts; a sulfur sensitizer; a selenium sensitizer; and reduction sensitizers including polyamine, and stannous chloride. 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, singly 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, and a trimethine dye. These sensitization techniques mentioned above, are described in US—A—2,688,545, 2,912,329, 3,397,060, 3,615,635 and 3,628,964; GB—A—1,195,302, 1,242,588 and 1,293,862; DE—A—2,030,326 and 2,121,780; and JP—A—4936/1968 and 14030/1969. 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 desired 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 purposes thereof. As additives described above, there are mentioned, for example, stabilizers and

antifogging agents such as azaindenes, triazoles, tetrazoles, imidazolium salts, tetrazolium salts and polyhydroxy compounds; hardeners such as aldehyde series, aziridine series, isoxazole series, vinylsulfonic series, acryloyl series, carbodiimimde series, maleimide series, methanesulfonic ester series and triazine series; development accelerators such as benzyl alcohol and polyoxyethylene series compounds; image stabilizers such as chroman series, coumaran series, bisphenol series and phosphorous ester series; lubricants such as waxes, glycerides of higher fatty acids and higher esters of higher fatty acids. 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, and an alklai salt of a reaction product between styrene maleic anhydride copolymer and p-aminobenzenesulfonic acid are effective. As matting agents, there may be mentioned methyl polymethacrylate, polystyrene and alkali-soluble polymers. 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 and vinyl esters, 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 and alkyl vinyl ether-maleate copolymer.

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 polystyrene. 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, and the diffusion transfer process. Among uses described above, it is particularly effectively used for color photography to which color development is applied.

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, indazalone series compounds and cyanoacetyl compounds and as cyan couplers, phenol series compounds, and naphthol series compounds.

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.

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 disclosd 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 comprising silver iodobromide containing 2 mole% of silver iodide.

The obtained emulsion was divided into six portions, to each of which, tetramethylthiourea or a thioether represented by the formula [I] 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. These emulsions were designated as Em — 1 to Em — 6. There are shown in Table 1 added amounts of tetramethylthiourea and thioether [I] and results with respect to grain shapes after treatment obtained by observation through an electron microscope.

TABLE 1

Emulsion No.	Added amount of tetramethyl-thiourea mg/mole AgX	Added amount of thioether [I] mg/mole AgX	Shape of grain after solvent treatment	Grain size distribution after treatment with the solvent (%)	Period of time for solvent treatment (minute)
Em — 1	—	—	octahedral	8	60
Em — 2	5	—	rounded at the vertex of crystals (1/8r)	8	60
Em — 3	120	—	spherical	9	60
Em — 4	—	150	rounded at the vertex of crystals (1/8r)	8	60
Em — 5	—	700	spherical	9	60
Em — 6	25	—	comprising mainly spherical grains with containing 10% of confetto-shaped grains	9	30

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$$\begin{array}{l} CH_2NHCOCH_2CH_2COOH \\ | \\ CH_2SCH_2CH_2SC_2H_5 \end{array} \qquad [I]$$

To the resultant emulsion, 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 phenylmercaptotetrazole were added. Then, as couplers, 15 g of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amylphenoxyacetamido)benzamide-5-pyrozolone dissolved in 30 ml of ethyl acetate and 15 ml of dibutyl 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 the 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 12. Particulars of samples are shown in Table 2.

TABLE 2

Sample No.	Emulsion No.	Period of time for chemical ripening (minute)
1	Em — 1	120
2	Em — 1	140
3	Em — 2	90
4	Em — 2	110
5	Em — 3	40
6	Em — 3	60
7	Em — 4	90
8	Em — 4	110
9	Em — 5	40
10	Em — 5	60
11	Em — 6	40
12	Em — 6	60

Twelve Samples described above were expressed through an optical wedge, 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 (Standard)	Em — 1	120	0.05
3 (The present invention)	Em — 2	400	0.04
4 (The present invention)	Em — 2	600	0.05
5 (Comparative example)	Em — 3	170	0.04
6 (Comparative example)	Em — 3	200	0.11
7 (The present invention)	Em — 4	350	0.04
8 (The present invention)	Em — 4	520	0.05
9 (Comparative example)	Em — 5	200	0.04
10 (Comparative example)	Em — 5	210	0.10
11 (Comparative example)	Em — 6	180	0.04
12 (Comparative example)	Em — 6	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.

