(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 462 543 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **91109909.1**

(51) Int. Cl.[5]: **G03C 1/015**, G03C 1/035

(22) Date of filing: **17.06.91**

(30) Priority: **18.06.90 JP 159360/90**

(43) Date of publication of application:
27.12.91 Bulletin 91/52

(84) Designated Contracting States:
DE FR GB

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

(72) Inventor: **Ito, Yoshiro, c/o Konica Corporation**
No. 1, Sakura-machi
Hino-shi, Tokyo 191(JP)
Inventor: **Matsuzaka, Syoji, c/o Konica Corporation**
No. 1, Sakura-machi
Hino-shi, Tokyo 191(JP)

(74) Representative: **Henkel, Feiler, Hänzel & Partner**
Möhlstrasse 37
W-8000 München 80(DE)

(54) Silver halide emulsions having high sensitivity and pressure resistance.

(57) The present invention is disclosed a silver halide emulsion that contains silver halide grains having a seed phase. The improvement is that said silver halide grains have not been subjected to either desalting or washing with water prior to the completion of the formation of the silver halide grains.

EP 0 462 543 A1

BACKGROUND OF THE INVENTION

This invention relates to silver halide emulsions which can advantageously be coated on supports to form silver halide photographic materials. This invention relates particularly to silver halide emulsions that have high sensitivity and pressure resistance.

A class of silver halide emulsions conventionally known to have high sensitivity are core/shell emulsions that comprise grains having a "core/shell" structure which have a high AgI content phase in the interior surrounded by a low AgI content phase as shown in Unexamined Published Japanese Patent Application No. 138538/1985. From the viewpoint of high sensitivity, monodisperse emulsions are known to be preferred as reported on page 91 of "Interactions Between Light and Materials", which is the preprint for the 1980 Tokyo Symposium on the Advances in Photography.

As also shown in Unexamined Published Japanese Patent Application No. 138538/1985, supra, monodisperse core/shell emulsions can be produced by a process which consists of the step of nucleation using seeds and the step of crystal growth, with desalting and washing with water being effected in each step. This process is not only cost-effective in large-scale production but also capable of achieving an improvement in monodispersity.

However, the conventional silver halide emulsions containing core/shell grains of the type described above have not been completely satisfactory in pressure resistance and suffer from the problem of fogging by pressure. Further, the emulsions prepared by the prior art method described above have also not been completely satisfactory in sensitivity.

SUMMARY OF THE INVENTION

An object, therefore, of the present invention is to provide silver halide emulsions that have high sensitivity and which yet have sufficiently good pressure resistance to be free from the problem of fogging by pressure.

This object of the present invention can be attained by a silver halide emulsion that contains silver halide grains having a seed phase, which emulsion is characterized in that said silver halide grains have not been subjected to either desalting or washing with water prior to the completion of the formation of the silver halide grains.

DETAILED DESCRIPTION OF THE INVENTION

The term "silver halide grains having a seed phase" as used herein means those silver halide grains which are formed by a process consisting of two separate steps, nucleation and crystal growth, and which consist of a nuclear seed phase and a portion that has grown from said phase. An emulsion composed of such silver halide grains having a seed phase may be prepared by a process that comprises the steps of nucleation, separating the resulting emulsion into three or more portions, storing them for at least one day, and permitting crystals to grow from one of the divided portions. In this process, the step of crystal growth following nucleation may be performed in several stages.

The term "seed phase" as used in the present invention means grains in a silver halide emulsion that has been separated into three or more portions at a stage prior to the completion of crystal growth and which is subsequently stored for at least one day.

The silver halide emulsion of present invention contains silver halide grains that have a seed phase as defined above and that have not been subjected to either desalting or washing with water prior to the completion of crystal growth stage. This emulsion can be obtained by a process that does not contain either the step of desalting or the step of washing with water prior to the completion of crystal growth.

The mechanism behind the present invention is not completely clear but probably the absence of the steps of desalting and washing with water prior to the completion of the crystal growth stage of silver halide grains will contribute to a substantial decrease in lattice imperfections and defects, thereby producing an emulsion having satisfactory sensitivity and high resistance to fogging by pressure.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in detail. In the following description, those silver halide grains which have a seed phase and which have not been subjected to either desalting or washing with water prior to the completion of their crystal growth stage will be referred to as the "silver halide grains of the present invention".

The silver halide grains of the present invention have a seed phase. A seed phase is formed when grains are formed from seed grains. An example of the method for forming grains using seed grains is described in Unexamined Published Japanese Patent Application No. 138538/1985, supra, in which grain growth is effected starting from seed grains. The seed grains may have any silver halide composition (they do not necessarily have to contrain silver iodide or to be composed of silver bromide).

The nuclei to be formed in the nucleation stage for the process of forming the silver halide grains of the present invention may have any silver halide composition and it is also unnecessary for them to contain silver iodide or to be composed of silver bromide. Preferably they are composed of silver iodobromide with a silver iodide content of at least 20 mol%, preferably at least 30 mol%.

