⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 407 576 A1**

⑫ EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

㉑ Application number: **89901593.7**

㉒ Date of filing: **18.01.89**

(86) International application number:
PCT/JP89/00039

(87) International publication number:
WO 89/06831 (27.07.89 89/16)

㉚ Priority: **18.01.88 JP 7851/88**
18.01.88 JP 7852/88
18.01.88 JP 7853/88
04.08.88 JP 194861/88
04.08.88 JP 194862/88
05.08.88 JP 195778/88

㊸ Date of publication of application:
16.01.91 Bulletin 91/03

(84) Designated Contracting States:
DE GB NL

(51) Int. Cl.5: **G03C 1/015**, G03C 1/08

(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma Minami Ashigara-shi
Kanagawa 250-01(JP)

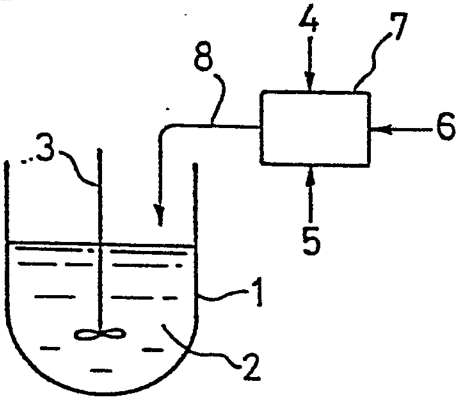
(72) Inventor: **URABE, Shigeharu**
Fuji Photo Film Co., Ltd. 210, Nakanuma
Minami-Ashigara-shi Kanagawa 250-01(JP)
Inventor: **AIDA, Shun-ichi**
Fuji Photo Film Co., Ltd. 210, Nakanuma
Minami-Ashigara-shi Kanagawa 250-01(JP)

(74) Representative: **Patentanwälte Dr. Solf & Zapfapf**
Zeppelinstrasse 53
D-8000 München 80(DE)

(54) SILVER HALIDE PHOTOGRAPHIC MATERIAL AND PROCESS FOR ITS PREPARATION.

(57) A silver halide photographic material and a process for its preparation are disclosed. This material has a silver halide emulsion layer containing photosensitive silver halide grains obtained by adding previously prepared fine silver halide grains to a reaction vessel for formation of grain nuclei and/or growth of crystals to thereby form nuclei and/or allow crystals to grow in said reaction vessel and subjecting to reduction sensitization. It has a high photographic speed, suffers less fogging, and gives good graininess.

Fig. 1



TITLE MODIFIED
see front page

SPECIFICATION

SILVER HALIDE PHOTOGRAPHIC MATERIALS AND PRODUCTION PROCESS THEREOF

TECHNICAL FIELD

This invention relates to a silver halide photographic material useful in the field of photography and a process of producing it. More particularly, the invention relates to a silver halide photographic material having high sensitivity and a fine graininess.

BACKGROUND ART

The fundamental performance required for a photographic silver halide emulsion is a high sensitivity, low fog, and a fine graininess.

For increasing the sensitivity of an emulsion, it is required (1) to increase the number of photons being absorbed by one grain, (2) to increase the efficiency of conversing the photoelectrons generated by light absorption into silver clusters (latent images), and (3) to increase the development activity for effectively utilizing the latent images formed. The increase of the grain size increases the number of photons being absorbed by one grain but reduces the image quality. The increase of the development activity is an effective means for increasing the sensitivity but is generally accompanied by the reduction of graininess in the case of a parallel type development such as color development. For increasing the sensitivity without accompanied by the reduction in graininess, it is most preferred to increase the efficiency of converting photoelectrons into latent images, that is, to increase the quantum sensitivity. For increasing the quantum sensitivity, it is necessary to remove inefficient steps such as re-combination, latent image dispersion, etc. It is known that a reduction sensitization method of forming small silver nuclei having no development activity in the inside or at the surface of silver halide is effective for inhibiting the occurrence of re-combination.

Also, James et al found that when after vacuum-degassing a coated film of a silver halide emulsion subjected to gold and sulfur sensitization, a sort of reduction sensitization, i.e., a heat treatment under a hydrogen gas atmosphere was applied thereto, the sensitivity could be increased in a low fog level as compared to an ordinary reduction sensitization. The sensitization method is well known as a hydrogen sensitization and is effective as a high sensitizing means in an experimental scale. Furthermore, in the field of astrophotography, the hydrogen sensitization has been practically used.

A reduction sensitization has been investigated from old. Carroll disclosed the usefulness as a reduction sensitizer of tin compounds in U.S. Patent 2,487,850, Lowe et al disclosed of polyamine compounds in U.S. Patent 2,512,925, and Fallens et al disclosed of thiourea dioxide series compounds in British Patent 789,823. Furthermore, Collier compared properties of silver nuclei prepared by various reduction sensitization methods in Photographic Science and Engineering, Vol. 23, page 113 (1979). She employed a method of using dimethylamineborane, stannous chloride, hydrazine, high pH ripening, and low pAg ripening. Methods of reduction sensitization are further disclosed in U.S. Patents 2,518,698, 3,201,254, 3,411,917, 3,779,777 and 3,930,867. Not only the selection of reduction sensitizers but also the using methods of reducing agents are disclosed in JP-B-57-33572 and JP-B-58-1410 and JP-A-57-179835. (The term "JP-B" and "JP-A" as used herein mean an "examined Japanese patent publication", and an "unexamined published Japanese patent application", respectively.). Furthermore, techniques for improving the storage stability of emulsions reduction sensitized are disclosed in JP-A-57-82831 and JP-A-60-178445.

In spite of such various investigations, the increasing width of sensitivity is insufficient as compared with the hydrogen sensitization of subjecting light-sensitive materials to a hydrogen gas treatment under vacuo. This is reported in Journal of Imaging Science, Vol. 29, page 233 (1985) by Moisar et al.

Conventional techniques for reduction sensitization are insufficient for the requirements for recent high-speed high-image quality photographic light-sensitive materials. Also, the means of hydrogen sensitization has a disadvantage that if the light-sensitive material is allowed to stand in the air after the hydrogen sensitization, the sensitization effect is lost. Accordingly, in the case of photographic light-sensitive materials for which specific apparatus can not be used, the utilization of the sensitizing method is difficult.

Light-sensitive silver halide grains for high-speed silver halide photographic materials are generally gold-sulfur sensitized at the surfaces of the grains and also since a reduction sensitization and a gold sensitization are used together, it causes severe formation of fog, various investigations on the reduction sensitization for the insides of grains have been carried out.

On the other hand, in a conventional production process for photographic silver halide grains, the grains are generally produced by reacting an aqueous silver salt solution and an aqueous halide solution in an aqueous colloid solution in a reaction vessel. A single jet method of placing an aqueous solution of protective colloid such as gelatin and an aqueous halide solution in a reaction vessel and adding thereto an aqueous silver salt solution with stirring over a period of a certain time and a double jet method of placing an aqueous gelatin solution in a reaction vessel and adding thereto an aqueous silver salt solution and an aqueous halide solution over a period of certain time are known. The double jet method provides silver halide grains having a narrower grain size distribution and in the method, the halide composition can be freely changed with the growth of the grains.

Also, it is known that the growing rate of silver halide grains is greatly influenced by the concentration of silver ions (halogen ions) in a reaction solution, the concentration of a silver halide solvent, the distance between grains, grain sizes, etc. In particular, the heterogeneity of the concentration of silver ions or halogen ions formed from an aqueous silver salt solution and an aqueous halide solution added to a reaction vessel makes differ the growing rate by each concentration, which results in forming a silver halide emulsion having heterogeneity. Thus, it is necessary to quickly uniformly mixing the aqueous silver salt solution and the aqueous halide solution supplied to the aqueous colloid solution to react them for homogenizing the concentration of silver ions or halogen ions in the reaction vessel.

However, in the conventional method of adding an aqueous halide solution and an aqueous silver salt solution onto the surface of an aqueous colloid solution in a reaction vessel, the concentrations of the halogen ions and the silver ions become higher at the vicinities of the added positions of the reaction solutions, which makes it difficult to produce homogeneous silver halide grains.

As a method of improving the localization of the concentrations, there are known the techniques disclosed in U.S. Patent 3,415,650, British Patent 1,323,464, and U.S. Patent 3,692,283.

In these methods, a hollow rotary mixer (the inside thereof is filled with an aqueous colloid solution, and more preferably, the mixer is partitioned into an upper room and a lower room by a disk) of an intermediate size having slits at the cylindrical wall is disposed in an reaction vessel filled with an aqueous colloid solution so that the rotary axis thereof is perpendicular, an aqueous halide solution and an aqueous silver salt solution are supplied from the upper and lower openings thereof into the mixer rotating at a high speed through feed pipes to quickly mixing them and to cause reaction (when the mixer is separated into the upper room and the lower room by a separation disk, the aqueous halide solution and the aqueous silver salt solution supplied into the upper and lower rooms are diluted with an aqueous colloid solution filled in each room and are quickly mixed with each other at the vicinity of the outlet slits of the mixer to cause the reaction), and silver halide grains formed by the centrifugal force caused by the rotation of the mixer are ejected into the aqueous colloid solution in the reaction vessel to grow the grains.

On the other hand, a technique of preventing the heterogeneous growth of silver halide grains by improving the localization of the concentrations is disclosed in JP-B-55-10545. This method is a technique in which an aqueous halide solution and an aqueous silver salt solution are separately supplied into a mixer filled with an aqueous colloid solution through feed pipes from the lower open portions, said mixer being placed in a reaction vessel filled with an aqueous colloid solution, the reaction solutions are abruptly stirred and mixed by means of lower stirring blades (turbine blades) equipped to the mixer to grow silver halide grains, and the silver halide grains thus grown are immediately discharged into the aqueous colloid solution in the reaction vessel from the upper open portion of the mixer by upper stirring blades disposed at the upper portion of the aforesaid lower stirring blades.

JP-A-57-92523 also discloses a production method of silver halide grains for improving the heterogeneity of the concentrations. This method is a production method of silver halide grains by separately supplying an aqueous halide solution and an aqueous silver salt solution into a mixer filled with an aqueous colloid solution from the open lower portion thereof, said mixer being placed in a reaction vessel filled with an aqueous colloid solution, to dilute both the reaction solutions with the aforesaid aqueous colloid solution, abruptly stirring and mixing both the reaction solutions by means of lower stirring blades equipped to the mixer, and immediately discharging the silver halide grains thus grown into the aqueous colloid solution in the reaction vessel from the upper open portion of the mixer, wherein both the reaction solutions diluted with the aqueous colloid solution are passed through the gap formed between the inside wall of the mixer and the tops of the stirring blades without passing through each gap between the stirring blades, whereby both the reaction solutions are abruptly sheared and mixed at the gap portion to form silver halide grains.

However, although in the aforesaid methods, the local heterogeneity of the concentrations of silver ions and halogen ions in a reaction vessel can be surely overcome, in these methods, the heterogeneity of the concentrations yet exists in the mixer and, in particular, there is a considerably large concentration distribution at the vicinities of the nozzles for supplying the aqueous silver salt solution and the aqueous halide solution, at the lower portions of the stirring blades, and the stirring portion. Furthermore, the silver halide grains supplied to the mixer together with the protective colloid pass through such portions having the heterogeneous concentration distribution and more seriously, the silver halide grains abruptly grow in these portions. In other words, in the aforesaid methods, a concentration distribution exists in the mixer and the growth of silver halide grains occurs abruptly in the mixer, whereby the object of uniformly growing silver halide grains in a state having no concentration distribution is not attained.