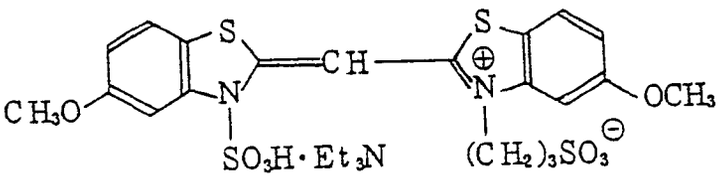
As apparent from Table 3, in the emulsion of the present invention, it was found that, in spite of a slight change in grain shapes, it has a remarkably enhanced sensitivity as compared with an emulsion comprising ordinary octahedral crystal grains and also is able to reach a higher level of sensitivity as compared with Em — 3 and Em — 5 comprising spherical grains or Em — 6 containing confetto-like grains, and further, increase in fogging generated by chemical ripening is mild, giving thereby the improved anti-progress of fogging.

Example 2

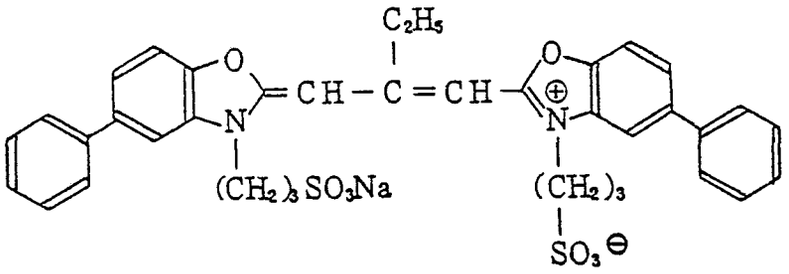
To Em — 1 to Em — 6 in Example 1, 0.45 ml of a 0.2% by weight aqueous chloroauric acid tetrahydrate solution and 1.5 ml of a 0.25% by weight aqueous sodium thiosulfate dihydrate solution based on one mole of AgX were added respectively and subjected to chemical ripening at 46°C for 110, 80, 30, 80, 30 and 30 minutes, respectively.

Thereafer 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.

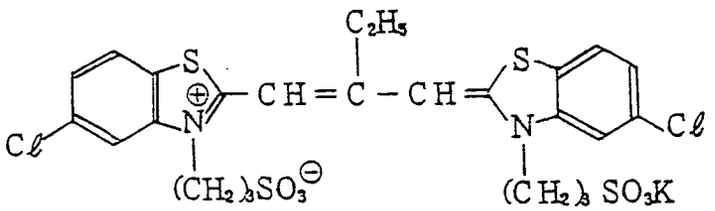
(1)



(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. 13 to 30.

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)	Dye	Sample No.	Emulsion No.	Period of time for chemical ripening (minute)	Dye
13	Em — 1	110	(1)	22	Em — 4	80	(1)
14	Em — 1	110	(2)	23	Em — 4	80	(2)
15	Em — 1	110	(3)	24	Em — 4	80	(3)
16	Em — 2	80	(1)	25	Em — 5	30	(1)
17	Em — 2	80	(2)	26	Em — 5	30	(2)
18	Em — 2	80	(3)	27	Em — 5	30	(3)
19	Em — 3	30	(1)	28	Em — 6	30	(1)
20	Em — 3	30	(2)	29	Em — 6	30	(2)
21	Em — 3	30	(3)	30	Em — 6	30	(3)

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Eighteen 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. Samples other than Sample Nos. 13, 16, 19, 22, 25 and 28 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*
13	0.04	100	22	0.04	370
14	0.04	100	23	0.04	350
15	0.04	100	24	0.04	370
16	0.04	400	25	0.04	200
17	0.04	420	26	0.04	180
18	0.04	380	27	0.04	180
19	0.04	170	28	0.04	170
20	0.04	170	29	0.04	180
21	0.04	180	30	0.04	180

* 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. 13 to 15 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

A 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 was divided into two portions. 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 each were added to both two portions and tetramethylthiourea and thiourea [I] were added in an amount of 5 mg and 150 mg to each portions, respectively and the resultant emulsions were subjected to chemical ripening at 46°C. Subsequently, the additives were added in the same manner as in Example 1, followed by coating and drying. These samples are designated as Sample Nos. 31 and 32. After completion of heat treatment of Sample Nos. 31 and 32 together with Sample Nos. 1, 3, and 7 at 55°C under a relative humidity (R.H.) of 80% for 72 hours, the same developing treatment and sensitometry as in Example 1 were conducted to compare with samples prepared without heat treatment. The results where shown in Table 8.