The silver halide grains of the present invention may have any silver halide composition. Preferably, they comprise silver iodobromide, silver iodochloride, silver chloroiodobromide and other compositions that contain silver iodide, and silver iodobromide and silver chloroiodobromide are used with particular advantage.

The silver halide grains of the present invention are preferably core/shell grains having a high I content phase (which may be a nuclear seed phase) that is surrounded by a shell forming the outermost layer. More preferred are core/shell silver halide grains in which the core forming a high AgI content phase (which core is hereinafter referred to as the "high I core") has a AgI content of at least 10 mol%, more preferably at least 15 mol%, and most preferably at least 20 mol%. The shell preferably has a AgI content of not more than 10 mol%, more preferably not more than 7 mol%. The shell of such core/shell grains preferably accounts for 10 - 90% of the total volume of the grains, with 15 - 80% being more preferred and 20 - 70% being particularly preferred.

Also preferred are silver halide grains in which the high I core is separated from the shell by an intermediate layer having a AgI content somewhere between the AgI contents of the core and the shell. In this case, the intermediate layer preferably accounts for 3 - 60% of the total volume of the grains, with the range of 5 - 50% being more preferred.

The details of the distribution of silver iodide in core/shell silver halide grains can be checked by various methods of physical measurements such as the luminescence measurement at low temperatures and the X-ray diffraction described in A Summary of the Proceedings of the 1981 Annual Meeting of the Society of Photographic Science and Technology of Japan.

In a standard method of X-ray diffraction, Cu is used as the target and $K\alpha$ emission of Cu is used as the radiation source, with a diffraction curve for a (420) face of a silver halide being measured by the powder method at a tube voltage of 40 kV and a tube current of 100 mA. To enhance the resolving power of the measuring apparatus, the slit width and scan recording speed are generally selected at appropriate values and the stepping angle of the goniometer is set at 0.02 degrees, with the diffraction angle being corrected with a reference sample such as silicon being placed in the cell. The sample of silver halide emulsion to be measured is generally used in a dry state with gelatin being removed with an enzyme. According to this method of measurement, the presence of at least 5 mol% AgI in the core can be verified by the fact that in an X-ray diffraction scan for the silver halide emulsion of interest, the diffraction angle accounts for at least 10% of the peak intensity at any point in the range of diffraction intensity for 5 mol% or more AgIBr which corresponds to the $K\alpha_1$ emission of Cu.

The silver halide grains of the present invention can be prepared by various means. In the case of silver halide compositions that contain iodine, the advantages of the present invention are particularly significant if the silver halide grains are prepared by the following method. Stated more specifically, if the silver halide grains of the present invention are of a type that contains iodine such as in the case of silver iodobromide or silver chloroiodobromide, iodide ions may be added during grain growth in the form of an ion solution such as a potassium iodide solution. Alternatively, iodide ions may be added as grains having a smaller solubility product than the growing silver halide grains. The supply of iodine is preferably effected by adding silver halide grains having the smaller solubility product (as described below in detail).

In a preferred embodiment, the silver halide grains of the present invention (which are to be conveniently referred to as "AgX grains (1)" in the following description of the process of grain growth) are grown in the presence of fine silver halide grains having a solubility product comparable to or less than that of AgX grains (1) (which fine silver halide grains are conveniently referred to as "AgX grains (2)") during at least part of the process of the growth of AgX grains (1).

The term "comparable to or less than" means that the solubility product of AgX grains (2) is equal to or smaller than that of AgX grains (1). The term "solubility product" as used herein has the same meaning as generally defined in chemistry.

In the preferred embodiment described above, AgX grains (2) whose solubility product is comparable to or less than that of AgX grains (1) are present during at least part of the process of the growth of AgX

grains (1) and said AgX grains (1) are permitted to grow in the presence of said AgX grains (2). In this embodiment, the AgX grains (2) may be used in such a way that they are present until the end of supply of elements (e.g. a solution of halide ion and a solution of silver ion) that cause the growth of AgX grains (1).

The AgX grains (2) generally have a smaller average size than the AgX grains (1) and they may sometimes have a larger size. Further, the AgX grains (2) are usually such that they are substantially free of light sensitivity. The AgX grains (2) preferably have an average size of 0.001 - 0.7 μm, more preferably 0.01 - 0.3 μm, with the range of 0.1 - 0.01 μm being particularly preferred.

The AgX grains (2) are preferably permitted to be present in a suspension system providing a site for the preparation of AgX grains (1) (which system is hereinafter referred to as the "mother liquor") for a time period not later than the end of the growth of AgX grains (1).

The AgX grains (2) may be allowed to be present in the mother liquor before seed grains that form a seed phase, or they may be added to the mother liquor containing seed grains prior to a grain growth composition. Alternatively, the AgX grains (2) may be added during the addition of elements that cause grain growth. If desired,the AgX grains (2) may be added in separate portions during two or more of the time periods described above.

The AgX grains (2) and the elements that cause grain growth may be added at a time, or continuously, or intermittently.

The AgX grains (2) and the elements that cause grain growth are preferably added to the mother liquor by a multi-jet method such as a double-jet method at rates that match the growth of grains under such conditions that pH, pAg, temperature and other parameters are controlled.

