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(54) **Silver halide emulsion**

(57) The present invention provides a silver halide emulsion showing high sensitivity and high image quality, which comprises water, a dispersion medium and silver halide grains, wherein from 60 to 100% of the total projected area of the silver halide grains are tabular grains having: an aspect ratio (projected area diameter/

thickness) of from 2.6 to 300; AgI content (mol%) of from 88 to 100; and a projected area diameter of grain (μm) of 0.2 to 10, and the tabular grains have from 3 to 10^4 planes per a grain of twin defect plane parallel to the main plane.

EP 1 528 428 A2

DescriptionFIELD OF THE INVENTION

[0001] The present invention relates to a silver halide (hereinafter referred to as "AgX") emulsion useful in the photographic field.

BACKGROUND OF THE INVENTION

[0002] Concerning the advantage on using tabular grains as photosensitive AgX grains of an AgX photosensitive material, JP-A-58-113928 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and JP-A-2-838 can be referred to. There are known the following literatures concerning AgI tabular grain emulsions.

1) JP-A-59-119344. The patent claims a tabular grain emulsion, wherein 50% or more of the entire projected area of the grains accounts for face centered cubic crystal structural (referred to as γ -type) tabular grains (γ -type content is about 90 mol%) having a thickness of less than 0.3 μm and an average aspect ratio of 8 or more.

2) JP-A-59-119350. The patent claims a tabular grain emulsion, wherein 50% or more of the entire projected area of the grains accounts for tabular grains having a thickness of less than 0.3 μm and an average aspect ratio of 8 or more. The patent claims the same γ -type tabular grains as in the example in 1) and newly β -type AgI tabular grains. These grains are both formed by merely adding Ag^+ and X^- by a double jet method on the same solution condition from beginning to end, and crystal defect is not sufficiently controlled. In the example in 2), grains in Fig. 3 (diameter: 2.3 μm) and grains in Fig. 4 (diameter: 11.4 μm , thickness: 0.32 μm) are disclosed as β -type tabular grains. The grains in Fig. 3 are polydispersed grains containing many low aspect ratio grains, and the grains in Fig. 4 are large-sized tabular grains [the ratio of (sensitivity/granularity) is low] that cannot be generally used in photographs, i.e., thick tabular grains. The tabular grains also contain low aspect ratio grains having a diameter of 0.3 μm or more and an aspect ratio of 2 or less.

[0003] The absorption coefficient of blue light of AgI near 410 nm is from several ten to one hundred times larger than that of AgBr, and the light is almost absorbed during passes through a thin tabular grain having a thickness of about 0.1 μm in the thickness direction, thus absorption efficiency is very excellent. The development of photographic materials of high sensitivity and high quality utilizing AgI grains is desired.

SUMMARY OF THE INVENTION

[0004] An object of the present invention is to provide an AgX emulsion providing higher sensitivity and high quality to conventional AgX emulsions.

[0005] The present invention was achieved by the following modes.

(I) Modes for carrying out the invention

[0006]

(1) A silver halide emulsion comprising at least water, a dispersion medium and silver halide grains, wherein from 60 to 100%, preferably from 80 to 100%, more preferably from 90 to 100%, and still more preferably from 95 to 100%, of the total projected area of the silver halide grains are tabular grains having: an aspect ratio (projected area diameter/thickness) of from 2.6 to 300; preferably from 3.1 to 300, more preferably from 5 to 200, and still more preferably from 7 to 100; AgI content (mol%) of from 80 to 100, preferably from 88 to 100, more preferably from 90 to 100, and still more preferably from 94 to 100; a projected area diameter (μm) of grain of 0.2 to 20, preferably from 0.2 to 10, more preferably from 0.2 to 8, and still more preferably from 0.4 to 6; and a thickness (μm) of preferably from 0.01 to 0.4, more preferably from 0.02 to 0.3, still more preferably from 0.03 to 0.2, and particularly preferably from 0.03 to 0.1, and the tabular grains have from 3 to 10^4 planes per a grain of twin defect plane 1 parallel to the main plane, preferably from 5 to 3,000, more preferably from 6 to 500, and still more preferably from 8 to 100.

(2) The silver halide emulsion as described in the above item (1), wherein the twin defect plane 1 is a stacking fault plane formed by the stack of γ -type crystal phase on the {001} face of β -type crystal phase or the stack of β -type crystal phase on the {111} face of γ -type crystal phase.

(3) The silver halide emulsion as described in the above item (1), wherein the tabular grains have a layer of β -type

crystal phase and a layer of γ -type crystal phase parallel to the main plane, and the content of the γ -type crystal phase (mol%) of from 0.01 to 50, preferably from 0.05 to 30, more preferably from 0.2 to 15, and still more preferably from 1 to 10.

(4) The silver halide emulsion as described in the above item (3), wherein the {001} face of β -type crystal phase and the {111} face of γ -type crystal phase are both parallel to the main plane.

(5) The silver halide emulsion as described in the above item (1), wherein the tabular grains further have from 1 to 10^4 planes per a grain of twin defect plane 2 parallel to the main plane, preferably from 1 to 10^3 , more preferably from 1 to 100, and still more preferably from 1 to 10, and the twin defect plane 2 is a stacking fault plane formed when a γ -type crystal phase is stacked on the {111} face of a γ -type crystal phase, preferably the stacking fault plane is a contact plane formed by the contact of two γ -type crystals with each other on the {111} face, and more preferably the two γ -type crystal phases are in the relationship of mirror symmetry to the twin defect plane 2.

(6) The silver halide emulsion as described in the above item (1), wherein the shape of the main plane of the tabular grain is a hexagon or a hexagon having rounded corners, and the adjacent edge ratio (the edge length of the longest edge/the edge length of the shortest edge) of the six edge lengths (when the corners are rounded, the lengths of six edges formed by extending the straight line parts of the edges) = A1 is from 1.0 to 3.5 on one tabular grain, preferably from 1.0 to 3.0, and more preferably from 1.0 to 2.5.

(7) The silver halide emulsion as described in the above item (1), wherein the shape of the main plane of the tabular grain is a triangle or a triangle having rounded corners, and the triangle has the adjacent edge ratio of the three edge lengths in one triangle (the edge length of the longest edge/the edge length of the shortest edge) = A1 of from 3.51 to ∞ , preferably from 4 to ∞ , and more preferably from 6 to ∞ .

(8) The silver halide emulsion as described in the above item (1), wherein in the projected area ratio of the tabular grains., the main plane shape of the tabular grain is [hexagonal tabular grains described in the item (6)]/triangular tabular grains described in the item (7)] of from 1/5 to 5/1, preferably from 1/3 to 3/1, and more preferably from 1/2 to 2/1.

(9) The silver halide emulsion as described in the above item (1), wherein the defect planes 1 or 2 are present in the region of from 60 to 100% of the thickness of the tabular grain, preferably from 80 to 100%, and more preferably from 90 to 100%.

(10) The silver halide emulsion as described in the above item (1), wherein the defect planes 1 or 2 are present in the region of from 1 to 59% of the thickness of the tabular grain, preferably from 5 to 50%, and more preferably from 1 to 30%.

(11) The silver halide emulsion as described in the above item (9) or (10), wherein in the tabular grains, (distance A4 between one main plane and the defect plane 1 nearest to the main plane) / (distance A5 between the other main plane and the defect plane 1 nearest to the main plane) = A2 is from 0.3 to 3, preferably from 0.5 to 2 and more preferably from 0.8 to 1.3.

(12) The silver halide emulsion as described in the above item (1), wherein the shortest distance (nm) of the distances between the defect planes 1 in the tabular grains is from 0.1 to 30, preferably from 0.3 to 20, and more preferably from 0.3 to 10.

(13) The silver halide emulsion as described in the above item (1), wherein in 30 to 100% of the total number of the defect planes 1 present in the tabular grains, preferably from 60 to 100%, the distance between the defect planes 1 (nm) is from 0.1 to 30, preferably from 0.3 to 20, and more preferably from 0.3 to 15.

(14) The silver halide emulsion as described in the above item (1), wherein when the position of one main plane is taken as 0 and the position of the other main plane is taken as 100, the distance between planes of the defect planes 1 present between 30 to 70, preferably from 40 to 60, and more preferably from 45 to 55 is from 0.1 to 30 nm, preferably from 0.3 to 20 nm, and more preferably from 0.3 to 15 nm.

(15) The silver halide emulsion as described in the above item (1), wherein the tabular grains do not substantially contain a screw dislocation line.

(16) The silver halide emulsion as described in the above item (1), wherein the tabular grains do not substantially contain a blade-like dislocation line.

(17) The silver halide emulsion as described in the above item (1), wherein the grains of low aspect ratio (the aspect ratio of 1.6 or less, preferably 2 or less, and more preferably 2.4 or less) having a projected area diameter (μm) of 0.4 or more, preferably 0.3 or more, more preferably 0.2 or more, and still more preferably 0.15 or more have a number ratio (the number of non-tabular grains/the number of tabular grains) = A3 of from 0 to 0.7, preferably from 0 to 0.5, more preferably from 0 to 0.3, still more preferably from 0 to 0.1, and most preferably from 0 to 0.03.

(18) The silver halide emulsion as described in the above item (1), wherein the variation coefficient (standard deviation/mean value) of the fluctuation of the projected area diameters of the tabular grains is from 0.01 to 0.6, preferably from 0.01 to 0.4, more preferably from 0.01 to 0.35, still more preferably from 0.01 to 0.30, still yet preferably from 0.02 to 0.25, and most preferably from 0.02 to 0.20.

(19) The silver halide emulsion as described in the above item (1), wherein the variation coefficient of the fluctuation

of the thickness of the tabular grains is from 0.01 to 0.6, preferably from 0.01 to 0.4, more preferably from 0.01 to 0.3, and still more preferably from 0.01 to 0.2.

(20) The silver halide emulsion as described in the above item (1), wherein the variation coefficient of the fluctuation of the number of the defect planes 1 or 2 among grains is from 0.01 to 0.6, preferably from 0.01 to 0.4, more preferably from 0.01 to 0.3, and still more preferably from 0.02 to 0.2.

(21) The silver halide emulsion as described in the above item (1), wherein the variation coefficient of the fluctuation of the distance between the defect planes 1 in the grain and among grains is from 0.01 to 0.6, preferably from 0.01 to 0.4, more preferably from 0.01 to 0.3, and still more preferably from 0.02 to 0.2.

(22) The silver halide emulsion as described in the above item (3), wherein when the tabular grains are measured by powder X-ray diffraction measurement with $\text{CuK}\beta$ -ray, [diffraction intensity corresponding to {400} face of a γ phase/ diffraction intensity corresponding to {203} face of a β phase] = A4 is from 0.003 to 30, preferably from 0.01 to 30, more preferably from 0.01 to 10, still more preferably from 0.03 to 5, and still yet preferably from 0.1 to 1.

(23) The silver halide emulsion as described in the above item (1), wherein from 20 to 100 number%, preferably from 60 to 100 number%, and more preferably from 80 to 100 number% of the tabular grains do not contain the defect planes 2.

