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(54) Silver halide-photographic light-sensitive material.

(57) A silver halide photographic light-sensitive material improved in sensitivity, graininess and preservability is provided, comprising a support having thereon a silver halide emulsion layer containing silver halide tabular grains having a diameter of not less than 0.3 μm and a ratio of 1/d of less than 0.4, in which the the thickness of a tabular grain is denoted by d and the distance between the tabular grain's principal plane and its twin plane nearest to the principal plane is denoted by 1, and the tabular grains accounting for not less than 50% of the total projected area of silver halide grains contained in said emulsion layer.

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FIELD OF THE INVENTION

The present invention relates to a tabular grain light-sensitive silver halide emulsion having high sensitivity, graininess and preservability. Further, the present invention relates to a silver halide photographic light-sensitive material having high sensitivity, graininess and preservability.

BACKGROUND OF THE INVENTION

Giving a high sensitivity to a light-sensitive silver halide emulsion is the most useful means to improve a photographic light-sensitive material in various properties. For example, high-sensitivity color photographic light-sensitive materials used in recent years are developed by raising the sensitivity of an emulsion. And, with respect to image quality, it is widely known that graininess can be improved by use of a silver halide comprising small grains having a high sensitivity. Further, in the manufacture of X-ray photographic light-sensitive materials, a technique for raising the sensitivity of a light-sensitive silver halide emulsion is indispensable in maintaining high sensitivity and, concurrently, in providing high sharpness by reducing the amount of crossover light. Accordingly, there have so far been made a variety studies to raise the sensitivity of light-sensitive silver halide emulsions.

Especially, techniques for raising the sensitivity using tabular silver halide grains were often disclosed in recent years, examples of which can be seen in Japanese Pat. O.P.I. Pub. Nos. 111935/1983, 111936/1983, 111937/1983, 113927/1983 and 99433/1984.

Since these tabular silver halide grains have surface areas larger than those of the so-called regular silver halide grains including hexahedral and octahedral grains when compared in equal volumes, these can adsorb larger amounts of sensitizing dyes on their surfaces and, thereby, have an advantage of being highly sensitive.

Further, Japanese Pat. O.P.I. Pub. No. 92942/1988 discloses a technique to provide a high silver iodide content core inside of a tabular silver halide grain, and Japanese Pat. O.P.I. Pub. No. 151618/1988 discloses a technique to use hexagonal tabular silver halide grains, both of which are effective in providing high sensitivities. In addition, Japanese Pat. O.P.I. Pub. Nos. 106746/1988, 183644/1989 and 279237/1989 disclose techniques concerning the composition distribution of tabular silver halide grains.

With respect to the crystal structure of tabular silver halide grains, there have been disclosed several techniques which relate to parallel twin planes. Japanese Pat. O.P.I. Pub. No. 163451/1988 discloses a technique of employing tabular silver halide grains having two or more parallel twin plains in which the ratio of the distance between twin planes (a) to the grain thickness (b) is 5 or more. Described therein are a technique for raising the uniformity of distances between twin planes and the high sensitivity and improved graininess resulting therefrom.

WO No. 91/18320 describes that a high sensitivity is achieved by use of tabular silver halide grains in which the distance between twin planes is 0.012 μm or less. Japanese Pat. O.P.I. Pub. No. 165133/1993 describes a technique of using core/shell type twin silver halide grains in which the average of maximum distances between twin planes is 0.001 to 0.01 μm and the resultant improving effects in sensitivity, sharpness, pressure resistance, graininess, etc. These techniques aim at achievement of high sensitivities by narrowing the distance between twin planes.

Although various studies have been made as described above, the rise in sensitivity by use of tabular silver halide grains is mostly due to a spectral sensitizing effect, or an improvement in spectral sensitivity, and the rise in inherent sensitivity of silver halide grains themselves is still insufficient even when the above disclosed techniques are used. Accordingly, a further rise in inherent sensitivity of tabular silver halide grains themselves is indispensable for obtaining much higher sensitivities.

In order to raise the sensitivity of silver halide grains, it is useful to improve the uniformity of grains and, at the same time, it is also important to develop a technique for raising much more the sensitivity of individual silver halide grains.

Under such circumstances, the present inventors have conducted a study with close attention to individual silver halide grains, on the assumption that the relation between a principal plane and a twin plane may exert an influence upon the sensitivity.

SUMMARY OF THE INVENTION

Accordingly, a first object of the present invention is to provide a light-sensitive silver halide emulsion comprising tabular silver halide grains high in sensitivity and excellent in graininess and preservability, and a second object of the present invention is to provide a silver halide photographic light-sensitive material high in sensitivity and excellent in graininess and preservability.

The present invention is accomplished, through a study giving priority to the relation between a principal plane and a twin plane as stated above, by finding out the fact that the sensitivity is lowered as the distance between a principal plane and a twin plane becomes larger.