The AgX grains (2) and seed grains of silver halide may be prepared in the mother liquor or they may be added to the mother liquor after being prepared outside said liquor.

An ammoniacal silver salt solution is preferably used as the water-soluble silver salt solution in the preparation of AgX grains (2).

If AgX grains (1) are composed of silver iodobromide, AgX grains (2) are preferably composed of silver iodide or silver iodobromide that has a higher iodine content than the growing silver iodobromide grains. If AgX grains (1) are composed of silver chlorobromide, AgX grains (2) are preferably composed of silver bromide or silver chlorobromide having a higher bromine content than the growing silver chlorobromide grains. If AgX grains (1) are made of silver iodobromide, it is particularly preferred that AgX grains (2) are composed of silver iodide.

If AgX grains (1) are composed of silver iodobromide or silver chloroiodobromide, it is preferred that all iodine to be used for grain growth is added as AgX grains (2). If desired, part of such iodine may be supplied as an aqueous halide solution to an extent that is not deleterious to the advantages of the present invention.

If the silver halide grains of the present invention are to be formed using a solution of water-soluble silver salt and a solution of water-soluble halide, grain growth is preferably performed with the temperature of the mixture of the two solutions being adjusted to 20 - 90 °C, more preferably 30 - 80 °C.

The silver halide grains of the present invention have an average size of not greater than 5.0 μm, preferably in the range of 0.1 - 5.0 μm, more preferably 0.2 - 3.0 μm, with the range of 0.2 - 2.0 μm being most preferred.

The silver halide emulsion of the present invention may have any grain size distribution as illustrated by a polydisperse emulsion having a broad grain size distribution or a monodisperse emulsion having a narrow size distribution.

The silver halide emulsion of the present invention may be comprised of a single emulsion or a mixture of several kinds of emulsions.

A monodisperse emulsion is preferably used in the practice of the present invention. The silver halide emulsion of the present invention can be consistently obtained as an emulsion having a satisfactory degree of monodispersity.

A preferred monodisperse silver halide emulsion is such that the weight of silver halide grains whose size is within the range of ±20% of the mean value $\bar{r}$ is at least 60% of the total weight of all the silver halide grains present. More preferably, the relative weight is at least 70%, most preferably at least 80%, of the total weight of all the silver halide grains present.

The "mean grain size $\bar{r}$" is defined as the size ri of such grains that provide a maximum value of $n_i \times r_i^3$ where ni is the frequency of the grains having size ri (calculation is made to three significant digits, with the least significant figure being rounded). The grain size "ri" means the diameter of a spherical silver halide grain or the diameter of a circle equivalent in area to the projected image of a non-spherical grain. A typical method of grain size measurement consists of taking an electron micrograph of a grain of interest at a magnification of 1×10^4 - 5×10^4 and then measuring the diameter of the grain as observed on the print or

the area of the projected image (assuming that the measurement is performed on randomly selected 1,000 or more grains).

A highly monodisperse emulsion which is particularly preferred for the present invention is such that the width of distribution as defined by the following equation is no more than 20%, preferably no more than 15%:

$$\text{Coefficient of variation (\%)} = \frac{\text{Standard deviation of grain size}}{\text{Mean grain size}} \times 100.$$

In this equation, the "mean grain size" and "standard deviation of grain size" are assumed to be determined from "ri" as already defined above.

An applicable method of obtaining monodisperse emulsions comprises adding a solution of water-soluble silver salt and a solution of water-soluble halide to a gelatin solution containing seed grains by a double-jet method under controlled pAg and pH conditions.

The rates of addition can be determined with reference being made to the disclosures in Unexamined Published Japanese Patent Application Nos. 48521/1979 and 49938/1983.

During the formation and/or growth of silver halide grains, at least one metal ion selected from the group consisting of cadmium salts, zinc salts, lead salts, thallium salts, iridium salts (including complex salts), rhodium salts (including complex salts) and iron salts (including complex salts) may be added to have those metal elements incorporated in the interior of grains and/or in the surface layers thereof. Alternatively, reduction sensitization nuclei may be imparted to the interior of grains and/or to their surfaces by placing them in an appropriate reducing atmosphere.

The silver halide emulsion of the present invention may be chemically sensitized in the usual manner.

The silver halide emulsion of the present invention may be optically sensitized for a desired wavelength range using dyes that are known as sensitizing dyes in the photographic industry. Sensitizing dyes may be used either alone or in admixtures.

Antifoggants, stabilizers and other common additives may be added to the silver halide emulsion of the present invention. Gelatin is advantageously used as a binder for the emulsion.

When forming a light-sensitive material using the silver halide emulsion of the present invention, the emulsion layers and other hydrophilic colloidal layers in the light-sensitive material can be hardened. Plasticizers and dispersions (latices) of water-in-soluble or slightly soluble synthetic polymers can also be incorporated in those layers.

The silver halide emulsion of the present invention can be effectively used to form a color photographic material. When said emulsion is to be used in associated emulsion layers, color forming couplers are usually contained in it.