(24) The silver halide emulsion as described in the above item (1), wherein the tabular grains contain from 1 to 10^3 , preferably from 3 to 10^3 , and more preferably from 5 to 10^3 dislocation lines.

(25) The silver halide emulsion as described in the above item (1), wherein the tabular grains contain the defect plane 1 in an amount of Z1 in number and the defect plane 2 in an amount of Z2 in number, and the ratio of Z1/Z2 is 0.4 or less, preferably from 0 to 0.3, more preferably from 0 to 0.2, and still more preferably from 0 to 0.1.

(26) The silver halide emulsion as described in the above item (1), wherein the tabular grains contain the defect plane 1 Z1 in number and the defect plane 2 Z2 in number, and (Z1/Z2) is from 0.1 to 2.9.

(27) The silver halide emulsion as described in any of the above items (60) to (63), wherein the epitaxial parts have from 1 to 10^4 , preferably from 3 to 10^3 , dislocation lines in one epitaxial part.

(28) The silver halide emulsion as described in any of the above items (60) to (63), wherein from 20 to 100 number%, preferably from 60 to 100 number%, of the epitaxial parts do not have a dislocation line.

(29) The silver halide emulsion as described in the above item (30), wherein the density of the defect planes 1 that are formed at the time of the seed crystals formation is taken as Z3 (number of the planes/ μm) and the density of those formed after the seed crystals formation is taken as Z4, the ratio of (Z4/Z3) is from 0.03 to 30, preferably from 0.1 to 10, and more preferably from 0.2 to 5, in which the seed crystal represents the moiety in which the tabular particle grows by 0.1 μm of diameter at the formation of the particles.

(30) The silver halide emulsion as described in the above item (1), wherein the AgX emulsion is manufactured by the process comprising a seed crystal forming process of forming tabular seed crystals by adding an aqueous solution containing Ag^+ (Ag-1 solution) and an aqueous solution containing I^- (X-1 solution) to an aqueous solution containing at least water and a dispersion medium (dispersion medium solution 1), and a growing process of growing the seed crystals.

(31) The silver halide emulsion as described in the above item (30), wherein the seed crystal forming process comprises a tabular nucleus forming process and an Ostwald ripening process, and non-tabular grains are vanished and tabular grains are grown in the ripening process, and the tabular grain number ratio (the number of tabular grains/the total grain number) = A5 is increased to 1.5 to 10^6 times, preferably from 2 to 10^4 times, followed by a growing process.

(32) The silver halide emulsion as described in the above item (30) or (31), wherein at least the ripening process or the growing process is carried out in the presence of an AgX solvent so as to increase the solubility of AgX to 1.2 to 10^5 times the solubility at the time free of AgX solvent, preferably from 1.5 to 10^4 times, and more preferably from 2 to 10^3 times.

(33) The silver halide emulsion as described in the above item (31), wherein the temperatures in the nucleating process and the ripening process are different by 3 to 80°C , preferably by 6 to 80°C , and more preferably by 10 to 70°C , and the ripening temperature is higher than the nucleating temperature.

(34) The silver halide emulsion as described in the above item (31), wherein the temperatures in the nucleating process and the growing process are different by from 3 to 80°C , preferably by from 6 to 80°C , and more preferably from 10 to 70°C , and the growing temperature is higher than the nucleating temperature.

(35) The silver halide emulsion as described in the above item (31), wherein at least one of the pH and pAg of the aqueous solutions in the nucleating process and the growing process, or in the nucleating process and the ripening process are different by from 0.1 to 10, preferably by from 0.2 to 7, more preferably from 0.3 to 5, and still more preferably from 0.5 to 5, and preferably the pH value of the nucleating time is lower than the pH value at the time of the ripening and growing, more preferably the pAg value of the nucleating time is lower than at the time of the ripening and growing, wherein pAg means $-\log [\text{Ag}^+ \text{ concentration (mol/liter)}]$.

(36) The silver halide emulsion as described in the above item (32), wherein the AgX solvent is a compound capable

of forming a water-soluble complex (excluding gelatin) with Ag^+ .

(37) The silver halide emulsion as described in the above item (36), wherein the AgX solvent is an organic compound having from 1 to 100 thioether groups in a molecule.

(38) The silver halide emulsion as described in the above item (31), wherein in the growing process, AgX fine grains having an AgI content of from 88 to 100 mol%, preferably from 90 to 100 mol%, more preferably from 94 to 100 mol%, and an average projected area diameter of from 1 to 250 nm, preferably from 3 to 200 nm, more preferably from 6 to 100 nm are added, the added fine grains are dissolved and deposited on the tabular seed crystals to whereby grow the tabular seed crystals.

(39) The silver halide emulsion as described in the above item (38), wherein the fine grains are fine grains manufactured by a continuous manufacturing system of continuously feeding an aqueous solution containing Ag^+ (Ag-2 solution) and an aqueous solution containing I^- (I-2 solution) through hollow tubes to a continuous system mixer, both solutions are mixed in the mixer, and the mixed solution is continuously discharged through a liquid pipe.

(40) The silver halide emulsion as described in the above item (38), wherein the fine grains are fine grains manufactured by a batch system of adding (Ag⁺-2 solution) and (I⁻-2 solution) by a double jet method to the aqueous solution containing a dispersion medium (dispersion medium solution 2) in a batch system reaction vessel.

(41) The silver halide emulsion as described in the above item (38), wherein the fine grains are dodecahedral fine grains disclosed in Japanese Patent Application No. 2003-57156 or the dodecahedral fine grains having rounded corners or edges.

(42) The silver halide emulsion as described in the above item (38), wherein the fine grains are tetradecahedral fine grains disclosed in Japanese Patent Application No. 2003-57156 or the tetradecahedral fine grains having rounded corners or edges.

(43) The silver halide emulsion as described in the above item (38), wherein the fine grains are rectangular parallelepipeds, preferably rectangular parallelepipeds having an edge length ratio [(the edge length of the longest edge/the edge length of the shortest edge) of one grain] = A6 of from 1.0 to 1.5, preferably from 1.0 to 1.1, or cubes, or fine grains having rounded corners or edges.

(44) The silver halide emulsion as described in the above item (1) or (30), wherein from 1 to 10^4 defect planes 1 per a grain are also formed during grain growth, preferably from 2 to 10^3 .

(45) The silver halide emulsion as described in the above item (30), wherein the defect planes 1 are formed when the seed crystals are formed.

(46) The silver halide emulsion as described in the above item (30) or (31), wherein the temperature of the dispersion medium solution in the growing process is from 50 to 100°C, preferably from 60 to 95°C, and more preferably from 65 to 90°C, and pH is from 2 to 12, preferably from 3 to 12, and more preferably from 5 to 11.5.

(47) The silver halide emulsion as described in the above item (30) or (31), wherein $\text{pI} = -\log [\text{I}^- \text{ concentration (mol/liter)}]$ of the dispersion medium solution in the growing process is from 1 to 3, preferably from 1.5 to 2.7, and more preferably from 1.7 to 2.5.

(48) The silver halide emulsion as described in the above item (30), wherein when the concentration of the dispersion medium B1 of the solution in the reaction vessel at the time of the tabular grain growth is taken as Z6 and the concentration of the nucleus dispersion medium B2 at the time of the tabular nucleus formation is taken as Z7, the ratio of (Z6/Z7) is from 0.5 to 100, preferably from 1.0 to 100, more preferably from 1.3 to 50, and still more preferably from 2 to 50.

(49) The silver halide emulsion as described in the above item (31), wherein the ripening process is carried out while adding the Ag-1 solution and the X-1 solution.

(50) The silver halide emulsion as described in the above item (30), wherein the aqueous solution containing Ag^+ and the aqueous solution containing X^- that are added at the time of forming the silver halide emulsion are added to the solution in a reaction vessel directly under the liquid surface through hollow tubes, and the length of at least one tube in the solution is from 1 to 300 times the shortest distance (C1) between the addition port and the liquid surface, preferably from 1.3 to 300 times, and more preferably from 2 to 100 times.

(51) The silver halide emulsion as described in the above item (1), wherein the existing density of the defect plane 1 (the existing number/a thickness of 20 nm) is from 4 to 40, preferably from 6 to 40, more preferably from 8 to 30, and still more preferably from 10 to 30.

(52) The silver halide emulsion as described in the above item (35), wherein the solubility of AgX increases by the change of the pAg and/or the pH to 1.2 to 10^5 times the solubility before the change, preferably from 1.5 to 10^4 times, and more preferably from 2 to 10^3 times, preferably the change of the pAg and/or the pH is performed during the time from 10 seconds to 40 minutes after the initiation of grain formation by the addition of Ag-1 solution, preferably during the time from 30 seconds to 20 minutes, and preferably the change of the pAg is performed by the addition of I^- .

(53) The silver halide emulsion as described in the above item (30), wherein the concentration of the dispersion medium at the time of the nucleation of the tabular grains (at the time of the initiation of grain formation) is from

0.1 to 20 g/liter, preferably from 0.2 to 15 g/liter, more preferably from 0.3 to 10 g/liter, and still more preferably from 0.3 to 6.0 g/liter.

(54) The silver halide emulsion as described in the above item (30), wherein the concentration of the dispersion medium at the time of the grain growth of the tabular grains is from 0.1 to 100 g/liter, preferably from 1 to 30 g/liter, and more preferably from 3 to 20 g/liter.

(55) The silver halide emulsion as described in the above item (53) or (54), wherein the dispersion medium is gelatin.

(56) The silver halide emulsion as described in the above item (55), wherein the gelatin is gelatin in which one to all of the amino group, carboxylic acid group, imidazole group, hydroxyl group and thioether group are chemically modified, and the modification rate is from 10 to 100%, preferably from 30 to 100%, more preferably from 60 to 100%, and preferably the amino group is chemically modified.

(57) The silver halide emulsion as described in the above item (56), wherein the gelatin is chemically modified with an organic compound having from 0 to 50, preferably from 1 to 50, carbon atoms,

(58) The silver halide emulsion as described in the above item (55), wherein the methionine group content of the gelatin is from 0 to 60 $\mu\text{mol/g}$, preferably from 0 to 40 $\mu\text{mol/g}$, more preferably from 0 to 20 $\mu\text{mol/g}$, and still more preferably from 0 to 10 $\mu\text{mol/g}$.

(59) The silver halide emulsion as described in the above item (55), wherein the gelatin is amino group-modified gelatin, and preferably phthalated gelatin.

(60) The silver halide emulsion as described in the above item (1), wherein an epitaxial part of silver halide having an AgI content of from 0 to 40 mol%, preferably from 0 to 30 mol%, and more preferably from 0 to 20 mol%, is grown on the grain surfaces of the tabular grains (one or more sites of the main plane, edge, corner and arris).

(61) The silver halide emulsion as described in the above item (60), wherein the epitaxial part has an AgCl content of from 0 to 100 mol%, preferably from 30 to 100 mol%, and more preferably from 60 to 100 mol%.

(62) The silver halide emulsion as described in the above item (60), wherein the epitaxial part has an AgBr content of from 0 to 100 mol%, preferably from 30 to 100 mol%, and more preferably from 60 to 100 mol%.