For overcoming the heterogeneous distribution of the concentrations of silver ions and halogen ions by more completely mixing them, an attempt of separating the reaction vessel and the mixer from each other and supplying an aqueous silver salt solution and an aqueous halide solution into the mixer to mix abruptly them and to grow silver halide grains has been made. For example, JP-A-53-37414 and JP-B-48-21045 disclose a method and apparatus of producing silver halide grains by circulating an aqueous protective colloid solution (containing silver halide grains) in a reaction vessel from the bottom of the reaction vessel by means of a pump, equipping a mixer to the circulation system, supplying an aqueous silver salt solution and an aqueous halide solution into the mixer, and abruptly mixing both the aqueous solutions in the mixer to grow silver halide grains.

Also, U.S. Patent 3,897,935 discloses a method of circulating an aqueous protective colloid solution (containing silver halide grains) in a reaction vessel from the bottom of the reaction vessel and pouring an aqueous halide solution and an aqueous silver salt solution into the circulation system by means of a pump. Also, JP-A-53-47397 discloses a method and apparatus of producing silver halide grains by circulating an aqueous protective colloid solution (containing silver halide grains) in a reaction vessel from the reaction vessel by means of a pump, pouring first an aqueous alkali metal halide solution into the circulation system to disperse until the mixture becomes uniform, and then pouring an aqueous silver salt solution into the system followed by mixing to form silver halide grains.

These methods can surely change independently the flow rate of the aqueous solution in the reaction vessel being circulated to the circulation system and the mixing efficiency in the mixer and will be able to perform the growth of silver halide grains in a homogeneous condition of the concentration distribution, but after all, silver halide crystals sent from the reaction vessel together with the aqueous protective colloid solution grow quickly at the pouring inlets for the aqueous silver salt solution and the aqueous halide solution. Accordingly, as described above, it is in principle impossible to hemogenize the concentration distribution at the mixing portion or at the vicinities of the pouring inlets and, in other words, the object of uniformly growing silver halide grains in the state of having no concentration distribution can not be attained.

As described above, in a conventional process of preparing photographic silver halide grains, the heterogeneity of silver ion concentration in the range of causing the grain growth is unavoidable. Such a heterogeneity of silver ion concentration not only becomes a heterogeneity of the reductive atmosphere in the reaction vessel by itself but also causes the heterogeneity of the silver nucleus forming reaction by the heterogeneity in the case of using a reducing agent together. This is because, the silver nucleus forming reaction can be generally shown by $nAg^+ + ne^- \rightarrow Agn$ but the existence of the heterogeneity of silver ion concentration in the domain of causing the grain growth namely means that the left side of the aforesaid formula showing the silver nucleus forming reaction differs in each spot in the domain of causing the grain growth.

The object of this invention is to provide a silver halide emulsion having high sensitivity and good graininess and a process of producing a silver halide emulsion having high sensitivity and giving less fog. Also, the 2nd object of this invention is to provide a photographic light-sensitive material having high sensitivity and good graininess and also to provide a photographic light-sensitive material having high sensitivity and giving less fog.

DISCLOSURE OF INVENTION

As the results of various investigations, it has been found that the objects of this invention can be attained by the following invention.

(1) A silver halide photographic material having on a support at least one silver halide emulsion layer, characterized in that the light-sensitive silver halide grains contained in the silver halide emulsion layer are light-sensitive silver halide grains obtained by adding previously prepared silver halide grains having fine grain sizes into a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains to cause the nucleus formation and/or the crystal growth of the grains in the reaction vessel, and the silver halide grains are reduction sensitized.

(2) A silver halide photographic material having on a support at least one silver halide emulsion layer, characterized in that the light-sensitive silver halide grains contained in the silver halide emulsion layer are light-sensitive silver halide grains obtained by adding previously prepared silver halide grains having fine grain sizes into a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains under the condition capable of reduction sensitizing the silver halide grains to cause the nucleus formation and/or the crystal growth in the reaction vessel.

(3) The silver halide photographic material described in the above (1) or (2), wherein the silver halide grains having fine grain sizes are formed by mixing

an aqueous solution of a water-soluble silver salt and an aqueous solution of water-soluble halide(s) in a mixer disposed outside a reaction vessel of causing the nucleus formation and/or the crystal growth of the light-sensitive silver halide grains, and immediately after the formation, the fine silver halide grains are supplied to the reaction vessel for the nucleus formation and/or the crystal growth of the light-sensitive silver halide grains.

(4) The silver halide photographic material described in the above (2) or (3), wherein an oxidizing agent and/or an inhibitor exists in addition to the condition capable of causing reduction sensitization.

(5) The silver halide photographic material described in the above (2), (3), or (4), wherein the light-sensitive silver halide grains are silver iodobromide having a silver iodide content of from 3 mol% to 40 mol%.

(6) The silver halide photographic material described in the above (2), (3), or (4), wherein the halogen composition is silver chlorobromide, silver chloroiodide, or silver chloroiodobromide.

(7) A process of producing a silver halide photographic material having on a support at least one silver halide emulsion layer, which comprises producing the light-sensitive silver halide grains contained in the

silver halide emulsion layer by adding previously prepared silver halide grains having fine grain sizes into a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains to cause the nucleus formation and/or the crystal growth in the reaction vessel, said silver halide grains being reduction sensitized.

(8) A process of producing a silver halide photographic material having on a support at least one silver halide emulsion layer, which comprises producing the light-sensitive silver halide grains contained in the silver halide emulsion layer by adding previously prepared silver halide grains having fine grain sizes under the condition capable of reduction sensitizing the silver halide grains to a reaction vessel for causing the nucleus formation and/or the crystal growth of the silver halide grains to cause the nucleus formation and/or the crystal growth in the reaction vessel.

(9) The process of producing a silver halide photographic material described in the above (7) or (8), wherein the silver halide grains having fine grain sizes are formed by mixing an aqueous solution of a water-soluble silver salt and an aqueous solution of water-soluble halide(s) in a mixer disposed outside the reaction vessel for causing the nucleus formation and/or the

crystal growth of the light-sensitive silver halide grains and after the formation thereof are immediately supplied to the reaction vessel for causing the nucleus formation and/or the crystal growth of the light-sensitive silver halide grains.

(10) The process of producing a silver halide photographic material described in the above (8) or (9), wherein an oxidizing agent and/or an inhibitor exists in addition to the condition capable of reduction sensitizing.

(11) The process of producing a silver halide photographic material described in the above (8), (9), or (10), wherein the silver halide grains are silver iodobromide having a silver iodide content of from 3 mol% to 40 mol%.

(12) The process of producing a silver halide photographic material described in the above (8), (9), or (10), wherein the halogen composition is silver chlorobromide, silver chloroiodide, or silver chloroiodobromide.

Then, the present invention is explained in detail.

The production process of a silver halide emulsion is generally composed of the steps of grain formation, desalting, chemical sensitization, coating, etc. The grain formation is composed of a nucleus formation, ripening, growing, etc. These steps are not carried out in a definite order but as the case may be, the order of the steps is reversed or the steps are repeatedly carried out.

In this invention, a part or the whole of the grain formation in the aforesaid steps is carried out "under the condition capable of reduction sensitizing" or "under the condition capable of reduction sensitizing and further under the condition of existing an oxidizing agent and/or an inhibitor" (hereinafter, is referred to as "reduction sensitizing"). The silver halide grain formation is roughly divided into "nucleus formation" and "growth" and the "growth" is further divided into a narrow sense "growth" which is proceeded by supplying silver halide grains being supplied for the crystal grow from outside a reaction vessel for causing the crystal growth and "ripening" which is proceeded without supply of silver halide grains from outside. The reduction sensitization of this invention may be applied at any step of the aforesaid grain formation or after the grain formation. It is preferred that the grain growth is performed by adding silver halide grains having fine grain sizes under the condition capable of reduction sensitizing. In the case of performing a chemical sensitization using a gold sensitization together, it is preferred to perform the reduction sensitization prior to the chemical sensitization such that undesirable fog is not formed and it is more preferred that the reduction sensitization is applied to the inside of the silver halide grains and the content of reduced silver nuclei causing fog with the gold sensitization is reduced in the surface of the grains to which the gold sensitization is applied.

The reduction sensitization of this invention can be carried out by a method of adding a known reducing agent to a silver halide emulsion, a method of growing or ripening silver halide grains in an atmosphere of low pAg of from pAg of 1 to 7, called as silver ripening, or a method of growing or ripening silver halide grains in an atmosphere of high pH of from 8 to 11, called as high pH ripening. Also, two or more of the methods can be used together.

The method of adding a reduction sensitizer is preferred in the point capable of finely controlling the level of the reduction sensitization.

As the reduction sensitizers, there are known stannous salts, amines, polyamines, hydrazine derivatives, formamizinesulfinic acid, ascorbic acid derivatives, hydroquinone derivatives, silane compounds, borane compounds, etc. In this invention, the aforesaid compounds can be used and two or more compounds can be used together. As the reduction sensitizer, stannous chloride, thiourea dioxide, and dimethylamineborane are preferred. The addition amount of the reduction sensitizer depends upon the production condition of the silver halide emulsion but is properly in the range of from 10^{-7} to 10^{-3} mol per mol of silver halide.

An ascorbic acid derivative is also a preferred compound as the reduction sensitizer and in this case, the addition amount is properly in the range of from 5×10^{-5} to 1×10^{-1} mol per mol of silver halide.

The reduction sensitizer is added to the system of forming silver halide grains as a solution thereof in water, an alcohol, a glycol, a ketone, an ester, an amide, etc. The solution may be previously placed in a reaction vessel for causing the grain formation or may be added at a proper time of the grain formation. Also, the solution of the reduction sensitizers may be added in several times with the formation of grains or may be continuously added for a long period of time. The addition of a solution of a soluble silver salt or a solution of a soluble halide solution for controlling pAg for performing silver ripening or the addition of a solution of an acid or alkali for controlling pH for performing high pH ripening is performed by the same manner as the solution of a reduction sensitizer as described above.

In the reduction sensitization of this invention, an oxidizing agent and/or an inhibitor can exist with a reducing agent for controlling the level of the reduction sensitization. The coexistence of an oxidizing agent and/or an inhibitor in the reduction sensitization of this invention is mainly for two purposes. The first purpose is that the reducing agent added for practicing the reduction sensitization at a necessary time in the step of forming grains is inactivated by the addition of an oxidizing agent and/or an inhibitor when the reduction sensitization becomes unnecessary to stop the occurrence of unnecessary reduction sensitized nuclei. The use of the oxidizing agent and/or the inhibitor by the first purpose makes it possible to control the distribution of the reduction sensitized nuclei in the light-sensitive silver halide grains. The second purpose of using the oxidizing agent and/or the inhibitor is in that at performing the reduction sensitization by a reductive atmosphere of low pAg or high pH, or by a reducing agent, the extent of the reduction sensitization (the extent is considered to be influenced by the sizes or the number of reduced silver nuclei) is controlled to realize the optimum performance.