That is, the first object of the invention is attained by a light-sensitive silver halide emulsion comprising tabular grains in which the average projected area diameter is not less than 0.3 μm and the average of li/di values is less than 0.4, when the thickness of number i tabular grain is denoted by di and the distance between said tabular grain's principal plane and its twin plane nearest to the principal plane is denoted by li.

The second object of the invention is attained by a silver halide photographic light-sensitive material having a silver halide emulsion layer in which tabular grains having a diameter not less than 0.3 μm amount to 50% or more of the total projected area of the silver halide grains contained, and grains meeting the relation of l/d<0.4 amount to 50% or more of said tabular grains in number, when the thickness of the tabular grain is denoted by d and the distance between said tabular grain's principal plane and its twin plane nearest to the principal plane is denoted by 1.

Next, the invention is described in detail.

The light-sensitive silver halide emulsion of the invention may use any of those silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide, silver chloroiodobromide and silver chloride which are used in the usual silver halide emulsion. Among them, silver bromide, silver iodobromide and silver chloroiodobromide are particularly preferred.

The silver halide grains contained in the light-sensitive emulsion of the invention are tabular silver halide grains. The term tabular silver halide grains means grains having two parallel principal planes facing to each other, in which an average ratio of grain thickness to grain diameter, or an aspect ratio, is 1.3 or more, preferably 3 or more and more preferably in the range of 3 to 12.

In the invention, an average projected area diameter (hereinafter referred to as a grain size), which is given as the diameter of a circle corresponding to the projected area of said tabular silver halide grain (the diameter of a circle having the same projected area as said silver halide grain), is 0.3 μm or more, preferably in the range of 0.3 μm to 5 μm and more preferably in the range of 0.4 μm to 2 μm. In the invention said tabular grains having a diameter of 0.3 μm or more account for at least 50% of the total projected area of the grains contained in the emulsion layer, preferably not less than 60%, more preferably 70%.

The grain size can be determined by projecting said grain with an electron microscope at 10,000 to 70,000 power and then measuring the projected area on the print. The average grain size (ϕ) can be determined by the following equation:

$$\text{Average Grain Size } (\phi) = \Sigma nidi/n$$

where n is the number of test grains, and ni is the frequency of grains having a grain size of ϕi. (The number of test grains is 1,000 or more selected at random.)

Tabular silver halide grains belong to the twin crystal in crystallography. In the invention, twin crystals are silver halide crystals having one or more twin planes in a grain. The classification of forms of twin crystals is described in detail in Klein and Moisar, Photographishe Korrespondenz, Vol.99, P.99 and Vol.100, p.57.

The tabular silver halide grains of the invention have one or more twin planes in parallel to the principal plane. The twin plane can be observed with a transmission electron microscope: a typical method comprises the steps of preparing a sample by coating a light-sensitive silver halide emulsion on a support so as to have the principal planes of tabular silver halide grains contained oriented in parallel to the support, cutting off an about 0.1-μm thick section from the sample using a diamond cutter, and observing the section with a transmission electron microscope. When a grain has two or more twin planes, the twin plane according to the invention is the one nearest to the principal plane.

In the invention, the average of ratios of tabular grain thickness (d) to distance (1) between a principal plane and a twin plane nearest to the principal plane can be determined as follows: 100 or more tabular silver halide grains each having a cross section nearly perpendicular to the principal plane are arbitrarily selected by observing a section prepared as above using a transmission electron microscope, a d/l ratio is measured on each grain, and an averaging value is determined from measured values.

In the embodiment of the invention, the l/d ratio is less than 0.4, preferably in the range of 0.1 to less than 0.4 and more preferably in the range of 0.15 to 0.39. The proportion of grains which meet the relation of l/d < 0.4 can be determined by observing with a transmission electron microscope and counting the number of grain sections as mentioned above. In the embodiment of the invention, the percentage of grains meeting l/d < 0.4 is preferably 50% or more by number of grains. Thus, when the percentage is 50% or more, there have been remarkably achieved advantageous effects of the invention such as improved sensitivity and graininess and less lowering of sensitivity under high temperature and high humidity. The percentage of grains meeting l/d < 0.4 is more preferably 60% or more, further more preferably 70% or more.

The light-sensitive silver halide emulsion of the invention can be prepared by placing an aqueous solution containing a protective colloid and, if necessary, a seed emulsion in a reaction vessel, and adding thereto silver ions, halogen ions and, if necessary, a fine grain emulsion and a silver halide solvent to form grains through the steps of nucleus formation, Ostwald's ripening and grain growth.

In manufacturing the light-sensitive silver halide emulsion of the invention, there can be employed various methods which are well known in the art. That is, the single jet method, the double jet method and the triple jet method can be arbitrarily combined. Further, a method, which controls the pH and pAg of a reaction liquor where silver halide is formed correspondingly to the growth rate of the silver halide, can also be combined.

