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

(11) EP 0 736 797 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.10.1996 Bulletin 1996/41

(51) Int Cl.^{6}: **G03C 1/005**, G03C 1/015

(21) Application number: **96302435.1**

(22) Date of filing: **04.04.1996**

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **05.04.1995 JP 79999/95**

(71) Applicant: **KONICA CORPORATION**
Tokyo 163 (JP)

(72) Inventor: **Akahori, Hiromi**
Hino-shi, Tokyo (JP)

(74) Representative:
Ellis-Jones, Patrick George Armine
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(54) A silver halide photographic light-sensitive material and a manufacturing method of a silver halide emulsion

(57) A silver halide photographic light-sensitive material comprises a light-sensitive silver halide emulsion layer containing silver halide grains, said emulsion having been ultrafiltrated, wherein said silver halide grains have an aspect ratio of 2 to less than 5 and have an average silver chloride content of not less than 30 mol%.

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

The invention relates to a silver halide photographic light-sensitive material and a manufacturing method of a silver halide emulsion.

The invention relates particularly to a silver halide photographic light-sensitive material which can be subjected to rapid processing (for example, Dry to Dry processing of less than 30 seconds) and a manufacturing method of the same.

BACKGROUND OF THE INVENTION

Recently, in a light sensitive photographic material, rapid processing is demanded in addition to high sensitivity and high image quality. For example, in X-ray photographs for medical use, there is a strong demand for rapid developing in order to improve service to patients or processability, in addition to demand for high sensitivity and high image quality.

In order to realize rapid processing such as total processing time of less than 30 seconds, a light sensitive material is required to have excellent developability.

As a light sensitive material having excellent developability, a technique employing silver chloride containing tabular grains is known, which is disclosed in Japanese Patent O.P.I. Publication Nos. 63-281149/1988, 62-218959/1987 and 63-213836/1988. This technique makes rapid development possible and improves the affect of halide ions in a developer. There is, however, the problem that the light sensitive material comprising silver chloride-containing tabular grains gives yellow color to developed silver, and produces roller marks due to transport rollers, resulting in image quality deterioration.

The use of increased gelatin binder or the use of polymer latex is known as a means to prevent the roller marks. However, this means is not preferable since it has the disadvantages of lowered sensitivity and color staining due to residual sensitizing dyes produced during rapid processing.

SUMMARY OF THE INVENTION

Accordingly, an object of the invention is to provide a silver halide photographic light-sensitive material which prevents roller marks (pressure fog or pressure desensitizing) in rapid processing (for example, Dry to dry processing time of less than 30 seconds), even when an automatic processor is employed, and which has improved image tone and reduced staining after development, and a manufacturing method of a silver halide emulsion constituting said silver halide photographic light-sensitive material.

BRIEF EXPLANATION OF THE DRAWING

Fig. 1 shows a constitution of an ultrafilter used in the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present inventor has found that the above object can be attained by the followings:

The above object can be attained by a silver halide photographic light-sensitive material comprising at least one light-sensitive silver halide emulsion layer containing silver halide grains, said emulsion having been ultrafiltrated (hereinafter also called the emulsion in the invention), wherein said silver halide grains have an aspect ratio of 2 to less than 5 and have an average silver chloride content of not less than 30 mol%.

The above object is attained by said silver halide photographic light sensitive material, wherein the total processing time of the material is less than 30 seconds.

The above object is also attained by a manufacturing method of a silver halide emulsion containing silver halide grains having an aspect ratio of 2 to less than 5 and having an average silver chloride content of not less than 30 mol%, the method comprising an ultrafiltration step.

The silver halide photographic light-sensitive material in the invention and its manufacturing method will be detailed below.

The silver halide photographic light-sensitive material of the invention comprises at least one light-sensitive silver halide emulsion layer containing silver halide grains, wherein said silver halide grains have an aspect ratio of 2 to less than 5 and have an average silver chloride content of not less than 30 mol%. The average silver chloride content is preferably 40 to 90 mol%. The aspect ratio is 2 to less than 5, but is preferably 2.5 to 4.5 and more preferably 3 to 4.

The silver halide grains used in the invention are preferably prepared by methods detailed in US Patent Nos.

4,063,951, 4,386,156, 5,275,930 and 5,314,798.

In the invention, the silver halide grain projected area necessary to determine the aspect ratio is obtained by the sum area of the grains. The projected area to measure the total projected area and grain size is obtained as follows: The silver halide grains are spread out on a flat surface such that the grains form a dense, single layer, and photographed at a 10,000-50,000 magnification ratio by an electron microscope to obtain a print. The total projected area and grain size of the grains are obtained by measuring the grain area and grain size of the photographed grains (at least 1000 randomly sampled grains) on the print. The silver halide grains used in the invention have an aspect ratio of 2 to less than 5 which is defined in terms of grain size/grain thickness ratio. It is preferable that 50% of the total projected area are monodisperse twinned crystal grains having a thickness of less than 0.3 μm and an aspect ratio of 2 to less than 5. The thickness of the grains is obtained by observing the grains at an angle through an electron microscope.

The grain size distribution may be a monodisperse emulsion having a narrow distribution or a polydisperse emulsion having a broad distribution. The preferable silver halide emulsion used in the invention is, for example, a monodisperse emulsion containing silver halide grains having silver iodide localized in its interior. The preferable monodisperse emulsion herein referred to is an emulsion containing silver halide grains wherein at least 95% by weight or by grain number of the silver halide grains fall within ±40%, and preferably ±30% of an average grain size obtained by measuring according to a conventional method.

The crystal structure of the silver halide grains may be a structure such that the halogen composition of the exterior of the grains is different than the interior of the grains. For example, the emulsion may be a monodisperse emulsion containing core/shell type grains having two apparent layers in which a core having a high silver iodide content is covered with a shell layer having a low silver iodide content. The manufacturing method of the above described monodisperse emulsion is well known, and for example, is detailed in J. Phot. Sci., 12, 242-251 (1963), Japanese Patent O.P.I. Publication Nos. 48-36890/1973, 52-16364/1977, 55-142329/1980 and 58-49938/1983, British Patent No. 1,413,748 or US Patent Nos. 3,574,628 and 3,655,394.