The oxidizing agent which is used for the aforesaid purposes may be an inorganic compound or an organic compound. Suitable examples are iodide, hexacyano iron(III) salts, bromosuccinimide, quinone derivatives, periodates, persulfates, pentacyanonitrosyl iron acid salts, N(m-nitrobenzyl)quinolinium chloride, etc. Also, the compounds of following general formulae [I] to [III] are preferred as the oxidizing agents in this invention.

[I] $R - SO_2S - M$

[II] $R - SO_2S - R^1$

[III] $RSO_2S - L_m - SO_2S - R^2$

[wherein, R, R^1, and R^2, which may be the same or different, each represents an aliphatic group, an aromatic group, or a heterocyclic group; M represents a cation; L represents a divalent linkage group; and m represents 0 or 1.]

Practical examples of the compounds shown by general formula [I], [II], or [III] are shown below but the invention is not limited to them.

(1-1) CH_3SO_2SNa

(1-2) $C_2H_5SO_2SNa$

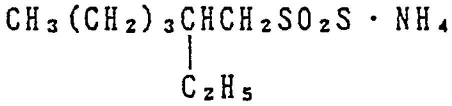
(1-3) $C_3H_7SO_2SK$

(1-4) $C_4H_9SO_2SLi$

(1-5) $C_6H_{13}SO_2SNa$

(1-6) $C_8H_{17}SO_2SNa$

(1-7)



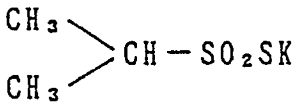
$CH_3(CH_2)_3CH(C_2H_5)CH_2SO_2S \cdot NH_4$

(1-8) $C_{10}H_{21}SO_2SNa$

(1-9) $C_{12}H_{25}SO_2SNa$

(1-10) $C_{16}H_{33}SO_2SNa$

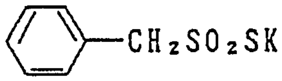
(1-11)



(1-12) $t-C_4H_9SO_2SNa$

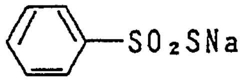
(1-13) $CH_3OCH_2CH_2SO_2S \cdot Na$

(1-14)

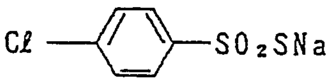


(1-15) $CH_2=CHCH_2SO_2SNa$

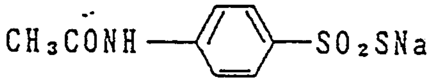
(1-16)



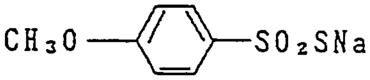
(1－17)



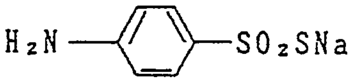
(1－18)



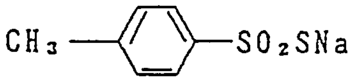
(1－19)



(1－20)

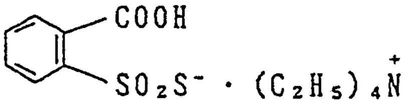


(1－21)

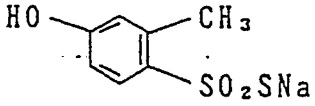


(1－22)

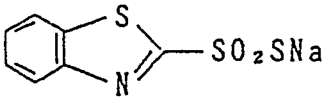
(1－23)



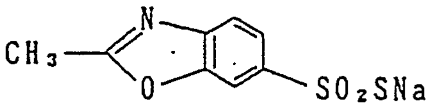
(1－24)



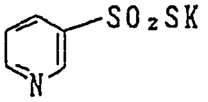
(1－25)



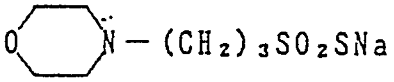
(1－26)



(1 - 27)



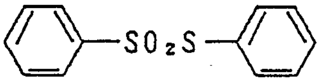
(1 - 28)



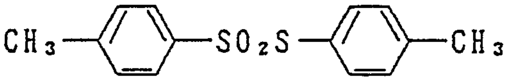
(2 - 1) $C_2H_5SO_2S-CH_3$

(2 - 2) $C_8H_{17}SO_2SCH_2CH_3$

(2 - 3)

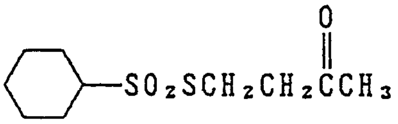


(2 - 4)

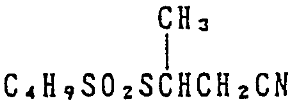


(2 - 5) $C_2H_5SO_2SCH_2CH_2CN$

(2 - 6)

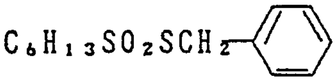


(2 - 7)

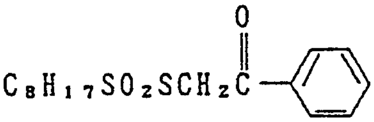


$$C_4H_9SO_2S\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CN$$

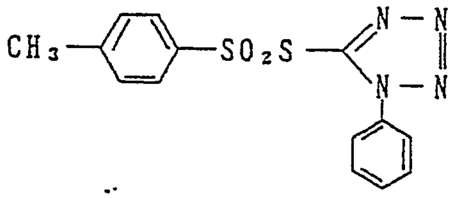
(2 - 8)



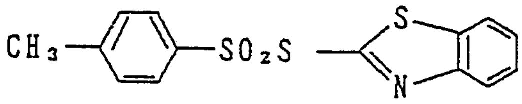
(2 - 9)



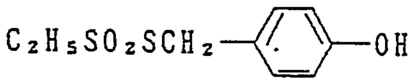
(2-10)



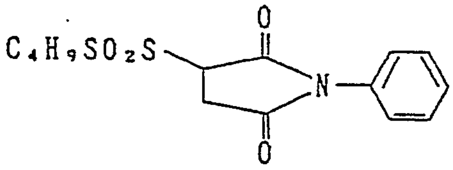
(2-11)



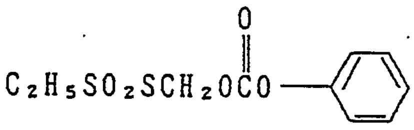
(2-12)



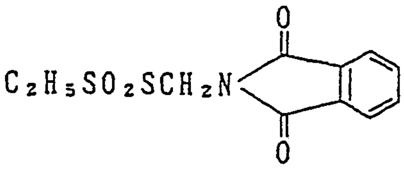
(2-13)



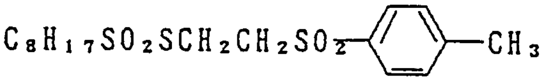
(2-14)



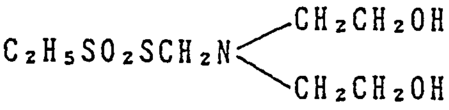
(2-15)



(2-16)



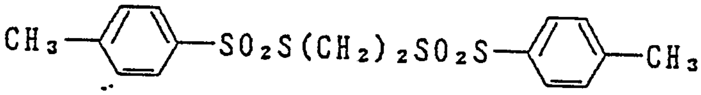
(2-17)



$C_2H_5SO_2SCH_2N\left<\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix}\right.$

(2-18) $C_2H_5SO_2SCH_2CH_2CH_2CH_2OH$

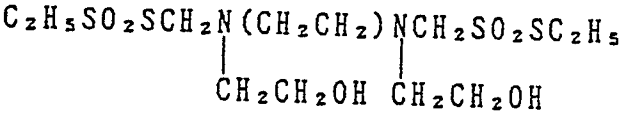
(3-1)



(3-2) $C_2H_5SO_2SCH_2CH_2SO_2CH_2CH_2SO_2SC_2H_5$

(3-3)

(3-4)



$$\begin{array}{l} C_2H_5SO_2SCH_2\underset{\displaystyle CH_2CH_2OH}{\underset{|}{N}}(CH_2CH_2)\underset{\displaystyle CH_2CH_2OH}{\underset{|}{N}}CH_2SO_2SC_2H_5 \end{array}$$

Furthermore, the inhibitor which is used for the aforesaid purposes may be an inorganic compound or an organic compound. For example, there are preferably soluble halides for controlling pAg and acids and alkalis as well as organic compounds capable of adsorbing on the surface of silver halide grain, which are used as so-called stabilizers, (e.g., mercapto compounds and heterocyclic compounds) for controlling pH.

In this case, however, in the case of using the compound capable of adsorbing on the surface of silver halide grains, the compound having a low inhibiting power for the growth of the silver halide grains by the compound is preferred.

The methods of using the oxidizing agents and/or the inhibitors described above may be preferably used as a combination thereof.

The amount of the oxidizing agent or the inhibitor and the selection of pAg or pH depend upon the kind and the amount of the reducing agent. The amount of the oxidizing agent is selected according to the oxidation-reduction potential of the reducing agent and the oxidizing agent and also for the purpose of using the oxidizing agent and, for example, in the case of controlling the extent of the reduction sensitization, the amount of the compound shown by general formula [I], [II], or [III] is preferably from 10^{-7} to 10^{-1} mol, more preferably from 10^{-6} to 10^{-2} mol, and particularly preferably from 10^{-5} to 10^{-3} mol per mol of silver halide.

For adding the aforesaid oxidizing agent, inhibitor, or compound for adjusting pAg or pH during the production step of the photographic emulsion, a method which is usually used in the case of adding additives to a photographic emulsion can be used. For example, a water-soluble compound can be added as an aqueous solution thereof of a proper concentration and a compound insoluble in water or sparingly soluble in water can be added as a solution thereof in an organic solvent miscible with water, such as alcoholos, glycols, ketones, esters, amides, etc., which does not give bad influences on the photographic characteristics. The time for adding the additives may be at any step during the grain formation of the silver halide emulsion. For inhibiting the unnecessary reduction sensitization which is the first purpose for using the oxidizing agent and/or the inhibitor, the additive may be added at the time when the reduction sensitization during the grain formation becomes unnecessary. For controlling the extent of the reduction sensitization which is the second purpose for using the oxidizing agent and/or the inhibitor, it is preferred to add the oxidizing agent and/or the inhibitor before the addition of the reducing agent or setting the reducing atmosphere (pAg, pH) but the addition may be at the same time or the order may be reversed.

It is important that the reduction sensitization proceeds substantially in the existence of the oxidizing agent and/or the inhibitor. The additive may be previously added to the reaction vessel or may be added at a proper time of the grain formation. The oxidizing agent and/or the inhibitor may be added as a solution thereof in several times with the growth of the grains or may be continuously added for a long period of time.

As the oxidizing agent which is used for controlling the extent of the reduction sensitization, the compounds of aforesaid general formulae [I] to [III] are preferred and the compound of general formula [I] is more preferred. The control of pAg by the addition of a soluble halide and the control of pH by the addition of acid are also preferably used for the second purpose. Also, if bad influences are not given to the growth of the grains, a means of reducing the temperature of the reaction vessel for causing the grain growth, etc., may be used.

Then, the production process of the silver halide grains of this invention is explained.

By adding silver halide grains having fine grain sizes previously prepared to a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains, the nucleus formation and/or the crystal growth of silver halide grains are performed in the reaction vessel.

That is, in this invention, it is important that the aqueous silver salt solution and the aqueous halide solution are not added to the reaction vessel for the nucleus formation and/or the crystal growth except for adjusting pAg of the emulsion in the reaction vessel, and further the aqueous protective colloid solution (containing silver halide grains) in the reaction vessel is not circulated into the mixer.

