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

(11) Publication number: **0 557 695 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **93100475.8**

(51) Int. Cl.^{5}: **G03C 1/015**

(22) Date of filing: **14.01.93**

(30) Priority: **31.01.92 JP 15846/92**

(43) Date of publication of application:
01.09.93 Bulletin 93/35

(84) Designated Contracting States:
DE FR GB NL

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

(72) Inventor: **Ishikawa, Sadayasu, c/o Konica**
Corporation
1 Sakura-machi
Hino-shi, Tokyo(JP)
Inventor: **Kasai, Shigetami, c/o Konica**
Corporation
1 Sakura-machi
Hino-shi, Tokyo(JP)

(74) Representative: **Henkel, Feiler, Hänzel &**
Partner
Möhlstrasse 37
D-81675 München (DE)

(54) Process for preparing silver halide photographic emulsion and silver halide color photographic light sensitive material.

(57) A silver halide color photographic light-sensitive material and a process for its preparation are disclosed. The material comprises a support and provided thereon, a silver halide photographic emulsion layer comprising core/shell silver halide grains having a core composed of silver halide containing silver iodide in an amount of 10 to 45 mol% and a shell composed of silver halide having a silver iodide content lower than that of the core, the silver halide grains being prepared by a process comprising the steps of maintaining a distance between cores in the range of 0.1 to 3.0 μm in an aqueous dispersion solution to form the core, followed by forming the shell on the formed core.

Rank Xerox (UK) Business Services
(3. 10/3.6/3.3. 1)

FIELD OF THE INVENTION

This invention relates to a process for preparing silver halide photographic emulsions useful in the field of photographic industry and the silver halide color photographic light sensitive materials applied with the emulsions and, particularly to the silver halide color photographic light sensitive materials low in fog, excellent in graininess and high in sensitivity.

BACKGROUND OF THE INVENTION

In recent years, the demands for the characteristics of silver halide photographic emulsions have become more and more serious and, particularly, there are more higher level demands for the photographic characteristics such as a high sensitivity, a low fog, a high gamma and so forth.

In relation to the tendency of making sensitivity and image quality higher, there have been increased the demands for reducing fog and improving graininess of silver halide photographic light sensitive materials.

To try to satisfy the above-mentioned demands, there have been energetically studies on emulsions comprising core/shell type silver halide grains having a silver iodobromide phase of high content of silver iodide. In particular, silver iodobromide emulsions containing core/shell type grains having inside the grains a high silver iodide-containing phase of not less than 10 mol% have come into the limelight, as the emulsions for color negative film. The typical examples of highly sensitive emulsions are disclosed in Japanese Patent Publication Open to Public Inspection (hereinafter abbreviated to as JP OPI Publication) Nos. 60-143331/1985, 62-3247/1987 and 62-7039/1987, respectively.

For forming cores having high iodine content when preparing a silver halide emulsion of a core/shell structure having a high silver iodide content inside, it is required to increase the solubility in the course of growing the grains, because silver iodide itself is low in solubility. For the countermeasure, it is well known to apply a method of elevating a temperature, adding a solvent, making pH and/or pAg higher or the like. However, in the above countermeasure, silver halide grains are coagulated each other when highly iodine containing cores are formed and, therefore, fog is produced and graininess is seriously deteriorated.

In the conventional techniques, as described above, it has been difficult to develop any silver halide photographic emulsions high in sensitivity, low in fog and improved on graininess so as to satisfactorily displaying the merits of high iodine containing core/shell type emulsions.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a process for preparing silver halide photographic emulsions in which the above-described problems can be improved so as to have a high sensitivity, a low fog and an improved graininess and also to provide a silver halide color photographic light sensitive material applied with the emulsions.

After energetically studying, the present inventors have discovered that the objects of the invention can be achieved as follows.

(1) A process for preparing a silver halide photographic emulsion comprising silver halide grains each formed of both of a core comprising silver halide containing silver iodide in an amount of 10 to 45 mol% in the presence of a dispersion medium and a shell comprising either silver halide covering the core and having a silver iodide content lower than that of the core; wherein the core is formed in an aqueous solution containing a dispersion medium in an amount of not less than 3.0 wt%.

(2) A silver halide color photographic light sensitive material comprising a support having at least one silver halide emulsion layer; wherein at least one of the emulsion layers contains the silver halide photographic emulsion prepared in the process described in the above paragraph (1) for preparing silver halide photographic emulsions.

DETAILED DESCRIPTION OF THE INVENTION

Each of the inventions of this patent application will be detailed below.

The silver halide emulsions relating to the invention are comprised of silver iodobromide having an average silver iodide content within the range of preferably, 3 to 20 mol% and more preferably, 5 to 15 mol%.

The silver halide grains of the silver halide emulsions of the invention are comprised of a silver bromide phase or a silver iodobromide phase each forming the surfaces of the grains (hereinafter referred sometimes to as a "shell") and an inner phase having high silver iodide content (hereinafter referred sometimes to as a "core"). The silver iodide content of a core is within the range of 10 to 45 mol% and, preferably, 20 to 40 mol%. The silver iodide content of a shell is within the range of, preferably, not more than 6 mol% and, more preferably, not more than 3 mol%.

The grains contained in the photographic emulsions of the invention are to have the so-called core/shell type structure. It is allowed either to make a silver iodide containing phase (i.e., an intermediate phase) present before forming a core and/or between the core and shell or to continuously vary the silver iodide content of the core and/or shell.

The silver iodide content of the intermediate phase is within the range of, preferably, 2 to 20 mol% and, more preferably, 5 to 15 mol%.

The differences of the silver iodide contents between a core and an intermediate phase and between an intermediate phase and a shell are preferably not less than 6 mol% and, more preferably, not less than 10 mol%, respectively.

In the embodiment mentioned above, it is also allowed to make another silver halide phase present in the center of the core, between the core and the intermediate phase and between the intermediate phase and the shell.

The volume of the shell is preferably, not less than 2% and, more preferably, within the range of 10 to 80%, each of the whole grain. The volume of the core is within the range of, preferably, 3 to 70% and, more preferably, 10 to 55%, each of the whole grain.

The emulsions relating to the invention are prepared in the presence of a dispersion medium, that is, they are prepared in a solution containing the dispersion medium.

The expression, "an aqueous solution containing a dispersion medium" herein stated means an aqueous solution in which a protective colloid is formed in the aqueous solution by making use of gelatin or a material capable of constituting another hydrophilic colloid (such as a material capable of serving as a binder) and, preferably means an aqueous solution containing colloidal gelatin.

When making use of gelatin as the above-mentioned protective colloid for embodying the invention, such a gelatin may be either lime-processed or acid-processed. The preparation of gelatin are detailed in Arthur Weiss, "The macromolecular Chemistry of Gelatin", Academic Press, 1964.