Also usable are colored couplers that are capable of color correction, competing couplers and those compounds which, upon coupling with the oxidation products of developing agents, release photographically useful fragments such as a development accelerator, a bleach accelerator, a developing agent, a silver halide solvent, a toning agent, a hardener, a foggant, an anti-foggant, a chemical sensitizer, a spectral sensitizer and a desensitizer.

When forming a light-sensitive material using the silver halide emulsion of the present invention, auxiliary layers such as a filter layer, an anti-halo layer and an anti-irradiation layer may be used in that light-sensitive material. Dyes that will flow out of the light-sensitive material or that will be bleached during development may be contained in those auxiliary layers and/or emulsion layers.

The light-sensitive material can also contain other additives including a formaldehyde scavenger, an optical brightening agent, a matting agent, a lubricant, an image stabilizer, a surfactant, a color fog preventing agent, a development accelerator, a development retarder and a bleach accelerator.

The support of the light-sensitive material may be composed of any materials including paper laminated with resins such as polyethylene, polyethylene terephthalate films, baryta paper, and triacetyl cellulose.

Using the light-sensitive material incorporating the silver halide emulsion of the present invention, color images can be obtained by performing known procedures of color photographic processing following imagewise exposure.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting. Before going into details of the respective examples, let us describe the preparation of the emulsions used in those examples.

Preparation of fine-grained AgI emulsion AI-1

A reaction vessel was charged with an aqueous solution containing 5 wt% of ossein gelatin. Under stirring at 40 °C, an aqueous solution of 3.5 N silver nitrate and an aqueous solution of 3.5 N potassium iodide, each weighing 1 mole, were added at a constant rate over a period of 30 min. During the addition, pAg was controlled at 13.5 by conventional pAg control means.

The resulting silver iodide grains had an average size of 0.06 μm and were composed of a mixture of β-AgI and γ-AgI.

This emulsion is hereunder referred to as emulsion AI-1.

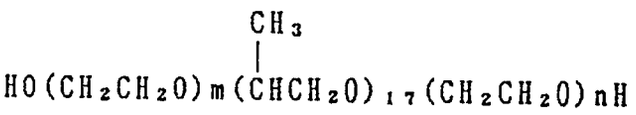
Preparation of seed emulsion N-1

Seed emulsion N-1 was prepared using the three aqueous solutions described below.

Aqueous solution (a-1):

Gelatin	40 g
10% Methanol solution of compound (I) identified below	20 ml
KBr	1.5 g
$MgSO_4$	18.4 g
10% Nitric acid solution	182.0 ml
Water	to make 9422 ml

Compound (I)



(av. mol. wt.≃1,300)

Aqueous solution (a-2):

$AgNO_3$	780 g
10% Nitric acid solution	65.0 ml
Water	to make 1951.2 ml

Aqueous solution (a-3):

Gelatin	41.1 g
KBr	980.0 g
10% Methanol solution of compound (I)	14.4 ml
Water	to make 3500 ml

To stirred aqueous solution (a-1) at 60° C, aqueous solutions (a-2) and (a-3) and 2.47 moles of fine-grained AgI emulsion (AI-1) were added by a triple-jet method over 156 min with pAg and pH being controlled at 7.8 and 2.0, respectively, with nitric acid and an aqueous solution of KBr. An aqueous solution containing 400 g of gelatin was added and dispersed in an aqueous gelatin solution containing silver halide grains in an amount equivalent to all the silver content to be added, whereby a seed emulsion N-1 was prepared.

Preparation of seed emulsion N-2

Seed emulsion N-2 was prepared using the four aqueous solutions described below.

Aqueous solution (b-1):	
Gelatin	126.7 g
10% Methanol solution of compound (I)	30.0 ml
28% Aqueous ammonia	792 ml
Water	to make 6423 ml
Aqueous solution (b-2):	
$AgNO_3$	1098.0 g
28% Aqueous ammonia	860.1 ml
Water	to make 1846.5 ml
Aqueous solution (b-3):	
Gelatin	136.4 g
KBr	1419.8 g
Water	to make 3409 ml
Emulsion solution (b-4) containing fine AgI grains:	
Fine-grained AgI emulsion (AI-1)	equivalent to 3.48 moles
4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene (hereunder abbreviated as "TAI")	10.87 g
Water	to make 7278 ml

To stirred aqueous solution (b-1) at 50 °C, 0.651 moles of seed emulsion N-1 was added and, further, with pAg and pH being controlled at 7.5 and 7.0, respectively, with acetic acid and an aqueous solution of KBr, aqueous solutions (b-2), (b-3) and (b-4) were added by a triple-jet method over 124 min.

An aqueous solution containing 400 g of gelatin was added and dispersed in an aqueous gelatin solution containing silver halide grains in an amount equivalent to all the silver content to be added, whereby a seed emulsion N-2 was prepared.

Preparation of seed emulsion N-3

Silver halide grains were prepared as in the case of seed emulsion N-2; thereafter, desalting and washing with water were performed in the usual manner and an aqueous solution containing 115 g of gelatin was added and dispersed, whereby a seed emulsion N-3 was prepared.