In this invention, by adding the silver halide grains of fine sizes previously prepared to the reaction vessel, the nuclei of the grains can be formed and further the growth of the crystals can be carried out in the reaction vessel.

Further, by adding the silver halide grains of fine sizes previously prepared to the reaction vessel in which the nuclei of the grains were previously formed by a conventionally known method, the growth of the crystals can also be carried out.

More specific methods of adding the fine silver halide are as follows.

(1) Method of supplying fine silver halide grains from a mixer outside the reaction vessel.

By immediately supplying the fine grains formed by mixing an aqueous solution of a water-soluble silver salt and an aqueous solution of water-soluble halides in a mixer disposed outside the reaction vessel for causing the nucleus formation and/or the crystal growth to the reaction vessel, the nucleus formation and/or the crystal growth of the silver halide core grains is carried out (hereinafter, is referred to as Method A).

The system of such a grain forming method is shown below by referring to Fig. 1.

In Fig. 1, a reaction vessel 1 contains an aqueous solution 2 of a protective colloid. The aqueous solution of the protective colloid is stirred by a propeller 3 attached to a rotary shaft. An aqueous solution of silver salt, an aqueous solution of halides, and an aqueous solution of a protective colloid are introduced into a mixer 7 outside the reaction vessel through feed systems 4, 5, and 6, respectively. (In this case, the aqueous protective colloid solution may be added as a mixture with the aqueous halide solution and/or the aqueous silver salt solution). These solution are quickly and strongly mixed in the mixer and the grains formed are immediately introduced into the reaction vessel 1 through a system 8.

The details of the mixer 7 are shown in Fig. 2. A reaction chamber 10 is formed in the mixer 7 and a stirring blade 9 fixed to a rotary shaft 11 is equipped in the reaction chamber 10. An aqueous silver salt solution, an aqueous halide solution, and an aqueous protective colloid solution are added to the reaction chamber 10 from three inlets (4, 5, and one inlet is omitted from the figure). By rotating the rotary shaft at a high speed (at least 1000 r.p.m., preferably at least 2000 r.p.m., and more preferably at least 3000 r.p.m.), the mixture is quickly and strongly mixed and a solution containing very fine grains thus formed is immediately discharged from an outlet 8. The very fine grains formed in the mixer are then introduced into the reaction vessel, easily dissolved due to the fineness of the grain size to form silver ions and halogen ions again, and cause the formation of homogeneous growth of grains. The halide composition of the very fine grains is selected such that it is same as the halide composition of silver halide grains being formed. The very fine grains introduced into the reaction vessel are dispersed in the reaction vessel by stirring in the reaction vessel to release halogen ions and silver ions of the halide composition being formed from each fine grain. The grains formed in the mixer is very fine, the number of the grains is very large, and since the silver ions and halogen ions (in the case of the growth of mixed crystals, the desired halogen ion composition is formed) are released from a very large number of grains and they are released over the whole protective colloid in the reaction vessel, the completely homogeneous nuclei formation and/or the growth of completely homogeneous grains can be caused. It is important that silver ions and halogen ions are never added to the reaction vessel as aqueous solution thereof except for pAg control and the protective colloid solution in the reaction vessel is not circulated in the mixer. The method can give an astonishing effect in the homogeneous growth of silver halide grains different from conventional methods.

The fine grains formed in the mixer have a very high solubility since the grain size thereof is very fine, dissolved when added to the reaction vessel to form silver ions and halogen ions again, and nuclei are formed or they are deposited on the grains already existing in the reaction vessel to cause the grain growth. In this case, however, since the fine silver halide grains have a high solubility, the fine grains cause so-called Ostwald ripening in the mixer before being added to the reaction vessel to increase the grain sizes. If the size of fine grains is increased, the solubility thereof is lowered with the increase of the size, the dissolution thereof in the reaction vessel is delayed, the grain growing rate is greatly reduced, and in some case, the fine grains cause the grain growth as the nuclei thereof without being dissolved.

These problems are solved by the following three techniques in this invention.

1) After the formation of the fine grains in the mixer, the fine grains are immediately added to the reaction vessel.

In this invention, by disposing the mixer very close to the reaction vessel and shortening the residence time of the solutions added to the mixer, and thus by immediately adding the fine grains formed to the reaction vessel, the occurrence of the Ostwald ripening is prevented. Practically, the residence time (t) of the solutions added to the mixer is shown as follows.

$$t = \frac{v}{a + b + c}$$

v: Volume (ml) of the reaction chamber in the mixer.

a: Addition amount (ml/min.) of a silver nitrate solution.

b: Addition amount (ml/min.) of a halide solution.

c: Addition amount (ml/min.) of a protective colloid solution.

In the production process of this invention, t is not longer than 10 minutes, preferably not longer than 5 minutes, more preferably not longer than 1 minute, and far more preferably not longer than 20 seconds. Thus, the fine grains formed in the mixer are immediately added to the reaction vessel without causing the increase of the grain size.

2) Solutions are strongly and efficiently stirred in the mixer.

In T.H. James, The Theory of the Photographic Process, page 93, there is described "Another form in addition to Ostwald ripening is coalescence. In coalescence ripening, crystals which were far apart are directly brought into contact with each other and adhere to each other to form large crystals, and hence the grain sizes change suddenly. Both of Ostwald ripening and coalescence ripening occur not only after the completion of deposition but also during deposition.". The coalescence ripening described in the aforesaid book is liable to occur when the grain sizes are very small and, in particular, it is liable to occur when stirring is insufficient. In the extreme case, it sometimes happens that large massive grains are formed. In this invention, the stirring blade of the reaction chamber can be rotated at a high rotation number since a closed type mixer shown in Fig. 2 is used but it is impossible in a conventional open type reaction vessel (i.e., in an open type reaction vessel, when a stirring blade is rotated at a high speed, the liquid is scattered by the centrifugal force and hence such as operation is unapplicable practically with an additional problem of foaming). That is, in this invention, it is possible to employ mixing by strong and efficient stirring for preventing the occurrence of the aforesaid coalescence ripening, which results in the formation of very fine grains having very fine grain sizes.

In this invention, the rotation number of the stirring blade is at least 1000 r.p.m., preferably at least 2000 r.p.m., and more preferably at least 3000 r.p.m.

3) Pouring of aqueous protective colloid solution into mixer.

The occurrence of aforesaid coelescence ripening can be markedly prevented by a protective colloid for silver halide grains. In this invention, an aqueous protective colloid solution is added to the mixer as follows:

(a) Aqueous protective colloid solution is added singly to the mixer.

The concentration of the protective colloid is at least 0.2% by weight, and preferably at least 0.5% by weight and the flow rate thereof is at least 20%, preferably at least 50%, and more preferably at least 100% of the sum of the flow rate of an aqueous silver nitrate solution and the flow rate of an aqueous halide solution.

(b) Protective colloid is incorporated in aqueous halide solution.

The concentration of the protective colloid is at least 0.2% by weight, and preferably at least 0.5% by weight.

(c) Protective colloid is incorporated in aqueous silver nitrate solution.

The concentration of the protective colloid is at least 0.2% by weight, and preferably at least 0.5% by weight. When gelatin is used, since gelatin silver is formed by silver ions and gelatin and gelatin silver forms silver colloid by causing photodecomposition and thermal decomposition, it is better to mix an aqueous silver nitrate solution and an aqueous protective colloid solution directly before use.

Also, aforesaid methods (a) to (c) may be used solely or as a combination thereof. Furthermore, the three methods may be simultaneously used.

(2) Method of adding a previously prepared silver halide fine grain emulsion.

In this invention, a method of adding a fine grain silver halide emulsion containing silver halide grains of fine grain size previously prepared to a reaction vessel to perform the formation of nuclei and/or the growth of the grains (hereinafter, is referred to as "Method B") can be used.

In this case, it is better as in the aforesaid case that the grain size of the previously prepared emulsion is fine. In the method, an aqueous silver salt solution and an aqueous halide solution are not added to the reaction vessel for causing the nucleus formation and/or the crystal growth except for pAg control of the emulsion in the reaction vessel as in the aforesaid method. The previously prepared emulsion may be previously washed with water and/or gelled before adding to the reaction vessel.

In this invention, gelatin is preferably used as the protective colloid.

As other high molecular compounds other than gelatin having a protective colloid action for silver halide grains for use in this invention, the following compounds are used.

(a) Polyacrylamide polymers:
homopolymer of acrylamide, copolymer of polyacrylamide and imidated polyacrylamide, and a copolymer of acrylamide and methacrylamide.

(b) Amino polymers:

(c) Polymers having thioether group:
the polymers having thioether groups shown in U.S. Patents 3,615,624, 3,860,428, and 3,706,564.

(d) Polyvinyl alcohol:

(e) Acrylic acid polymers:
acrylic acid homopolymer, acrylic acid ester polymer having amino group, and halogenated acrylic acid ester polymer.

(f) Polymers having hydroxyquinoline:

(g) Celluloses, starch:

(h) Acetals:

(i) Polyvinylpyrrolidone:

(j) Polystyrene:

Also, low molecular weight gelatin is used in this invention. The average molecular weight of gelatin is preferably not more than 30,000 and more preferably not more than 10,000.

When the synthetic protective colloids shown above, natural protective colloids, and low molecular weight gelatin are used, the formation of fine grain silver halide grains can be performed at a lower temperature than the case of using ordinary gelatin and silver halide having finer grain sizes can be provided.

The concentration of the protective colloid being added to the mixer in Method A is at least 0.2% by weight, preferably at least 1% by weight, and more preferably at least 2% by weight. In the case of incorporating the protective colloid in an aqueous silver nitrate solution and/or an aqueous halide solution, the concentration thereof is at least 0.2% by weight, preferably at least 1% by weight, and more preferably at least 2% by weight.

Also, in Method B, the concentration of the protective colloid in the reaction vessel at the preparation of the fine grain emulsion is at least 0.2% by weight, preferably at least 1% by weight, and more preferably at least 2% by weight.

In Method A described above, the temperature of the mixer is not higher than 40°C, and preferably not higher than 35°C and the temperature of the reaction vessel is not lower than 50°C, and preferably not lower than 60°C, and more preferably not lower than 70°C.

In Method B, the grain forming temperature for the fine grain emulsion being previously prepared is not higher than 40°C, and preferably not higher than 35°C and the temperature of the reaction vessel to which the fine grain emulsion is added is not lower higher than 50°C, preferably not lower than 60°C, and more preferably not lower than 70°C.

The grain size of the silver halide grains having fine grain sizes for use in this invention can be confirmed by a transmission type electron microscope on a mesh and the magnification thereof is preferably from 20,000 to 40,000. The grain size of the fine silver halide grains for use in this invention is not larger than 0.2 µm, preferably not larger than 0.1 µm, and more preferably not larger than 0.05 µm.

As described above, Method A can provide fine grains having finer grain sizes than Method B by employing the means of (1) fine silver halide grains are immediately added to the reaction vessel after the formation thereof,

(2) strong stirring is applied, (3) an aqueous solution of protective colloid is poured into the mixer, etc.

In the process of this invention, by using a silver halide solvent for the reaction system in the reaction vessel, a higher dissolution speed of the fine grains and a higher growing speed of the grains in the reaction vessel can be obtained.

As the silver halide solvent, there are water-soluble bromides, water-soluble chlorides, thiocyanates, ammonia, thioethers, thioureas, etc.