(63) The silver halide emulsion as described in the above item (60), wherein (the AgX molar amount of the epitaxial part/the AgX molar amount of the host grains) is from 10^{-5} to 2, preferably from 10^{-5} to 0.5, and more preferably from 10^{-3} to 0.3.

(64) The silver halide emulsion as described in the above item (1), wherein, with the tabular grains as the core grains, a shell part having a different composition from the composition of the core part is formed on the surface of the tabular grains in the region of from 1 to 100% of the surface, preferably from 5 to 100%, and the composition of the shell part is different by 0.1 to 60 mol% in at least one of Cl, Br and I, preferably by 0.2 to 20 mol%, and more preferably by 0.3 to 10 mol%.

(65) The silver halide emulsion as described in the above item (64), wherein the composition of the shell layer changes stepwise or continuously.

(66) The silver halide emulsion as described in the above item (1), (60) or (64), wherein the tabular grains contain one or more of a single substance and a compound of the atoms having atomic numbers of from 1 to 92 as the dope other than silver and halogen in one or more of the host tabular grains, the epitaxial phase and the shell phase in total amount of from 10^{-9} to 10^{-1} mol/mol AgX, and preferably from 10^{-8} to 10^{-2} mol/mol AgX.

(67) The silver halide emulsion as described in the above item (66), wherein the dope is a single substance of metal atoms (the atoms on the left side of the line connecting boron B and At in the long periodic table of elements), or a neutral body or an ionic body of the compounds containing the metal atoms, more preferably the dope is a single substance of transition metal atoms, or a neutral body or an ionic body of the compounds containing the transition metals.

(68) The silver halide emulsion as described in the above item (67), wherein the compound is a metal complex having from 1 to 3 of the metal atoms and from 2 to 20 ligands, and from one to all of the ligands are inorganic ligands and/or organic ligands having from 1 to 30 carbon atoms.

(69) The silver halide emulsion as described in the above item (68), wherein the metal complex is tetra- or hexa-coordination complex.

(70) The silver halide emulsion as described in the above item (68) or (69), wherein the metal complex has one or two of the organic ligands, and the remaining ligands are inorganic ligands.

(71) The silver halide emulsion as described in the above item (66), wherein the dope is a chalcogen atom (one or more of S, Se, Te), and the doping amount is from 10^{-2} to 10^{-8} mol/mol AgX, and preferably from 10^{-3} to 10^{-7} mol/mol AgX.

(72) The silver halide emulsion as described in the above item (1), (60) or (64), wherein the tabular grains contain reduced silver in one or more of the host tabular grains, the epitaxial phase and the shell phase in an amount of from 10^{-2} to 10^{-8} mol/mol AgX, and preferably from 10^{-3} to 10^{-7} mol/mol AgX.

(73) The silver halide emulsion as described in the above item (60), wherein the epitaxial part is formed by adding Ag^+ and X- to the tabular grains in the state of being adsorbed with an adsorbent other than gelatin in an amount

of from 20 to 100% of the saturation adsorption amount, preferably from 40 to 100%, and more preferably from 60 to 100%.

(74) The silver halide emulsion as described in the above item (73), wherein the adsorbent is one or more of a cyanine dye, an antifoggant, the above dope, a crystal habit controller, and a water-soluble dispersion medium.

(75) The silver halide emulsion as described in the above item (1), wherein when the emulsion is coated on a support, or when a chemical sensitizer is added to the emulsion and chemical ripening is performed, or when a sensitizing dye is added to the emulsion and spectral sensitization is performed, the emulsion is used by selecting the most preferred combination of the pAg of from 3 to 11, the pH of from 3 to 11, and the temperature of from 10 to 90°C.

(76) The silver halide emulsion as described in the above item (1), wherein an interstitial silver ion (AgI^+) concentration reducer is added to the emulsion and allowed to be adsorbed onto the grains to reduce the AgI^+ concentration to 0.8 to 0.001 times the concentration before addition, and preferably from 0.5 to 0.01 times.

(77) The silver halide emulsion as described in the above item (1), wherein the emulsion is a chemically sensitized emulsion with the addition of chalcogen chemical sensitizers (one or more of a sulfur sensitizer, an Se sensitizer and a Te sensitizer) in total amount of from 10^{-2} to 10^{-8} mol/mol AgX, preferably from 10^{-3} to 10^{-7} mol/mol AgX, and the emulsion grains contain chalcogen atoms (S, Se and Te) in total amount of from 10^{-2} to 10^{-8} mol/mol AgX, preferably from 10^{-3} to 10^{-7} mol/mol AgX, and/or the emulsion is a chemically sensitized emulsion with the addition of a gold sensitizer in an amount of from 10^{-2} to 10^{-8} mol/mol AgX, preferably from 10^{-3} to 10^{-7} mol/mol AgX, and the emulsion grains contain a gold atom in an amount of from 10^{-2} to 10^{-8} mol/mol AgX, preferably from 10^{-3} to 10^{-7} mol/mol AgX.

(78) The silver halide emulsion as described in the above item (60), wherein the epitaxial part is chemically sensitized and contains chalcogen atoms (S, Se and Te) in total amount of from 10^{-2} to 10^{-8} mol/mol AgX, preferably from 10^{-3} to 10^{-7} mol/mol AgX, and/or a gold atom in an amount of from 10^{-2} to 10^{-8} mol/mol AgX, preferably from 10^{-3} to 10^{-7} mol/mol AgX.

(79) The silver halide emulsion as described in the above item (1), wherein the emulsion is a spectrally sensitized emulsion by the addition of one or more cyanine dyes, and the adsorption amount of the cyanine dyes onto the AgX grains is from 1.0 to 100% of the saturation adsorption amount, preferably from 10 to 100%, and more preferably from 30 to 100%.

(80) The silver halide emulsion as described in the above item (32), wherein the AgX solvent is added during the time from 10 seconds to 40 minutes after the initiation of grain formation by the addition of Ag-1 solution, preferably from 30 seconds to 20 minutes.

(81) The silver halide emulsion as described in the above item (55), wherein from 10 to 100%, preferably from 30 to 100%, more preferably from 60 to 100%, and still more preferably from 80 to 100%, of the methionine groups of the gelatin are oxidized and the gelatin is modified by oxidants (sulfinyl groups, sulfonium groups).

(82) The silver halide emulsion as described in the above item (1), wherein the diameter of the tabular grain is from 0.3 to 2 μm .

(83) The silver halide emulsion as described in the above item (30), wherein in the manufacture of the emulsion the silver amount of the emulsion after grain formation and before the demineralization process of the emulsion is from 0.05 to 3 mol/liter, preferably from 0.08 to 3 mol/liter, more preferably from 0.10 to 3 mol/liter, and still more preferably from 0.12 to 3 mol/liter.

(84) The silver halide emulsion as described in the above item (1), wherein the content of the γ -type crystal phase of the tabular grains is from 5 to 60 mol%, preferably from 10 to 55 mol%, more preferably from 15 to 50 mol%, still more preferably from 20 to 45 mol%, and most preferably from 25 to 40 mol%.

(90) A photosensitive material comprising a support and one or more silver halide emulsion layers coated on one or both surfaces of the support, wherein at least one silver halide emulsion layer contains the photosensitive silver halide emulsion as described in the above item (1).

(91) The photosensitive material as described in the above item (90) is a photothermographic material, wherein said at least one silver halide emulsion layer contains the photosensitive silver halide emulsion, a photo-insensitive organic silver salt, a heat developer and a binder.

(92) The photosensitive material as described in the above item (90) is a photosensitive material for X-ray photographing.

(93) The photosensitive material as described in the above item (90) is a photosensitive material capable of receiving partially or entirely the lights in the region of from 300 to 800 nm, being sensitized and providing an image.

(94) The photosensitive material as described in the above item (90) is a photosensitive material having a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer.

(95) The photosensitive material as described in the above item (94) is a color photosensitive material containing a color coupler.

(96) The photosensitive material as described in the above item (94), wherein the silver halide emulsion as de-

scribed in the above item (1) is used at least in the blue-sensitive layer.

(97) The photosensitive material as described in the above item (90) or (94), wherein the silver halide emulsion as described in the above item (1) is used as the UV absorber, and preferably the emulsion is used in a layer farther than the blue-sensitive layer from the support.

(98) The photosensitive material as described in the above item (90) or (94), wherein the silver halide emulsion as described in the above item (1) is used in a yellow filter layer (a blue light-excluding layer), and preferably the emulsion is used between the blue-sensitive layer and the green-sensitive layer.

(99) The photosensitive material as described in the above item (90) is a photosensitive material to be exposed, sensitized, and provides a black-and-white image.

[0007] When the emulsion according to the present invention was used as a photosensitive emulsion in the embodiments of the invention, the improvement of (sensitivity/granularity) of the emulsion was confirmed.

Brief Description of the Drawings

[0008]

Fig. 1 is a model drawing showing the space lattices of β -type AgI crystal and γ -type AgI crystal. a) is an oblique view and b) is a top view.

Fig. 2 shows a low temperature TEM image of the sliced cross section of a tabular grain. Magnifications are about 150,000 magnifications.

Fig. 3 shows a transmission electron beam diffraction image of the sliced cross section of a tabular grain. (A) shows the diffraction example in the case where the incidence of the electron beam is 0° to the normal line of the cross section and (B) is the case of 15° .

Fig. 4 shows the structure of the grain obtained in Example 1. Magnifications are 5,400 magnifications.

Fig. 5 shows the structure of the grain obtained in Example 6. Magnifications are 4,100 magnifications.

Fig. 6 shows the structure of the grain obtained in Example 7. Magnifications are 7,500 magnifications.

Fig. 7 shows the structure of the grain obtained in Example 11. Magnifications are 4,000 magnifications.

Fig. 8 is a drawing showing the model of the lattice array image of the defect plane 1 and defect plane 2 of the tabular grain by a high resolution TEM. Magnifications are a little less than about 3,000,000 magnifications.

Description of Reference Numerals

[0009]

8-1: The interface between β -type crystal phase and γ -type crystal phase.

8-2: The interface between γ -type crystal phase and γ -type crystal phase.

DETAILED DESCRIPTION OF THE INVENTION

[0010] (II) The present invention is described in further detail below.

(II-1) Characteristics of grains

[0011] The diameter of a tabular grain is the equivalent-circle diameter of the projected area (the diameter of a circle having the same area as the projected area of a grain) when the grain is placed on a flat base plane in parallel with the main plane and viewed from the upside. The diameters of other grains are the equivalent-circle diameters of the projected areas when the grains are placed on a flat base plane and viewed from the upside.

[0012] A β -type crystal phase means a wurtzite hexagonal crystal structure and a γ -type crystal phase means a zinc blende face centered cubic crystal structure. With respect to the details of these crystal structures, the later-shown literature 1, and with respect to the X-ray analysis data on these crystal structures, the later-shown literature 2 can be referred to, respectively.