The hydrophilic colloids other than gelatin, which are applicable as the protective colloids include, for example, protein such as a gelatin derivative, a graft polymer of gelatin and other macromolecules, albumin and casein; a cellulose derivative such as hydroxyethyl cellulose, carboxymethyl cellulose and a cellulose sulfate; a sugar derivative such as sodium alginate and a starch derivative; and various kinds of synthesized hydrophilic macromolecular materials such as a monomer or copolymer of polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinyl pyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole or polyvinyl pyrazole.

In the case of using gelatin, it is desired to use those having a jelly strength of not lower than 200 in PAGI method.

The effects obtained in the invented preparation process include that aggregation of prepared silver halide grains is eliminated by making the gelatin concentration higher, at a desired temperature, inside a reaction system, so that the graininess and fog production can resultingly be improved. The gelatin concentration is to be not lower than 3 wt% and, preferably, within the range of 4 to 10 wt%. The expression, "the aggregation of silver halide grains", herein stated means the following two phenomena produced in the course of growing silver halide grains; namely, one phenomenon is that two or more silver halide grains are united in a body so as to be grown up as a single silver halide grain substantially so that a bulky grain may be produced; and the other phenomenon is that individual silver halide grains are united in a body in the stage where their configurations and sizes thereof remain as they are, so that a single lump is formed as the group of grains. When the present inventors tried to obtain an aggregation ratio [that is, the number of aggregated silver halide grains x 100/1000] (%) by making use of a scanning type electron microscope (manufactured by Nippon Electron Co., Ltd.) as a means for observing the aggregation degrees of the prepared silver halide grains and then by counting the number of the aggregated grain present in 1000 pieces of silver halide grains, it was proved that the higher the silver halide grain aggregation ratio of an emulsion is, the more the fog is produced and the graininess is deteriorated. The silver halide grains prepared in the preparation process of the invention are to have an aggregation ratio of, preferably, not higher than 10% and, more preferably, not higher than 5%.

In preparing the emulsions of the invention, it is essential to shorten the distance between silver halide grains when the cores are formed for forming the high iodine containing cores and to maintain the distance between the grains within the range of 0.1 to 3.0 μm and, preferably, 0.3 to 2.5 μm.

The distance between silver halide grains means the distance between the centers of adjoining grains, assuming that all silver halide grains are dispersed in the dispersion solution at an equal distance from one another. In other words, supposed spheres having a radius r from the center of the grains are assumed to occupy the entire dispersion solution in a state of face-centered cubic lattice. Accordingly, the distance between grains can be obtained from the following equation:

$$\text{Distance between the grains} = 2 \times \sqrt[3]{0.74 \times V/N \times 3/(4\pi)}$$

wherein V represents an amount of the dispersion solution; N represents the number of grains present in the dispersion solution; and 0.74 represents a volume occupied ratio of face-centered cubic lattice.

The silver halide emulsions prepared in the emulsion preparation methods of the invention may be those grown of seed crystals or those accompanying a nucleous production. Further, the configurations of the silver halide emulsions prepared therein may be either one of a regular crystal such as a cube, an octahedron, a tetradecahedron and so forth or twinned crystals of tabular-shaped emulsions.

The silver halide emulsions prepared in the invention may be comprised of any one of silver iodochloride, silver iodobromide and silver chloroiodobromide. In particular, silver iodobromide is preferred from the viewpoint that those having a high sensitivity can be prepared.

The silver halide emulsions prepared in the invention may be any desired one such as a polydispersed emulsion having a wide grain size distribution and a monodispersed emulsion having a narrow grain size distribution. They may also be an independent emulsion or a mixture of several types of emulsions. When preparing a light sensitive material by making use of the emulsions of the invention, it is desired to use a monodisperse type emulsion.

Therein, the monodisperse type silver halide emulsions are preferably those in which the content of the silver halide grains having a grain size within the range of ±20% around the average grain size r are preferably not less than 60%, more preferably not less than 70% and, further more preferably not less than 80%, based on the whole silver halide grains.

The term, "an average grain size r", is defined as grain size ri obtained when maximizing a product of ni x ri^3 in which ni represents a frequency of grains having grain size ri. (wherein, the significant figures are three figures and the minimum figures shall be rounded.)

The term, "grain size", stated herein means a grain diameter in the case of a globular-shaped silver halide grain and a diameter of a circular image having the same area as that of a projective image obtained in the case of the other configurated grains than the globular grains.

The above-mentioned grain sizes can be obtained by projecting a subject grain upon magnifying it 10,000 to 50,000 times through an electron microscope and then by practically measuring the diameter of the magnified grain image on a print or the area of the projected grain image, (in this case, number of the grains subject to measurement are to be not less than 1000 pieces.)

The particularly desirable highly monodispersed emulsions of the invention have a grain size distribution range of not wider than 20% and, more preferably, not wider than 15%. The grain size distribution mentioned above is defined by the following equation;

(Standard deviation)/an average grain size) x 100 = Grain size distribution range [%]

wherein an average grain size and a standard deviation are to be obtained from the above-defined grain size.

A monodisperse type emulsion can be prepared in the process that an aqueous silver salt solution and a water-soluble halide solution are added into a gelatin solution containing seed grains under controls of pAg and pH in a double-jet method. When determining a adding rate, it may be referred to JP OPI Publication Nos. 54-48521/1979 and 58-49938/1983.

Further as a process for preparing a highly monodispersed emulsion, it can be apply the growing process carried out in the presence of tetrazaindene, of which is disclosed in JP OPI Publication No. 60-122935/1985.

When preparing the silver halide emulsions of the invention, any well-known silver halide solvents such as ammonia, thioether, thiourea and so forth may be made present or no silver halide solvent may also be used.

In the courses of forming and/or growing grains, the silver halide grains may be added with metal ions by making use of at least one kind selected from the group consisting of a cadmium salt, a zinc salt, a lead salt, a thallium salt and an iridium salt (including the complex salts thereof) so that the inside and/or surfaces of the grains may contain these metal elements. Further, when putting the grains in a suitable reducible atmosphere, the inside and/or surfaces of the grains may be provided with reduction sensitization nuclei.

The silver halide grains may be either one of those capable of forming a latent image mainly on the surfaces thereof or those capable of forming a latent image mainly inside the grains. The grain sizes of the silver halides are within the range of 0.05 to 5.0 µm and, preferably, 0.1 to 3.0 µm.)

The silver halide emulsions of the invention may be those from which unnecessary soluble salts are removed after completing the growth of the silver halide grains, or those containing the unnecessary soluble salts as they are. If desired, the unnecessary soluble salts may be removed with reference to the method described in Research Disclosure (hereinafter abbreviated to as RD) No. 17643, Paragraph II. For the further details thereof, the soluble salts may be removed, in a noodle-washing method of gellating gelatin, after a flocculation is produced or from an emulsion already chemically ripened. It is further allowed to use a flocculation method utilizing an inorganic salt, an anionic surfactant, an anionic polymer (such as polystyrene sulfonic acid) or a gelatin derivative (such as acylated gelatin and carbamoylated gelatin).