In the invention, the above monodisperse emulsion is obtained by a method comprising the steps of supplying a silver ion and a halide ion to seed grains as growing nuclei and growing the seed grains.

The manufacturing method of the above described core/shell type emulsion is well known, and for example, J. Phot. Sci., 24, 198 (1976), US Patent Nos. 2,592,250, 3,505,068, 4,210,450 and 4,444,877 or Japanese Patent O.P.I. Publication No. 60-14331/1985 is referred to.

British Patent No. 2,112,157 or US Patent Nos. 4,414,310 and 4,434,226 disclose that, when 50% or more in terms of silver of silver halide grains are tabular silver halide grains having an aspect ratio (grain size/grain thickness ratio) of 2 to less than 5, the silver halide grains show elevated spectral sensitizing efficiency and improved image graininess and sharpness. The emulsion can be manufactured according to the description of these patent publications. The emulsion may be any of a surface latent image-forming emulsion forming a latent image on the surface of the grains, an internal latent image-forming emulsion forming a latent image in the grains or an emulsion forming a latent image both on the surface of the grains and in the grains.

In the invention the silver halide grains have an average silver chloride content of not less than 30 mol%, and the silver chloride content of an individual silver halide grain can be measured by analyzing a composition of the individual silver halide grain using an X-ray microanalyzer.

The silver chloride content of the individual silver halide grain is obtained by the following: The silver chloride content of at least 100 silver halide grains is measured with an X-ray microanalyzer, the standard deviation thereof is computed, and said standard deviation is divided by the average silver chloride content and multiplied by 100.

The measured results of the silver iodide content of an individual silver halide grain as measured by an analytical electron microscope are described in Nihon Shashin Gakkaishi, 53, 2, p. 125-128 (1990). There is also a disclosure in Journal of Imaging Science, Vol. 31, No. 1 (1987), P. 15-26 in which the fine structure inside the tabular grains on a halogen composition is analyzed through Low-temperature luminescence microscopy. There is further a disclosure in Journal of Imaging Science, Vol. 32, No. 4 (1988), P. 160-177 that, when silver chloride is precipitated on silver bromoiodide having silver iodide distribution in the grains, the silver iodide site-directs the precipitation site of the silver chloride.

Then, there is a disclosure in Nihon Shashin Gakkaishi, 35, p. 213 and after (1990) that non-uniformity of a halide composition in the grains can be observed directly at a low temperature through a transparent electron microscope. As shown above, a fine structure of an individual silver halide grain can be observed.

An emulsion used for the silver halide photographic light sensitive material of the present invention can be produced by a conventional method. For example, methods described in "Emulsion Preparation and Types" in Research Disclosure (RD) No. 17643 (December, 1978), pp. 22 to 23 and RD. No. 18716 (November, 1979), on page 648 can be used.

The emulsion used for the silver halide photographic light sensitive material of the present invention can be prepared by methods described in "The Theory of the Photographic Process" 4th Edition (1977), written by T.H. James, published by Macmillan Inc., on pp. 38 to 104, "Photographic Emulsion Chemistry" (1966) written by G.F. Duffin, published by Focal Press Inc., "Chimie et Physique Photographique" written by P. Glafkides, published by Paul Montel (1967) and "Making and Coating Photographic Emulsion" written by V.L. Zelikman and others, published by Focal Press Inc. (1964).

Namely, under a solution condition of a neutral method, an acid method and an ammonia method, mixing conditions of an ordinary mixing method, a reverse mixing method, a double jet method and a controlled double jet method, grain preparation conditions of a conversion method and a core/shell method, and their combinations can be selected for producing the emulsion.

At physical ripening or grain preparation, a cadmium, lead, zinc, thallium or iridium salt or their complexes or a rhodium salt or its complex may be added to the emulsion.

The silver halide emulsion in the invention is ultrafiltrated, particularly ultrafiltrated in preparation of silver halide grains, and preferably after the growth of silver halide grains. The term "ultrafiltration" (also called "dialysis") herein referred to is defined as described in M. Chenyan, "Ultrafiltration Handbook, Technomic Co., (1986). The specific examples applying ultrafiltration to a photographic element are described in Research Disclosure, Vol. 102, (1972), 10, Item 10208 and Vol. 131, (1975), 3, Item 13122 and the description is referred to.

The above Research Disclosure is published by Industrial Opportunities Ltd., Homewell, Havant·Hampshire, P09 1EG, England.

Ultrafiltration is also called diafiltration, which is well known as a purification method particularly useful for preparation or purification of grains. A membrane is generally used in the ultrafiltration, wherein unnecessary substances pass through the membrane and necessary substances such as silver halide grains do not.

The ultrafiltration comprises removing extra soluble salts to wash or concentrate a silver halide emulsion. The ultrafiltration is carried out as follows: A deflocculated silver halide emulsion is incorporated into a ultrafiltration module, and run such that unnecessary salts pass through the membrane to obtain a residual composition comprising a silver halide emulsion and a deflocculant. The selective removal is carried out by pressing a solution against a synthetic semipermeable membrane under pressure, so that molecules of less than a specific size selectively pass through the membrane and molecules of not less than the specific size do not.

The soluble salts and silver halide grains precipitated in a deflocculant-containing solution can be supplied to a vessel according to a conventional method. Subsequently, the solution may be supplied through a flow meter to the ultrafiltration module using a pump. The extra salts are removed as a permeation solution, and the rest is circulated in the vessel as a recirculation mode. In another embodiment, many ultrafiltration modules are aligned in series to supply the rest from the previous module to the inlet of the subsequent module. Before a solution is introduced into each module successively, the solution can be diluted for washing with a solvent. However, re-dilution of the solution is not necessary in view of concentration of the solution.