[0013] The crystal structure described in the above item (2) is shown in Fig. 1. When the grains are stacked as in Fig. 1 (B) (X^- is stacked on the position of Ag^+ on the base, and Ag^+ is stacked on the position of X^- on the base), this stack is β -type stack layer, and when the grains are stacked on the positions turned by 30° respectively as in (A), this stack is γ -type stack layer.

[0014] When a cross section of the tabular grain obtained by cutting in perpendicular to the main plane is photographed with a transmission electron microscope (TEM) at a low temperature of $-110^\circ C$ or less, a plenty of the defect

planes parallel with the main plane are observed, and this observation example is shown in Fig. 2. As can be seen in Fig. 2, the defect plane also has a part not completely parallel with the main plane. This is presumably due to various causes, e.g., the grain is curved, the grain has distortions, or the electron beam image is distorted. However, when the TEM image is viewed in a broader region not partially, the twin plane is more parallel with the main plane. "Parallel" means that the direction of the vector of the line of the defect plane observed with an electron microscope is in the range of from -10 to +10 to the direction of the vector of the main plane, more preferably -5 to +5.

[0015] There are the embodiment that the tabular grain substantially does not contain a screw dislocation line or a blade-like dislocation line and the embodiment of containing the dislocation line, and it is preferred to select these cases according to purposes. "Substantially does not contain" means that the number of a dislocation line is from 0 to 3 per a grain, preferably 0, and "Substantially contain" means that the number of a dislocation line is 4 or more per a grain, provided that the dislocation lines introduced at the time of preparing a hyper thin slice are excluded.

[0016] The examples of the cross section irradiated with electron beams, and the observation of the electron beam diffraction image are shown in Fig. 3. (A) is a diffraction image of the time being irradiated with electron beams in the perpendicular direction to the cross section, and (B) is a diffraction image of the time being irradiated at an angle of 75°.

[0017] Both (A) and (B) showed an electron beam diffraction pattern (split and a streaking phenomenon at diffraction point) peculiar to a twin defect plane. Accordingly, in the diffraction image of the time being irradiated with electron beams at an angle of from 0 to 30° to the normal line of the cross section, preferably from 0 to 20°, split points that the diffraction point split into 2 to 100, preferably 3 to 50, and a streaking image (an image of the split points arranged linearly) are given as compared with the diffraction point of a complete crystal.

[0018] Giving attention to the I⁻ atomic layer, β -type AgI crystal takes the order of stack of (A/B/A/B), but the stack order of γ -type AgI crystal is (A/B/C/A/B/C). As the defect plane 2, (A/B/C/B/A) type stack fault plane and (A/B/C/C/B/A) type stack fault plane are present. In general, since the latter is greater in energy of formation, the former is liable to occur.

[0019] The details of the crystal structures of the defect planes 1 and 2 can be obtained by photographing a low temperature TEM image of a hyper thin sliced cross section (100 nm or less in thickness) of a tabular grain with a high resolution TEM and obtaining the lattice array image. With respect to the details of photographing the image, the description in the later-described literature 11 can be referred to. Photographing is performed on the so-called Schelzer condition by arranging a crystal so that the crystal atoms are arrayed in rows in the incident direction of an electron beam. That is, in photographing, the direction of the skewer of skewered arrangement of atoms and the direction of incidence are made almost coincident. This means to take the incident direction in parallel to the crystal zone axis. The enlarged high resolution image of the skewered arrangement is the image of atomic arrangement. The example (a model drawing) is shown in Fig. 8. This is a model drawing of an example of observation by taking the direction of electron beam in the [100] direction of a β -type phase. One point corresponds to one AgI. The resolution of the point is about 0.1 nm, and the discrimination of Ag⁺ and I⁻ atoms cannot be resolved. Fig. 8-1 shows the interface between β -type crystal phase and γ -type crystal phase, which corresponds to the defect plane 1. 8-2 shows the interface between γ -type crystal phase and γ -type crystal phase, which corresponds to the defect plane 2. Further, well-known lattice constant and the distance between atoms of the image are almost coincident. β -Layer shows the (A/B) type stack layer structure and γ -layer shows the (A/B/C) type stack layer structure. Since γ -phase comes to the original position on layer A by stacking three layers, the stack angle (θ) to the main plane is, from $\cos\theta=1/3$, $\theta=70.53^\circ$. The angle in the figure almost coincides with the angle. The main contrast of the image is phase contrast. When the phase shift of transmitted wave passed without stopping and regularly-scattered wave scattered by the regularly arrayed atoms becomes about $n/2$, the contrast becomes the maximum. It is preferred to observe a high contrast image.

[0020] The skewered arrangement of atoms plays the role of regularly arranged micro-pore diffraction slits, and there are some images that correspond to the interference fringes between the electron beam waves coming out of the diffraction slits, so that the greatest care must be taken in handling. An atomic image of only one skewered arrangement (that is, one-atom image) is observed in, e.g., gold atoms, the reason is that transmitted waves and scattered waves are present also in that case. However, if the images coincide with the structures obtained from X-ray diffraction and electron beam diffraction, there are generally no problems.

[0021] In the electron diffraction of the defect planes, diffraction images containing diffraction data in various aspects can be preferably obtained by selecting the incident direction of electron beams almost in parallel to the direction of crystal zone axis, preferably by selecting the incident direction in the direction of crystal zone axis having low indexes.

[0022] In Fig. 8, the angle α of β -type phase is $\tan\alpha=(7.51/3.977)$ from the well-known lattice constant value, and $\alpha=62.1^\circ$. The angle in Fig. 8 is almost that angle.

[0023] The embodiment of the item (25) is more preferred as the item (26). The higher the density of the defect plane 1, the higher is the growth of the edge plane of the tabular grain, and the thickness of the tabular grain shows a tendency to become thinner. In the grains in the items (41) to (43), the defect planes 1 and 2 are also observed, but the existing density and the content of the γ -type crystal phase are different from those in the tabular grains in the existence of non-parallel twin defect plane and the like.

[0024] Dislocation lines can be introduced to the tabular grain by the embodiment of the item (24). For example, dislocation lines can be introduced by generating distortion in the crystal structure by doping the dopes described in the items (66) to (72). By performing doping in higher concentration and more locally, dislocation lines are introduced in higher density. When a lot of electrons and positive holes are generated by exposure, dislocation lines temporarily trap electrons and prevent recombination and dispersion of latent images, whereby the forming efficiency of developable latent images is increased. The examples of dislocation lines include screw dislocation lines, blade-like dislocation lines, and composite dislocation lines containing both of them.

[0025] At the joint part of the epitaxial part, dislocation lines are easily introduced due to the difference in structures of crystal lattices. Dislocation lines can be introduced by making use of the characteristic by the embodiment of the item (27). In addition, dislocation lines can be introduced by doping the above dopes.

[0026] One method of obtaining the γ -type crystal content is the method as described in the item (22).

[0027] Almost all the tabular grains have hexagonal or triangular main planes, and each apex angle of hexagon is about 120° , and the apex angle of triangle is about 60° . This is the reflection of the shape of the unit cell of β -type AgI, but there are cases where these apex angles a little vary by the distortion of TEM images and the like.

(II-2) AgX solvent

[0028] With respect to the specific examples of the compounds of AgX solvents, the description of literature 3 can be referred to. AgX solvents (SOL) are compounds that form a water-soluble complex with Ag^+ and increase the dissolution concentration of Ag^+ to 1.2 to 10^6 times, preferably from 1.5 to 10^5 times, more preferably from 2 to 10^4 , and still more preferably from 4 to 10^3 times. The concentration of the AgX solvents is from 10^{-7} to 3 mol/liter, preferably from 10^{-5} to 1 mol/liter, more preferably from 10^{-3} to 0.3 mol/liter. The solubility of the complex in one liter of water (molar amount) is from 10^{-3} to ∞ , preferably from 10^{-2} to ∞ , and more preferably from 0.1 to ∞ . The compounds are compounds exclusive of gelatin having a molecular weight of preferably from 17 to 10^4 , more preferably from 17 to 10^3 .

[0029] In the reaction of $[\text{Ag}^+ + \text{SOL} \rightarrow \text{Ag}^+ - \text{SOL}]$, $[\text{Ag}^+ - \text{SOL}] / [\text{Ag}^+] = K_1$ is from 0.2 to 10^6 , preferably from 0.6 to 10^5 , and more preferably from 2 to 10^4 .

[0030] As the specific examples of AgX solvents, straight chain or (saturated or unsaturated) cyclic compounds containing one or more of an amine group, a thioether group and a thiourea group are exemplified, and compounds further containing, if necessary, from 1 to 10^3 groups of water-soluble groups in one molecule are preferred. The water-soluble group here means a group having Gibbs free energy change ($-\Delta G$ KJ/mol) at the time of being dissolved in water, or heat of hydration (KJ/mol) of from 3 to 600, preferably from 10 to 400, and more preferably from 20 to 300, and as the specific examples, $-\text{OH}$, $-\text{SO}_3^-$, $-\text{COO}^-$ and $-\text{NH}_3^+$ are exemplified. With respect to the details of AgX solvents, the description in literature 6, Chapter 9 can be referred to. Compounds having from 1 to 10^3 groups of thioether groups in one molecule, preferably from 2 to 100 groups, are preferred.

(II-3) Dispersion medium

[0031] As the dispersion medium, conventionally well known various dispersion media can be used, and regarding the specific examples, the description in the literatures 3 to 5 can be referred to. The weight average molecular weight of the dispersion media is preferably from 3,000 to 10^6 , more preferably from 6,000 to 3×10^5 . The concentration of the dispersion media is preferably from 0.01 to 20 mass%, more preferably from 0.05 to 10 mass%. Gelatin is more preferred as a dispersion medium. The gelatins extracted from the bones and skins of cattle and pig, and bones, skins and scales of fishes are more preferred.

[0032] Alkali-processed gelatin and acid-processed gelatin are known. Gelatins obtained by processing these gelatins with one or more of acid, alkali, and hydrolytic enzyme to reduce the molecular weight (weight average molecular weight: from 3,000 to 60,000, preferably from 6,000 to 40,000) are preferred. Empty gelatins obtained by reducing their impurity content to 0 to 10^4 ppm, preferably from 0 to 10^3 ppm, and more preferably from 0 to 100 ppm are preferred.

[0033] Gelatins in which one to all of the amino group, carboxylic acid group, imidazole group, hydroxyl group and thioether group are chemically modified are preferred, and the modification rate is from 1 to 100%, preferably from 10 to 100%, more preferably from 30 to 100%, and still more preferably from 60 to 100%. Chemically modified gelatin with an organic compound group (R^1) having from 1 to 50 carbon atoms, preferably from 2 to 20 carbon atoms, e.g., gelatin in which the amino group is phthalated, succinated, trimellitated, and acetylated, esterified gelatin in which the carboxylic acid group is modified, gelatin in which an alkyl group is introduced to the thioether group of the methionine group (Met), gelatin in which sulfonium is added to said group, and gelatin in which said group is subjected to oxidation with an oxidizing agent whereby to be changed to a sulfinyl group or a sulfonyl group are preferred, and gelatin having a sulfinyl group are more preferred. Oxidizing agents have standard equilibrium potential (volt, V) of oxidation reduction of from 0.7 to 4, preferably from 1 to 3, are preferred, and H_2O_2 is more preferred. The methionine content of gelatin may be from 0 to 100 $\mu\text{mol/g}$, but preferably from 0 to 40 $\mu\text{mol/g}$, more preferably from 0 to 20 $\mu\text{mol/g}$, and still more

preferably from 0 to 10 $\mu\text{mol/g}$. Gelatin subjected to oxidation treatment with these oxidizing agent, gelatin subjected to the above alkali process, and gelatin having the above methionine content in which the amino group is chemically modified as above are preferred.