The silver halide emulsions of the invention may be chemically sensitized in any ordinary methods. To be more concrete, it is allowed to make independent or combination use of a sulfur sensitization method, a selenium sensitization method, a reduction sensitization method, a noble metal sensitization method in which gold or other noble metal compounds are used, and so forth.

The silver halide emulsions of the invention may be optically sensitized to any desired wavelength regions by making use of the dyes as the sensitizing dyes well-known in photographic industry. Such a sensitizing dye may be used independently or in combination. The emulsions are also allowed to contain not only the sensitizing dye but also a dye having no spectrally sensitizing function in it salt or a compound substantially incapable of absorbing any visible rays of light, that is so-called the supersensitizer for enhancing the sensitizing functions of the sensitizing dye.

The silver halide emulsions of the invention are allowed to be added with an antifoggant, a stabilizer and so forth. As the binders for the emulsions, it is advantageous to use gelatin. Emulsion layer and other hydrophilic colloidal layers may be hardened and a plasticizer and the dispersed matter (i.e., a latex) of a water-insoluble or soluble synthetic polymer may be contained therein.

The emulsion layers of a color light sensitive material are applied with couplers. Further, a competing coupler having a color compensation effect and a compound such as a development accelerator, a developing agent, a silver halide solvent, a color toner, a layer hardener, a foggant, an antifoggant, a chemical sensitizer, a spectral sensitizer and a desensitizer, each capable of releasing a photographically useful fragment upon coupling to the oxidized products of a developing agent.

A light sensitive material may be provided with an auxiliary layer such as a filter layer, an antihalation layer and an antiirradiation layer. Inside the above-given layers and/or the emulsion layers, it is allowed to contain therein a dye capable of being released from a light sensitive material or being bleached.

The light sensitive materials are allowed to be added with a matting agent, a lubricant, an image stabilizer, a formalin scavenger, a UV absorbent, a fluorescent whitening agent, a surfactant, a development accelerator and a development retarder.

As for the supports, paper laminated with polyethylene or the like, a polyethylene terephthalate film, baryta paper, a cellulose triacetate film may be used.

EXAMPLES

Now, the invention will be detailed concretely with reference to the examples thereof. It is, however, understood that the invention shall not be limited thereto.

Example-1

(Preparation of a silver halide emulsion)

(Preparation of globular-shaped seed emulsion T-I)

A monodispersed globular-shaped seed emulsion was prepared in the following process.

(Solution A)

Ossein gelatin	80 g
Potassium bromide	47.4 g
A 10% methanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	20 cc
Add water to make	8.0 liter

(Solution B)

Silver nitrate	1.2 kg
Add water to make	1.6 liter

(Solution C)

Ossein gelatin	32.2 g
Potassium bromide	840 g
Add water to make	1.6 liter

(Solution D)

Aqueous ammonia	470 cc

(Solution B) and (Solution C) were added, in a double-jet method, for 11 minutes into (Solution A) which was violently stirred at 40°C, so that the nuclei were produced. The pBr was kept at 1.60 in the whole course.

After that, taking 12 minutes, the temperature was lowered to 30°C and a ripening treatment was further carried out for 18 minutes. The KBr concentration in the ripening step was 0.07 mols per liter and the ammonia concentration was 0.63 mols per liter.

After completing the ripening treatment, the pH was adjusted to be 6.0 and a desalting treatment was carried out in an ordinary method. When the resulting emulsion grains were observed through an electron microscope, they were proved to be a globular-shaped emulsion having two twinned crystal faces parallel to each other and an average grain size of 0.428 µm.

(Emulsion of the invention EM-1)

Octahedral twinned crystallized monodisperse type emulsion EM-1 relating to the invention was prepared by making use of the following 7 kinds of solutions.

(Solution A)

Ossein gelatin	268.2 g
Distilled water	4.0 liter
A 10% methanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	1.5 cc
Seed emulsion (T-1)	0.341 mol
An aqueous 28 wt% ammonia solution	528.0 cc
An aqueous 56 wt% acetic acid solution	795.0 cc
A methanol solution containing 0.001 mol of iodine	50.0 cc
Add distilled water to make	5930.0 cc

(Solution B)

An aqueous 3.5N ammoniacal silver nitrate solution, (the pH was adjusted with ammonium nitrate to be pH = 9.0)

(Solution C)

An aqueous 3.5N potassium bromide solution containing 4.0 wt% of gelatin

(Solution D)

Fine-grain containing emulsion comprising 3.0 wt% of gelatin and silver iodide fine grains (having an average grain size of 0.05 µm)	0.844 mol

The preparation process will be shown below.

Two litre of each of 7.06 mol of silver nitrate and an aqueous solution containing 7.06 mol of potassium iodide was added to 5000 cc of a 6.0 wt% gelatin solution containing 0.06 mol of potassium iodide by taking 10 minutes. The pH in the course of forming the fine grains was controlled with nitric acid so to be 2.0. The temperature was controlled to be 40 °C. After completing the formation of the grains, the pH was adjusted with an aqueous sodium carbonate solution so as to be pH = 6.0.

(Solution E)

A fine-grained emulsion comprising silver iodobromide grains (having an average grain size of 0.04 µm) containing 1 mol% of silver iodide	2.20 mol

This solution was prepared in the same manner as in Solution D, except that the temperature in the course of forming the fine grains was controlled to be 30 °C.

(Solution F)

An aqueous 1.75 N potassium bromide solution

(Solution G)

An aqueous 56 wt% acetic acid solution

(Solution B), (Solution C) and (Solution D) were added to (Solution A) kept at 70 °C in a reaction chamber in a double-jet method by taking 163 minutes and, successively, (Solution E) was independently and constantly added thereinto by taking 12 minutes, so that the seed crystals were grown up to have a grain size of 1.349 µm.

The rates of adding (Solution B) and (Solution C) were functionally varied timewise so as to meet the critical growth rate and the solutions were then added at a suitable adding rates so that any small-sized grains other than the growing seed crystals may not be produced and may not be polydispersed by an Ostwald ripening phenomenon. (Solution D), that was a silver iodide grain emulsion, was supplied by varying the supplying rate (in a mol ratio) corresponding to the supplying rate of an aqueous ammoniacal silver nitrate solution, as shown in Table 1, so as to meet the grain sizes (or the adding periods of time), so that a core/shell type silver halide emulsion having a multilayered structure could be prepared.

The pAg and pH in the course of forming crystals were each controlled as shown in Table 1 by making use of Solutions F and G. The pAg and pH were measured by making use of a silver sulfide electrode and a glass electrode in an ordinary method.