Preparation of seed emulsion N-4

To 500 ml of a 2.0% aqueous gelatin solution heated to 40 °C, 250 ml of an aqueous solution of 4 M (molar concentration) $AgNO_3$ and 250 ml of an aqueous solution of 4 M KBr/KI (98:2 in molar ratio) were added by a controlled double-jet method over 35 min in accordance with the disclosure in Unexamined Published Japanese Patent Application No. 45437/1975, with pAg and pH being controlled at 9.0 and 2.0, respectively. An aqueous gelatin solution containing silver halide grains in an amount equivalent to all the silver content to be added was adjusted to pH 5.5 with an aqueous solution of potassium carbonate and, thereafter, an aqueous solution containing 20 g of gelatin was added and dispersed, whereby a seed emulsion N-4 was prepared.

Preparation of seed emulsion N-5

Seed emulsion N-5 was prepared using the three aqueous solutions described below.

Aqueous solution (c-1):	
Gelatin	32.96 g
10% Methanol solution of compound (I)	20 ml
KBr	0.74 g
TAI	0.18 g
28% Aqueous ammonia	117 ml
Water	to make 7518 ml
Aqueous solution (c-2):	
$AgNO_3$	1144.4 g
28% Aqueous ammonia	896.4 ml
Water	to make 1924 ml
Aqueous solution (c-3):	
Gelatin	18.7 g
KBr	763.8 g
KI	21.8 g
TAI	2.2 g
Water	to make 1871 ml

To stirred solution (c-1) at 40 °C, 0.32 moles of seed emulsion N-4 was added and, further, with pAg and pH being controlled at 8.8 and 7.5, respectively, with acetic acid and an aqueous solution of KBr, aqueous solutions (c-2) and (c-3) were added by a double-jet method over 35 min. An aqueous solution containing 300 g of gelatin was added and dispersed in an aqueous gelatin solution containing silver halide grains in an amount equivalent to all the silver content to be added, whereby a seed emulsion N-5 was prepared.

Preparation of seed emulsion N-6

Silver halide grains were prepared as in the case of seed emulsion N-5; thereafter, desalting and washing with water were performed in the usual manner and an aqueous solution containing 128 g of gelatin was added and dispersed, whereby a seed emulsion N-6 was prepared.

Preparation of emulsion EM-1

Emulsion EM-1 was prepared using the four aqueous solutions described below.

Aqueous solution (d-1):	
Gelatin	89.44 g
10% Methanol solution of compound (I)	30.0 ml
28% Aqueous ammonia	528.0 ml
Water	to make 4380 ml
Aqueous solution (d-2):	
$AgNO_3$	1534.4 g
28% Aqueous ammonia	1201.9m
Water	to make 2580.4 ml
Aqueous solution (d-3):	
Gelatin	140.3 g
KBr	1460.5 g
Water	to make 3507 ml
Emulsion solution (d-4) containing fine AgI grains:	
Fine-grained AgI emulsion (AI-1)	equivalent to 0.498 moles
TAI	7.4 g
Aqueous solution of 10% potassium hydroxide	21.0 ml
Water	to make 1950 ml

To vigorously stirred aqueous solution (d-1) at 60°C, 0.367 moles of seed emulsion N-2 was added and, thereafter, pH and pAg were properly adjusted with acetic acid and an aqueous solution of KBr.

Subsequently, with pH and pAg being controlled as shown in Table 1, aqueous solutions (d-2), (d-3)

and (d-4) were added by a triple-jet method at the flow rates respectively shown in Tables 2, 3 and 4.

After the end of addition, an aqueous solution of phenylcarbamylated gelatin was added and the grains were permitted to settle and agglomerate by adjusting the pH of the mixed solution, followed by desalting and washing with water. Thereafter, pH and pAg were adjusted to 5.80 and 8.06, respectively, at 40 °C. As a result, a monodisperse AgIBr emulsion was obtained that had an average grain size of 0.8 μm, an average AgI content of 12.6 mol% and a grain size distribution of 11.2%.

The AgI contents and relative volumes of the respective phases of emulsion EM-1 are shown in Table 5.

Table 1

Grain growth conditions of emulsion EM-1

Ag(%)	0		29.2		29.2		56		100
pH	7.0	A	7.0	C	6.0	A	6.0	A	6.0
pAg	7.8	A	7.8	C	9.7	B	10.1	A	10.1

Notes: A indicates constant pH or pAg;B indicates gradual decrease; and C indicates sudden decrease.