[0034] In addition, gelatin in which the imidazole group is oxaminated by the application of the oxidizing agent, gelatin acid amidated by acid anhydride, and gelatin in which (imidazole residue- R^1) is formed are preferred. As the modifiers, ethoxyformic anhydride, methyl-p-nitrobenzene-sulfonate and iodoacetic acid can be used. Gelatin in which the guanidyl group of arginine is reacted with the oxidizing agent, or reacted with acid anhydride, and gelatin in which the amine group is sulfamidated by the application of a sulfamide agent can be used.

[0035] When the emulsion of the invention is applied to photothermographic materials, gelatin in which the amino group is modified with the above R^1 is preferably used as the dispersion medium. The modification rate is from 30 to 100 mol%, preferably from 60 to 100 mol%, and more preferably from 80 to 100 mol%, and phthalated gelatin is more preferred. With respect to the details of these modified gelatins and oxidizing agents, literatures 3 to 5 can be referred to.

[0036] These dispersion media can be added at any time, e.g., before grain formation, after grain formation, and just before coating of an emulsion. It is preferred that the weight average molecular weight of the dispersion medium added after grain formation is from 1.1 to 50 times the dispersion medium added during grain formation, preferably from 1.5 to 20 times, and the methionine content of the former is from 0 to 100 times the latter, preferably from 20 to 100 times.

(II-4) Addition solution

[0037] The aqueous solution containing Ag^+ (Ag^+ solution) is an aqueous silver salt solution having a dissolution amount (molar amount) in one liter of water of 25°C of from 0.1 to ∞ , preferably from 0.3 to ∞ . For example, silver nitrate, silver sulfate, and silver oxalate are exemplified, and silver nitrate is more preferred. The aqueous solution containing I^- (I^- solution) is an aqueous iodide salt solution having the same dissolution amount (molar amount) of from 0.1 to ∞ , preferably from 0.3 to ∞ . For example, NaI, KI and NH_4I are exemplified, and NaI and KI are more preferred.

One or more of Cl^- and Br^- can be added to an aqueous solution containing I^- in an amount necessary to achieve the above embodiment. These compounds can be added to both solutions without containing a dispersion medium. A dispersion medium can be added to one or more of both solutions, preferably to both solutions, in an amount of from 0.01 to 20 mass%, preferably from 0.05 to 10 mass%, and more preferably from 0.1 to 5 mass%. A dispersion medium is preferably added. The addition solutions mean the Ag^+ solution and the I^- solution, and the temperature of the addition solution is room temperature, or temperatures of from 1 to 99°C, and the optimal temperature can be selected from 5 to 90°C. The temperature is more preferably from (room temperature+3°C) to 99°C, more preferably from (room temperature+6°C) to 90°C, and the difference between the temperature of the addition solution and the solution in the reaction vessel is preferably from 0 to 30°C, more preferably from 0 to 20°C, and still more preferably from 0 to 10°C. The temperature of the addition solution can be controlled by installing the addition system with a temperature controlling device. It is preferred to use the addition system as disclosed in Japanese Patent Application No. 2003-99256 in addition.

[0038] The pH of the addition solution is from 2 to 11, preferably from 2.5 to 9.5, and the optimal temperature can be selected in the above range. Japanese Patent Application No. 2003-57156 can be referred to as to the addition method of Ag^+ solution and X^- solution.

(II-5) Preparation of tabular grain emulsion

[0039] In the first place, tabular seed crystal is formed and grown to tabular grains. The seed crystal can be formed by one process, but it is preferred to provide a nucleation process and a ripening process.

[0040] At first, the most preferred seed crystal is formed. That is, tabular seed crystal uniform in grain structural characteristics among grains is formed. If the grain structural characteristics are fluctuated, the tabular grains obtained by growing the seed crystal become polydispersed grains. The characteristics mean that the defect plane structural characteristics parallel to the main plane are uniform, and the grain substantially does not have dislocation lines (a screw dislocation line and a blade-like dislocation line) other than the defect planes. For forming the seed crystal, Ag-1 solution and X-1 solution are added by double jet addition under the optimal reaction solution conditions and uniformly mixed to form AgX nuclei. At this time, if the formed nuclei are all tabular grain nuclei, the nuclei may enter the growing process as tabular seed crystal. In many cases, non-tabular grain nuclei are formed besides tabular grain nuclei. In such a case, it is preferred to make the non-tabular grain nuclei disappear by Ostwald ripening, to whereby grow tabular grains and increase the percentage of tabular grain number (A5).

[0041] The ripening can be performed while the addition of Ag^+ solution and X^- solution is ceased, or can be performed while adding both solutions at a low speed. It is preferred to select the most preferred addition speed. For accelerating the ripening, it is preferred to add AgX solvent by the embodiment as described in the item (32). For accelerating the ripening, it is preferred to increase the ripening temperature higher than the temperature of nucleus formation by the

embodiment as described in the item (33). When a desired seed crystal is obtained, the seed crystal is then grown under appropriate conditions. The seed crystal is grown under the conditions less in the increase of the thickness and diameter fluctuation. When Ag^+ and X^- are added in the form of ionic aqueous solutions, the defect planes parallel to the main plane are liable to occur even during grain growth. Accordingly, when a low temperature TEM image of a hyper thin sliced cross section of a formed tabular grain is observed, the defect planes are observed throughout the region of thickness as shown in Fig. 3.

[0042] The reason for this is due to the fact that the stack fault is liable to occur since the energy difference in the structures between β -type and γ -type shown in Fig. 1 is small. When tabular grains are grown according to the methods in the items (38) to (40), since the grain growth becomes oversaturated low growth ruled by the solubility of AgX fine grains, the selecting growing property of the edge of tabular grain becomes high, so that thinner tabular grains can be obtained and preferred.

[0043] The descriptions in literatures 3 and 5 can be referred to, as to the methods of the items (38) to (40). The fine grains are prepared by using Ag-1 solution and X-1 solution, but they are to be called Ag-2 solution and X-2 solution for the purpose of discrimination. For accelerating the dissolution of the fine grains added and controlling the frequency of formation of the defect planes, it is preferred to use AgX solvent in the embodiment in the item (32).

[0044] AgX solvent can be added at any stage of before initiating nucleus formation, at the time of concluding grain growth, and until the subsequent washing of the emulsion. Further, when the added solvent becomes unnecessary, the solvent can be partially or completely nullified by adding a nullifier. For example, in the case of NH_3 and an amine compound, the solvent can be nullified by adding acid (e.g., HNO_3) to whereby lower the pH lower than the acid dissociation constant value pKa, to make quaternary salts of nitrogen atoms. In the case of a thioether group-containing compound, the nullification can be performed by adding the oxidizing agent (e.g., H_2O_2) to whereby make an -S(O)-group of the thioether group. With respect to the oxidation of the thioether group, the description of (II-3) can be referred to. That is, pH adjustment, oxidation and nullification by decomposition are used. From 10 to 100 mol%, preferably from 20 to 90 mol%, of the solvent added after the ripening can be nullified, but the embodiment of from 0 to 10 mol% can also be used.

[0045] By increasing Ag^+ concentration in solution in a reactor vessel, the AgX solvent is combined with Ag^+ on the surfaces of grains and accelerates the formation of γ -type phase to whereby increase the probability of the formation of the defect planes 1 and 2, and has the effect of increasing the forming rate of tabular grain edge.

[0046] When the dispersion medium concentration of the dispersion medium solution 1 at the time of nucleus formation is made low, the probability of the formation of the defect plain 1 and the probability of the formation of tabular seed crystal is liable to increase. In this point, the dispersion medium concentration is from 0.1 to 20 g/liter, preferably from 0.3 to 10 g/liter, more preferably from 1 to 10 g/liter.

(II-6) Others

[0047] Regarding the details of [the adsorbents in the items (73) and (74)], [the dope compounds and the methods in the items (66) to (71)], and [the compounds in the item (76)], literatures 3 and 5 can be referred to. As the compounds in the item (76), antifoggants are effective.

[0048] The emulsion of the invention can be subjected to chemical sensitization by the addition of chemical sensitizers. As the chemical sensitizers, chalcogen sensitizers (sulfur, selenium and tellurium sensitizers), noble metal sensitizers (gold and metal compounds belonging to the group VIII), and reduction sensitizers can be used alone or in combination of two or more in various ratios.

[0049] The grains have a large blue light absorption coefficient in 430 nm or shorter wavelengths but the blue light absorption coefficient in the wavelengths longer than that is small. Accordingly, when emulsion 1 is used in a blue-sensitive layer of a photosensitive material, it is preferred that one to twenty kinds of sensitizing dyes for a blue-sensitive layer are added and allowed to be adsorbed onto the grains, followed by spectral sensitization. When the emulsion is used in a green-sensitive layer, one to twenty kinds of sensitizing dyes for a green-sensitive layer are added, and when the emulsion is used in a red-sensitive layer, one to twenty kinds of sensitizing dyes for a red-sensitive layer are added, and then spectral sensitization is performed. These sensitizing dyes are preferably used according to the embodiment described in the item (79).

[0050] When sensitizing dyes are adsorbed onto emulsion grains and irradiated with light, it is preferred to add a compound (PED) that absorbs 1 photon and giving from 2 to 4 electrons to AgX grains in an addition amount of from 10^{-8} to 10^{-1} mol/mol AgX, preferably from 10^{-6} to 10^{-2} mol/mol AgX. Regarding the details of the compounds, literature 7 can be referred to.

[0051] Regarding the AgX emulsion of the invention, compounds to be used and the addition amounts, manufacturing methods and the application, and others, JP-A-2000-201810, paragraphs [0067] to [0087], JP-A-2001-25561, item (I-8), and literature 5 can be adopted.

[0052] With respect to the application of the emulsion of the invention to photothermographic materials, the descrip-

tion of literature 8, and the application to other photographic materials, the description of literature 9 can be respectively referred to.

[0053] With respect to the photo-insensitive organic silver salt, heat developer, binder and support described in the item (91), the description of literature 8 can be referred to.

Literatures:

[0054]

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EXAMPLE

[0055] The present invention is described in further detail below with reference to examples, however the present invention is not limited thereto. The grain formation in the invention was performed under preferred stirring. In the determination addition of Ag⁺ solution and X⁻ solution, a highly precise constant flow pump was used. In the addition of Ag⁺ solution and X⁻ solution; the addition system disclosed in Japanese Patent Application No. 2003-99256 (the length of the hollow liquid tube in the solution in a reaction vessel was 8 times the shortest distance (C1) from the addition port to the liquid surface) was used, unless otherwise indicated.