TABLE 8

	Developed immediately before coating		Developed after heat-treatment	
Sample No.	Sensitivity*	Fog	Sensitivity*	Fog
1 (Standard)	100	0.04	80	0.07
31 (Comparative example)	220	0.04	110	0.09
1 (The present invention)	400	0.04	380	0.05
32 (Comparative example)	200	0.04	120	0.11
7 (The present invention)	350	0.04	320	0.05

* The sensitivity was expressed by an exposure amount which gives a fog density of plus 0.1, in terms of its relative value, assuming the sensitivity of Sample No. 1 immediately after coating as 100.

From the results in Table 8, in cases where a solvent for a silver halide is added during chemical ripening, Sample Nos. 31 and 32 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 (free from a solvent) 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 — 7. In the same manner as in Example 1, this emulsion was subjected to solvent treatment with 150 mg/mole AgX of thioether [1] at 50°C for 60 minutes and washed with water. The average grain size and the distribution of Em — 7 after solvent treatment were 0.83 μm and 39%, respectively.

Thereafter, there were conducted chemical ripening with chloroauric acid and sodium thiosulfate, addition of additives, coating and drying to prepare Sample No. 33.

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 — 8 and Em — 9, which have an average grain size of 1.0 μm and 0.5 μm, respectively, and contain 2 mole% of iodine and the resultant emulsions were subjected to solvent treatment with 150 mg/l mole AgX of thioether 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 — 8 and Em — 9 at a proportion defined by an equation, Em — 8: Em — 9 = 7: 3 in terms of the ratio between weights of silver halide in Em — 8 and Em — 9, additives were added in the same manner as described in Example 1, and the mixture was coated to obtain Sample No. 34.

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 9.

Further, observation of silver halide grains in Sample Nos. 33 and 34 by the use of an electron microscopic photography revealed that each of them comprises octahedral grains having roundness (1/8 r) at the vertex angle thereof.

TABLE 9

Sample No.	Emulsion No.	Sensitivity*	Fog	r
33	Em — 7	75	0.04	1.55
34	Em — 8 + Em — 9 (7:3) (The present invention)	100	0.03	1.60

*The sensitivity was expressed in terms of the relative sensitivity, assuming the sensitivity of Sample No. 34 as 100.

As apparent from Table 9, 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 the method as disclosed in 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 was prepared. This emulsion was divided and to each emulsion tetramethylthiourea or thioether [1] 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. These emulsions were designated as Em — 10 to Em — 14. Added amounts of tetramethylthiourea and thioether [1] and results of observation on grain shapes after treatment obtained through an electron microscope are shown in Table 10.

TABLE 10

Emulsion No.	Added amount of tetramethylthiourea mg/mole AgX	Added amount of thioether [I] mg/mole AgX	Shape of grain after solvent treatment	Grain size distribution after solvent treatment (%)
Em — 10	—	—	tetradecahedral	8
Em — 11	5	—	rounded at the vertex of crystals (1/8 r) spherical	8
Em — 12	120	—		9
Em — 13	—	150	rounded at the vertex of crystals (1/8 r)	8
Em — 14	—	770	spherical	9

With respect to Em — 10 to 14, 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 11 to prepare Sample Nos. 35 to 44. With respect to samples thus obtained development treatment and sensitometry were conducted in the same manner as in Example 1. There are shown particulars of samples in Table 11 and results obtained by sensitometry in Table 12.

TABLE 11

Applied sample No.	Emulsion No.	Period of time for chemical ripening (minute)
35	Em — 10	120
36	Em — 10	140
37	Em — 11	90
38	Em — 11	110
39	Em — 12	40
40	Em — 12	60
41	Em — 13	90
42	Em — 13	110
43	Em — 14	40
44	Em — 14	60

TABLE 12

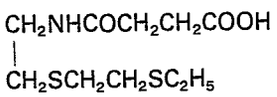
Sample No.	Emulsion No.	Sensitivity*	Fog
35 (Standard)	Em — 10	100	0.04
36 (Standard)	Em — 10	110	0.05
37 (The present invention)	Em — 11	380	0.04
38 (The present invention)	Em — 11	600	0.05
39 (Comparative example)	Em — 12	180	0.04
40 (Comparative example)	Em — 12	200	0.11
41 (The present invention)	Em — 13	340	0.04
42 (The present invention)	Em — 13	500	0.05
43 (Comparative example)	Em — 14	180	0.04
44 (Comparative example)	Em — 14	210	0.10