Table 2

Profile of the addition of (d-2)

time (min)	rate of addition (ml/min)
0	2.3
20.0	3.4
32.9	4.2
48.8	5.4
67.9	6.9
92.4	9.3
98.1	14.0
105.4	16.1
108.7	19.9
115.9	29.0
122.6	45.7
125.7	62.8
128.5	76.9
138.5	98.7
140.2	103.7

Table 3

Profile of the addition of (d-3)

time (min)	rate of addition (ml/min)
0	2.2
10.3	2.7
24.3	3.5
41.3	4.6
62.9	6.2
92.4	8.8
92.6	12.3
98.5	18.0
105.1	23.2
110.3	32.5
114.3	37.8
119.9	56.7
124.1	88.7
125.4	106.4
140.2	111.7

Table 4

Profile of the addition of (d-4)

time (min)	rate of addition (ml/min)
0	7.1
14.2	9.4
32.0	12.8
56.8	18.5
92.4	28.5
92.6	8.2
98.5	8.2
102.0	9.1
105.4	10.3
105.7	3.1
112.7	4.3
118.9	6.1
123.5	8.8
125.7	11.1
138.5	17.5

Table 5

	First phase (seeds)	Second phase	Third phase	Fourth phase	Fifth phase
AgI content (mol%)	35	35	10	3	0
Relative volume (%)	3.5	25.5	6.6	58.6	5.8

Preparation of emulsion Em-2

Emulsion EM-2 was prepared in entirely the same manner as emulsion EM-1 except that N-3 was used as the seed emulsion. Emulsion Em-2 was a monodisperse silver iodobromide emulsion having an average grain size of 0.8 μm, an average silver iodide content of 12.6 mol% and a grain size distribution of 11.2%.

Preparation of emulsion EM-3

Emulsion EM-3 was prepared in entirely the same manner as emulsion Em-1 except that seed emulsion N-5 was used. Emulsion EM-3 was a monodisperse silver iodobromide emulsion having an average grain size of 0.8 μm, an average silver iodide content of 11.4 mol% and a grain size distribution of 11.2%.

Preparation of emulsion EM-4

Emulsion EM-4 was prepared in entirely the same manner as emulsion EM-1 except that N-6 was used as the seed emulsion. Emulsion EM-4 was a monodisperse silver iodobromide emulsion having an average grain size of 0.8 μm, an average silver iodide content of 11.4 mol% and a grain size distribution of 11.2%.

Preparation of Emulsion EM-5

Emulsion EM-5 having the AgI contents and relative volumes of the respective phases as shown in Table 6 was prepared by repeating the procedure for the preparation of emulsion EM-1. Emulsion EM-5 was a monodisperse silver iodobromide emulsion having an average grain size of 0.80 μm, an average silver iodide content of 6.0 mol% and a grain size distribution of 11.2%.

Table 6

	First phase (seeds)	Second phase	Third phase	Fourth phase	Fifth phase
AgI content (mol%)	35	35	10	3	0
Relative volume (%)	3.5	5.0	6.0	79.7	5.8

Preparation of emulsion EM-6

Emulsion EM-6 was prepared in entirely the same manner as emulsion EM-5 except that N-3 was used as the seed emulsion. Emulsion EM-6 was a monodisperse silver iodobromide emulsion having an average grain size of 0.8 μm, an average silver iodide content of 6.0 mol% and a grain size distribution of 11.2%.

Preparation of emulsion EM-7

Emulsion EM-7 was prepared in entirely the same manner as emulsion EM-5 except that N-5 was used as the seed emulsion. Emulsion EM-7 was a monodisperse silver iodobromide emulsion having an average grain size of 0.8 μm, an average silver iodide content of 4.8 mol% and a grain size distribution of 11.2%.

Preparation of emulsion EM-8

Emulsion EM-8 was prepared in entirely the same manner as emulsion EM-5 except that N-6 was used as the seed emulsion. Emulsion EM-8 was a monodisperse silver iodobromide emulsion having an average grain size of 0.8 μm, an average silver iodide content of 4.8 mol% and a grain size distribution of 11.2%.

The characteristics of emulsions EM-1 to EM-8 are summarized in Table 7 with respect to the seed emulsion used, its AgI content, whether the seed emulsion was desalted or not, and the total I content of each emulsion.

Table 7

Emulsion No.	Seed emulsion No.	I content of seed emulsion (mol%)	Desalting of seed emulsion	Total I content (mol%)	Remarks
EM-1	N-2	35	no	12.6	invention
EM-2	N-3	35	yes	12.6	comparison
EM-3	N-5	2	no	11.4	invention
EM-4	N-6	2	yes	11.4	comparison
EM-5	N-2	35	no	6.0	invention
EM-6	N-3	35	yes	6.0	comparison
EM-7	N-5	2	no	4.8	invention
EM-8	N-6	2	yes	4.8	comparison

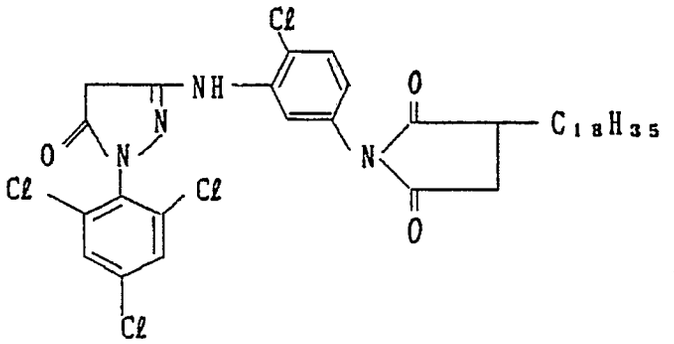
The examples of the present invention are specifically described below.