EXAMPLE 1

[0056] Dispersion medium solution 1 [10 g of alkali-processed deionized ossein gelatin of cattle (Gel), 1.25 liters of H₂O, and 5 ml of KI-1 solution (an aqueous solution containing KI 10 g/liter), pH: 7.0] was put in a reaction vessel and the temperature was set at 67°C. Ag-1 solution [containing 100 g/liter of AgNO₃] and X-1 solution [containing 97.8 g of KI and 3 g of gelatin in 1 liter, pH: 7.0] were added thereto at a rate of 10 ml/minute for 3 minutes. pl of the solution was about 2.6. This is nucleus formation.

[0057] To the reaction vessel were then added 5 ml of KI-1 solution, 150 ml of AgX solvent 1 solution (a methanol solution containing 50 g/liter of AgX solvent 1), and (a heated gelatin aqueous solution containing 10 g of Gel and NaOH). The pH of the reaction solution was raised to 9.3 with NaOH, the temperature was increased to 78°C, and subjected to ripening for 16 minutes. During this period of time, Ag-1 solution and X-1 solution were added at a rate of 5 ml/minute. This is a ripening process.

[0058] In the next place, Ag-1 solution and X-1 solution were added thereto by controlled double addition (CDJ addition) while maintaining pl=-Log[I⁻ concentration = 2.3 mol/liter]. Ag-1 solution was added at an initial flow rate of 10 ml/minute and an accelerated flow rate of 0.05 ml/minute for 70 minutes. This is a growing process.

[0059] After stirring the solution for 1 minute, 1 ml of the emulsion was taken out and sensitizing dye 1 was adsorbed by the saturation adsorption amount. The TEM image of the carbon replica film of the grains was photographed. Ninety-seven (97) percent or more of the entire projected area of the grains accounted for tabular grains having an aspect ratio of 3 or more. Triangular tabular grains having 3.51 or more of A1 accounted for 53% of the projected area, and hexagonal tabular grains having 3.5 or less of A1 accounted for 47% of the projected area.

EXAMPLE 2

[0060] The same procedure as in Example 1 was performed except for omitting the addition of AgX solvent 1.

5 EXAMPLE 3

[0061] The same procedure as in Example 1 was performed except for omitting the temperature increase after nucleus formation.

10 EXAMPLE 4

[0062] The same procedure as in Example 1 was performed except that Ag⁺ solution and X⁻ solution were added with a tube having a length of 1.3 times or less the length of C1.

15 EXAMPLE 5

[0063] The same procedure as in Example 1 was repeated except for performing nucleus formation, ripening and growth at pH 7.

20 COMPARATIVE EXAMPLE 1

[0064] A tabular grain emulsion having an average grain diameter of 11.4 μm was prepared according to Example 9 of JP-A-59- 119350.

25 EXAMPLE 6

[0065] Dispersion medium solution 2 [6 g of Gel, 1.25 liters of H₂O, and 5 ml of KI-1 solution, pH: 7.0] was put in a reaction vessel and the temperature was raised to 70°C. Ag-1 solution and X-1 solution were added at a rate of 8 ml/minute for 100 seconds. A heated aqueous solution containing 14 g of Gel and 150 ml of AgX solvent 1 solution were added, and pH was adjusted to 9.1 with NaOH. The temperature was elevated to 77°C and ripening was performed for 16 minutes. During this period of time, Ag-1 solution and X-1 solution were added at a rate of 5 ml/minute.

[0066] Ag-1 solution and X-1 solution were then added by CDJ addition while maintaining pl = 2.3. Ag-1 solution was added at an initial flow rate of 8 ml/minute and an accelerated flow rate of 0.05 ml/minute for 80 minutes. The same procedure as in Example 1 was repeated hereinafter, and photographing of the TEM image of the grains and preparation of a coating sample were performed.

EXAMPLE 7

[0067] The same procedure as in Example 6 was repeated except for performing growing at pl=2.5.

40 EXAMPLE 8

[0068] The same procedure as in Example 6 was repeated except for performing growing at pl=2.1.

45 EXAMPLE 9

[0069] The same procedure as in Example 6 was repeated and grain formation was stopped at a half of the growing time, and entered washing process.

50 EXAMPLE 10

[0070] The same procedure as in Example 6 was repeated but Ag⁺ solution and X⁻ solution were not added in growing time, and previously prepared AgI fine grains were added in the same silver amount. The amount of 1/3 was added at the time of initiating growing, 1/3 was added 10 minutes after, and 1/3 was added 7 minutes after. The temperature was lowered 25 minutes after, thus the grain formation was concluded.

Preparation of AgI fine grains:

[0071] Dispersion medium solution 3 [20 g of gelatin Ge2 having a weight average molecular weight of 15,000, 1.25 liters of H₂O, and 1 ml of KI-1 solution, pH: 6.0] was put in a reaction vessel, and Ag-2 solution [containing 200 g of AgNO₃ in 1 liter] and X-2 solution [containing 195.5 g of KI and 8 g of Ge2 in 1 liter, pH: 6.0] were added at 22°C with vigorously stirring at 50 ml/minute for 10 minutes by double jet addition. After the addition, the reaction solution was stirred for 1 minute, and then concentrated by ultrafiltration to about half an amount. A TEM image was photographed by a direct method. The grain diameter was about 18 nm.

[0072] The characteristics and photographic characteristics (sensitivity/granularity) of the obtained tabular emulsion are summarized in Table 1 below. (Sensitivity/granularity) is shown as a relative value with the value of the sample in Comparative Example 1 as 100. CV value is the CV value of the fluctuation of diameter, tabular rate shows [the total of the projected areas of tabular grains having (aspect ratio >3) / the total of the projected areas of all the grains] x 100 (%).

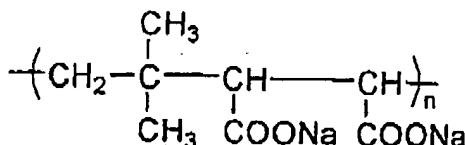
[0073] The ratio of the projected area (%) of (triangular tabular grains/hexagonal tabular grains) of the grains obtained in Examples 6 and 7 were about (37/63) and (26/74) respectively.

EXAMPLE 11

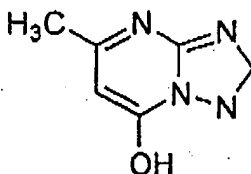
[0074] Dispersion medium solution 3 (3.5 g of Gel, 1.25 liters of H₂O, and 4 ml of KI-1 solution, pH: 6.5) was put in a reaction vessel and the temperature was raised to 71°C. Ag-1 solution and X-1 solution were added at a rate of 7 ml/minute for 90 seconds. A heated aqueous solution containing 17 g of Gel and 150 ml of AgX solvent 1 solution were added, and pH was adjusted to 9.2 with NaOH. The temperature was raised to 77°C, and ripening was performed for 16 minutes. During the time, Ag-1 solution and X-1 solution were added at a rate of 5 ml/minute.

[0075] In the next place, Ag-1 solution and X-1 solution were added thereto by CDJ addition while maintaining pH=2.8. Ag-1 solution was added at an initial flow rate of 6 ml/minute and an accelerated flow rate of 0.05 ml/minute for 78 minutes. The same procedure as in Example 1 was repeated hereinafter, and photographing of the TEM image of the grains and preparation of a coating sample were performed. The ratio of hexagonal tabular grains having A1 of 3.5 or less accounted for about 98%, and the ratio of hexagonal tabular grains having A1 of 3.0 or less accounted for about 95%, which is shown in Fig. 7.

[0076] In the tabular grains manufactured in Examples 1 to 11, the same parallel twin planes (containing twin planes parallel to the main planes from 5 to 10⁴ planes per a grain) as shown in Fig. 2 were observed, but parallel twin planes were not observed in Comparative Example 1 at all.

Precipitant 1

Average molecular weight: 1.2×10^5

Antifoggant 1

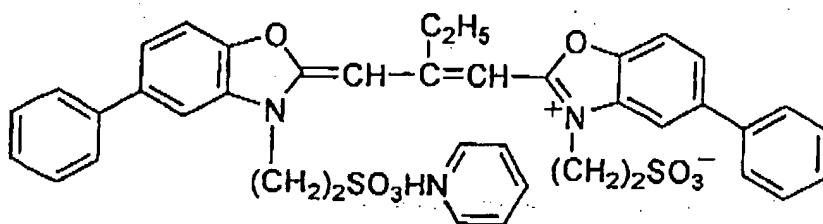
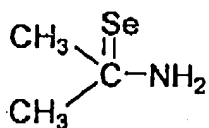
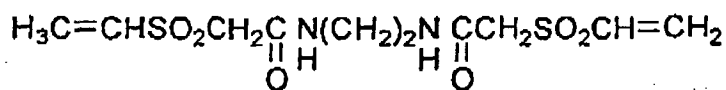
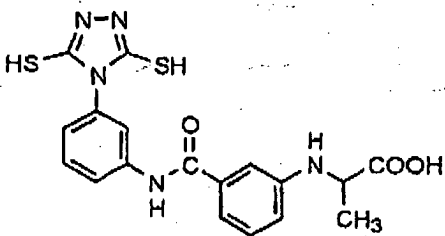
Sensitizing Dye 1Chemical Sensitizer 1:Na₂S₂O₃=1:2 (by mol)Hardening agent 1PX 1AgX Solvent 1

TABLE 1

Sample	Blue Light Exposure (sensitivity/granularity)	-Blue Light Exposure (sensitivity/granularity)	Average (diameter/thickness) (μm)	CV	Tabular Rate (%)
Example 1	280	282	2.1/0.15	0.19	>97
Example 2	150	152	1.4/0.33	0.28	>80
Example 3	240	245	1.9/0.18	0.24	>95
Example 4	230	232	1.8/0.20	0.25	"
Example 5	250	252	1.95/0.17	0.21	"
Comparative Example 1	100	100	11.4/0.32	0.42	<90
Example 6	300	303	2.2/0.12	0.22	>97
Example 7	260	261	1.6/0.22	0.18	"
Example 8	285	287	2.4/0.1	0.26	"
Example 9	248	250	1.3/0.08	0.21	"
Example 10	290	292	2.4/0.1	0.25	"
Example 11	303	306	1.5/0.20	0.15	"

Preparation of emulsion coating sample:

[0077] Precipitant 1 was added to each emulsion in Examples and Comparative Example, the temperature was lowered to 30°C, and each emulsion was washed with water by a precipitation washing method. pH was adjusted to 6.4, the temperature was raised to 40°C and the emulsion was re-dispersed. pAg of the emulsion was adjusted to 5.5 with an AgNO₃ solution and a KI solution. Sensitizing dye 1 was added at 40°C in an amount of 90% of the saturation amount. Then, the temperature was raised to 60°C, and chemical sensitizer 1 was added in a total amount of 3.5×10^{-4} mol/mol AgX, and ripening was performed for 50 minutes. The temperature was lowered to 40°C, PX1 was added in an amount of 10^{-3} mol/mol AgX, and then the antifoggant was added in an amount of 3×10^{-3} mol/mol AgX. pH was adjusted to 6.4 and pAg to 5.5, and stirring was performed for further 40 minutes.