Moreover, the silver halide composition of grains may be varied by applying the conversion method anytime during silver halide formation. Or, halide ions and silver ions may be added in the form of silver halide fine grains.

In the manufacture of light-sensitive silver halide emulsion of the invention, it is necessary to control the distance between a principal plane and a twin plane of a tabular grain as well as the thickness of a tabular grain. In order to achieve them, it is necessary to control the formation and growth of principal plane and twin plane.

The twin plane can be controlled, no matter whether a seed emulsion is used or not, by appropriately selecting factors, which exert influences upon the supersaturation state at the time of nucleus formation, such as gelatin concentration, temperature, iodine ion concentration, pBr, ion supplying rate, stirring rate, kind of gelatin, as well as by selecting a proper combination of amounts and kinds of adsorptive additives. Further, this control can also be made by properly selecting the conditions of Ostwald's ripening and grain growth, such as gelatin concentration, temperature, iodine ion concentration, pBr, ion supplying rate, stirring rate, kind of gelatin, kind and amount of silver halide solvent. Details of supersaturation factors can be seen, for example, in the specifications of Japanese Pat. O.P.I. Pub. Nos. 92942/1988 and 213637/1984.

The principal plane can be controlled by properly selecting factors, such as gelatin concentration, temperature, iodine ion concentration, pBr, ion supplying rate, stirring rate, kind of gelatin, kind and amount of silver halide solvent, throughout the whole process including nucleus formation, Ostwald's ripening and grain growth.

In the manufacture of light-sensitive silver halide emulsion of the invention, there can be used a seed emulsion, which is prepared by a method well known in the art such as the single jet method or the controlled double jet method. The halide composition of the seed emulsion may be arbitrarily selected from silver bromide, silver iodide, silver chloride, silver iodobromide, silver chlorobromide, silver chloroiodide and silver chloroiodobromide. Among them, preferred are silver bromide and silver iodobromide.

When a seed emulsion is used, such a seed emulsion preferably comprises grains having twin planes. The shape of seed grains is not particularly limited. In manufacturing the light-sensitive silver halide emulsion of the invention using a seed emulsion, silver halide nuclei are formed in the step of manufacturing the seed emulsion; therefore, the twin plane can be controlled by selecting an appropriate combination of factors exerting influences upon the supersaturation state during nucleus formation, such as gelatin concentration, temperature, iodine ion concentration, pBr, ion supplying rate, stirring rate, kind of gelatin, etc.

In the embodiment of the invention, the grain size distribution of tabular silver halide grains is preferably 25% or less, more preferably 20% or less and most preferably 15% or less. The grain size distribution is given by the equation of:

Grain Size Distribution (%) = (Standard Deviation of Grain Size/Average Grain Size) × 100

The tabular silver halide grains of the invention may be uniform in halide composition, or may contain localized silver iodide, but preferred are those in which silver iodide is localized at their centers.

In the manufacture of the tabular silver halide grains, silver halide solvents, such as ammonia, thioether and thiourea, may be used if necessary.

The silver halide grains used in the light-sensitive silver halide emulsion of the invention may contain a metallic element at their inner portions and/or surfaces; that is, metallic ions may be incorporated in these grains by adding at least one metallic salt or metallic complex salt selected from cadmium salts, zinc salts, lead salts, thallium salts, iridium salts (including complex salts), rhodium salts (including complex salts) and iron salts (including complex salts), in the process of forming grains and/or the process of growing grains. Or, there may be formed reduction-sensitized specks at inner portions and/or surfaces of grains by placing these grains in a reducing environment.

In carrying out the invention, gelatins are favorably used as the dispersion medium for a protective colloid of silver halide grains. Suitable gelatins include alkali-processed gelatins, acid-processed gelatins, low molecular weight gelatins (molecular weight: 20,000 to 100,000) and phthalated gelatins. Other types of hydrophilic colloids can also be used, examples of which include those described in Research Disclosure (hereinafter referred to as RD), Vol.176, No.17643 (Dec., 1978).

The light-sensitive silver halide emulsion of the invention may be subjected, after grains have grown, to desalting for the removal of soluble salts, or it may contain soluble salts left unremoved. When such salts are removed, desalting can be performed according to the method described in RD, Vol.176, No.17643 (Dec., 1978).

The silver halide photographic light-sensitive material of the invention is a silver halide photographic light-sensitive material containing the foregoing light-sensitive silver halide emulsion of the invention and includes, for example, black-and-white silver halide photographic light-sensitive materials (e.g., light-sensitive materials for X-ray photography, light-sensitive materials for printing, negative light-sensitive materials for popular use), color photographic light-sensitive materials (e.g., color negative light-sensitive materials, color reversal light-sensitive materials, light-sensitive materials for color printing), light-sensitive materials for diffusion transfer, and heat-developable light-sensitive materials.