Example 1

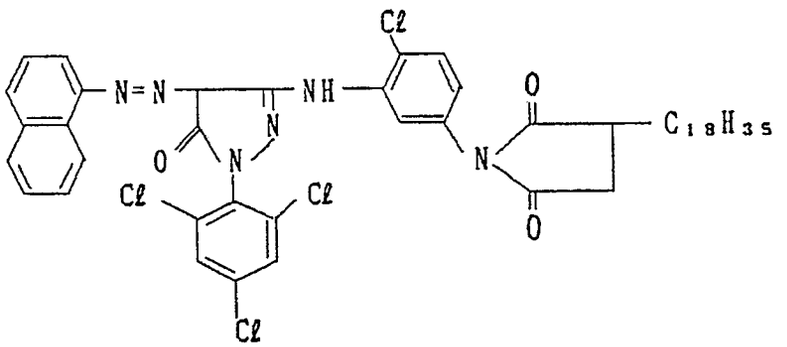
Each of the emulsions EM-1 to EM-8 was subjected to gold-plus-sulfur sensitization in an optimal way. Each of those emulsions was then sensitized spectrally to have sensitivity to green light by addition of sensitizing dyes (I) and (II) (see below) in respective amounts of 100 mg and 65 mg per mole of AgX. Subsequently, the emulsions were stabilized by addition of TAI and 1-phenyl-5-mercaptotetrazole.

Further, magenta coupler (M-1) (see below), magenta coupler (M-2) (also see below) and colored magenta coupler (CM-1) (also see below) were dissolved in di-t-nonyl phthalate in respective amounts of 5 x 10^{-3} moles, 6.2 x 10^{-3} moles and 4.0 x 10^{-3} moles, respectively, per mole of AgX, and the resulting solution was dispersed in an aqueous solution containing gelatin. The thus prepared dispersion was added to each emulsion. Thereafter, a spreading agent, a hardener and other common photographic additives were added to prepare coating solutions, which were applied to subbed film bases in the usual manner. The applied solutions were dried to prepare sample Nos. 101 - 108.

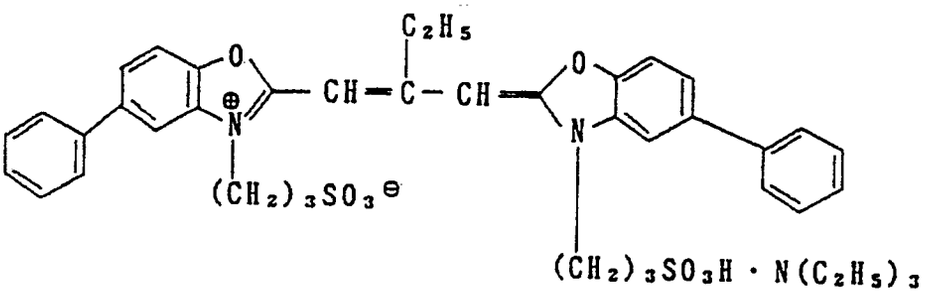
M-1



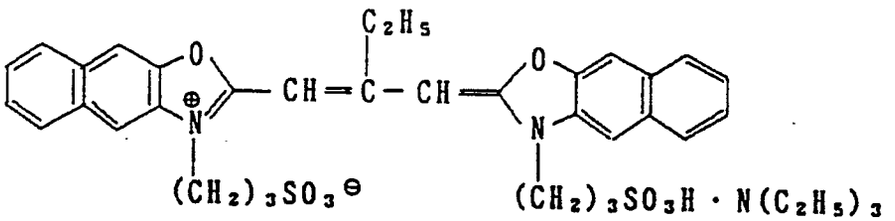
CM-1



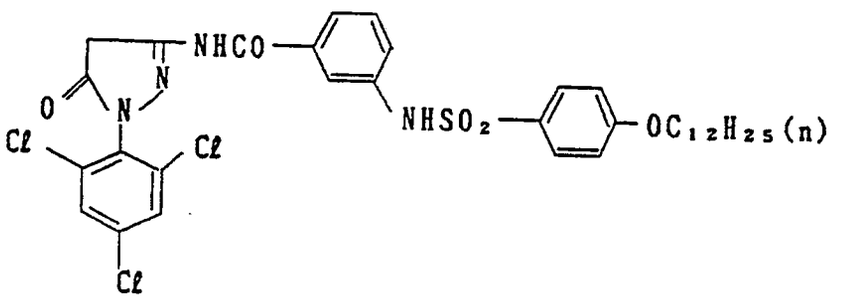
Sensitizing dye I



Sensitizing dye II



M-2



Each of the samples was subjected to wedge exposure through a yellow filter in the usual manner and subsequently processed by the following scheme.

Processing scheme (38° C)	
Color development	3 min and 15 sec
Bleaching	6 min and 30 sec
Washing with water	3 min and 15 sec
Fixing	6 min and 30 sec
Washing with water	3 min and 15 sec
Stabilizing	1 min and 30 sec
Drying	

The solutions used in the steps of color development, bleaching, fixing and stabilizing had the following recipes.