*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 12, an emulsion having silver halide grains consisting of tetradecahedral crystals according to the present invention exhibits a remarkably higher sensitivity as compared with an emulsion having tetradecahedral crystal grains which have not been subjected to solvent treatment, though 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 — 12 and Em — 14 in which crystals are formed into spherical shapes by solvent treatment with increased amount of solvent, and thereby the degree of progress 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 emulsion having cubic crystals 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 — 15 to Em — 18. In Table 13 are shown added amounts of solvents and result of observation on grain shapes after treatment obtained through an electron microscope.



[I]

TABLE 13

Emulsion No.	Added amount of ammonium rhodanide mg/mole AgX	Added amount of tetra-methylthiourea mg/mole AgX	Added amount of thioether [I] mg/mole AgX	Shape of grain after solvent treatment	Grain size distribution after solvent treatment (%)
Em — 15	—	—	—	cubic	8
Em — 16	150	—	—	spherical	10
Em — 17	—	50	—	slightly rounded at the vertex of crystals (1/8 r)	9
Em — 18	—	—	70	slightly rounded at the vertex of crystals (1/8 r)	9

To Em — 15 to Em — 18, 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. 45 to 52. There are shown particulars of samples in Table 14 and results obtained by sensitometry in Table 15.

TABLE 14

Sample No.	Emulsion No.	Period of time for chemical ripening (minute)
45	Em — 15	20
46	Em — 15	30
47	Em — 16	10
48	Em — 16	20
49	Em — 17	5
50	Em — 17	10
51	Em — 18	20
52	Em — 18	30

TABLE 15

Sample No.	Emulsion No.	Sensitivity*	Fog
45	Em — 15	100	0.04
46	Em — 15	130	0.06
47	Em — 16	120	0.04
48	Em — 16	200	0.10
49	Em — 17	100	0.04
50	Em — 17	120	0.12
51	Em — 18	110	0.04
52	Em — 18	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 Table 15, an emulsion having cubic crystals exhibit a lower sensitivity as compared with the emulsion according to the present invention and further accelerates fogging which is liable to be induced during chemical sensitization.

Comparative Example 2

According to the method as disclosed in Japanese Provisional Patent Publication No. 48521/1979, a monodisperse emulsion having tetradecahedral crystals (giving appearances of triangle and octagon) which comprises silver iodobromide containing 2 mole% of silver iodide and has an average grain size of 0.8 μm was prepared. This emulsion was divided and to each of emulsions ammonium rhodanide, tetramethylthiourea or thioether was added; then the emulsions thus obtained were subjected to solvent treatment at 50°C for 60 minutes, followed by adjustment of the pAg value to 8.2. The emulsions thus obtained are designated as Em — 19 to Em — 22. Added amounts of solvents and results of observation on grain shapes after treatment obtained through an electron microscope are shown in Table 16.

TABLE 16

Emulsion No.	Added amount of ammonium rhodanide mg/mole AgX	Added amount of tetramethylthiourea mg/mole AgX	Added amount of thioether [I] mg/mole AgX	Shape of grain after solvent treatment	Grain size distribution after solvent treatments (%)
Em — 19	—	—	—	tetradecahedral	8
Em — 20	75	—	—	spherical (1/4 r)	9
Em — 21	—	5	—	spherical (1/5 r)	9
Em — 22	—	—	70	spherical (1/4 r)	9

To Em — 19 to 22, 0.4 ml of a 0.2% by weight aqueous chloroauric tetrahydrade solution and 4.5 ml of a 0.25% by weight aqueous sodium thiosulfate solution were added and these 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. The emulsions thus obtained were designated as Sample Nos. 53 to 60. There are shown particulars of the applied samples in Table 17 and the results obtaned by sensitometry in Table 18.

TABLE 17

Sample No.	Emulsion No.	Period of time for chemical ripening (minute)
53	Em — 19	30
54	Em — 19	40
55	Em — 20	20
56	Em — 20	30
57	Em — 21	20
58	Em — 21	30
59	Em — 22	20
60	Em — 28	30

TABLE 18

Sample No.	Emulsion No.	Sensitivity*	Fog
53	Em — 19	100	0.04
54	Em — 19	120	0.06
55	Em — 20	130	0.04
56	Em — 20	160	0.11
57	Em — 21	110	0.04
58	Em — 21	140	0.12
59	Em — 22	160	0.04
60	Em — 22	200	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.