In making the silver halide photographic light-sensitive material which uses the light-sensitive silver halide emulsion of the invention, the light-sensitive silver halide emulsion is subjected to physical ripening, chemical ripening and spectral sensitization and, further, various additives are added thereto according to specific requirements. Suitable additives and other materials include, for example, those shown in RD Nos. 17643 (Dec.,1978), 18716 (Nov.,1978) and 308119 (Dec.,1989). Locations where there are shown are as follows:

Additives	RD-17643		RD-18716		RD-308119	
	Page	Class.	Page	Class.	Page	Class.
Chemical sensitizers	23	III	648 upper right		996	III
Sensitizing dyes	23	IV	648-649		996-8	IV
Desensitizing dyes	23	IV			998	IV
Dyes	25-26	VIII	649-650		1003	VIII
Development accelerators	24	XXI	649 upper right			
Antifoggants ·stabilizers	24	IV	649 upper right		1006-7	VI
Whitening agents	24	V			998	V
Hardeners	26	X	651 left		1004-5	X
Surfactants	26-7	XI	650 right		1005-6	XI
Antistatic agents	27	XII	650 right		1006-7	XIII
Plasticizers	27	XII	650 right		1006	XII
Slipping agents	27	XII				
Matting agents	28	XVI	650 right		1008-9	XVI
Binders	26	XXII			1003-4	IX
Supports	28	XVII			1009	XVII

EXAMPLES

The following examples illustrate the various aspects of the invention but are not intended to limit it.

Example 1

Preparation of Tabular Twin Crystal Seed Emulsion (Seed Emulsion T-1)

Seed emulsion T-1 comprising tabular twin crystals was prepared in the following manner:

Solution A1	
Ossein gelatin	24.2 g
Deionized water	9657 ml
Sodium polypropyleneoxy-polyethyleneoxy-disuccinate (10% ethanol solution)	6.78 ml
KBr	10.8 g
10% Nitric acid	114 ml
Solution B1	
2.5N Aqueous $AgNO_3$	2825 ml
Solution C1	
KBr	824 g
KI 23.5 g	
Deionized water is added to make up to 2825 ml	
Solution D1	
1.75N Aqueous KBr	an amount to control the silver potential as described later

Using a stirring machine described in Japanese Pat. Exam. Pub. Nos. 58255/1983 and 58289/1983, nuclei were formed by adding 463.3 ml each of solutions B1 and C1 to solution A1 in 2 minutes at 35°C according to the double jet method.

After stopping the addition of solutions B1 and C1, the temperature of solution A1 was raised to 60°C in 60 minutes, and then the pH was adjusted to 5.0 with 3% aqueous KOH. Subsequently, solutions B1 and C1 were added again by the double jet method at addition rates of 55.4 ml/min, respectively. During the heating from 35°C to 60°C and during the re-addition of solutions B1 and C1 by the double jet method, the silver potential was maintained at +8 mv and +16 mv, respectively, by the addition of solution D1.

After the addition, the pH was adjusted to 6 with 3% aqueous KOH, followed by desalting and washing. The resultant seed emulsion comprised grains having an average grain size of 0.59 µm and an average aspect ratio of 9.8.

Preparation of Tabular Twin Crystal Seed Emulsions (Seed Emulsions T-2 to T-13)

Seed emulsions T-2 to T-13 each comprising tabular twin crystals were prepared by varying the amount of gelatin, kind of gelatin and amount of KBr contained in solution A1, addition rate, addition time, temperature and silver potential in the preparation of seed emulsion T-1.

Preparation of Grown Emulsions (Emulsions EM-1 to EM-13)

Grown emulsion EM-1 was prepared from seed emulsion T-1 by the following procedure:

In an aqueous gelatin solution of 60°C containing sodium polypropyleneoxy-polyethyleneoxy-disuccinate was dissolved 0.11 mol equivalent of seed emulsion T-1 per mol silver of grown emulsion to be prepared. Then, a silver nitrate solution and a halide solution containing potassium bromide and potassium iodide, which had been prepared so as to give an average silver iodide content of 1.55 mol% finally, were added in 107 minutes by the controlled double jet method with the reaction liquor maintained at pH 5.8, pAg 8.8 and 60°C. Obtained was emulsion EM-1 comprising tabular silver iodobromide grains having an average grain size of 1.03 μm and an average aspect ratio of 4.83.

Emulsions EM-2 to EM-13 comprising tabular silver iodobromide grains were prepared by repeating the procedure of emulsion EM-1, except that seed emulsions T-2 to T-13 were used by turns in place of seed emulsion T-1, and that the pAg and addition time were varied.

Emulsions EM-1 to EM-13 were desalted by the usual method and then re-dispersed under the conditions of 50°C, pAg 7.8 and pH 5.85.

The resultant emulsions EM-1 to EM-6 were made into respective sections according to the method described above, and the sections were observed with a transmission electron microscope to determine the average of ratios of tabular grain thickness (d) to distance between a principal plane and a twin plane nearest to the principal plane (1). The results obtained are shown in Table 1.