For example, there are thiocyanates (U.S. Patents 2,222,264, 2,448,534, and 3,320,069), ammonia, thioether compounds (U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439, and 4,276,347), thione compounds (e.g., JP-A-53-144319, JP-A-53-82408, and JP-A-55-77737), amine compounds (e.g., JP-A-54-100717), thiourea derivatives (e.g., JP-A-55-2983), imidazoles (e.g., JP-A-54-100717, and substituted mercaptotetrazoles (e.g., JP-A-57-202531).

The halide composition of the emulsion obtained by the present invention may be silver iodobromide, silver chlorobromide, silver chloroiodobromide, or silver chloroiodide and according to this invention, silver halide mixed crystal grains having a homogeneous microscopic distribution of halide, that is, "complete homogeneity" are obtained.

As an example of the silver halide emulsion grains having "complete homogeneity" tabular silver iodobromide emulsion grains having a silver iodobromide phase are explained.

The "completely homogeneous silver iodide distribution" in this invention completely differs from a conventional silver iodide distribution and a more microscopic distribution. Hitherto, as a means for measuring the silver iodide distribution of silver iodobromide grains, Analytical Electron Microscopy has been well used. For example, in M.A. King, M.H. Lorretto, T.J. Maternaghan, and F.J. Berry, The Investigation of Iodide Distribution by Analytical Electron Microscopy, "Progress in Basic Principles of Imaging Systems; International Congress of Photographic Science", 1986 (Köln), there is described the topographic result of the content of silver iodide in tabular silver iodobromide grains.

The size of the probe for electron ray irradiation used in the investigations is 50 Å but actually, the electron beam is broarded by the elastic scattering of electron and the diameter of the spot of the electron irradiated onto the surface of the sample becomes about 300 Å. Accordingly, a finer silver iodide distribution than the diameter can not be measured by the method. In

JP-A-58-113927, a silver iodide distribution was measured by the same manner but the size of the spot of the electron been used was 0.2 µm.

Therefore, it is impossible to clarify a more microscopic (positional change of the order of 100 Å or less) silver iodide distribution by these measurement methods. The microscopic silver iodide distribution can be observed by a direct method of using a transmission type electron microscope at a low temperature described, for example, in J.H. Hamilton, Photographic Science and Engineering, Vol. 11, page 57, (1967) and Takekimi Shinozawa, Journal of the Society of Photographic Science and Technology of Japan, Vol. 35, No. 4, page 213, (1972). That is, silver halide grains taken out under safe light such that the emulsion grains are not printed out are placed on a mesh for electron microscopic observation and the observation of the sample is carried out in the state of being cooled by liquid nitrogen or liquid helium for preventing the occurrence of damages (print out, etc.) of the sample by electron beams.

In this case, as the acceleration electric voltage for the electron microscope is higher, clearer transmitted images are obtained but 200 Kvolts is preferred for grains having a thickness up to 0.25 µm and 1,000 Kvolts is preferred for grains having a thicker thickness. Since as the acceleration voltage is higher, the damage of the grains by the irradiated electron beams becomes severer, it is more preferred to cool the sample by liquid helium than by liquid nitrogen.

The photographing magnification can be properly changed according to the size of the grains but is from 20,000 to 40,000 magnifications.

When the transmission type electron microphotograph of tabular silver iodobromide grains is photographed as described above, a very fine annular ring-like striped pattern is observed at the portion of the silver iodobromide phase. An example thereof is shown in Fig. 3. The tabular grains shown in the figure are grains composed of tabular silver bromide grain as the core and silver iodobromide containing 10 mol% of silver iodide as the shell formed at the outside of the core and the structure can be clearly confirmed by the transmission type electron microphotograph. That is, since the core portion is silver bromide and is, as a matter of course, homogeneous, homogeneous flat images only are obtained but, on the other hand, a very fine annular ring-like striped pattern is clearly confirmed in the silver iodobromide phase. The striped pattern has a very fine interval as the order of 100 Å or less, which shows a very microscopic heterogeneity. It can be clarified by various methods that the very fine striped pattern shows the heterogeneity of the silver iodide distribution but more directly, the aforesaid fact can be clearly concluded from that when the tabular grains are annealed under the condition wherein iodide ions can move in the silver halide crystal (e.g., 250°C, 3 hours), the striped pattern is completely vanished.

The annular ring-like striped pattern showing the heterogeneity of the silver iodide distribution of the tabular silver iodobromide emulsion grains described above is clearly observed in the transmission type electron microphotograph attached to JP-A-58-113927 cited above and also is clearly shown in the transmission type electron microphotograph in the King et al investigation cited above. From these facts, it is clear the conventional silver iodobromide grains prepared in a definite silver iodide content for obtaining a homogeneous silver iodide distribution have a very microscopically heterogeneous distribution of silver iodide contrary to the intention for the production thereof and neither the technique for homogenizing the distribution nor the production process for such silver halide grains has been disclosed. The present invention discloses the silver halide emulsion having the completely homogeneous microscopic silver iodide distribution and the production process thereof.

As described above, the silver halide grains having "the completely hemogeneous silver iodide distribution" can be clearly distinguished from conventional silver halide grains by observing the transmitted images of the grains using the cooling type transmission electron microscope. That is, in the inside of the silver halide grains containing silver iodide of this invention, there exist at most two lines caused by the heterogeneity of silver iodide at an interval of 0.2 µm in the direction crossing the lines, preferably there exist one such line, and more preferably there exists no such a line.

The lines constituting the annular ring-like striped pattern showing the microscopic heterogeneity of silver iodide occur in the form of crossing the growing direction of the grains, which results in concentrically distributing these lines from the center of the grains. For example, in the case of the tabular grains shown in Fig. 3, the lines constituting the annular ring-like striped pattern showing the heterogeneity of silver iodide rectangularly cross the growing direction of the tabular grains, whereby the lines become parallel to the edge of the grain, the direction rectangularly crossing the line directs to the center of the grain, and the lines distribute concentrically around the center of the grains.

As a matter of course, if the content of silver iodide is abruptly changed during the growth of the grains, the boundary line can be observed as a similar line to above by the aforesaid observation method but such a change of the content of silver iodide constitutes a single line only and can be clearly distinguished from those constituted by plural lines caused by the microscopic heterogeneity of silver iodide. Furthermore, the line originated in the change of the content of silver iodide can be clearly confirmed by measuring the content of silver iodide at both sides of the line by the analytical electron microscope described above. Such a line by the change of the content of silver iodide is utterly different from the lines originated in the microscopic heterogeneity of silver iodide and shows "a macroscopic silver iodide distribution".

Also, when the content of silver iodide is substantially continuously changed during the growth of the grains, the aforesaid line of showing the macroscopic change of the content of silver iodide is not observed since there is not abrupt change of the content of silver iodide and thus if there are at least three lines with an interval of 0.1 µm, it shows that there is the microscopic heterogeneity of the content of silver iodide.

Thus, "the silver halide grains having a completely homogeneous silver iodide distribution" of this invention are grains having at most two lines, preferably one line, more preferably no line showing the microscopic silver iodide distribution with an interval of 0.2 µm in the direction of rectangularly crossing the line in the transmitted images of the grain obtained by using a cooling type transmission electron microscope. Furthermore, it is preferred that the grains account for at least 60%, preferably at least 80%, and more preferably at least 90% of the whole grains.

Conventional silver halide grains which are called silver halide grains containing, for example, homogeneous silver iodide are prepared by simply adding silver nitride and a mixture of halides having a definite composition (a definite content of iodide) to a reaction vessel by a double jet method at the growth of grains and thus in such grains, the macroscopic silver iodide distribution may be surely constant but the microscopic silver iodide distribution is not homogeneous. In this invention, such grains are called as grains having "a constant halogen composition" and are clearly distinguished from the grains of this invention showing "the complete homogeneity".

Furthermore, the process of this invention is very effective in the production of pure silver bromide or pure silver chloride. According to a conventional production process, the local existence of silver ions and halogen ions in a reaction vessel is unavoidable and silver halide grains in the reaction vessel are brought into other circumstance than other homogeneous portions by passing through such a local heterogeneous portion, whereby not only the growth thereof becomes heterogeneous but also reduced silver or fogged silver is formed at the portion of a high silver ion concentration. Accordingly, there is no heterogeneous distribution of halide in silver bromide or silver chloride but another heterogeneity as described above occurs. This problem is completely solved by the process of this invention.

Thus, for the photographic emulsion layers of the photographic light-sensitive materials of this invention, silver bromide, silver iodobromide, silver iodochlorobromide, or silver chlorobromide can be used. The preferred silver halide in this invention is silver iodobromide having a silver iodide content of from 3 mol% to 40 mol%, silver chlorobromide, silver chloroiodide, or silver chloroiodobromide. In the case of silver iodobromide having a silver iodide content of less than 3 mol%, the feature of the "completely homogeneous" mixed crystals by the process of this invention is less. Also, since mixed crystals containing silver chlorobromide, silver chloroiodide, or silver chloroiodobromide have a high solubility and are liable to become heterogeneous, the feature of the "completely homogeneous" mixed crystals by the process of this invention is liable to occur.

The silver halide grains for use in this invention can be selected from normal crystals containing no twin plane and the examples of crystals described in Shashin Kogyo no Kiso; Ginen Shashin Hen (The Bases of photographic Industry; Silver Salt Photography), page 163, edited by Nippon Shashin Gakkai (published by Corona Sha), such as single twin having one twin plane, parallel multiple twin having at least 2 parallel twin planes, non-parallel multiple twin having at least 2 non-parallel twin planes, etc., according to the purpose. In the case of normal crystals, cubic grains composed of (100) planes, octahedral grains composed of (111) planes, or the dodecahedral grains composed of (110) planes disclosed in JP-B-55-42737 and JP-A-60-222842. Furthermore, the (h11) plane grains such as (211) plane grains, the (hh1) plane grains such as (331) plane grains, the (hk0) plane grains such as (210) plane grains, or the (hk1) plane grains such as (321) plane grains reported in Journal of Imaging Science, Vol. 30, page 247, (1986) can be used according to the purpose although some modification is required in the preparation process thereof. Tetradecahedral grains having both a (100) plane and a (111) plane in one grain, grains having both a (100) plane and a (110) plane, or grains having both a (111) plane and a (110) plane can be also used according to the purpose.

The grain sizes of the silver halide obtained may be fine grains of not more than 0.1 micron or large size grains up to 10 microns in the diameter of the projected area, and also the emulsion may be a mono-dispersed emulsion having a narrow distribution or a polydispersed emulsion having a broad distribution.

A so-called mono-dispersed silver halide emulsion having such narrow grain size distribution that at least 80% of the whole grains are within ±30% of the mean grain size by number or by weight can be used in this invention. Also, for satisfying the gradation for the light-sensitive material, in emulsion layers having a substantially same color sensitivity, two or more kinds of mono-dispersed silver halide emulsions each having different grain sizes can be used in a same emulsion layer as a mixture thereof or may be coated as double layers. Furthermore, two or more kinds of polydispersed silver halide emulsions can be used as a mixture or double layers or a combination of a mono-dispersed emulsion and a polydispersed emulsion can be used as a mixture or double layers.

The photographic emulsion of this invention is prepared by the aforesaid process but may be partially prepared by a conventional process.