Table 1

Adding time (min)	Grain size (μm)	Flow rate of (Solution D)	pH	pAg
Intermediate phase				
0.0	0.428	10.3	7.2	7.8
23.1	0.584	10.3	7.2	7.8
38.0	0.669	10.3	7.2	7.8
Core				
50.1	0.726	30.0	7.2	7.8
82.6	0.887	30.0	7.2	7.8
82.6	0.887	30.0	6.5	9.4
Shell				
112.7	0.952	10.3	6.5	9.4
122.0	0.976	10.3	6.5	9.4
141.6	1.054	7.7	6.5	9.4
141.6	1.054	0.0	6.5	9.4
163.0	1.249	0.0	6.5	9.7

After completing the formation of the grains, a desalting treatment was carried out in accordance with the method described in JP Application No. 3-41314/1991. Thereafter, gelatin was so added as to be re-dispersed and the pH and pAg were adjusted to be 5.80 and 8.06 at 40 ° C, respectively.

From the scanning type electron microscopic photograph of the resulting emulsion grains, it was proved to be an octahedral twinned crystallized monidisperse type emulsion having an average grain size of 1.349 μm and a distribution range of 10.3%.

Further, the amounts of adding distilled water and ossein gelatin applicable to the preparation of (Solution A) were adjusted in the same preparation process as in EM-1, so that the emulsions for the invention, EM-2 and EM-3, could be prepared.

Still further, the amounts of adding distilled water and ossein gelatin and the iodine composition of the cores each applicable to the preparation of (Solution A) were adjusted in the same preparation process as in EM-1, so that the emulsions for comparison, EM-4, EM-5, EM-6 and EM-7, were prepared.

The resulting EM-1 through EM-7 were each photographed through a scanning type electron microscope [manufactured by Nippon Electron Co., Ltd.], so that the aggregation ratios of silver halide grains were obtained.

Table 2 shows collectively the preparation conditions for EM-1 through EM-7 and the results.

Table 2

Emulsion No.	Max.value of iodine composition in forming cores (mol%)	Distance between the grains in forming cores (µm)		Gelatin content in forming cores (%)	Grain size distribution (%)	Aggregation ratio of silver halide grains (%)
		Initial stage of forming cores	Final stage of forming cores			
EM-1 (Invention)	30	2.17	2.39	4.3	10.3	2.0
EM-2 (Invention)	30	0.40	0.85	4.4	10.1	2.2
EM-3 (Invention)	30	1.70	2.11	3.5	11.5	4.1
EM-4 (Comparison)	5	2.17	2.39	4.3	10.2	3.6
EM-5 (Comparison)	30	4.26	5.14	4.3	32.6	3.7
EM-6 (Comparison)	30	2.17	2.39	1.0	14.0	48.6
EM-7 (Comparison)	30	4.77	5.98	1.4	29.6	21.1

As is obvious from Table 2, emulsions EM-1 through EM-3 each prepared by applying the preparation process of the invention were remarkably improved in the aggregation ratios. Among the comparative emulsion, the aggregation ratios of EM-4 and EM-5 were as low as those of the emulsions of the invention. The aggregation ratio of EM-4 resulted from lowering the maximum value of the iodine composition of the cores down to be out of the scope of the invention. On the other hand, the grain size distribution of EM-5 was seriously deteriorated, due to the inter-grain distances widened to be out of the scope of the invention.

Example-2

(Preparation of a light sensitive material sample)

A multilayered color photographic light sensitive material was prepared in the following manner. Emulsions EM-1 through EM-7 were each subjected to the optimum gold-sulfur sensitization and, making use of the resulting emulsions, the layers having the following compositions were each formed over a triacetate cellulose film support in order from the support.

In the following every description, the amounts of the components added to the silver halide photographic light sensitive materials are indicated in terms of grams per sq.meter unless otherwise stated. The amounts of silver halides and colloidal silver are indicated by converting them into the silver contents thereof. The amounts of the sensitizing dyes are indicated in terms of the mol numbers thereof per mol of silver halides.

The constitution of multilayered color photographic light sensitive material-1 (in which emulsion EM-1 of the invention) was used) was as follows.

Layer 1 : An antihalation layer	
Black colloidal silver	0.16
UV absorbent (UV-1)	0.20
High boiling organic solvent (Oil-1)	0.16
Gelatin	1.23

Layer 2 : An intermediate layer	
Compound (SC-1)	0.15
High boiling organic solvent (Oil-2)	0.17
Gelatin	1.27

Layer 3 : A low-speed red-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.38μm and a silver iodide content of 8.0 mol%)	0.50
Silver iodobromide emulsion (having an average grain size of 0.27μm and a silver iodide content of 2.0 mol%)	0.21
Sensitizing dye (SD-1)	$2.8\text{x}10^{-4}$
Sensitizing dye (SD-2)	$1.9\text{x}10^{-4}$
Sensitizing dye (SD-3)	$1.9\text{x}10^{-5}$
Sensitizing dye (SD-4)	$1.0\text{x}10^{-4}$
Cyan coupler (C-1)	0.48
Cyan coupler (C-2)	0.14
Colored cyan coupler (CC-1)	0.021
DIR compound (D-1)	0.020
High boiling solvent (Oil-1)	0.53
Gelatin	1.30

Layer 4 : A medium-speed red-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.52µm and a silver iodide content of 8.0 mol%)	0.62
Silver iodobromide emulsion (having an average grain size of 0.38µm and a silver iodide content of 8.0 mol%)	0.27
Sensitizing dye (SD-1)	$2.3\text{x}10^{-4}$
Sensitizing dye (SD-2)	$1.2\text{x}10^{-4}$
Sensitizing dye (SD-3)	$1.6\text{x}10^{-5}$
Sensitizing dye (SD-4)	$1.2\text{x}10^{-4}$
Cyan coupler (C-1)	0.15
Cyan coupler (C-2)	0.18
Colored cyan coupler (CC-1)	0.030
DIR compound (D-1)	0.013
High boiling solvent (Oil-1)	0.30
Gelatin	0.93

Layer 5 : A high-speed red-sensitive layer	
Silver iodobromide emulsion (EM-1)	1.27
Sensitizing dye (SD-1)	$1.3\text{x}10^{-4}$
Sensitizing dye (SD-2)	$1.3\text{x}10^{-4}$
Sensitizing dye (SD-3)	$1.6\text{x}10^{-5}$
Cyan coupler (C-2)	0.12
Colored cyan coupler (CC-1)	0.013
High boiling solvent (Oil-1)	0.14
Gelatin	0.91

Layer 6 : An intermediate layer	
Compound (SC-1)	0.09
High boiling organic solvent (Oil-2)	0.11
Gelatin	0.80