[0078] The emulsion was coated on a PET base and dried with a protective layer containing hardening agent 1 (0.01 g/g of gelatin). The emulsion was put in a closed container and preserved at 40°C for 15 hours to whereby accelerate hardening reaction. The coated products of the emulsions of Examples 1 to 11 were taken as Samples 1 to 11, and

the coated product of the emulsion in Comparative Example 1 was taken as Comparison 1.

[0079] A sample obtained by subjecting each coated sample to exposure with blue light for 10^{-2} sec. (the light of the wavelength of 450 nm or lower) through an optical wedge, and a sample obtained by subjecting each coated sample to exposure with blue light (the light of the wavelength of 500 nm or higher) were development processed with a pyrogallol developer as described in literature 5 at 40°C for 50 minutes. Each sample was immersed in a stopping solution for 1 minute, immersed in a fixing solution (Super Fuji Fix) for 30 minutes and fixed, washed, and dried. After the sensitometry, the result of the ratio of (sensitivity/granularity) is shown in Table 1. It was confirmed that the samples in the invention were excellent in (sensitivity/granularity) as compared with the sample in Comparative Example.

[0080] The sensitivity was shown as the reciprocal of exposure amount (lux·sec.) necessary to give the density of (fog + 0.2). The granularity was obtained by subjecting each sample to even exposure with the light quantity giving the density of (fog + 0.2) for 10^{-2} sec., performing development process, measuring the fluctuation of density by using a circular opening having a diameter of 48 μ m with a micro-densitometer, and finding rms granularity σ . The details are described in literature 10, Chapter 21, Clause E.

EXAMPLE 12

[0081] Dispersion medium solution 4 (3.5 g of Gel, 1.25 liters of H₂O, and 7 ml of KI-1 solution, pH: 6.1) was put in a reaction vessel and the temperature was raised to 73°C. Ag-1 solution and X-2 solution were added at a rate of 7 ml/minute for 90 seconds. An aqueous solution containing 3 g of Gel, NaOH and KI, and 150 ml of AgX solvent 1 solution were added to adjust pH to 9.2 and pl to 2.4. The temperature was raised to 77°C, and ripening was performed for 16 minutes. During the time, Ag-1 solution and X-2 solution were added at a rate of 7 ml/minute.

[0082] In the next place, a heated aqueous solution containing 12 g of Ge3 (alkali-processed phthalated gelatin having a phthalation rate of the amino group of 95%) was added and pH was adjusted to 7.5. Then, with maintaining pl=2.4, Ag-2 solution and X-2 solution were added by CDJ addition. Ag-1 solution was added at an initial flow rate of 7 ml/minute and an accelerated flow rate of 0.06 ml/minute for 76 minutes.

[0083] Ag⁺ solution and X⁻ solution in Examples 12 and 13 were added with a tube having a length of 2 times the length of C1. X-2 solution shows KI solution (containing 98 g of KI in 1 liter).

EXAMPLE 13

[0084] Dispersion medium solution 5 (10 g of gelatin containing 40 μ mol/g of methionine, 1.25 liters of H₂O, 0.5 g of KI, and pH was adjusted to 10.5 with NaOH) was put in a reaction vessel and the temperature was raised to 75°C. AgNO₃ aqueous solution (containing 50 g/liter of AgNO₃) and KI aqueous solution (containing 50 g/liter of KI) were added into the liquid at a rate of 5 ml/minute for 10 minutes. After ripening for 3 minutes, HNO₃ solution was added and pH was adjusted to 9.0.

[0085] In the next place, an aqueous H₂O₂ solution (3 mass%) was added to oxidize the Met group of the gelatin to make the Met content 0 μ mol/g. Then, 80 ml of AgX solvent 1 solution was added, and pH was adjusted to 10 with NaOH. Then, with maintaining pl=2.4, Ag-3 solution (containing 170 g/liter of AgNO₃) and X-3 solution (containing 170 g/liter of KI) were added by CDJ addition. Ag-3 solution was added at an initial flow rate of 2.0 ml/minute and an accelerated flow rate of 0.1 ml/minute in total amount of 800 ml. The same procedure as in Example 1 was repeated hereinafter, and photographing of the TEM image of the grains and preparation of a coating sample were performed.

EXAMPLE 14

[0086] Dispersion medium solution 6 (containing 0.9 g of gelatin, 1.25 liters of H₂O, and 8 ml of KI-1 solution, pH of 6.5) was put in a reaction vessel and the temperature was set at 70°C. Ag-1 solution and X-1 solution were then added to the reaction vessel at a rate of 8 ml/minute for 90 seconds. In the next place, a gelatin aqueous solution (containing 10 g of gelatin and 0.2 g of KI, pH was 9.0) was added, the temperature was raised to 78°C, and then 160 ml of AgX solvent 1 was added. Ripening was performed by the addition of Ag-1 solution and X-1 solution at a rate of 5 ml/minute for 10 minutes. Then, with maintaining pl=2.4, Ag-1 solution and X-1 solution were added by CDJ addition for 80 minutes. Ag-1 solution was added at an initial flow rate of 8 ml/minute and an accelerated flow rate of 0.08 ml/minute.

[0087] By the same process as in Example 1 hereafter, preparation of coating samples and evaluation of photographic properties of the emulsions obtained in Examples 12, 13 and 14 were performed, and TEM images of the grains were photographed. In both samples, tabular grains having an aspect ratio of 3 or more accounted for 97% or more of the entire projected area of the grains. The ratio (%) of the tabular grains having A1 of 3.5 or less accounting for in the projected area, (the number of the defect planes/grain), the ratio of γ -phase, and the photographic properties are shown in Tables 2 and 3 below.

[0088] (The number of the defect planes/grain) of the emulsions in other examples was in the range of 20 to 100,

and the number of twin defect planes 2 was in the range of 0 to 3.

TABLE 2

Sample	Blue Light Exposure (sensitivity/granularity)	-Blue Light Exposure (sensitivity/granularity)	Average (diameter/thickness) (μm)	CV	Tabular Rate (%)
Example 12	290	292	2.3/0.12	0.16	>97
Example 13	250	252	1.5/0.20	0.18	>97
Example 14	300	301	1.0/0.08	0.17	>97

TABLE 3

Sample	Percentage Of A1>3.51	Percentage of A1<3.5	Defect plane 1 Number/ Grain	Defect plane 2 Number/ Grain	γ -Phase Ratio (%)
Example 12	60	40	50	0	30

TABLE 3 (continued)

Sample	Percentage Of A1>3.51	Percentage of A1<3.5	Defect plane 1 Number/ Grain	Defect plane 2 Number/ Grain	γ -Phase Ratio (%)
Example 13	57	43	31	2	17
Example 1	53	47	50	0	30
Example 11	2	98	40	1	26
Example 14	10	30	37	1	19

Claims

1. A silver halide emulsion comprising water, a dispersion medium and silver halide grains, wherein from 60 to 100% of the total projected area of the silver halide grains are tabular grains having: an aspect ratio (projected area diameter/thickness) of from 2.6 to 300; AgI content (mol%) of from 88 to 100; and a projected area diameter of grain (μm) of 0.2 to 10, and the tabular grains have from 3 to 10^4 planes per a grain of twin defect plane 1 parallel to the main plane, wherein the twin defect plane 1 is a stacking fault plane formed by the stack of γ -type crystal phase on the {001} face of β -type crystal phase or the stack of β -type crystal phase on the {111} face of γ -type crystal phase.
2. The silver halide emulsion as claimed in claim 1, wherein the tabular grains have a layer of β -type crystal phase and a layer of γ -type crystal phase parallel to the main plane, and the content of the γ -type crystal phase (mol%) of from 0.01 to 50.
3. The silver halide emulsion as claimed in claim 1, wherein the {001} face of β -type crystal phase and the {111} face of γ -type crystal phase are both parallel to the main plane.
4. The silver halide emulsion as claimed in claim 1, wherein the tabular grains further have from 1 to 10^4 planes per a grain of twin defect plane 2 parallel to the main plane, and the twin defect plane 2 is a stacking fault plane formed when a γ -type crystal phase is stacked on the {111} face of a γ -type crystal phase.
5. The silver halide emulsion as claimed in claim 4, wherein the tabular grains contain the twin defect plane 1 in an amount of Z1 in number and the defect plane 2 in an amount of Z2 in number, and the ratio of Z1/Z2 is 0.4 or less.