That is, in the preparation of the light-sensitive silver halide grains of this invention, the whole grains may be prepared by the process of this invention or the process of this invention is applied for preparing a part of the grains and remaining grains may be prepared by a conventional process. For example, the core or the shell only of core/shell type silver halide grains having a different halogen composition between the inside and the surface layer of the grain is prepared by the process of this invention and the other may be prepared by a known process or a combination of the process of this invention and a conventional process may be used for the preparation of the inside and the surface layer having a same halogen composition. In the preparation of grains having similar junction structure (epitaxial grains), the preparation of the host and the preparation of the guest may be separately performed by the process of this invention and a conventional process, respectively.

Also, the photographic emulsion layers of the photographic light-sensitive material of this invention may contain a photographic emulsion which is not prepared by the production process of this invention. Such a photographic emulsion can be prepared by the process described in P. Glafkides, Ciemie et Physique Photographique, published by Paul Montel, 1967, G.F. Duffin, Photographic Emulsion Chemistry, published by Focal Press, 1966, and V.L. Zelikman et al, Making and Coating Photographic Emulsion, published by Focal Press, 1964. That is, an acid process, a neutralization process, an ammonia process, etc., can be used and as a system of reacting a soluble silver salt and a soluble halide, a single jet process, a double jet process or a combination thereof may be used. A so-called reverse mixing process of forming silver halide grains in the existence of excess silver ions can be also used. As one system of the double jet process, a so-called controlled double jet process of keeping a constant pAg in a liquid phase of forming silver halide grains can be also used. According to the process, a silver halide emulsion containing silver halide grains having a regular crystal form and almost uniform grain sizes can be obtained.

The aforesaid silver halide emulsion composed of regular grains is obtained by controlling pAg and pH during the formation of the grains. The details thereof are described, for example, in Photographic Science and Engineering, Vol. 6, pages 159-165 (1962), Journal of

Photographic Science, Vol. 12, pages 242-251 (1964), U.S. Patent 3,655,394, and British Patent 1,413,748.

Also, tabular grains having an aspect ratio of at least 3 can be used in this invention. The tabular grains can be easily prepared by the methods described in Cleve, Photographic Theory and Practice, page 131 (1930), Gutoff, Photographic Science and Engineering, Vol. 14, pages 248-257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048, and 4,439,520 and British Patent 2,112,157. In the case of using the tabular grains, there are advantages of increasing covering power, increasing the color sensitizing efficiency by sensitizing dyes, etc., as described in detail in U.S. Patent 4,434,226 cited above. As the silver halide emulsion for use in this invention, a tabular grain silver halide emulsion is preferred. In particular, tabular grains wherein grains having an aspect ratio of from 3 to 8 account for at least 50% of the whole projected areas are preferred.

The crystal structure may be uniform, differs in halogen composition between the inside and the outer portion thereof, or a layer structure. These emulsion grains are disclosed in British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877 and Japanese Patent Application 58-248469. Also, silver halides each having different composition may be junctioned to each other by an epitaxial junction or a silver halide may be junctioned to other compound than silver halide, such as silver rhodanate, lead oxide, etc.

It is preferred that the silver halide emulsion of this invention has a distribution or a structure in regard to the halogen composition in the grains thereof. The typical ones are core/shell type or double layer structure type grains having a different halogen composition between the inside and the surface layer thereof as disclosed in JP-B-43-13162 and JP-A-61-215540, JP-A-60-222845, and JP-A-61-75337. In such grains, the form of the core portion is same as the form of the whole grain having shell thereon in one case and is different from the whole grain in another case. Practically, the core portion has a cubic form and the form of the whole grain having the shell is cube or octahedron. On the contrary, in other case, the form of the core portion is octahedron and the form of the whole grain having the shell is cube or octachedron. Also, in still other case, the core portion is a clear regular grain and the whole grain having the shell is slightly deformed or is amorphous. Furthermore, the core/shell grains of this invention may have not only a simple double structure but also a triple or more structure as disclosed in JP-A-60-222844 or a structure formed by attaching a thin silver halide layer having a different composition to the surface of the grain having a core/shell structure.

For forming the inside structure of the grains, grains having not only the aforesaid wrapping structure but also a so-called junction structure can be formed. Examples thereof are disclosed in JP-A-59-133540, JP-A-58-108526, EP 199290A2, JP-B-58-24772, and JP-A-59-16254. The crystals being junctioned can be junctioned to the edge or corner portions or the place portions of host crystals with a different composition from that of the crystals becoming the host. Such junction crystals which can be formed may be homogeneous in halogen composition or have a core/shell type structure. In the case of the junction structure, a combination of silver halides each other can be as a matter of course employed but a combination of silver halide and other silver salt compound having no rock salt structure, such as silver rhodanate, silver carbonate, etc., can be employed as the junction structure. Also, a non-silver salt compound such as PbO can be used if junction structure is possible.

In the case of the silver iodobromide grains having such a structure in, for example, core/shell type grains, the silver iodide content of the core portion may be high and the silver iodide content of the shell portion may be low, or on the contrary the silver iodide content of the core portion may be low and that of the shell portion may be high. Similarly, in the grains having a junction structure, the silver iodide content may be higher in the host crystal and relatively lower in the junction crystal or the relation may be the contrary.

Also, the boundary portion between the portions of the grain having the aforesaid structure, said portions each having different halogen composition, may form a clear boundary, may form an uncertain boundary by forming mixed crystals by the difference in halogen composition, or may have a continuously changing structure positively formed.

The silver halide emulsion for use in this invention may be subjected to the treatment of providing roundness to the grains as disclosed in EP 0096727 B1 and EP 0064412 B1 or the surface modification treatment as disclosed in DE 2306447 C2 and JP-A-60-221320.

The silver halide emulsion for use in this invention is preferably of a surface latent image type but an internal latent image type emulsion can be used by selecting a suitable developer or a suitable development condition as disclosed in JP-A-59-133542. Also, a shallow internal latent image type emulsion having covered thereon a thin shell can also be used according to the purposes.

In this invention, it is very important to apply a chemical sensitization such as a reduction sensitization, a sulfur sensitization, and a gold sensitization. The portion being chemically sensitized differs according to the composition, structure, and form of the emulsion grains or the purpose of using the emulsion. There is a case of forming the chemically sensitized nucleus in the inside of the grain, the case of forming the chemically sensitized nucleus in the position near the surface of the grain, or the case of forming the chemically sensitized nucleus at the surface thereof. The present invention is effective for any case described above but the case of forming the chemically sensitized nucleus in the vicinity of the surface is particularly preferred. In other words, the surface latent image type emulsion is more effective than the internal latent image type emulsion in this invention.

The chemical sensitization can be carried out using active gelatin as described in T.H. James, The Theory of the Photographic Process, 4th ed., pages 67-76 (1977), MaCmillan and also can be carried out using sulfur, selenium, tellurium, gold, platinum, palladium, iridium, or a combination of these sensitizers at pAg of from 5 to 10, pH of from 5 to 8, and a temperature of from 30 to 80°C as described in Research Disclosure, Vol. 120, 12008, (April, 1974); Research Disclosure, Vol. 34, 13452, (June, 1975), U.S. Patents 2,642,361, 3,297,446, 3,772,031, 3,857,711, 3,901,714, 4,266,018, and 3,904,415 and British Patent 1,315,755. The chemical sensitization is most favorably carried out in the existence of a gold compound and a thiocyanate compound or in the existence of the sulfur-containing compound described in U.S. Patents 3,857,711, 4,266,018, and 4,054,457 or a sulfur-containing compound such as hypo, thiourea compounds, rhodanine compounds, etc. Furthermore, the chemical sensitization can be carried out in the existence of a chemical sensitization aid. As the chemical sensitization aid, a compound which is known to inhibit the formation of fog and increase the sensitivity in the step of the chemical sensitization, such as an azaindene, azapyridazine, and azapyrimidine is used. Examples of the chemical sensitization aid are described in U.S. Patents 2,131,038, 3,411,914, and 3,554,757, JP-A-58-126526, and C.F. Duffin, Photographic Emulsion Chemistry, published by Focal Press, 1966, pages 138-143.

In the case of performing the chemical sensitization using a gold salt, it is preferred that the formation of fog by the reaction of reduced silver nuclei and the gold salt by the addition of the aforesaid oxidizing agent and/or the inhibitor prior to the formation of grains in the domain. For example, in the case of using a gold salt in the chemical sensitization of the surface of grains, it is preferred that the formation of the grains in the domain of at least 0.001 µm from the surface of the grain is carried out in the existence of the oxidizing agent and/or the inhibitor.

The photographic emulsion for use in this invention can contain various kinds of compounds for inhibiting the formation of fog during the production, the storage, or photographic processing of the light-sensitive materials or stabilizing the photographic performance thereof. That is, there are many compounds known as antofiggants or stabilizers, such as azoles (e.g., benzothiazolium salt, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazole, nitrobenzotriazoles, mercaptotetrazoles (in particular, 1-phenyl-5-mercaptotetrazole), etc.), mercaptopyrimidines, mercaptotriazines, thioketo compounds (e.g., oxazolinethione), azaindenes (e.g., triazaindenes, tetraazaindenes (in particular, 4-hydroxy-substituted (1,3,3a,7)-tetraazaindenes), pentaazaindenes, etc. For example, the compounds described in U.S. Patents 3,954,474 and 3,982,947 and JP-B-52-28660 can be used.

The silver halide emulsions for use in this invention may be spectrally sensitized by methine dyes, etc. The dyes for use include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes. Particularly useful dyes are dyes belonging to cyanine dyes, merocyanine dyes, and complex merocyanine dyes.

For these dyes can be applied nuclei ordinarily utilized for cyanine dyes as basic heterocyclic nuclei. That is, pyrroline nuclei, oxazoline nuclei, thiazoline nuclei, pyrrole nuclei, oxazole nuclei, thiazole nuclei, selenazole nuclei, imidazole nuclei, tetrazole nuclei, pyridine nuclei, etc.; the nuclei formed by fusing an aliphatic hydrocarbon ring to the aforesaid nuclei; and the nuclei formed by fusing an aromatic hydrocarbon ring to the aforesaid nuclei, such as indolenine nuclei, benzindolenine nuclei, indole nuclei, benzoxazole nuclei, naphthoxazole nuclei, benzothiazole nuclei, naphthothiazole nuclei, benzoselenazole nuclei, benzimidazole nuclei, quinoline nuclei, etc., can be applied for the dyes described above. These nuclei may be substituted on carbon atoms.

For merocyanine dyes or complex merocyanine dyes may be applied 5-memberd or 6-membered heterocyclic nuclei such as pyrazoline-5-one nuclei, thiohydantoin nuclei, 2-thiooxazolidine-2,4-dione nuclei, thiazolidine-2,4-dione nuclei, rhodanine nuclei, thiobarbituric acid nuclei, etc., as a nucleus having a ketomethylene structure.

These sensitizing dyes may be used singly or as a combination thereof. A combination of sensitizing dyes is frequently used for the purpose of super-color sensitization. Typical examples of the combinations are described in U.S. Patents 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,616,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, and 4,026,707, British Patents 1,344,281 and 1,507,803, JP-B-43-4936 and JP-B-53-12375, and JP-A-52-110618 and JP-A-52-109925.