Various filtration methods are known, and any filtration method can be used in the invention. In Fig. 1, the ultrafiltration unit 100 has a conventional convenient structure, and is used in the invention. For example, the useful ultrafiltration unit and a method employing the same are described in Research Disclosure, Vol. 102 (1972/10), Item 10208; Hagemaier et al., Research Disclosure, Vol. 131 (1975/3), Item 13122; Bonnet, Research Disclosure, Vol. 135 (1975/7), Item 13557; German Patent No. 2,436,461 and US Patent No. 2,495,918.

As described in Fig. 1, the reaction vessel is composed of the ultrafiltration unit 100, the tube 102, whereby the outlet communicates with the inlet in the ultrafiltration unit, forming a loop, and the pump 104, promoting a flow. As illustrated by the arrow 106, a halogenide solution is incorporated into the reaction vessel through the first inlet tube 108. Similarly, as illustrated by the arrow 110, a silver halide solution is incorporated into the reaction vessel through the second inlet tube 112. The water-soluble salt containing solution is separated from the silver halide dispersion solution by the filtration unit and discharged through the first outlet tube 114 as illustrated by the arrow 116. The second outlet tube 118 and the control valve 120 enable removal of the silver halide dispersion solution as illustrated by the arrow 122.

Ultrafiltration is preferably carried out by circulating a dispersion solution in the reaction vessel which passes through the semipermeable membrane in the ultrafiltration unit to produce the pressure difference necessary to cross the semipermeable membrane. Generally, said membrane comprises small holes which are permeable to molecules having not more than a specific molecular weight but impermeable to molecules having a molecular weight exceeding the specific molecular weight or silver halide grains in the dispersion solution. The membrane is selected from those having characteristics allowing permeation of compounds having a molecular weight (permeation cut-off molecular weight) of preferably about 500 to 300,000, and more preferably about 500 to 50,000.

In the invention, this cut-off molecular weight limit can be easily varied beyond the above molecular weight ranges. Apparently, the cut-off molecular weight limit can not be larger than that of a deflocculant.

Generally, the specific permeation cut-off molecular weight is selected depending on the silver halide grain size before ultrafiltration, a dispersing medium and/or another low molecular weight compound (retentate) to be remained in the dispersion solution after separation of soluble salts. The molecular weight of soluble reaction products (for example, alkali metal nitrates) in a halide or salt solution is lower, and therefore, a permeation cut-off molecular weight necessary to selectively obtain silver halide grains and a peptizer agent which may be present in the dispersion solution is easily selected.

The pressure applied to the dispersion solution contacting the ultrafiltration membrane may be broadly varied. In the reaction vessel, the pressure of the dispersion solution against the ultrafiltration membrane is preferably 100 palg (7.03 kg/cm^2) to 500 palg, and more preferably 5 palg to 10 palg, the pressure at the outlet of the retentate is not more than 10 palg (0.703 kg/cm^2). The pressure difference across the membrane is preferably 40 to 60 palg (2.81 to 4.22 kg/cm^2). As a matter of course, the pressure beyond the above pressure ranges can also be applied depending upon the structure of the reaction vessel or the ultrafiltration membrane, the dispersion solution viscosity, the retentate concentration or purity of the desirable retentate.

The membrane used in the ultrafiltration is typically an anisotropic membrane comprising an extremely thin membrane of fine vesicular structure provided on a thicker porous support. The useful membrane material is selected from various polymers such as polyvinyl chloride, polyvinyl carboxylate, polyvinyl formate, polyvinyl acetate, polyvinyl alcohol, polysulfone, polyvinyl ether, polyacrylamide, polyimide, polyester, polyfluoroalkylene (for example, polytetrafluoroethylene), polyvinylidene fluoride, and celluloses, for example, cellulose or cellulose esters such as cellulose acetate, cellulose butyrate and cellulose acetate butyrate.

Fig. 1 shows a simple loop including a single ultrafiltration unit, and said loop can be varied as long as it is within the scope of the invention. In addition to a single ultrafiltration unit, for example, two or more ultrafiltration units connected in series can be used. Further, two or more parallel loops can be used. A complex loop can also be used. When the ultrafiltration unit 100 has a relatively high cut off molecular weight, the removed medium can be supplied, as illustrated by the arrow 116, to a second ultrafiltration unit having a lower cut off molecular weight.

The retentate in the second ultrafiltration unit can be returned to a reaction vessel. Another embodiment is an example in which a part of the ultrafiltrated liquid is directly returned through the tube 114 to a reaction vessel and the rest is discarded.

The amount of a dispersion medium removed by ultrafiltration can be controlled to any desirable extent by adjusting liquid flow velocity in the reaction vessel and/or the liquid pressure difference across the ultrafiltration membrane.

The reduction of the pressure difference across the ultrafiltration membrane can prevent any phase of the precipitates. The ultrafiltration speed can be mechanically reduced. The volume of a silver halide emulsion, which is obtained after addition of a silver salt and a halide is completed at the same time, as the total volume percentage of added components is widely varied depending on characteristics of a desired silver halide emulsion.

The silver halide grains newly formed in the presence of a deflocculant are washed or purified by passing a newly precipitated silver halide emulsion through an ultrafiltration module. The flow or washing of the silver halide emulsion through the ultrafiltration module is continued until soluble salts such as a nitrate ion and halogenide ions are substantially removed from the emulsion. Typically, the silver halide emulsion is passed through the ultrafiltration module several times, and the filtration time depends on factors such as the soluble salt concentration formed during grain formation, melt weight, and the content ratio of silver halide to the deflocculant. Generally, it is practical and preferable that the silver halide emulsion is washed until pAg is reduced to not more than 8. It is generally recognized that repeated washing cycles reduce the soluble salt content according to material balance.

The silver halide photographic light sensitive material can be sensitized by methine dyes or other spectrally sensitizing dyes. The dyes used include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. The specifically useful dyes include cyanine dyes, merocyanine dyes, and complex merocyanine dyes. These dyes comprise a conventional nucleus, and the nucleus includes a pyrroline, oxazoline, thiazoline, pyrrole, oxazole, thiazole, selenazole, imidazole, tetrazole and pyridine nucleus, and nuclei in which these nuclei are condensed with a hydrocarbon ring, for example, an indolenine, benzindolenine, indole, benxoxazole, naphthoxazole, benzothiazole, naphthothiazole, benzoselenazole, benzimidazole or quinoline nucleus. The above mentioned nucleus may have a substituent.