Layer 7 : A low-speed green-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.38µm and a silver iodide content of 8.0 mol%)	0.61
Silver iodobromide emulsion (having an average grain size of 0.27µm and a silver iodide content of 2.0 mol%)	0.20
Sensitizing dye (SD-4)	$7.4\text{x}10^{-5}$
Sensitizing dye (SD-5)	$6.6\text{x}10^{-4}$
Magenta coupler (M-1)	0.18
Magenta coupler (M-2)	0.44
Colored magenta coupler (CM-1)	0.12
High boiling solvent (Oil-2)	0.75
Gelatin	1.95

Layer 8 : A medium-speed green-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.59µm and a silver iodide content of 8.0 mol%)	0.87
Sensitizing dye (SD-6)	2.4×10^{-4}
Sensitizing dye (SD-7)	2.4×10^{-4}
Magenta coupler (M-1)	0.058
Magenta coupler (M-2)	0.13
Colored magenta coupler (CM-1)	0.070
DIR compound (D-2)	0.025
DIR compound (D-2)	0.002
High boiling solvent (Oil-2)	0.50
Gelatin	1.00

Layer 9 : A high-speed green-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 1.00µm and a silver iodide content of 8.0 mol%)	1.27
Sensitizing dye (SD-6)	1.4×10^{-4}
Sensitizing dye (SD-7)	1.4×10^{-4}
Magenta coupler (M-2)	0.084
Magenta coupler (M-3)	0.064
Colored magenta coupler (CM-1)	0.012
High boiling solvent (Oil-1)	0.27
High boiling solvent (Oil-2)	0.012
Gelatin	1.00

Layer 10 : A yellow filter layer	
Yellow colloidal silver	0.08
Color-stain inhibitor (SC-2)	0.15
Formalin scavenger (HS-1)	0.20
High boiling solvent (Oil-2)	0.19
Gelatin	1.10

Layer 11 : An intermediate layer	
Formalin scavenger (HS-1)	0.20
Gelatin	0.60

Layer 12 : A low-speed blue-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 1.00µm and a silver iodide content of 8.0 mol%)	1.22
Silver iodobromide emulsion (having an average grain size of 0.27µm and a silver iodide content of 2.0 mol%)	0.03
Sensitizing dye (SD-8)	4.9×10^{-4}
Yellow coupler (Y-1)	0.75
DIR compound (D-1)	0.010
High boiling solvent (Oil-2)	0.30
Gelatin	1.20

Layer 13 : A medium-speed blue-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 0.59µm and a silver iodide content of 8.0 mol%)	0.30
Sensitizing dye (SD-8)	1.6×10^{-4}
Sensitizing dye (SD-9)	7.2×10^{-5}
Yellow coupler (Y-1)	0.10
DIR compound (D-1)	0.010
High boiling solvent (Oil-2)	0.046
Gelatin	0.47

Layer 14 : A high-speed blue-sensitive layer	
Silver iodobromide emulsion (having an average grain size of 1.00µm and a silver iodide content of 8.0 mol%)	0.85
Sensitizing dye (SD-8)	7.3×10^{-5}
Sensitizing dye (SD-9)	2.8×10^{-5}
Yellow coupler (Y-1)	0.11
High boiling solvent (Oil-2)	0.046
Gelatin	0.80

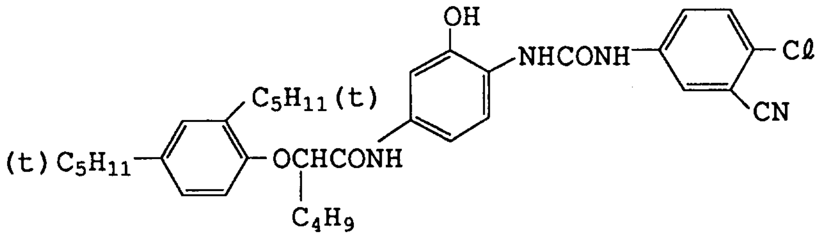
Layer 15 : Protective layer 1	
Silver iodobromide emulsion (having an average grain size of 0.08µm and a silver iodide content of 1.0 mol%)	0.40
UV absorbent (UV-1)	0.065
UV absorbent (UV-2)	0.10
High boiling solvent (Oil-1)	0.07
High boiling solvent (Oil-3)	0.07
Formalin scavenger (HS-1)	0.40
Gelatin	1.31

Layer 16 : Protective layer 2	
Alkali-soluble matting agent (having an average particle size of 2µm)	0.15
Polymethyl methacrylate (having an average particle size of 3µm)	0.04
Lubricant (WAX-1)	0.04
Gelatin	0.55

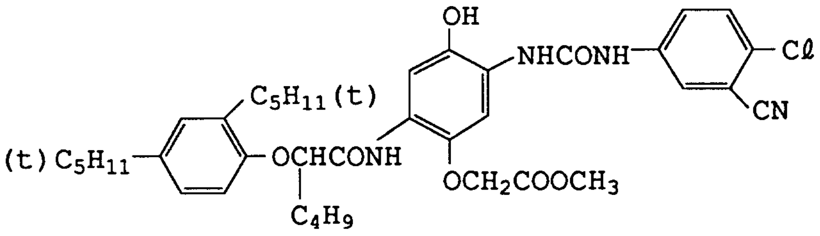
Besides the above-given compositions, there were added with coating aid Su-1, dispersing aid Su-2, a viscosity controller, layer hardeners H-1 and H-2, stabilizer ST-1, two kinds of antifoggants AF-1 and AF-2 having the weight average molecular weights of 10,000 and 1,100,000, respectively, and antiseptic DI-1. The amount of DI-1 added was 9.4 mg/m^2.

The structures of the compounds applied to the resulting samples were as follows.