The emulsion may contain a dye having no spectral sensitizing activity by itself or a material which does not substantially absorb visible light and shows super color sensitizing activity together with the sensitizing dye(s).

The sensitizing dye(s) may be added to the silver halide emulsion in any step of the preparation of the emulsion, which is known to be useful. Most usually, the addition thereof is performed after the completion of the chemical sensitization and before coating but the sensitizing dye may be added simultaneously with the addition of a chemical sensitizer to perform simultaneously the spectral sensitization and the chemical sensitization as described in U.S. Patents 3,628,969 and 4,225,666, the spectral sensitization can be performed prior to the chemical sensitization as described in JP-A-58-113928, or the spectral sensitization can be initiated by adding the sensitizing dye before the completion of the formation of the precipitation of the silver halide grains. Furthermore, the aforesaid compounds can be dividedly added, that is, a part of these compounds may be added prior to the chemical sensitization and the residues may be added after the chemical sensitization as disclosed in U.S. Patent 4,225,666, or the method disclosed in U.S. Patent 4,183,756 may be used as well as the compounds may be added in any step of forming the silver halide grains.

The addition amount can be from 4×10^{-6} to 8×10^{-3} mol per mol of silver halide and in the more preferred case that the size of the silver halide grains is from 0.2 to 1.2 µm, the effective addition amount is from about 5×10^{-5} to 2×10^{-3} mol.

For the light-sensitive materials of this technique can be used aforesaid various additives but in addition to these additives, various other additives can be also used according to the purposes.

These additives are described in more detail in Research Disclosure, Item 17643 (December, 1978) and ibid., Item 18716 (November, 1979) and they are summarized in the following table.

Additives	RD-17643	RD-18716
1. Chemical Sensitizer	Page 23	Page 648, right column
2. Sensitivity Increasing Agent		do
3. Spectral Sensitizer, Super Color Sensitizer	Pages 23-24	Page 648, right column-page 649, right column
4. Whitening Agent	Page 24	
5. Antifoggant and Stabilizer	Pages 24-25	Page 649, right column
6. Light Absorbent, Filter Dye, Ultraviolet Absorbent	Pages 25-26	Page 649, right column-page 650, left column
7. Stain Inhibitor	Page 25, right column	Page 650, left-right columns
8. Dye Image Stabilizer	Page 25	
9. Hardening Agent	Page 26	Page 651, left column
10. Binder	Page 26	do
11. Plasticizer, Lubricant	Page 27	Page 650, right column
12. Coating Aid, Surface Active Agent	Pages 26-27	do
13. Antistatic Agent	Page 27	do

[BRIEF EXPLANATION OF THE DRAWINGS]

Fig. 1 is a schematic view showing an emulsion reaction vessel which can be used for the process of this invention.

1: Reaction vessel

2: Aqueous protective colloid solution

3: Propeller

4: Addition system of aqueous halide solution

5: Addition system of aqueous silver salt solution

6: Addition system of aqueous protective colloid solution

7: Mixer

Fig. 2 is the detailed view showing a mixer which can be used for this invention.

4, 5, and 7 are same as in Fig. 1.

8: Introduction system to reaction vessel

9: Stirring blade

10: Reaction chamber

11: Rotary shaft

Fig. 3 is a transmission type electron microphotograph showing the crystal structure of conventional tabular silver halide grains having not completely homogeneous iodide distribution of silver iodobromide phase.

BEST MODE FOR PRACTICING THE INVENTION

Then, the present invention is further explained by referring to the examples.

Example 1 Silver Iodobromide Tabular Grains

Silver Iodobromide Fine Grain Emulsion I-A:

To 2.6 liters of a 2.0% by weight a gelatin solution containing 0.026M of potassium bromide were added 1200 ml of a solution of 1.2M of silver nitrate and 1200 ml of an aqueous halide solution containing 1.11M of potassium bromide and 0.09M of potassium iodide with stirring by a double jet method over a period of 15 minutes. The gelatin solution was kept at 35°C during the addition. Thereafter, the emulsion obtained was washed by an ordinary flocculation method, and after dissolving therein 30 g of gelatin, pH and pAg thereof were adjusted to 6.5 and 8.6, respectively. The mean grain size of the silver iodobromide fine grains (silver iodide content 7.5%) obtained was 0.07 µm.

Tabular Silver Bromide Core Emulsion I-B:

To 2 liters of an aqueous solution of 0.8% by weight gelatin containing 0.09M of potassium bromide were added 30 cc of an aqueous solution of 2.0M of silver nitrate and 30 cc of an aqueous solution of 2.0M of potassium bromide with stirring by a double jet method. During the addition, the gelatin solution in the reaction vessel was kept at 30°C. Thereafter, the temperature of the system was raised to 75°C and 40 g of gelatin was added thereto. Thereafter, an aqueous solution of 1.0M of silver nitrate was added thereto to adjust pBr to 2.55 and thereafter, a solution of 150 g silver nitrate was added thereto with accelerating flow rate (the flow rate at immediately before the end of the addition was 10 times that of the start) over a period of 60 minutes and simultaneously a solution of potassium bromide was added thereto by a double jet method such that pBr became 2.55.

Thereafter, the emulsion formed was cooled to 35°C, washed with water by an ordinary flocculation method, and after dissolving therein 60 g of gelatin at 40°C, pH and pAg thereof were adjusted to 6.5 and 8.6, respectively. The tabular silver bromide grains were mono-dispersed tabular grains having a mean diameter corresponding to circle of 1.4 µm, a grain thickness of 0.2 µm, and a coefficient of variation of circle-corresponding diameters of 15%.

Tabular Silver Iodobromide Emulsion I-C (Comparison Emulsion):

Emulsion I-B containing silver bromide corresponding to 50 g as silver nitrate was dissolved in 1.1 liters of water and the temperature and pBr thereof were kept at 75°C and 1.5, respectively. Then, 1 g of 3,6-dithiaoctane-1,8-diol was added thereto and immediately thereafter, a solution of 100 g of silver nitrate and a potassium bromide solution containing 7.5M of potassium iodide in an equivalent amount to silver nitrate were added thereto at constant flow rates over a period of 50 minutes. Thereafter, the emulsion formed was washed with water by an ordinary flocculation method and pH and pAg thereof were adjusted to 6.5 and 8.6, respectively. The center portion of the silver iodobromide tabular grains was silver bromide, the outer annular portion thereof was silver iodobromide containing 7.5M% of silver iodide, the mean circular-corresponding grain diameter was 2.3 µm and the thickness of the grain was 0.30 µm.

Tabular Silver Iodobromide Emulsion I-D (Comparison Emulsion):

By following the same procedure as the case of preparing Emulsion I-C except the following procedure, Emulsion I-D was prepared. That is, in place of adding the aqueous silver nitrate solution and the aqueous halide solution to the reaction vessel, the fine grain emulsion I-A was added to the reaction vessel in an amount of 100 g calculated as silver nitrate at a constant flow rate over a period of 50 minutes. The mean circle-corresponding diameter of the tabular grains obtained was 2.4 µm and the thickness of the grain was 0.31 µm.

Tabular Iodobromide Emulsions I-E, F, G, and H (Comparison Emulsions):

In the preparation of Tabular Silver Iodobromide Emulsion I-C, after 2 minutes since the initiation of the addition of the aqueous silver nitrate solution and the mixed solution of potassium iodide and potassium bromide, each of the reduction sensitizers shown in Table 1 was added and other procedure was same as that for Emulsion I-C to provide Emulsions I-E, F, G, and H. The grain sizes thereof were same as that of Emulsion I-C.

Tabular Silver Iodobromide Emulsions I-I, J, and K (Invention):

In the preparation of Tabular Iodobromide Emulsion I-D, after 2 minutes since the addition of the fine grain emulsion I-A, each of the reduction sensitizers shown in Table 1 was added and other procedure was same as that for Emulsion I-D to provide Emulsions I-I, J, and K. The grain sizes thereof were same as that of Emulsion I-D.

Tabular Silver Iodobromide Emulsions I-L, M, N, and O (Comparison Emulsions):

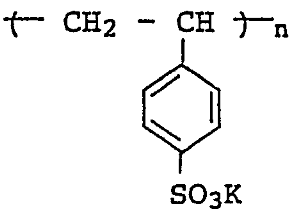
In the preparation of Tabular Silver Iodobromide Emulsions I-E, F, G, and H, directly before the addition of the silver nitrate solution and the mixed solution of potassium iodide and potassium bromide, each of the oxidizing agents shown in Table 1 was added and other procedure was same as those for Emulsions I-E, F, G, and H to provide Emulsions I-L, M, N, and O. The grain sizes were same as that of Emulsion I-C.

Tabular Silver Iodobromide Emulsion I-P, Q, and R (Invention):

In the preparation of Tabular Silver Iodobromide Emulsions I-I, J, and K, directly before the addition of the fine grain emulsion I-A, each of the oxidizing agents shown in Table 1 was added and other procedure was same as those for Emulsions I-I, J, and K to provide Emulsions I-P, Q, and R. The grain sizes thereof were same as those of Emulsion I-D.

To each of the Emulsions I-C to I-R thus prepared was added a spectral sensitizing dye 5-chloro-5'-phenyl-3,3'-(3-sulfopropyl)-9-ethyloxacarbocyanine (240 mg/mol-Ag and after adding thereto sodium thiosulfate (8×10^{-6} mol/mol-Ag), the emulsion was most favorably chemically sensitized at 60°C. After finishing the chemical sensitization, 100 g of each emulsion (containing 0.08 mol of Ag) was dissolved at 40°C and following additives (1) to (4) were successively added thereto with stirring.

(1) 4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	3%	2 cc
(2) $C_{17}H_{35}$-O-$(CH_2CHO)_{25}$-H	2%	2.2 cc

(3)  2% 1.6 cc

n = ca.3000)

(4) 2,4-Dichloro-6-hydroxy-s-triazine sodium 2% 3 cc

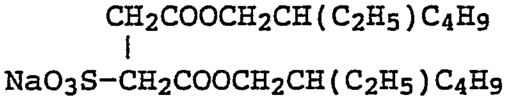
A coating composition for surface protective layer was prepared by successively adding following components (1) to (5) with stirring.

(1) Aqueous 14% gelatin solution 56.8 g

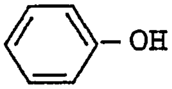
(2) Polymethyl methacrylate fine particles (average particle size 3.0 μm) 3.9 g

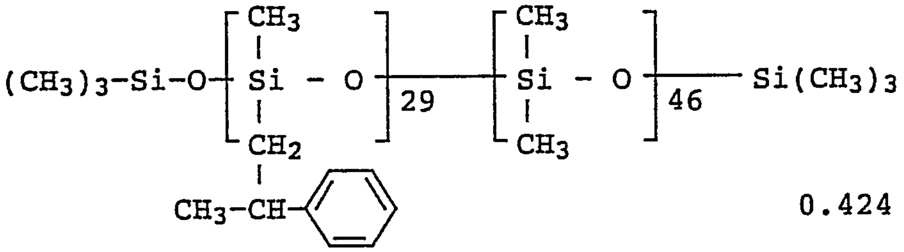
(3) Emulsifying Agent:

Gelatin 10% 4.24 g



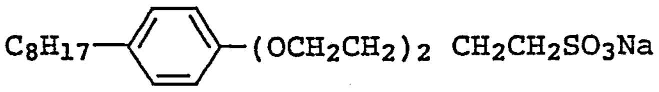
$NaO_3S-\underset{}{CH_2COOCH_2CH(C_2H_5)C_4H_9}$ with $CH_2COOCH_2CH(C_2H_5)C_4H_9$ 10.6 mg

 72% 0.02 cc

 0.424 g

(4) H_2O 68.8 cc

(5)



4.3% 3 cc

Both the emulsion coating composition and the coating composition for surface protective layer thus obtained were coated on a polyethylene terephthalate film support by a simultaneous extrusion method at a volume ratio of 103 : 45 at coating. The coated silver amount was 3.1 g/m^2.