The merocyanine dyes or complex cyanine dyes have, as a nucleus having a ketomethine nucleus, a 5- or 6-membered heterocyclic nucleus such as a pyrazoline-5-one, thiohydantoin, 2-thioxazolidine-2,4-dione, thiazolidine-2,4-dione, rhodanine or thiobarbituric acid nucleus.

These dyes are described in German Patent No. 929,080, US Patent Nos. 2,231,658, 2,493,748, 2,503,766, 2,519,001, 2,912,329, 3,655,394, 3,656,959, 3,672,897 and 3,649,217, British Patent No. 1,242,558 or Japanese Patent Publication No. 44-14030/1969.

These dyes may be used singly or in combination, but are often used in combination. The typical examples include those described in US Patent Nos. 2,688,545, 2,977,299, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,679,428, 3,703,377 and 3,837,862, British Patent No. 1,344,281 or Japanese Patent Publication No. 43-4936/1968.

The sensitizing dye may be added at any time of during grain formation, before, during or after chemical ripening or before coating, but is added preferably several times.

In the silver halide photographic light sensitive material of the invention, a crossover cut layer may be provided between the emulsion layer and the support. This layer may be a subbing layer provided between the hydrophilic colloid layer and the support or a dye layer provided between the emulsion layer and the subbing layer. The dye used in the subbing layer includes oxonol dyes having a pyrazolone or barbituric acid nucleus, azo dyes, azomethine dyes, anthraquinone dyes, arylidene dyes, styryl dyes, triarylmethane dyes, merocyanine dyes and cyanine dyes. The dye used in the dye layer may be dispersed in the form of fine particles. The dye includes exemplified compounds (I-2, 4, 6, 8, 9, 11, 12, 13 through 27, II-2, 5, 6, III-3, 4, 6, 8, 9, 10, 11, 12, 14 through 28, IV-3, 5, 6, 8, 10 through 16, and V-3, 5, 6, 7) disclosed on pages 6-12 of Japanese Patent O.P.I. Publication No. 2-264247/1990, and any of these can be used.

The above compounds can be easily synthesized according to the methods disclosed in International Patent No. 88/04794, European Patent Nos. 0274723A1, 276,566 and 299,435, Japanese Patent O.P.I. Publication Nos. 52-92716/1977, 55-155350/1980, 55-155351/1980, 61-205934/1986 and 48-68623/1973 or US Patent Nos. 2,527,583, 3,486,897, 3,746,539, 3,933,798, 4,130,429 and 4,040,841.

For the emulsion used in the silver halide photographic light-sensitive material of the invention, various additives for photographic use can be used in a step before or after physical ripening or chemical ripening. The additives used in such a step include various compounds described in Research and Disclosure (RD) Nos. 17643, 18716 and 308119 can be used.

Locations where the compounds are described in these three (RD) are shown below:

Additive	RD-17643		RD-18716	RD-308119	
	Page	Classification	Page	Page	Classification
Chemical Sensitizer	23	III	648 upper right	996	III
Sensitizing Dye	23	IV	648-649	996-8	IVA
Desensitizing Dye	23	IV		998	IVB
Dye	25-26	VIII	649-650	1003	VIII
Development Accelerating Agent	29	XXI	648 upper right		
Stabilizing Agent	24	IV	649 upper right	1006-7	VI
Brightening Agent	24	V		998	V
Hardener	26	X	651 left	1004-5	X
Surfactant	26-27	XI	650 right	1005-6	XI
Plasticizer	27	XII	650 right	1006	XII
Slipping Agent	27	XII			
Matting Agent	28	XVI	650 right	1008-9	XVI
Binder	26	XXII		1003-4	IX
Support	28	XVII		1009	XVII

The support used in the silver halide photographic light-sensitive material of the invention includes a support described on RD above. The suitable support includes a polyethyleneterephthalate film. In order to enhance adhesivity of the surface of the support to a coating layer, a subbing layer may be provided on the support or corona discharge and UV ray irradiation may be given to the surface.

The light sensitive material may be comprised of hydrophilic layers such as a silver halide emulsion layer, a protective layer, an intermediate layer, a filter layer, a UV absorbing layer, an antistatic layer, an antihalation layer and a backing layer.

Gelatin or other synthetic polymers can be used as a protective colloid in the hydrophilic layer.

As gelatin, lime-processed gelatin, acid-processed gelatin or gelatin derivatives may be used. The synthetic polymers other than gelatin include a cellulose derivative such as hydroxyethylcellulose, a homopolymer or copolymer of polyvinyl alcohol, partially acetal polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid and polyacrylamide. In the invention, when a light sensitive material is processed with an automatic processor comprising development, fixing, washing (or stabilizing) and drying steps, the total processing time which takes from developing to drying is preferably less than 30 seconds.

The total processing time referred to herein is the time (so-called Dry to Dry processing time) taken from entry of the leading edge of light sensitive material in the developing tank solution of the automatic processor to the delivery of the leading edge out of the drying zone of the automatic processor. The total processing time is preferably less than 30 seconds, and more preferably 15 to 25 seconds.

It is essential to contain in developer 1,4-dihydroxy benzenes, and optionally p-aminophenols or pyrazolidones as a developing agent.

The addition amount of 1,4-dihydroxybenzene is preferably 0.01 to 0.7 mol, and more preferably 0.1 to 0.5 mol per liter of developer.

The addition amount of p-aminophenols or pyrazolidones is preferably 0.0005 to 0.2 mol, and more preferably 0.001 to 0.1 mol per liter of developer.

The sulfites used in the developer include sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, and potassium metabisulfite. The amount used of the sulfite is 0.1 to 2.0 mol, and preferably 0.1 to 1.0 mol per liter of developer. In a concentrated developer the maximum addition amount is preferably up to 3.0 mol per liter of developer.