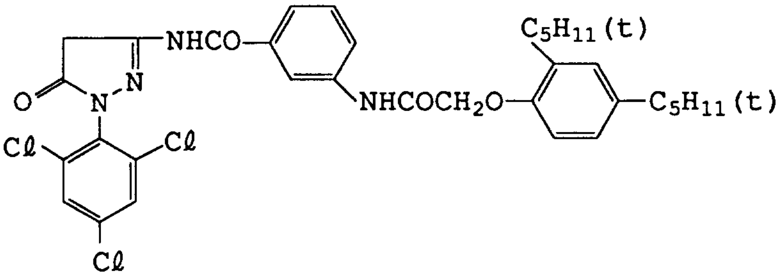
C-1



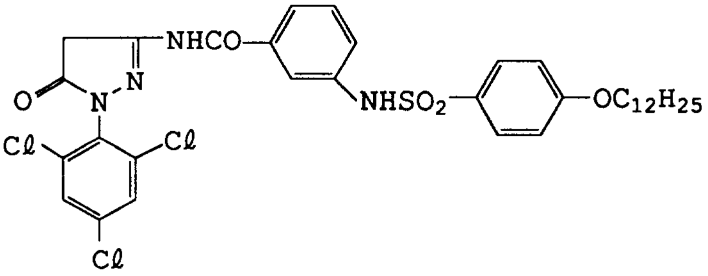
C-2



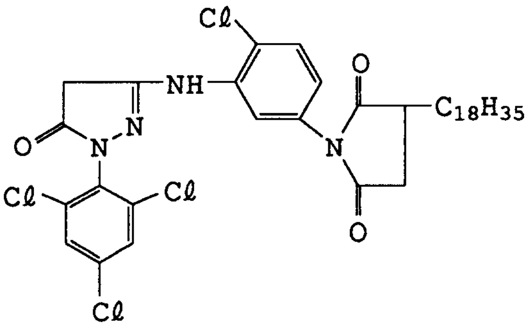
M-1



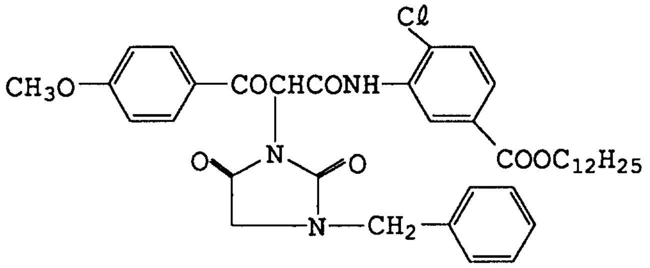
M-2



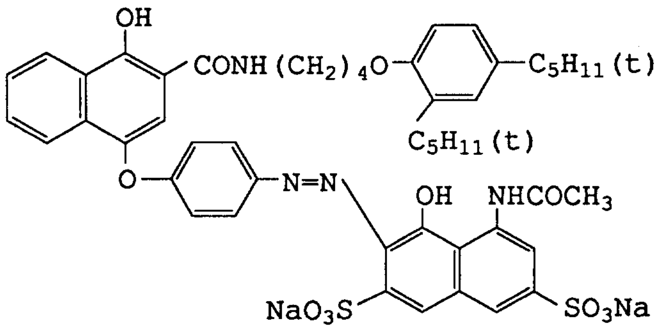
M-3



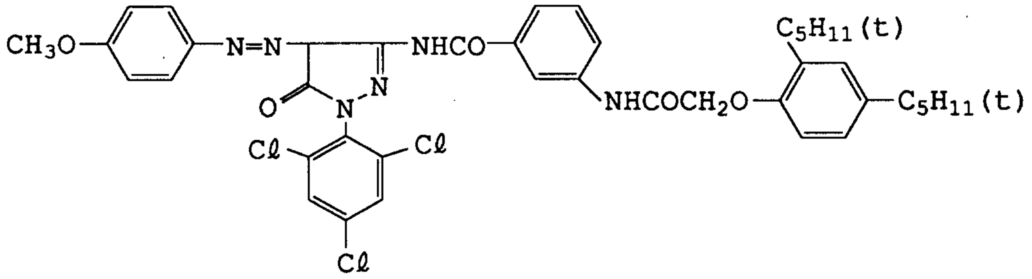
Y-1



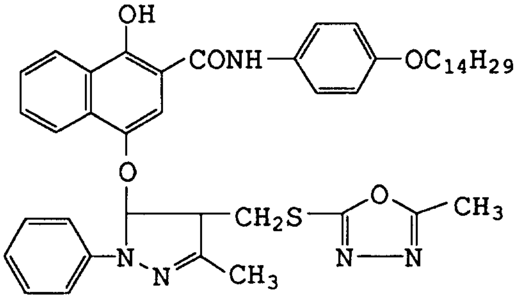
CC-1



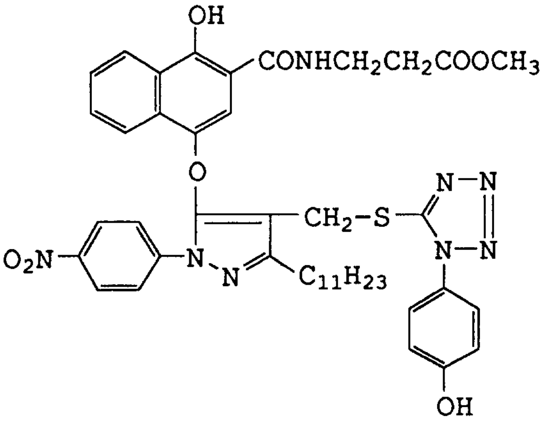
CM-1



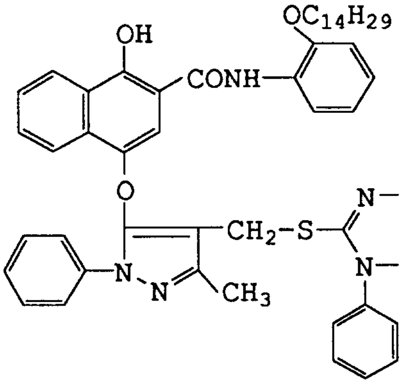
D-1



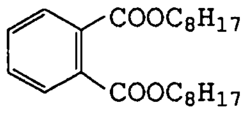
D-2



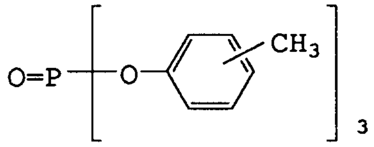
D-3



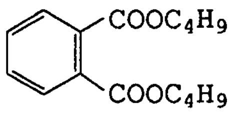
Oil-1



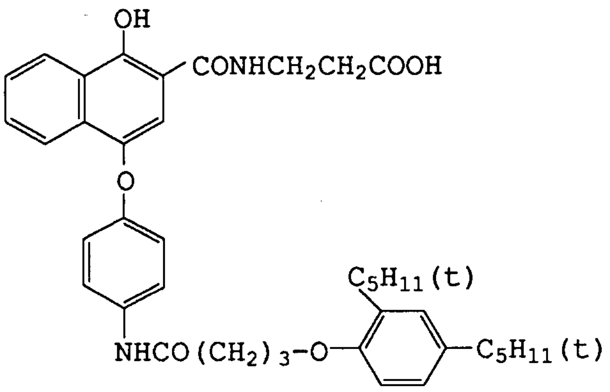
Oil-2



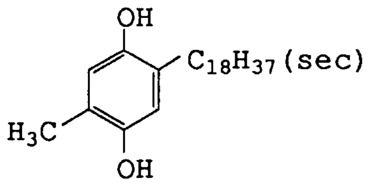
Oil-3



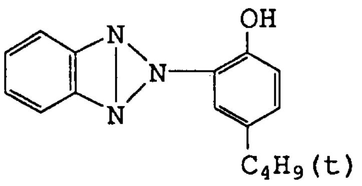
SC-1



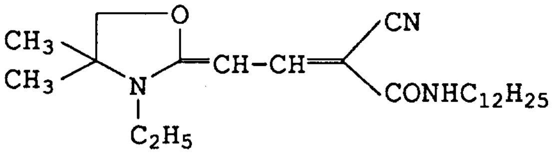
SC-2



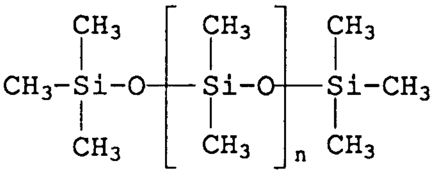
UV-1



UV-2



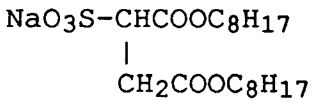
WAX-1



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

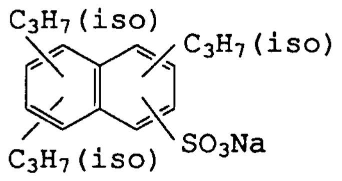
Weight average molecular weight MW : 3,000