Table 1

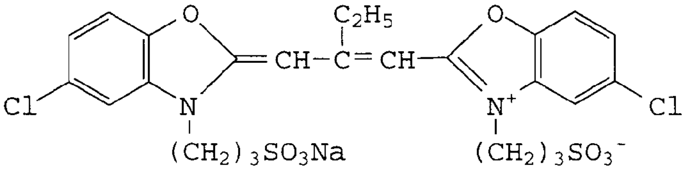
Emulsion	Grain diameter	[1/d]* av.	[1/d<0.4]**	
EM-1	1.03	0.45	35%	Comparison
EM-2	1.03	0.39	55%	Invention
EM-3	1.14	0.38	58%	Invention
EM-4	1.39	0.35	60%	Invention
EM-5	1.35	0.34	71%	Invention
EM-6	1.14	0.33	84%	Invention
EM-7	1.12	0.24	90%	Invention
EM-8	1.16	0.19	92%	Invention
EM-9	1.15	0.14	92%	Invention
EM-10	0.35	0.33	81%	Invention
EM-11	0.35	0.42	43%	Comparison
EM-12	0.27	0.35	62%	Comparison
EM-13	0.27	0.45	34%	Comparison

* The average of 1/d

** Percentage of grains meeting 1/d < 0.4

Subsequently, each of these emulsions was spectrally sensitized by adding an optimum amount of methanol solution of the following spectral sensitizing dye (I), and then subjected to gold or sulfur sensitization under an optimum condition using ammonium thiocyanate, chloroauric acid or sodium thiosulfate. After the sensitization, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added to each emulsion in an amount of 1.0 g per mol of silver.

Spectral sensitizing dye (I)

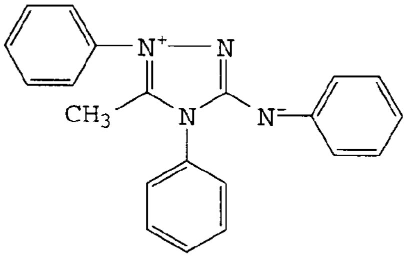
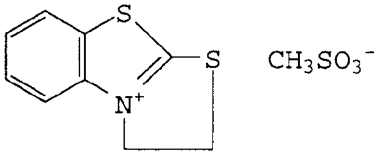


Emulsions EM-1 to EM-13 were made into coating solutions for emulsion layer by adding additives shown below. Thus, as shown in Table 2, emulsions were blended and then additives were added thereto to prepare the coating solutions. A coating solution for protective layer shown below was prepared at the same time. Both solutions were coated simultaneously and double-sidedly on a support at a speed of 80 m/min using two sliding hopper type coaters so as to give a silver weight of 2.0 g/m^2 and a gelatin coating weight of 3.1 g/m^2 on one side, followed by drying for 2 minutes and 20 seconds. Sample Nos.l to 6 were thus obtained. The support used was prepared by coating, on a polyethylene terephthalate film base for X-ray photography having a thickness of 175 μm and tinted with blue to a density of 0.15, a subbing solution comprising a 10 wt% aqueous dispersion of a copolymer having a monomer ratio of 50 wt% glycidyl methacrylate, 10 wt% methyl methacrylate and 40 wt% butyl methacrylate.

Table 2

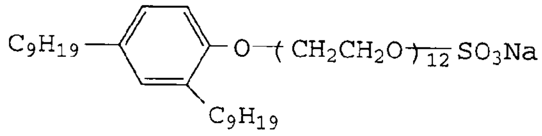
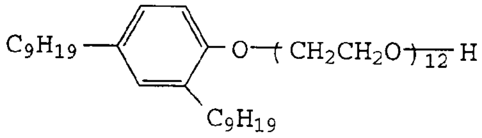
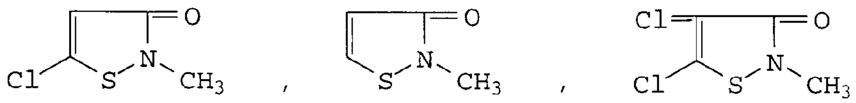
Sample No.	Emulsion	Blend ratio	[l/d<0.4]	
14	EM-1/EM-5	25/75	62%	Invention
15	EM-1/EM-5	50/50	53%	Invention
16	EM-1/EM-5	75/25	44%	Comparison

The additives employed in the emulsions are as follows. Addition amounts are shown in amounts per mol of silver halide.