To the developing solution, a chelating agent whose chelate stability constant against iron ion is 8 or more can be contained. The iron ion referred here means a ferric ion (Fe^{3+}).

The chelating agent whose chelate stability constant against iron is 8 or more includes an organic carboxylic acid chelating agent, an organic phosphoric acid chelating agent, an inorganic phosphoric chelating agent or a polyhydroxy compounds.

To the developing solution, a hardener which strengthen layer physical property through hardening reaction with gelatin in the light-sensitive material during photographic processing. As a hardener, for example, glutaric aldehyde, α-methylglutaric aldehyde, β-methylglutaric aldehyde, maleic dialdehyde, succinic dialdehyde, methoxysuccinic aldehyde, methylsuccinic dialdehyde, α-methoxy-β-ethoxyglutaric aldehyde, α-n-buthoxyglutaric aldehyde, α,α-dimethoxysuccinic dialdehyde, β-isopropyl succinic aldehyde, α,α-diethylsuccinic dialdehyde, butylmaleic dialdehyde or bisulfite adducts thereof.

pH of the developing solution is preferably 9.00 to 12.00, and more preferably 9.00 to 11.50. An alkali agent or a buffer agent used for regulating pH includes pH regulators such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, boric acid, sodium triphosphoric acid and potassium triphosphoric acid.

As a fixing solution, fixing solutions containing fixing agents such as sodium thiosulfate and ammonium thiosulfate can be used. Of them, in terms of fixing speed, ammonium thiosulfate is preferred. The amount used of these fixing agents is about 0.1 to 6 mol/liter.

To the fixing solution, an aqueous solution of aluminium salt can be added as a hardener. In addition, aluminum chloride, aluminium sulfate and potash alum can be used.

To the fixing solution, malic acid, tartaric acid, citric acid, gluconic acid or their derivatives can be used independently or two or more thereof can be used in combination. It is effective that these compounds are added by 0.001 mol or more and especially effective to add 0.005 to 0.03 mol per 1 liter of fixing solution.

pH of the fixing solution is preferably 3.8 or more and more preferably 4.2 to 7.0. When considering fixing hardening and the odor of sulfite, 4,3 to 4.8 is still more preferable.

EXAMPLES

The examples of the invention will be explained below, but the invention is not limited thereto.

Example 1

This example can be employed as a photographic light sensitive material for radiography and a light sensitive material suitable for rapid processing was used in the invention.

(Preparation of silver bromochloride emulsion) (Emulsions A-1, A-2)

The silver bromochloride emulsion was prepared using the following A, B and C solution.

[Solution A]

Ossein gelatin	6 g
Ten % ethanol solution of Polyisopropylene-polyethyleneoxydisuccinate sodium salt	1 ml
Distilled water	700 ml.

[Solution B]

$AgNO_3$	170 g
Distilled water	410 ml

[Solution C]

Sodium chloride	35.1 g
Sodium bromide	47.6 g
Iridium hexachloride	50 μg
Ten % ethanol solution of Polyisopropyleneoxy-disuccinate sodium salt	3 ml
Ossein gelatin	11 g
Distilled water	407 ml.

Sodium chloride was added to Solution A at 40°C to obtain EAg of 120mV. Solutions B and C were added thereto by a double-jet method using a mixing stirrer described in Japanese Patent Publication Nos. 57-92523/1982 and 57-92524/1982. The addition is carried out as shown below, wherein the addition amount was gradually increased over the total addition time of 25 minutes to give a constant EAg.

Seven minutes after the addition, EAg was varied from 120 mV to 100 mV using a sodium chloride solution, and thereafter, the 100 mV EAg was maintained to completion of the addition. In order to maintain EAg constant, EAg was adjusted using a 3 mol/liter sodium chloride solution.

Addition time (minutes)	Solution B (ml/minute)	Solution C (ml/minute)
0	5.4	5.3
7	5.4	5.3
10	22.0	21.6
25	22.0	21.6

In order to measure EAg, metal silver electrode and double junction saturated Ag/AgCl comparative electrode were employed. (As the constitution of electrodes, double junction disclosed in Japanese Patent Publication No. 57-197534/1982 was employed.)

The roller tube quantitative pump capable of varying the flow rate was used in adding Solutions B and C. During the addition, it was observed through an electron microscope that new grains were not produced in the emulsion. Further, during the addition, pH was maintained at 3.0 with a 3% aqueous nitric acid solution.

After completion of addition of Solutions B and C, the resulting emulsion was subjected to Ostwald ripening, and divided into two parts. One emulsion was desalted at 40°C by the use of an aqueous Demol N (a condensate of a naphthalene sulfonic acid salt with an aldehyde, produced by Kao Atlas Co., Ltd.) solution and an aqueous magnesium sulfate solution, washed with water (CW), mixed with 600 ml of an aqueous gelatin solution containing 15 g of ossein gelatin and redispersed with stirring at 55°C for 30 minutes. Thus, 750 ml of silver bromochloride emulsion (A-1-1) was obtained which contained cubic silver halide grains having a silver chloride content of 60 mol% and having an average grain size of 0.4 μm. The other emulsion was ultrafiltrated, mixed with 600 ml of an aqueous gelatin solution containing 15 g of ossein gelatin and redispersed with stirring at 55°C for 30 minutes. Thus, 750 ml of silver bromochloride emulsion (A-1-2) was obtained which contained cubic silver halide grains having a silver chloride content of 60 mol% and having an average grain size of 0.4 μm.

Silver bromochloride emulsion (A-2-1) was prepared in the same manner as in emulsion (A-1-1), except that the sodium chloride and sodium bromide contents of Solution C were varied. Emulsion (A-2-1) contained cubic silver halide grains having a silver chloride content of 20 mol%. Silver bromochloride emulsion (A-2-2) was prepared in the same manner as in emulsion (A-1-2), except that the sodium chloride and sodium bromide contents of Solution C were varied. Emulsion (A-2-2) contained cubic silver halide grains having a silver chloride content of 20 mol%.