Comparing the results shown in Tables 16 and 18 with those in Examples 1 to 5, it is found that tetradecahedral grains constituted of crystals giving appearances of octagon and triangle are liable to be formed into spherical grains by adding a solvent in a relatively small amount. Further, they exhibit less sensitization effect and accelerate fogging which is liable to be induced during chemical sensitization, resulting in reduced performance as compared with octahedral crystals and tetradecahedral crystals having other shapes.

Comparative Example 3

According to a controlled double-jet method with the pAg value being maintained at 8.0, an octahedral series emulsion having an average grain size of 0.65 μm was prepared. This emulsion was divided into three portions and to each of the divided emulsions tetramethylthiourea was added in an amount shown in Table 19 and the emulsions thus obtained were subjected to ripening followed by adjustment of pAg to 8.2 at 40°C after desalting and washing with water according to an ordinary method. These emulsions were designated Em — 23 to 25. The results of observation on grain shapes of these emulsions through an electron microscope are shown in Table 19.

TABLE 19

Emulsion No.	Added amount of tetramethylthiourea mg/mole AgX	Shape of grain after solvent treatment	Grain size distribution after solvent treatment (%)	Period of time for solvent treatment (minute)
Em — 23		octahedral	10	60
Em — 24	5	rounded at the vertex of crystals 1/6 r	12	60
Em — 25	25	spherical	14	60

To each of the emulsion, 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 and subjected to chemical ripening at 46°C. After completion of the ripening, to these emulsion 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and phenylmercaptotetrazole were added. Then, as couplers, 15 g of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amylphenoxyacetamido)benzamide-5-pyrozolone dissolved in 30 ml of ethyl acetate and 15 ml of dibutyl phthalate was mixed with 20 ml of a 10% by weight aqueous alkanole B (alkylnaphthalene-sulfonate, 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 the emulsions, thus obtained dispersion was added, applied on a triacetate film support so that the amount of Ag thereon is 20 mg/dm^2, followed by drying to prepare Sample Nos. 61 to 66. Particulars of the samples are shown in Table 20.

TABLE 20

Sample No.	Emulsion No.	Period of time for chemical ripening (minute)
61	Em — 23	110
62	Em — 23	130
63	Em — 24	90
64	Em — 24	110
65	Em — 25	45
66	Em — 25	65

These samples were exposed through an optical wedge and in the same manner as in Example 1 were subjected to color forming, development, bleaching, and fixing treatment, followed by drying after washing with water. The sensitivity of a magenta color image obtained was evaluated. The results are shown in Table 21.

TABLE 21

Sample No.	Fog	Sensitivity*
61	100	0.45
62	125	0.51
63	150	0.53
64	170	0.61
65	130	0.62
66	150	0.72

*The sensitivity was expressed by an exposure amount which gives a fog density of plus 0.1 in terms of its relative value, assuming the sensitivity of Sample 61 as 100.

As apparent from Table 21, the same effectiveness on sensitization as obtained by the silver iodobromide emulsion in Example 1 was not obtained even if a silver chlorobromide emulsion was subjected to solvent treatment to thereby form a slight roundness.

Claims

1. A monodispersed silver halide emulsion having silver halide grains which have octahedral crystals or tetradecahedral crystals constituted mainly of the face (111) and comprise substantially silver iodobromide grains, characterized in that said grains exhibit roundness at the vertices of the crystal faces, the radius or curvature of said roundness being, for octahedral crystals 1/10 r — 1/6 r with respect to the angle of the vertex, wherein r is the length of one side in a triangle supposedly formed by extending sides of one arbitrary outer surface of a crystal and, for tetradecahedral crystals, 1/10 r — 1/6 r with respect to the angle, wherein r is a length of the longest side in a polygon having the largest area selected from polygons which are supposedly formed by extending sides of each outer surface in crystals.

2. The silver halide emulsion according to claim 1, wherein 20% of the total number of silver halide grains contained in said silver halide emulsion have a roundness of said radius of curvature at the vertices of the crystal face.

3. The silver halide emulsion according to claim 1, wherein the grain size distribution of silver halide grains contained in said silver halide emulsion has a breadth of 13% or less in terms of the coefficient of variation.