Su-1

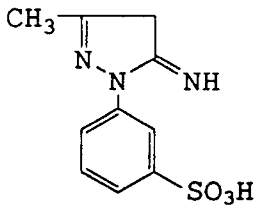


$$\begin{array}{l}NaO_3S\text{-}CHCOOC_8H_{17}\\ \qquad\quad |\\ \qquad\quad CH_2COOC_8H_{17}\end{array}$$

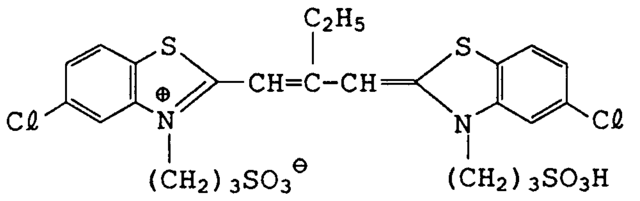
Su-2



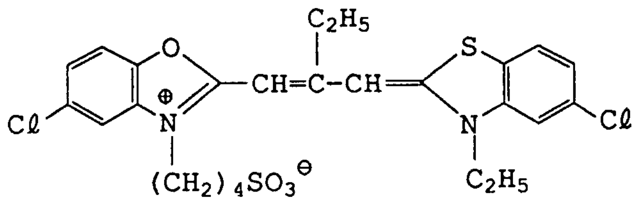
HS-1



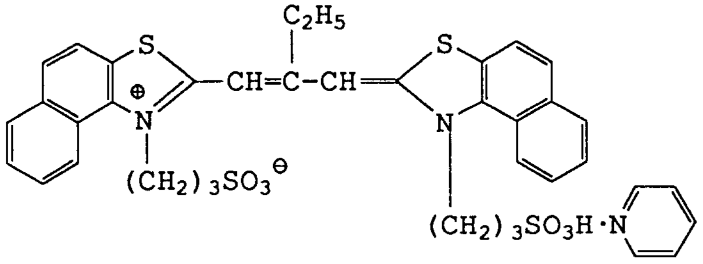
SD-1



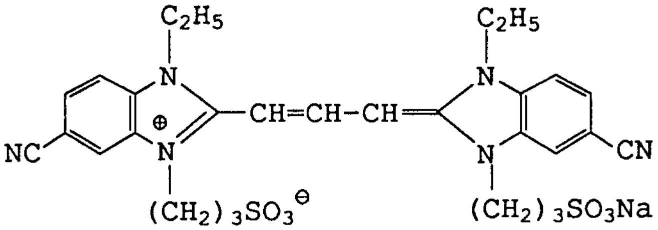
SD-2



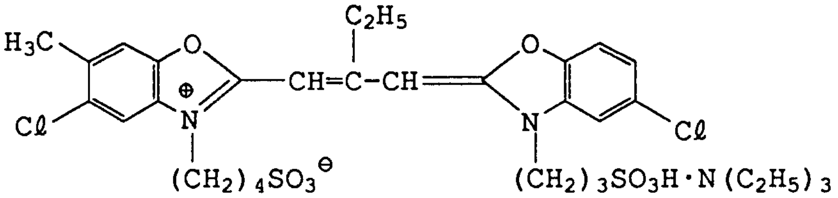
SD-3



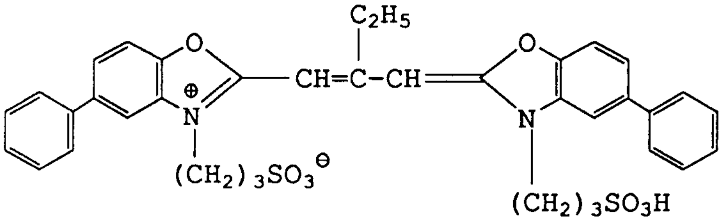
SD-4



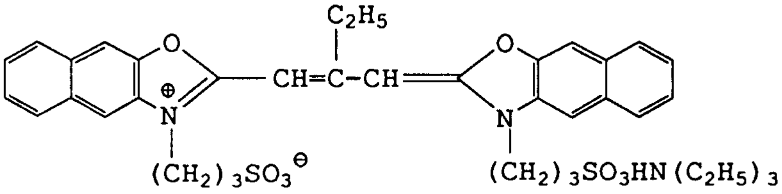
SD-5



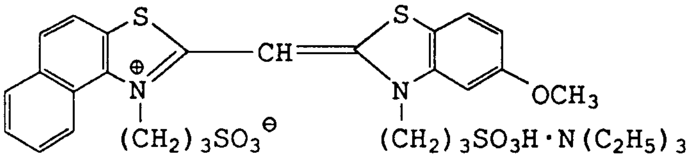
SD-6



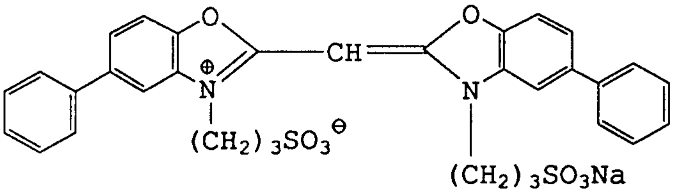
SD-7



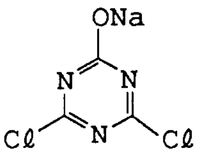
SD-8



SD-9



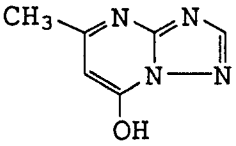
H-1



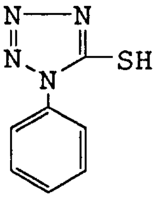
H-2

$(CH_2=CHSO_2CH_2)_2O$

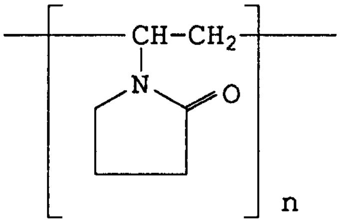
ST-1



AF-1

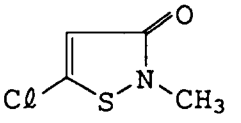


AF-2

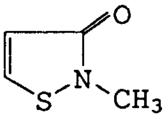


n : polymerization degree

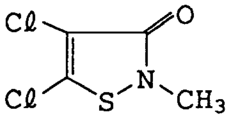
DI-1 (A mixture of the following 3 components)



(Component A)



(Component B)



(Component C)

Components A : B: C = 50 : 46 : 4 (in mol ratio)

Also with the use of emulsions EM-2 through EM-7, multilayered color photographic light sensitive materials, sample-2 through sample-7, were each prepared respectively, as shown in Table 3, in the same manner except that emulsion EM-1 of sample-1 was replaced by the above-mentioned emulsions.