(Emulsion B)

In a reaction vessel with a stirrer were placed a solution of an ossein gelatin having a high methionine content (containing 59.7 μmol of methionine per 1 g of gelatin) in which 90 g of the ossein gelatin is dissolved in 6000 g distilled water, 0.5 mol of $CaCl_2 \cdot 2H_2O$ and 118.5 g of NaBr. The resulting solution was kept at 40°C, and the pH was adjusted to 5.1 with NaOH or HNO_3. A 0.5 mol silver nitrate solution was added in four minutes in a silver amount of 1.6% based on the total silver amount to be used. The silver nitrate solution was further added in 55 minutes at a progressively increasing addition rate (the rate at the end of the addition was 10 times the rate the beginning of the addition) in a remaining silver amount of 98.4%. At 4, 16, and 36 minutes after beginning of precipitation, 30 cc of a 37 mM adenine solution was added and at 10 minutes after beginning of precipitation, 3.78 g of a 3 M $CaCl_2$ solution was added to the precipitation. While the adenine and $CaCl_2$ solutions were added, the addition of silver was suspended for one minute, and the additives were uniformly mixed. Thus, 4 mol of Ag was precipitated.

The resulting emulsion was divided into two parts. One emulsion was desalted at 40°C by the use of an aqueous Demol N (a condensate of a naphthalene sulfonic acid salt with an aldehyde, produced by Kao Atlas Co., Ltd.) solution and an aqueous magnesium sulfate solution, washed with water (CW), mixed with 600 ml of an aqueous gelatin solution containing 15 g of ossein gelatin and redispersed with stirring at 55°C for 30 minutes. Thus, 750 ml of tabular silver bromochloride emulsion (B-1) was obtained which contained tabular silver halide grains having an average silver chloride content of 20 mol%, an average grain size of 0.4 µm, a deviation coefficient of 0.25 and an aspect ratio of 4. The other emulsion was ultrafiltrated, mixed with 600 ml of an aqueous gelatin solution containing 15 g of ossein gelatin and redispersed with stirring at 55°C for 30 minutes. Thus, 750 ml of tabular silver bromochloride emulsion (B-2) was obtained which contained tabular silver halide grains having an average silver chloride content of 20 mol%, an average grain size of 0.4 µm, a deviation coefficient of 0.25 and an aspect ratio of 4. The above described emulsions are collectively shown in Table 1 (Emulsions Cs described later are also shown). AR represents an aspect ratio, and, as described above, CW and UF represent water washing and ultrafiltration, respectively.

Table 1

Emulsion	Silver halide grains	AgCl content (mol%)	AR	Grain shape	Average grain size (µm)
A-1-1	CW	60	1	Cubic	0.4
A-1-2	UF				
A-2-1	CW	20	1	Cubic	0.4
A-2-2	UF				
B-1	CW	20	4	Tabular	0.4
B-2	UF				
C-1-1	CW	25	9	Tabular	0.4
C-1-2	UF				
C-2-1	CW	100	9	Tabular	0.4
C-2-2	UF				
C-3-1	CW	50	4	Tabular	0.4
C-3-2	UF				
C-4	UF	94	3	Tabular	0.4
C-5	UF	60	4	Tabular	0.4
C-6	UF	85	3	Tabular	0.4

(Emulsion C-1)

An emulsion was prepared in the same manner as in Emulsion B, except that 112.5 g of NaBr was added. Thus, tabular silver bromochloride emulsions (C-1-1) and (C-1-2) were obtained which contained tabular silver halide grains having an average silver chloride content of 25 mol%, an average grain size of 0.4 µm, a deviation coefficient of 0.25 and an aspect ratio of 9.

(Emulsion C-2)

An emulsion was prepared in the same manner as in Emulsion B, except that NaBr was not added. Thus, tabular silver chloride emulsions (C-2-1) and (C-2-2) were obtained which contained tabular silver chloride grains having an average grain size of 0.4 µm, a deviation coefficient of 0.25 and an aspect ratio of 9.

(Emulsion C-3)

An emulsion was prepared in the same manner as in Emulsion B, except that 75 g of NaBr was added. Thus, tabular silver bromochloride emulsions (C-3-1) and (C-3-2) were obtained which contained tabular silver halide grains having an average silver chloride content of 50 mol%, an average grain size of 0.4 µm, a deviation coefficient of 0.25

and an aspect ratio of 4.

(Emulsion C-4)

An emulsion was prepared in the same manner as in Emulsion B, except that 9.3 g of NaBr was added. Thus, tabular silver bromochloride emulsions (C-4-1) and (C-4-2) were obtained which contained tabular silver halide grains having an average silver chloride content of 94 mol%, an average grain size of 0.4 μm, a deviation coefficient of 0.25 and an aspect ratio of 3.

(Emulsion C-5)

An emulsion was prepared in the same manner as in Emulsion B, except that 60 g of NaBr was added and ultrafiltration (UF) was not carried out. Thus, tabular silver bromochloride emulsions (C-5) was obtained which contained tabular silver halide grains having an average silver chloride content of 60 mol%, an average grain size of 0.4 μm, a deviation coefficient of 0.25 and an aspect ratio of 4. (Emulsion C-6)

An emulsion was prepared in the same manner as in Emulsion B, except that 22.5 g of NaBr was added and ultrafiltration (UF) was not carried out. Thus, tabular silver bromochloride emulsions (C-6) was obtained which contained tabular silver halide grains having an average silver chloride content of 85 mol%, an average grain size of 0.4 μm, a deviation coefficient of 0.25 and an aspect ratio of 3.

(Preparation of light sensitive material sample)

While each of the above obtained emulsions was kept at 50°C, 150 mg/mol of silver halide of the following sensitizer (A) and 15 mg/mol of silver halide of the following sensitizer (B) were added thereto, and then 7.0×10^{-4} mol per mol of silver halide of ammonium thiocyanate, and suitable amount of chloroauric acid and sodium thiosulfate were added for chemical sensitization. Thereafter, the above-mentioned silver iodide fine grain emulsion was added in an amount of 6.0×10^{-4} mol per mol of silver and 3×10^{-2} mol per mol of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added thereto for stabilizing.