4. The silver halide emulsion according to claim 1, wherein the silver halide comprises iodobromide containing 10 mole% or less of silver iodide.

5. A manufacturing method for a silver halide emulsion characterised in that a monodispersed silver halide emulsion having monodispersed silver halide grains which comprise octahedral crystals or tetradecahedral crystals constituted mainly of the face (111) and which substantially comprise silver iodobromide grains is subjected, after formation of said silver halide grains, to treatment with a thioether or thiourea solvent until the radius of curvature of roundness at the vertices of the crystal faces of said silver halide grains is, for octahedral crystals, 1/10 r — 1/6 r with respect to the angle of the vertex, wherein r is a length of one side in a triangle supposedly formed by extending sides of one arbitrary outer surface of the crystal, and for tetradecahedral crystals, 1/10 r — 1/6 r with respect to the angle, wherein r is a length of the longest side in a polygon having the largest area selected from polygons which are supposedly formed by extending sides of each outer surface in crystals; followed by desalting and chemical ripening.

6. The manufacturing method according to claim 5, wherein the silver halide emulsion to be treated with a solvent is an emulsion prepared by the Ammonia method.

7. The manufacturing method according to claim 5, wherein the silver halide to be treated with a solvent is silver iodobromide containing 10 mole% or less of silver iodide.

8. The manufacturing method according to claim 5, wherein the grain size distribution of silver halide grains to be treated with a solvent has a breadth of 10% or less in terms of the coefficient of variation.

Patentansprüche

1. Monodisperse Silberhalogenidemulsion mit Silberhalogenidkörnchen, die oktaedrische Kristalle oder tetradekaedrische Kristalle mit der Hautpfläche [111] aufweisen und im wesentlichen aus Silberjodbromidkörnchen bestehen, dadurch gekennzeichnet, daß die Körnchen an den Scheitelpunkten der Kristallflächen abgerundet sind, wobei der Krümmungsradius dieser Rundung bei oktaedrischen Kristallen 1/10 r—1/6 r (r = Länge einer Seite in einem durch Verlängern der Seiten einer beliebigen Außenfläche eines Kristalls vermutlich gebildeten Dreieck) in bezug auf den Scheitelwinkel und bei tetradekaedrischen Kristallen 1/10 r—1/6 r (r = Länge der längsten Seite in einem Polygon mit der größten Fläche von Polygonen, die vermutlich beim Verlängern der Seiten jeder Außenfläche bei Kristallen gebildet werden) in bezug auf den Winkel beträgt.

2. Silberhalogenidemulsion nach Anspruch 1, dadurch gekennzeichnet, daß 20% der Gesamtzahl der Silberhalogenidkörnchen in dieser Silberhalogenidemulsion an den Scheitelpunkten der Kristallfläche eine Rundung des Krümmungsradius' aufweisen.

3. Silberhalogenidemulsion nach Anspruch 1, dadurch gekennzeichnet, daß die Korngrößenverteilung der Silberhalogenidkörnchen in dieser Silberhalogenidemulsion eine Breite, ausgedrückt als prozentuale quadratische Streuung, von 13% oder weniger aufweist.

4. Silberhalogenidemulsion nach Anspruch 1, dadurch gekennzeichnet, daß das Silberhalogenid aus Silberjodbromid mit 10 Mol-% oder weniger Silberjodid besteht.

5. Verfahren zur Herstellung einer Silberhalogenidemulsion, dadurch gekennzeichnet, daß eine monodisperse Silberhalogenidemulsion mit monodispersen Silberhalogenidkörnchen aus oktaedrischen Kristallen oder tetradekaedrischen Kristallen mit der Hauptfläche [111], die hauptsächlich aus Silberjodbromidkörnchen bestehen, nach Bildung der Silberhalogenidkörnchen so lange mit einem Thioether- oder Thioharnstofflösungsmittel behandelt, bis der Krümmungsradius der Rundung an den Scheitelpunkten der Kristallflächen der Silberhalogenidkörnchen bei oktaedrischen Kristallen 1/10 r—1/6 r (r = Länge einer Seite in einem durch Verlängern der Seiten einer beliebigen Außenfläche eines Kristalls vermutlich

gebildeten Dreieck) in bezug auf den Scheitelwinkel und bei tetradekaedrischen Kristallen 1/10 r—1/6 r (r = Länge der längsten Seite in einem Polygon mit der größten Fläche von Polygonen, die vermutlich beim Verlängern der Seiten jeder Außenfläche bei Kristallen gebildet werden) beträgt, anschließend entsalzt und schließlich einer chemischen Reifung unterworfen wird.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die mit einem Lösungsmittel zu behandelnde Silberhalogenidemulsion aus einer nach dem Ammoniakverfahren hergestellten Emulsion besteht.

7. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das mit einem Lösungsmittel zu behandelnde Silberhalogenid aus einem Silberjodbromid mit 10 Mol-% oder weniger Silberjodid besteht.

8. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die Korngrößenverteilung der mit einem Lösungsmittel zu behandelnden Silberhalogenidkörnchen eine Breite, ausgedrückt als prozentuale quadratische Streuung, von 10% oder weniger aufweist.

Revendications

1. Emulsion monodispersée à base d'halogénure d'argent comportant des grains d'halogénure d'argent, ayant des cristaux octaèdriques ou tétradécaèdriques constitués principalement de la face (111) et comprenant substantiellement des grains d'iodobromure d'argent, caractérisée en ce que lesdits grains sont arrondis aux sommets des faces de cristaux, le rayon de courbure des parties arrondies étant pour les cristaux octaèdriques de 1/10 r—1/6 r par rapport à l'angle de pointe, r étant une longueur d'un côté dans un triangle que l'on suppose formé en prolongeant les côtés d'une surface extérieure arbitraire d'un cristal et, pour les cristaux tétradécaèdriques de 1/10 r—1/6 r par rapport à l'angle, r étant une longueur du plus grand côté dans un polygone ayant la plus grande aire choisi parmi des polygones que l'on suppose être formés en prolongeant les côtés de chaque surface extérieure dans les cristaux.

2. Emulsion à base d'halogénure d'argent selon la revendication 1, dans laquelle 20% du nombre total de grains d'halogénure d'argent contenus dans ladite émulsion d'halogénure d'argent ont une partie arrondie présentant ledit rayon de courbure aux sommets de la face des cristaux.

3. Emulsion à base d'halogénure d'argent selon la revendication 1, dans laquelle la granulométrie des grains d'halogénure d'argent contenus dans ladite émulsion d'halogénure d'argent présente une largeur de 13% ou moins exprimée en termes du coefficient de variation.

4. Emulsion à base d'halogénure d'argent selon la revendication 1, dans laquelle l'halogénure d'argent comprend de l'iodobromure d'argent contenant 10 moles% ou moins d'iodure d'argent.

5. Procédé de fabrication d'une émulsion à base d'halogénure d'argent, caractérisé en ce qu'une émulsion monodispersée à base d'halogénure d'argent présentant des grains d'halogénure d'argent monodispersés, lesquels comprennent des cristaux octaèdriques ou des cristaux tétradécaèdriques constitués principalement de la face (111) et qui comprennent substantiellement des grains d'iodobromure d'argent, est soumise, après formation desdites grains d'halogénure d'argent, à un traitement avec un solvant de thioéther ou de thiourée jusqu'à ce que le rayon de courbure des parties arrondies aux sommets des faces des cristaux desdits grains d'halogénure d'argent soit pour les cristaux octaèdriques de 1/10 r—1/6 r par rapport à l'angle de pointe, r étant une longueur d'un côté dans un triangle que l'on suppose formé en prolongeant les côtés d'une surface extérieure arbitraire du cristal, et pour les cristaux tétradécaèdriques de 1/10 r—1/6 r par rapport à l'angle, r étant une longueur du plus grand côté dans un polygone ayant l'aire la plus grande, choisi parmi des polygones que l'on suppose être formés en prolongeant les côtés de chaque surface extérieure dans les cristaux; procédé suivi d'une désalination et d'un mûrissement chimique.

6. Procédé de fabrication selon la revendication 5, dans lequel l'émulsion à base d'halogénure d'argent devant être traité avec un solvant est une émulsion préparée par le procédé ammoniacal.

7. Procédé de fabrication selon la revendication 5, dans lequel l'halogénure d'argent devant être traité avec un solvant est un iodobromure d'argent contenant 10 moles% ou moins d'iodure d'argent.

8. Procédé de fabrication selon la revendication 5, dans lequel la granulométrie des grains d'halogénure d'argent devant être traité avec un solvant présente une largeur de 10% ou moins exprimée en termes du coefficient de variation.