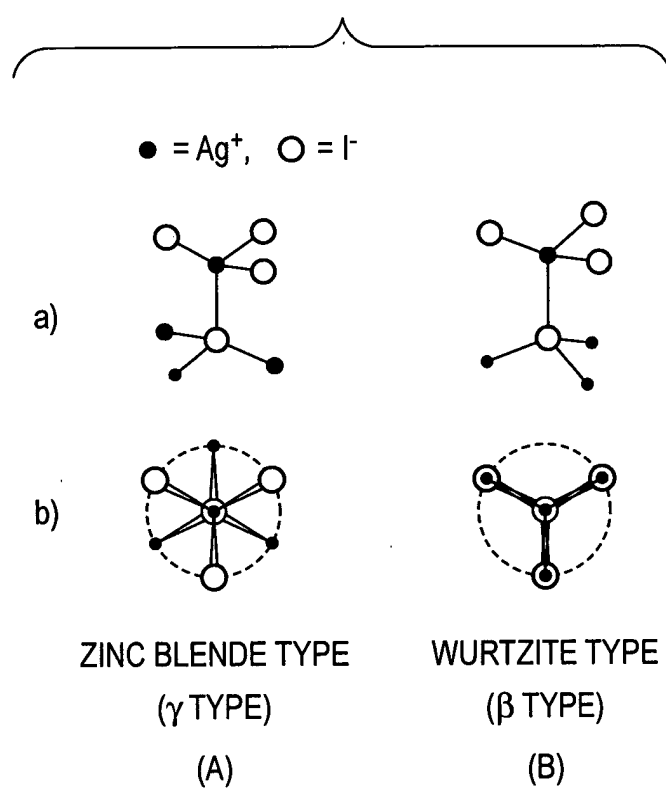
FIG. 1

FIG. 2



x ABOUT 150,000

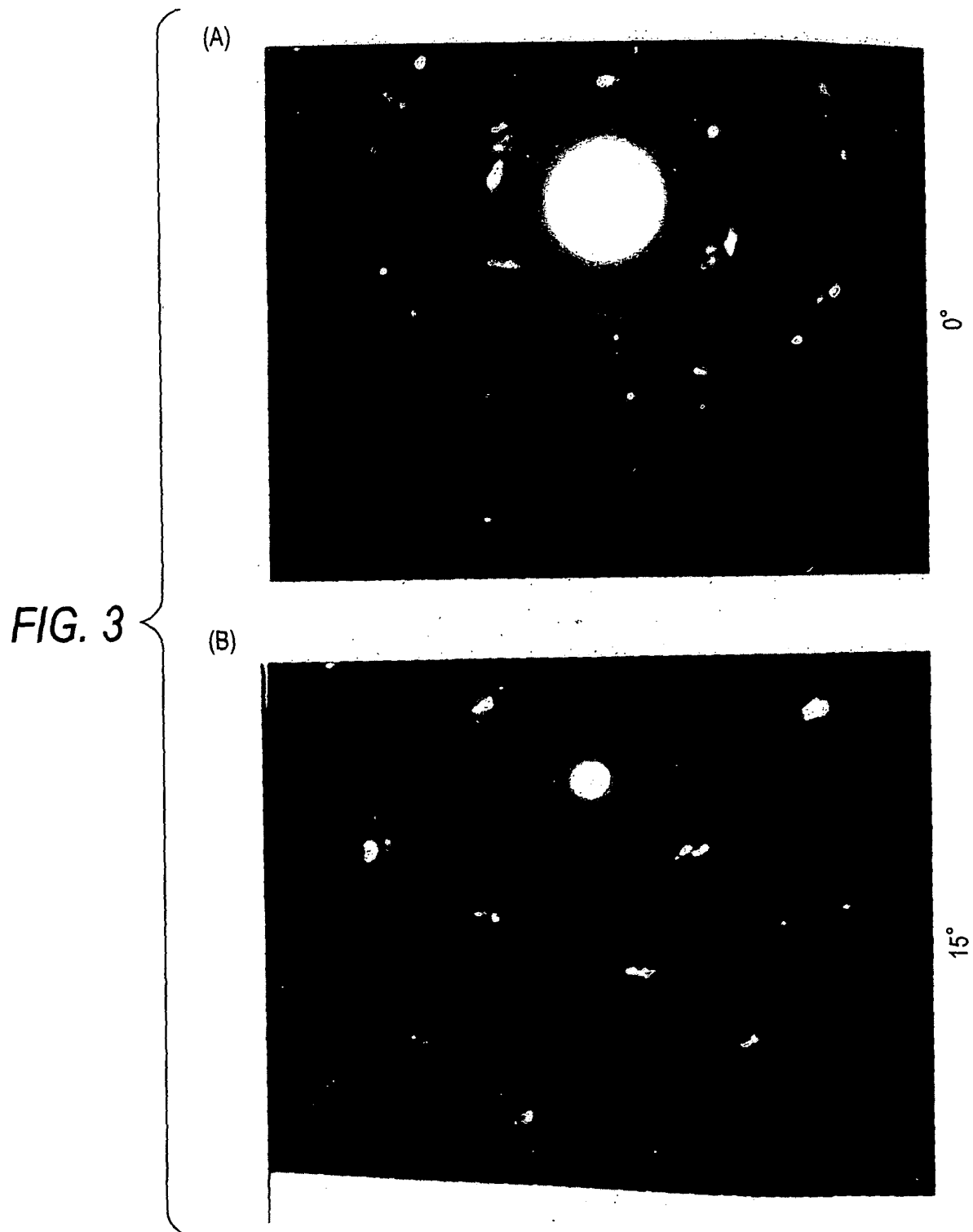
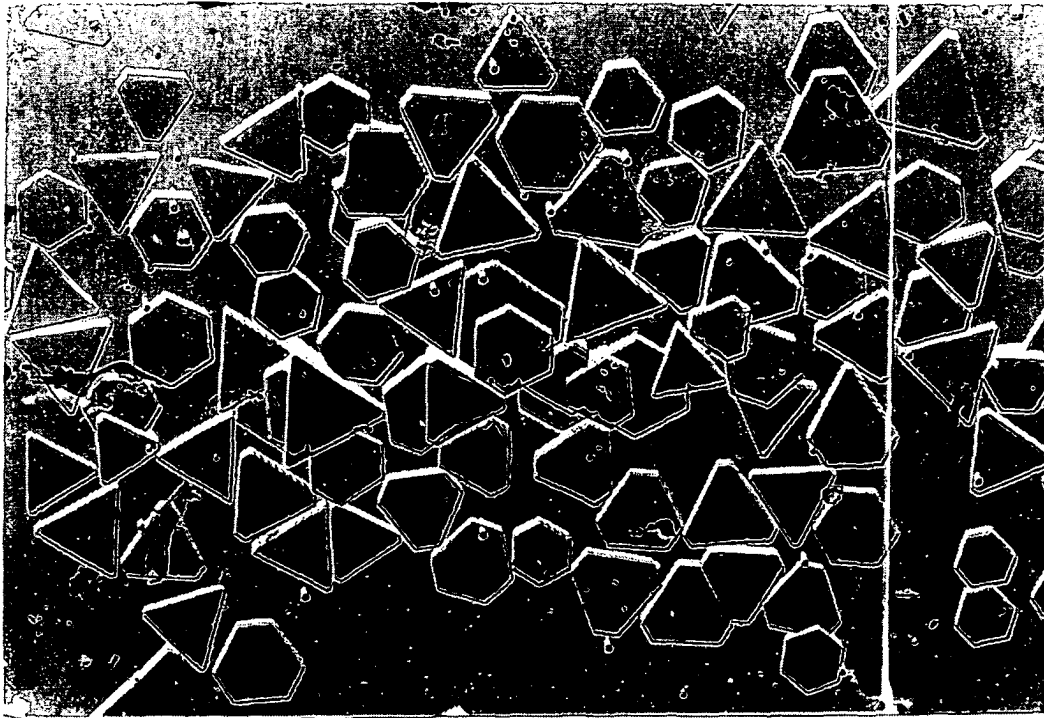
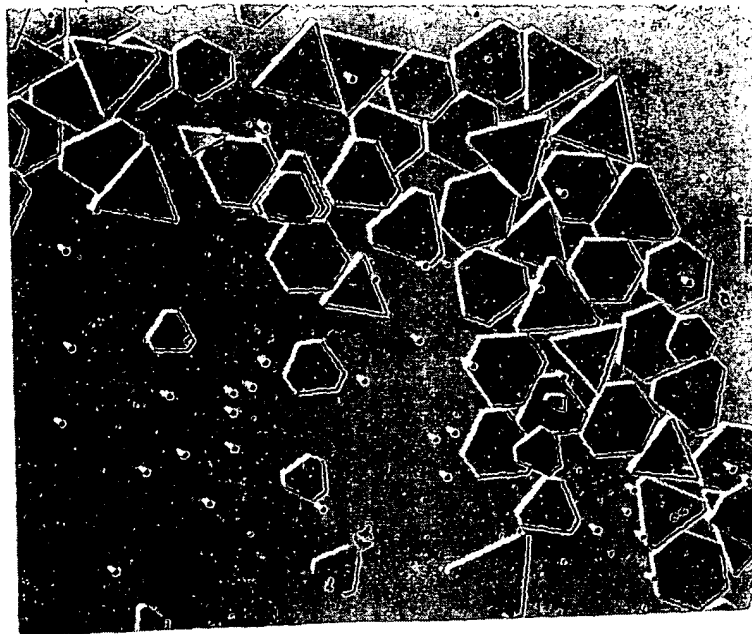


FIG. 4



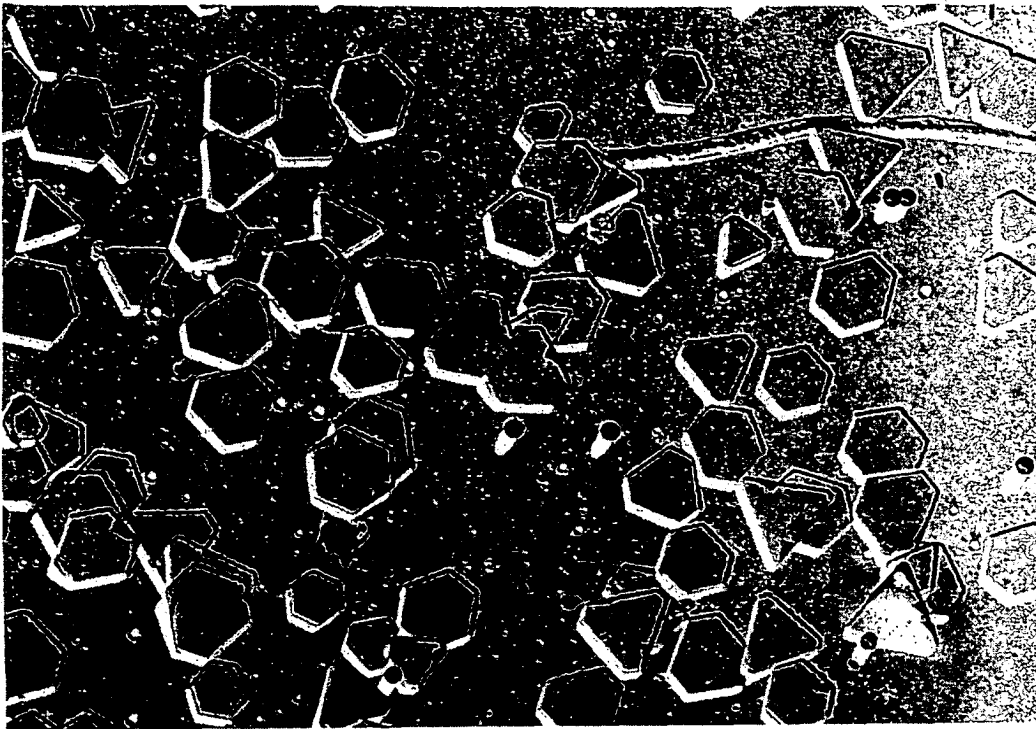
x 5400

FIG. 5



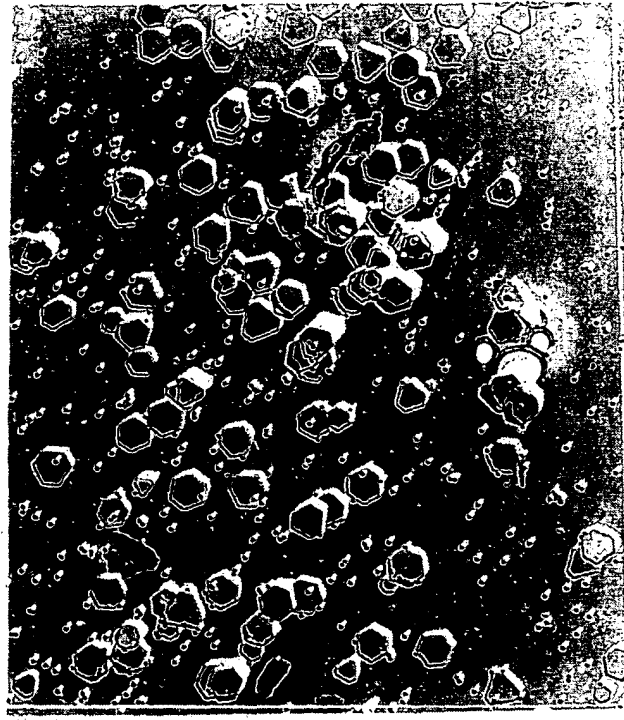
x 4100

FIG. 6



x 7500

FIG. 7



x 4000

FIG. 8