Color developing solution

4-Amino-3-methyl-N-ethyl-N-(ß-hydroxy-ethyl)aniline sulfate salt	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine hemisulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Nitrilotriacetic acid trisodium salt (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Water	to make 1000 ml
pH	adjusted to 10.0

Bleaching solution

Ethylenediaminetetraacetic acid iron ammonium salt	100.0 g
Ethylenediaminetetraacetic acid diammonium salt	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml
Water	to make 1000 ml
pH	adjusted to 6.0 with aqueous ammonia

Fixing solution

Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g
Water	to make 1000 ml
pH	adjusted to 6.0 with acetic acid

Stabilizing solution	
Formaldehyde (37% aq. sol.)	1.5 ml
Konidax (Konica Corp.)	7.5 ml
Water	to make 1000 ml

The processed samples were measured for relative sensitivity using green light. The results are shown in Table 8. The "relative sensitivity" is the relative value of the reciprocal of the amount of exposure that provides a fog density + 0.3, with the value for sample No. 108 being taken as 100.

Table 8

Sample No.	Emulsion No.	Desalting of seed emulsion	Relative sensitivity	Remarks
101	EM-1	no	140	invention
102	EM-2	yes	102	comparison
103	EM-3	no	133	invention
104	EM-4	yes	103	comparison
105	EM-5	no	138	invention
106	EM-6	yes	101	comparison
107	EM-7	no	132	invention
108	EM-8	yes	100	comparison

As will be understood from Table 8, emulsions EM-1, -3, -5 and -7 which were within the scope of the present invention had higher sensitivity than the comparative emulsions which were prepared by subjecting the seed emulsion to the steps of desalting and washing with water.

Example 2

In Example 2, the samples prepared in Example 1 were evaluated for their pressure resistance by the following procedure.

Sample Nos. 101 - 108 were left in an atmosphere of 23°C and 55% r.h. for 24 h. Under the same humidity condition, the surface of each sample on the emulsion side was scratched with a diamond stylus (0.025 mm$^{\phi}$) under a load of 3 g at a speed of 10 mm/sec. The samples were also subjected to a 90°C bend test (bent for 90 degrees around a stainless steel pipe) under the same humidity condition.

Those samples were imagewise exposed and subsequently processed as in Example 1. The changes in magenta density in the fogged areas were measured with a microdensitometer and the results are shown in Table 9.

Table 9

Sample No.	Change in fog*1 due to scratching with diamond stylus	Change in fog*2 due to bending	Remarks
101	17	16	invention
102	94	93	comparison
103	24	23	invention
104	95	94	comparison
105	18	17	invention
106	97	98	comparison
107	26	25	invention
108	100	100	comparison

*1, *2: "Change in fog" is expressed in relative values, with the change (increase) in fog for sample No. 108 being taken as 100.

As is clear from Table 9, the samples within the scope of the present invention had better pressure resistance than the comparative samples since they experienced smaller changes in fog irrespective of whether they were scratched with the diamond stylus or bent for 90 degrees.

As described on the foregoing pages, the silver halide emulsion of the present invention has high sensitivity and yet experiences a very small amount of fogging by pressure.

Claims

1. A silver halide emulsion comprising silver halide grains having a seed phase, the improvement wherein said silver halide grains have not been subjected to either desalting or washing with water prior to the completion of the formation of the silver halide grains.

2. A silver halide emulsion according to Claim 1 wherein the silver halide grains are essentially composed of silver iodobromide.

3. A silver halide emulsion according to Claim 1 wherein the silver halide grains have an average size of 0.2 to 2.0 μm.

4. A silver halide emulsion according to Claim 1 which is comprised of mono-dispersed emulsion having a coefficient of variation of no more than 0.15.

5. A silver halide emulsion according to Claim 1 wherein the silver halide grains are core/shell type grains.

6. A silver halide emulsion according to Claim 5 wherein the core of said silver halide grain contains more than 20 mol % of silver iodide and the shell of said silver halide grain contains less than 7 mol % of silver iodide.

7. A silver halide emulsion according to Claim 1 wherein said emulsion is a mono-dispersed emulsion having a coefficient of variation of no more than 0.15, said silver halide grains are a core/shell type grains having an average size of 0.2 to 2.0 μm being essentially composed of silver iodide contained with the concentration of more than 20 mol % in the core and of less than 7 mol % in the shell.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 9909

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	DE-A-3 410 790 (KONISHIROKU PHOTO INDUSTRY CO. LTD.) * page 12, lines 6 - 10 *	1-7	G 03 C 1/015 G 03 C 1/035
Y	EP-A-0 309 119 (KONICA CORPORATION) * examples; p.4, l.48-53 *	1-7	
D,Y	PATENT ABSTRACTS OF JAPAN vol. 9, no. 308 (P-410)(2031) 04 December 1985, & JP-A-60 138538 (KONISHIROKU SHASHIN KOGYO K.K.) 23 July 1985, * the whole document *	1-7	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	30 September 91	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document