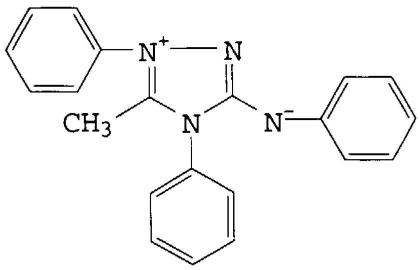
Sensitizing dye (A) :

5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)oxacarbocyanine sodium salt anhydride

Sensitizing dye (B) :

5,5'-di-(butoxycarbonyl)-1,1'-di-ethyl-3,3'-di-(4-sulfobutyl)benzimidazolocarbocyanine sodium salt anhydride

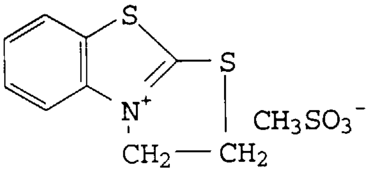
The additives added to each of the above obtained emulsions (light sensitive silver halide coating solution) were as follows: The amount is in terms of a weight amount per mol of silver halide.



	150 mg
t-Butyl-catechol	400 mg

Polyvinyl pyrrolidone (molecular weight 10,000)	1.0 g
Styrene-maleic acid anhydride copolymer	2.5 g
Trimethylpropane	10 g
Diethylene glycol	5 g
Nitrophenyl-triphenyl phosphonium chloride	50 mg
Ammonium 1,3-dihydroxybenzene-4-sulfonic acid	4 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	1.5 mg

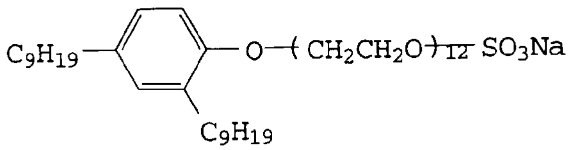
Compound (H)



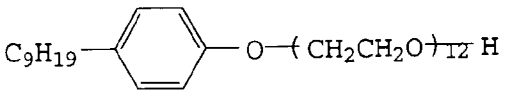
Compound (H)	70 mg
$n\text{-}C_4H_9OCH_2CH(OH)CH_2N(CH_2COOH)_2$	1 g

Additives used in a protective layer are as follows: The amount is in terms of a weight amount per gram of gelatin.

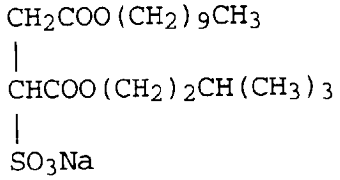
Polymethylmethacrylate Matting agent having an area average grain size of 7 µm)	7 mg
Colloid silica (an average grain size of 0.013 µm)	70 mg
Sodium salt of 2,4-dichloro-6-hydroxy-1,3,5-triazine	30 mg
$(CH_2=CHSO_2CH_2)_2O$	36 mg



12 mg

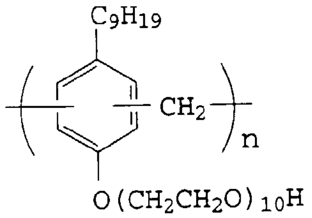


2 mg



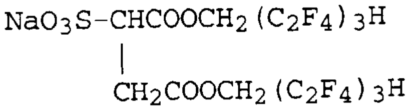
$$\begin{array}{l} CH_2COO(CH_2)_9CH_3 \\ | \\ CHCOO(CH_2)_2CH(CH_3)_3 \\ | \\ SO_3Na \end{array}$$

7 mg



15 mg

(a mixture of n=2-5)



$$\begin{array}{l} NaO_3S\text{-}CHCOOCH_2(C_2F_4)_3H \\ \qquad\quad | \\ \qquad\quad CH_2COOCH_2(C_2F_4)_3H \end{array}$$

3 mg

$F_{19}C_9O\text{-}(CH_2CH_2O)_{10}\text{-}CH_2CH_2OH$ 3 mg

A light sensitive material sample was prepared using the above obtained coating solution according to the following. Employing two slide hopper coaters, the photographic emulsion layer was coated at a coating speed of 80 m/minute simultaneously on both sides of a support to give a gelatin coating weight per one side of 2.0 g/m^2 and a silver coating weight per one side of 1.6 g/m^2. Similarly, the protective layer was coated simultaneously on both sides of a support to give a gelatin coating weight per one side of 1.15 g/m^2. Thereafter, the resulting material was dried for 2 minutes and 20 seconds to obtain a light sensitive material sample. The support was a blue colored 175 μm polyethylene terephthalate film base for radiography on which a subbing layer was provided by coating an aqueous dispersion of 10 wt% glycidyl methacrylate-methylacrylate-butylmethacrylate (50:10:40 by weight ratio) copolymer.

Developer or developer replenisher was prepared according to the following procedures:

Preparation of processing compositions

(Developer)(for 12 liter)

Part A

Potassium hydroxide	450 g
Potassium sulfite	2280 g
Sodium bicarbonate	132 g
Pentasodiumdiethylenetriaminepentaacetate	120 g
5-Methylbenzotriazole	1.6 g
1-Phenyl-5-mercaptotetrazole	0.8 g
Hydroquinone	340 g

Water added to 9.5 liter.

Part B (for 12 liter)

Glacial acetic acid	170 g
Triethylene glycol	185 g
1-Phenyl-3-pyrazolidone	76 g
5-nitroindazol	0.4 g

The above Part A was added to a 25°C 5 liter water in a 50 liter tank while stirring, Part B was added, and then water added to 12 liter. The resulting solution was allowed to stand at 25°C for 24 hours, and its pH adjusted to 10.45 at 25°C with an aqueous potassium or acetic acid solution. Thus, developer was obtained.

(Starter)

Glacial acetic acid	230 g
Potassium bromide	200 g
Water added to 1.5 liter.	

The above obtained developer was used as developer replenisher, and, at the beginning of processing, 20 ml of the above starter per 1 liter of the above developer were incorporated to prepare a starting developer.