Table 3

Sample No.	=	2	3	4	5	6	7
Emulsion used	=	EM-2	EM-3	EM-4	EM-5	EM-6	EM-7

The resulting samples were each exposed wedgewise to white light and were then treated in the following processing steps.

Processing steps

1. Color developing	3min.15sec.	38.0±0.1 °C
2. Bleaching	6min.30sec.	38.0±3.0 °C
3. Washing	3min.15sec.	24~41 °C
4. Fixing	6min.30sec.	38.0±3.0 °C
5. Washing	3min.15sec.	24~41 °C
6. Stabilizing	3min.15sec.	38.0±3.0 °C
7. Drying		50 °C or lower

The compositions of the processing solutions used in each of the processing steps were as follows.

⟨Color developer⟩	
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline•sulfate	4.75 g
Sodium sulfite, anhydrous	4.25 g
Hydroxylamine•¤sulfate	2.0 g
Potassium carbonate, anhydrous	37.5 g
Sodium bromide	1.3 g
Trisodium•nitrilotriacetate, (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Add water to make	1 liter
Adjust pH to be	pH = 10.1

⟨Bleacher⟩	
Iron ammonium ethylenediamine tetraacetate	100.0 g
Diammonium ethylenediamine tetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
Add water to make	1 liter
Adjust pH with aqueous ammonia to be	pH = 6.0

⟨Fixer⟩	
Ammonium thiosulfate	175.0 g
Sodium sulfite, anhydrous	8.5 g
Sodium metasulfite	2.3 g
Add water to make	1 liter
Adjust pH with acetic acid to be	pH = 6.0

⟨Stabilizer⟩	
Formalin (in an aqueous 37% solution)	1.5 cc
Konidux (manufactured by Konica Corp.)	7.5 cc
Add water to make	1 liter

Immediately after the samples were prepared, the relative fog, the relative sensitivity and the graininess of each sample were evaluated by making use of red light (R).

The results thereof will be shown in Table 4.

Table 4

Sample No	Invention or comparison	Red-sensitive layer		
		Relative fog	Relative sensitivity	Graininess
1	Invention	100	100	100
2	Invention	100	105	102
3	Invention	103	99	110
4	Comparison	101	65	105
5	Comparison	105	69	104
6	Comparison	131	95	146
7	Comparison	128	67	149

The above-mentioned relative fog is a value relative to the minimum density (DMin.). Such a relative fog as defined above is expressed by a value relative to the Dmin value of Sample-1 which is obtained through red light and regarded as the value of 100.

The above-mentioned relative sensitivity is a value relative to the reciprocal of the exposure quantity capable of giving a density of Dmin + 0.15. Such a relative sensitivity as defined above is expressed by a value relative to the red sensitivity obtained from Sample-1 which is regarded as the value of 100.

The above-mentioned graininess is expressed by a value relative to the standard deviation (i.e., RMS value) of a density variation produced when scanning a density of Dmin + 0.15 through a microdensitometer having an aperture scanning area of $250 \mu m^2$. Such an RMS value is the smaller the value is, the better and in such a case, the effects can be displayed higher. Such a graininess as mentioned above is expressed by the RMS value obtained from Sample-1, which is regarded as the value of 100.

As is obvious from the results shown in Table 4, sample-1 through sample-3 of the invention containing emulsions EM-1 through EM-3 relating to the invention are each high in sensitivity, low in fog and improved in graininess. Among these samples, sample-1 and sample-2 each applied with emulsions EM-1 and EM-2 each satisfying the best combination of the invention are particularly excellent. In contrast to the above, sample-4 through sample-7 each applied with comparative emulsion EM-4 through EM-7 are deteriorated in sensitivity, fog and graininess.

Claims

1. A silver halide color photographic light-sensitive material comprising a support and provided thereon, a silver halide photographic emulsion layer comprising core/shell silver halide grains having a core composed of silver halide containing silver iodide in an amount of 10 to 45 mol% and a shell composed of silver halide having a silver iodide content lower than that of said core, said silver halide grains being prepared by a process comprising the steps of:
   maintaining a distance between cores in the range of 0.1 to 3.0 μm in an aqueous dispersion solution containing a dispersion medium of not less than 3.0 % by weight to form said core; and
   forming said shell on said formed core.

2. The material of claim 1, wherein said silver halide grains are composed of silver iodobromide containing a silver iodide content of 3 to 20 mol%.

3. The material of claim 1, wherein the silver iodide content of said shell is not more than 6 mol%.

4. The material of claim 1, wherein the volume of said shell is not less than 2 %, and the volume of said core is 3 to 70 %.

5. The material of claim 1, wherein said dispersion medium is colloidal gelatin.

6. The material of claim 1, wherein said aqueous dispersion solution contains gelatin in an amount of 4 to 10 % by weight.

7. The material of claim 1, wherein the aggregation ratio of said silver halide grains is not higher than 10 %.

8. A process for preparing a silver halide photographic emulsion comprising core/shell silver halide grains having a core composed of silver halide containing silver iodide in an amount of 10 to 45 mol% and a shell composed of silver halide having a silver iodide content lower than that of the core, comprising the steps of:
   maintaining a distance between cores in the range of 0.1 to 3.0 µm in an aqueous dispersion solution containing a dispersion medium of not less than 3.0 % by weight to form said core; and
   forming said shell on said formed core.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 0475

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)
X,Y	EP-A-0 147 868 (FUJI PHOTO FILM COMPANY LTD.) * claims 1-16; example 1 *	1-8	G03C1/015
Y	PHOTOGRAPHIC SCIENCE AND ENGINEERING vol. 26, no. 2, March 1982, WASHINGTON US pages 61 - 64 R.JAGANNATHAN, J.S.WEY 'Interparticle Effect on Crystal Growth-AgBr System' * Definition of variable r1 on page 62, left column, lines 5-7 and tables I and III * * 'Experimental' on p.62, especially last two lines of left column *	1-8	
A	JOURNAL FUR SIGNALAUFZEICHNUNGSMATERIALIEN vol. 12, no. 3, May 1984, BERLIN DD pages 149 - 162 M.SZÜCS 'Kristallwachstum in photographischen Emulsionen' * last paragraph of part 2. *	1-8	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 MAY 1993	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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