1,1-Dimethylol-1-bromo-1-nitromethane	70 mg
t-Butyl-catechol	400 mg
Polyvinylpyrrolidone	1.0 g
Styrene-maleic anhydride copolymer	2.5 g
Nitrophenyl-triphenylphsphonium chloride	50 mg
Ammonium 1,3-dihydroxybenzene-4-sulfonate	2 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	1.5 g
	150 mg
	70 mg
$C_4H_9OCH_2CH(OH)CH_2N(CH_2COOHH)_2$	1 g
1-Phenyl-5-mercaptotetrazole	15 mg

Coating Solution for Protective Layer

Next, a coating solution for protective layer of the following composition was prepared. Amounts of additives are per liter of coating solution.

Lime-processed inert gelatin	68 g
Acid-processed gelatin	2 g
Sodium i-amyl-n-decylsulfosuccinate	1 g
Polymethyl methacrylate (matting agent, area average particle size: 3.5 μm)	1.1 g
Silicon dioxide particles (matting agent, area average particle size: 1.2 μm)	0.5 g
RUDOX AM (colloidal silica made by E.I.Du Pont de Nemours and Co.)	30 g
$(CH_2=CHSO_2CH_2)_2O$ (hardener)	500 mg
$C_4F_9SO_3K$	2 mg
$C_{12}H_{25}CONH(CH_2CH_2O)_5H$	2.0 g
	1.0 g
	0.4 g
 (50:46:4)	0.1 g

Photographic properties of these samples Nos.1 to 16 were also evaluated.

Each sample was held between two intensifying screens (KO-250) and then irradiated, through an aluminum wedge, in 0.05 second with X-rays at a tube voltage of 80 kvp and a tube current of 100 mA, followed by processing with the following developer and fixer in an automatic processor (SR X-502).

Developer Recipe

Part-A (to be made up to 12 liters)

Potassium hydroxide	450 g
Potassium sulfite (50% solution)	2280 g
Diethylenetetraminepentaacetic acid	120 g
Sodium hydrogencarbonate	132 g
5-Methylbenzotriazole	1.2 g
1-Phenyl-5-mercaptotetrazole	0.2 g
Hydroquinone	340 g
Water is added to make up to	5000 ml

Part-B (to be made up to 12 liters)

Glacial acetic acid	170 g
Triethylene glycol	185 g
1-Phenyl-3-pyrazolidone	22 g
5-Nitroindazole	0.4 g

Starter	
Glacial acetic acid	120 g
Potassium bromide	225 g
Water is added to make up to	1.01 liter

Fixer Recipe	
Part-A (to be made up to 18 liters)	
Ammonium thiosulfate (70 wt/vol%)	6000 g
Sodium sulfite	110 g
Sodium acetate trihydrate	450 g
Sodium citrate	50 g
Gluconic acid	70 g
1-(N,N-dimethylamino)-ethyl-5-mercaptotetrazole	18 g
Part-B	
Aluminum sulfate	800 g

Developer part-A and part-B were simultaneously added to about 5 liters of water, water was added thereto with stirring to make up 12 liters, and the pH was adjusted to 10.40 with glacial acetic acid. A developing replenisher was thus obtained.

To 1 liter of this developing replenisher was added the above starter in an amount of 20 ml/l. The pH was then adjustment to 10.26 to obtain a solution ready for use.

To prepare a fixer, fixer part-A and part-B were added simultaneously to about 5 liters of water, and water was added thereto with stirring to make up 18 liters, followed by pH adjustment to 4.4 with sulfuric acid and sodium hydroxide. Obtained was a fixing replenisher ready for use.

Temperatures of the respective processes were developing: 35°C, fixing: 33°C, washing: 20°C and drying: 50°C. Processing time was 45 seconds in terms of dry to dry.

The processed samples were subjected to sensitometry, in which the sensitivity was given by a reciprocal of the exposure necessary to obtain a density of fog + 0.5 and expressed in a value relative to the sensitivity of sample No.1 which was set at 100. The results are shown in Table 3.

Table 3

Sample	Sensitivity	
No-1	100	Comparison
No-2	115	Invention
No-3	125	Invention
No-4	132	Invention
No-5	138	Invention
No-6	140	Invention
No-7	145	Invention
No-8	150	Invention
No-9	159	Invention
No-10	41	Invention
No-11	25	Comparison
No-12	10	Comparison
No-13	10	Comparison
No-14	132	Invention
No-15	124	Invention
No-16	102	Comparison

It can be understood from the table that sample Nos.2 to 9, and sample No.10 according to the invention have higher sensitivities when compared with samples No.1 and No.11, respectively.

It is noted from the comparison of sample Nos.12 and 13 that when the grain diameter is less than 0.3 μm, high sensitivity cannot be accomplished even when the percentage of grains which meet l/d < 0.4 is 50% or more. It is further noted from the comparison of sample Nos.14 to 16 that even when blended emulsions are used, effects of the present invention can be achieved when the percentage of grains meeting l/d < 0.4 is 50% or more.