The developer was replenished with 300 ml of developer replenisher per 1 m^3 of light sensitive material sample in the invention.

(Fixer formulation)

Part A (for 38 liter)

Ammonium	6080 g
Disodium ethylenediamine tetraacetate (dihydrate)	0.76 g
Sodium sulfite	456 g
Boric acid	266 g
Sodium hydroxide	190 g
Glacial acetic acid	380 g
Water added to 9.5 liter.	

Part B (for 38 liter)

Aluminium sulfate (in terms of anhydride)	380 g
Sulfuric acid(50 wt%)	228 g
Water added to 1.9 liter.	

Mixing of each part

The above Parts A and B was added to 20 liter of 20°C water in a 50 liter tank while stirring, and then water added to 38 liter. The pH was adjusted to 4.30 at 25°C with an aqueous acetic acid solution. Thus, fixer was obtained. (The content of Al^{3+} was 58.5 millimole per 1 liter of fixer.) Fixer replenisher was the same as the fixer.

The fixer was replenished with 300 ml of fixer replenisher per 1 m^3 of light sensitive material sample in the invention.

In this example, evaluation was carried out according to the following methods:

(Evaluation of remaining stain)

The unexposed sample was processed using an automatic processor obtained by modifying SRX-502 (produced by Konica Corporation) according to the following processes. The total processing time was 29.0 seconds.

Processes	Processing Temperature	Processing Time	Replenishing Amount
Insertion		0.8 seconds	
Development and cross-over	35°C	8.7 seconds	300 ml/m^2
Fixing and cross-over	33°C	5.5 seconds	300 ml/m^2
Washing and cross-over	18°C	4.8 seconds	7.0 liter/m^2
Squeezing	45°C	3.8 seconds	
Drying	55°C	5.4 seconds	
Total Time taken		29.0 seconds	

The remaining stain of the resulting samples was visually observed and evaluated according to the following five criteria.

5 : No stain, and excellent

4 : Slight stain, and good

3 : A little stain, but applicable

2 : A little more stain, and application limit

1 : Much stain, and not applicable

(Evaluation of silver image tone)

The above prepared samples were exposed to give an optical density of 1.2 after development, and subjected to development using the above automatic processor. The developed samples were stored for 7 days at 50°C and 80%RH. The silver image tone of the resulting samples was observed through a viewing box, and evaluated according to the following four criteria. The optical density was measured by Sakura densitometer PDA-65 (produced by Konica Corporation).

4 : Genuine Black

3 : A little reddish stain

2 : Reddish stain

1 : Yellowish stain (Evaluation of roller marks)

The above prepared samples were exposed to give a density of 1.0, and subjected to development in the same manner as above. The roller marks of the developed samples was observed, and evaluated according to the following five criteria.

Evaluation criteria

5 : No pressure patches.
4 : Faint pressure patches are observed at film edges, but no problem in view of practical application.
3 : Faint pressure patches are observed at film center portions, but no problem in view of practical application.
2 : Apparent pressure patches are observed at film edges, and problematic in view of practical application
1 : Apparent pressure patches are observed at film center portions, and problematic in view of practical application.

The results are shown in Table 2.

Table 2

Sample No.	Emulsion No.	Grains	Remaining stain	Silver image tone	Roller marks	Remarks (μm)
1	A-1-1	CW	1	1	1	Comparative
2	A-1-2	CW	1	1	1	Comparative
3	B-1	CW	2	2	2	Comparative
4	C-1-1	CW	2	1	3	Comparative
5	C-2-1	CW	3	1	3	Comparative
6	C-3-1	CW	2	1	2	Comparative
7	A-1-2	UF	1	2	1	Comparative
8	A-2-2	UF	2	2	1	Comparative
9	B-2	UF	2	1	2	Comparative
10	C-1-2	UF	2	2	1	Comparative
11	C-2-2	UF	2	2	1	Comparative
12	C-3-2	UF	5	5	5	Invention
13	C-4	UF	5	4	5	Invention
14	C-5	UF	5	5	4	Invention
15	C-6	UF	5	5	5	Invention

As is apparent from comparison of the inventive samples (sample Nos. 12 through 15) with the comparative samples (sample Nos. 1 through 11) in Table 2, the present invention reduces roller marks produced when super rapidly processing light sensitive material through an automatic processor (in Dry to Dry processing of less than 30 seconds).

The present invention further shows improved silver image tone and reduced remaining stain after development.

Claims

1. A silver halide photographic light-sensitive material comprising a light-sensitive silver halide emulsion layer containing silver halide grains, said emulsion having been ultrafiltrated, wherein said silver halide grains have an aspect ratio of 2 to less than 5 and have an average silver chloride content of not less than 30 mol%.

2. The silver halide photographic light-sensitive material of claim 1, wherein said silver halide grains have an aspect ratio of 2.5 to 4.5.

3. The silver halide photographic light-sensitive material of claim 1, wherein said silver halide grains have an aspect ratio of 2.5 to 4.5 and have an average silver chloride content of not less than 40 to 90 mol%.

4. The silver halide photographic light-sensitive material of claim 1, wherein the total processing time of silver halide photographic light-sensitive material is less than 30 seconds.

5. A method of manufacturing a silver halide emulsion containing silver halide grains having an aspect ratio of 2 to less than 5 and having an average silver chloride content of not less than 30 mol%, the method comprising the step of:

   mixing a silver ion with a halide ion in a dispersion medium to obtain a silver halide emulsion; and
   ultrafiltrating the resulting emulsion using a ultrafiltration unit.

6. The method of claim 5, wherein said silver halide grains have an aspect ratio of 2.5 to 4.5.

7. The method of claim 5, wherein said silver halide grains have an aspect ratio of 2.5 to 4.5 and have an average silver chloride content of not less than 40 to 90 mol%.

8. The method of claim 5, wherein a pressure difference across a ultrafiltration membrane of the ultrafiltration unit is 40 to 60 palg.

9. The method of claim 5, further comprising a step of ripening the silver halide emulsion between the mixing step and the ultrafiltration step.

FIG. 1