Subsequently, each sample was divided into two portions, which were then stored for 7 days under the following different conditions, respectively:

Condition A: 23°C, 55% RH

Condition B: 40°C, 80% RH

After storing, the samples were subjected to exposure, development and sensitometry in the same manner as the above. The difference in sensitivity between condition A and condition B was determined on each sample, and recorded as a value relative to the difference in sensitivity of sample No.1 which was set at 100. The results are shown in Table 4, where the fluctuation in sensitivity becomes smaller as the value becomes smaller.

Table 4

Sample	Sensitivity fluctuation	
No-1	100	Comparison
No-2	91	Invention
No-3	89	Invention
No-4	86	Invention
No-5	79	Invention
No-6	77	Invention
No-7	75	Invention
No-8	71	Invention
No-9	66	Invention
No-10	88	Invention
No-11	102	Comparison
No-12	105	Comparison
No-13	104	Comparison
No-14	88	Invention
No-15	89	Invention
No-16	100	Comparison

It will be understood that sample Nos.2 to 10 according to the invention are less in sensitivity fluctuation and excellent in stability, as compared with sample Nos.1, 11, 12 and 13, even when stored under high temperature and high humidity conditions. Sample Nos.14 and 15 are also less in sensitivity fluctuation and superior as compared to sample No.16. This was an unexpected outcome which had not been intended by the invention.

Example 2

Preparation of Grown Emulsions (Emulsions EM-14 to EM-19)

Using seed emulsion T-1 prepared in Example 1, emulsion EM-14 was prepared in the following manner:

In an aqueous gelatin solution of 60°C containing sodium polypropyleneoxy-polyethyleneoxy-disuccinate was dissolved 0.11 mol equivalent of seed emulsion T-1 per mol silver of grown emulsion to be prepared. Then, a silver nitrate solution and a halide solution containing potassium bromide and potassium iodide, which had been prepared so as to give an average silver iodide content of 4.5 mol% finally, were added in 107 minutes by the controlled double jet method with the reaction liquor maintained at pH 5.8, pAg 8.8 and 60°C. The resultant emulsion EM-14 comprised tabular silver iodobromide grains having an average grain size of 0.86 μm and an average aspect ratio of 3.13.

Emulsions EM-15 to EM-19 comprising tabular silver iodobromide grains were prepared by repeating the procedure of emulsion EM-14, except that seed emulsions T-2 to T-6 were used by turns in place of seed emulsion T-1, and that the pAg and addition time were varied.

These emulsions EM-14 to EM-19 were subjected to desalting by the usual method and then redispersed under the conditions of 40°C, pAg 7.8 and pH 5.85.

The resultant emulsions EM-14 to EM-19 were made into sections according to the method described above, and the sections were observed with a transmission electron microscope to determine the average of ratios of tabular grain thickness (d) to distance between a principal plane and a twin plane nearest to the principal plane (1) and the percentage of grains which meet l/d < 0.4. The results are shown in Table 4.

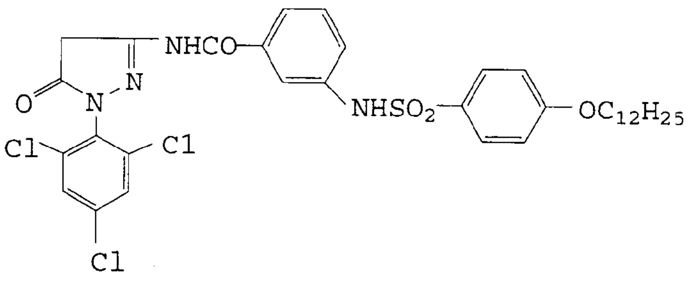
Table 5

Emulsion	[l/d]* av.	[l/d<0.4]**	
EM-14	0.46	35%	Comparison
EM-15	0.39	56%	Invention
EM-16	0.38	57%	Invention
EM-17	0.36	60%	Invention
EM-18	0.34	71%	Invention
EM-19	0.33	82%	Invention

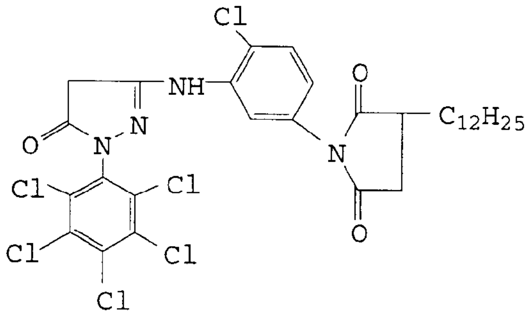
Subsequently, each of these emulsions was spectrally sensitized by adding an optimum amount of methanol solution of the following spectral sensitizing dye (I), and then subjected to gold or sulfur sensitization under an optimum condition using ammonium thiocyanate, chloroauric acid or sodium thiosulfate. After the sensitization, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added to each emulsion in an amount of 1.0 g per mol of silver. Each of the resultant emulsions EM-14 to EM-19 was made into a coating solution by adding additives so as to give the following composition and then coated on a triacetyl cellulose film support. Sample Nos.17 to 22 were thus obtained. The addition amounts shown below are grams per square meter unless otherwise indicated. The amount of silver halide is expressed in an amount of silver present.

Emulsion	1.27
Magenta coupler M-1	0.336
Magenta coupler M-2	0.256
Colored magenta coupler CM-1	0.048
High boiling solvent Oil-1	1.08
High boiling solvent Oil-2	0.048
Gelatin	2.00

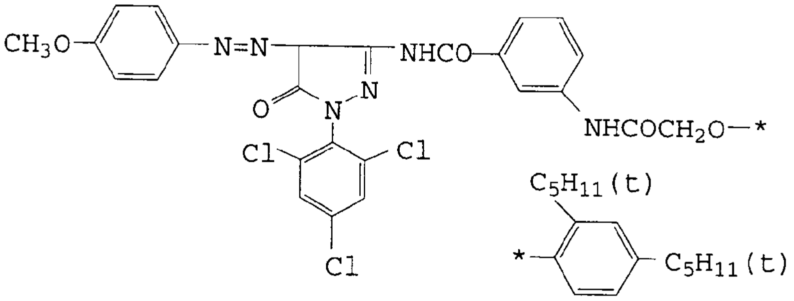
M-1



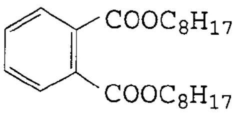
M-2



CM-1



Oil-1



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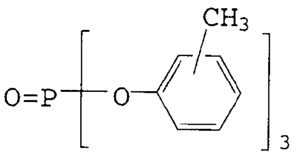

These samples were exposed to white light, processed by the following processes, subjected to sensitometry and subjected to evaluation of RMS graininess.

Processing (at 30°C)	
Color developing	2 min 40 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec
Drying	

Compositions of processing solutions used in the respective processes were as follows:

Color Developer	
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine·1/2sulfate	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

Water is added to make up to 1 liter, and the pH is adjusted to 10.0.

Bleacher	
Ammonium ferric ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g

Water is added to make up to 1 liter, and the pH is adjusted to 6.0 with aqueous ammonia.

Fixer	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g

Water is added to make up to 1 liter, and the pH is adjusted to 6.0 with acetic acid.

Stabilizer

Formalin (37% aqueous solution)	1.5 ml
Koniducks (product of Konica Corp.)	7.5 ml

Water is added to make up to 1 liter.

The sensitivity is given as a reciprocal of exposure to give a density of fog density + 1.0 and recorded as a value relative to the sensitivity of sample No.7 which is set at 100. The RMS graininess is a value 1000 times the fluctuation in density when a density of minimum density + 1.0 is scanned using a microdensitometer having an opening aperture scanning area of 250 μm, and is expressed in a value relative to the RMS value of sample No.17 which is set at 100. The evaluation results are shown in Table 6.

Table 6

Sample	Sensitivity	RMS Graininess	
No-17	100	100	Comparison
No-18	109	94	Invention
No-19	121	93	Invention
No-20	130	91	Invention
No-21	135	89	Invention
No-22	137	88	Invention

It can be understood from the table that sample Nos.18 to 22 according to the invention have higher sensitivities and better RMS graininesses when compared with sample No.17.

Claims

1. A silver halide photographic light-sensitive material comprising a support having thereon a silver halide emulsion layer, wherein said silver halide emulsion layer comprises silver halide tabular grains having a diameter of not less than 0.3 μm and a ratio of 1/d of less than 0.4, in which the the thickness of a tabular grain is denoted by d and the distance between the tabular grain's principal plane and its twin plane nearest to the principal plane is denoted by 1, accounting for not less than 50% of the total projected area of silver halide grains contained in said emulsion layer.

2. The photographic material of claim 1, wherein said tabular grains have an average aspect ratio of 3 or more.

3. The photographic material of claim 2, wherein the aspect ratio is 12 or less.

4. The photographic material of claim 1, wherein said tabular grains have a diameter of 0.3 to 5 μm.

5. The photographic material of claim 4, wherein said tabular grain have a diameter of 0.4 to 2 μm.

6. The photographic material of claim 1, wherein the ratio of 1/d is 0.15 to 0.39.

7. The photographic material of claim 1, wherein said tabular grains having a diameter of not less than 0.3 μm account for not less than 60% of the total projected area of the grains.

8. A silver halide photographic light-sensitive material comprising a support having thereon a silver halie emulsion layer, wherein said silver halide emulsion layer comprises silver halide tabular grains having a diameter of 0.3 to 5μm, an aspect ration of 3 to 12 and a ratio of 1/d of 0.15 to 0.39, when the the thickness of a tabular grain is denoted by d and the distance between the tabular grain's principal plane and its twin plane nearest to the principal plane is denoted by 1, accounting for not less than 50% of the total projected area of silver halide grains contained in said emulsion layer.