These samples were exposed (1/100 second) using a sensitometer through a yellow filter and an optical wedge, developed using RD-III Developer (made by Fuji Photo Film Co., Ltd.) for an automatic processor for 30 seconds at 35°C, and then fixed, washed and dried by ordinary processes. Then, the photographic sensitivity was measured. Each photographic sensitivity was shown by the relative value of the reciprocal of the exposure amount necessary for obtaining the optical density of fog value +0.5 and that of Sample 101 was shown as 100.

Table 1

Sample	Emulsion	Reduction Sensitizer	Amount (mol/ mol-Ag)	Oxidizing Agent	Amount (mol/ mol-Ag)	Photographic Performance	
						Fog	Sensitivity
101 Comparison	I - C	-	-	-	-	0.12	100
102 "	I - D	-	-	-	-	0.10	180
103 "	I - E	Dimethylamineborane	$3x10^{-6}$	-	-	0.18	170
104 "	I - F	"	$1x10^{-5}$	-	-	0.22	160
105 "	I - G	Thiourea Dioxide	$1x10^{-4}$	-	-	0.24	160
106 "	I - H	L-Ascorbic Acid	$2x10^{-3}$	-	-	0.21	170
107 Invention	I - I	Dimethylamineborane	$1x10^{-5}$	-	-	0.14	347
108 "	I - J	Thiourea Dioxide	$1x10^{-4}$	-	-	0.15	355
109 "	I - K	L-Ascorbic Acid	$2x10^{-3}$	-	-	0.14	339
110 Comparison	I - L	Dimethylamineborane	$3x10^{-6}$	Ox - 1	$5x10^{-5}$	0.14	162
111 "	I - M	"	$1x10^{-5}$	Ox - 1	"	0.15	170
112 "	I - N	Thiourea Dioxide	$1x10^{-4}$	Ox - 2	"	0.16	160
113 "	I - O	L-Ascorbic Acid	$2x10^{-3}$	Ox - 3	"	0.15	174
114 Invention	I - P	Dimethylamineborane	$1x10^{-5}$	Ox - 1	"	0.11	355
115 "	I - Q	Thiourea Dioxide	$1x10^{-4}$	Ox - 2	"	0.11	363
116 "	I - R	L-Ascorbic Acid	$2x10^{-3}$	Ox - 3	"	0.10	339

Ox-1: $C_2H_5SO_2SNa$

Ox-2: $C_8H_{17}SO_2SNa$

Ox-3: $C_{16}H_{33}SO_2SNa$

As shown in Table 1, the addition of the reduction sensitizer increased the sensitivity but in Samples 103 to 106 using the emulsions the grain growth of which was carried out by adding an aqueous silver nitrate solution and an aqueous halide solution in the existence of the reduction sensitizer, the increase of fog was severe, while in Samples 107 to 109 using the emulsions the grain growth of which was carried out by the process of this invention, the increasing width of fog was less and the sensitivity increasing width by the reduction sensitization was large, which shows that the emulsions having high sensitivity and less fog, which is the object of this invention, has been provided.

By the co-existence of the compound of general formula [I] as an oxidizing agent at the reduction sensitization, the formation of fog can be reduced without giving bad influences on the sensitivity but the sensitivity of Samples 110 to 113 using the emulsions the grain growth of which during the reduction sensitization was carried out by the addition of an aqueous silver nitrate solution and an aqueous halide solution is greatly lower than Samples 107 to 109 of this invention having almost same fog as those of these samples. On the other hand, Samples 114 to 116 using the emulsions the reduction sensitization of which was carried out in the existence of the oxidizing agent by the process of this invention show almost same fog as Sample 102 using the emulsion without being reduction sensitized and have very high sensitivity.

Example 2

By following the same procedure as Example 1, Emulsions I-C, D, H, K, O and R were prepared and each emulsion was most favorable chemically sensitized at 60°C by adding thereto sodium benzenethiosulfonate (2×10^{-4} mol/mol-Ag), sodium thiosulfate (1×10^{-5} mol/mol-Ag), chloroauric acid (2×10^{-5} mol/mol-Ag), and potassium thiocyanate (3.2×10^{-4} mol/mol-Ag). After finishing the chemical sensitization, each of the emulsions was coated as in Example 1 to provide Coated Samples 201 to 206. Each sample was exposed, processed and tested as in Example 1 except that the yellow filter was not used at the exposure and the results obtained are shown in Table 2. The sensitivity was shown relative values with that of Sample 201 being 100. Sodium benzenethiosulfonate used in this example is a compound belonging to general formula [I] gave almost no influence on the fog and sensitivity of Emulsions I-C and I-D but reduced the fog value without substantially changing the sensitivity on Emulsions I-H, K, O and R. However, when the amount thereof was increased, the fog value was not changed too much.

As shown in Table 2, in the case of using a gold sensitization together, Samples 204 and 206 of this invention showed very high sensitivity and low fog. On the other hand, in Samples 203 and 205 using the emulsions the grain grow of which during the reduction sensitization was carried out by the addition of an aqueous silver nitrate solution and an aqueous halide solution, the increasing width of fog was severe and the sensitivity increasing width by the reduction sensitivity was less.

Table 2

Sample	Emulsion	Reduction Sensitizer	Amount (mol/ mol-Ag)	Oxidizing Agent	Amount (mol/ mol-Ag)	Photographic Performance	
						Fog	Sensitivity
201 Comparison	I - C	-	-	-	-	0.15	100
202 "	I - D	-	-	-	-	0.14	182
203 "	I - H	L-Ascorbic Acid	2×10^{-3}	-	-	0.33	155
204 Invention	I - K	"	"	-	-	0.18	355
205 Comparison	I - O	"	"	Ox - 3	5×10^{-5}	0.20	166
206 Invention	I - R	"	"	Ox - 3	"	0.15	363

Example 3 Silver Iodobromide Octahedral Grains

Emulsion 3-A [Comparison Example]

To 1.2 liters of an aqueous solution of 3.0% by weight gelatin containing 0.06M of potassium bromide was added 20 ml of an aqueous solution of 5% 3,6-dithiaoctane-1,8-diol and the reaction vessel was kept at 75°C. To the solution were added 50 cc of an aqueous solution of 0.3M of silver nitrate and 50 cc of an aqueous halide solution containing 0.063M of potassium iodide and 0.19M of potassium bromide by a double jet method over a period of 3 minutes, whereby silver iodobromide grains containing 25 mol% silver iodide having 0.2 µm in the diameter of the circle corresponding to the projected area were obtained to form nuclei. Thereafter, 60 ml of 3,6-dithiaoctane-1,8-diol was added thereto at 75°C and 800 ml of an aqueous solution containing 1.5M of silver nitrate and an aqueous halide solution containing 0.375M of potassium iodide and 1.13M of potassium bromide were simultaneously added thereto by a double jet method over a period of 100 minutes to form a 1st coating layer. In the aforesaid procedures, the pH of the system in the reaction vessel was kept at 6.5. The emulsion grains obtained were an octahedral silver iodobromide emulsion (containing 25 mol% silver iodide) of 0.95 µm in the mean diameter of the circle corresponding to the projected area.

Then, after adding 0.06 mol of hydrogen peroxide, an aqueous solution of 1.5M of silver nitrate and an equimolar amount of an aqueous solution of 1.5M of potassium bromide were simultaneously added to the emulsion as the core emulsion to form the shell (2nd coating layer) of silver bromide. The mol ratio of 1st coating layer/2nd coating layer was 1 : 1. The pH of the system at the formation of the shell was kept at 5.8. The emulsion grains obtained were a core/shell mono-dispersed octahedral grains containing 25 mol% silver iodide in the inside having 1.2 µm in mean circle corresponding diameter.

Emulsion 3-B [Comparison Example]

After forming an emulsion as in the case of Emulsion 3-A, 3,6-dithiaoctane-1,8-diol was added to the emulsion. Then, 800 ml of an aqueous solution of 1.5M of silver nitrate, 800 ml of an aqueous halide solution containing 0.375M of potassium iodide and 1.13M of potassium bromide, and 500 ml of an aqueous solution of 2% by weight gelatin were added into a mixer having strong stirring power and high stirring efficiency disposed near the reaction vessel by a triple jet method over a period of 100 minutes. In this case, the temperature of the mixer was kept at 30°C.

The very fine grains formed in the mixer were immediately introduced into the reaction vessel kept at 75°C to form a 1st coating layer. The pH in the system in the reaction vessel was kept at 6.5. Then, after adding thereto hydrogen peroxide, an aqueous solution containing 1.5M of silver nitrate, an aqueous solution containing 1.5M of potassium bromide, and an aqueous solution of 2% by weight gelatin were added to the mixer to form the shell (2nd coating layer) of silver bromide, whereby the grains of 1 : 1 in the ratio of 1st coating layer/2nd coating layer were obtained. The pH at the formation of the 2nd coating layer was kept at 5.8. The grains obtained were octahedral mono-dispersed core/shell emulsion grains having a circle corresponding diameter of 1.2 µm.

Emulsions 3-C and D [Comparison Examples]

By following the same procedure as the case of preparing Emulsion 3-A except that the pH at the formation of the core and the formation of the shell was changed as shown in Table 3, Emulsions 3-C and D were prepared. The grain sizes were almost same.

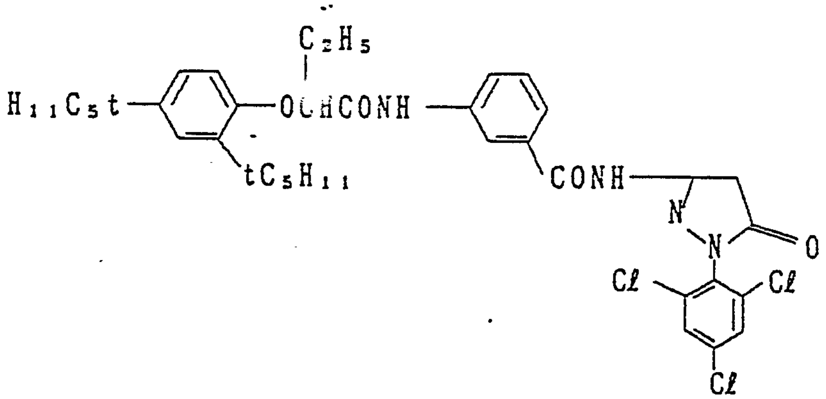
Emulsions 3-E and F [Invention]

By following the same procedure as the case of preparing Emulsion 3-B except that the pH at the formation of the core and the formation of the shell was changed as shown in Table 3, Emulsions 3-E and F were prepared. The grain sizes were almost same.

Each of the emulsions obtained as above was most favorably chemically sensitized at 56°C by adding sodium benzenethiosulfonate (2 x 10^{-4} mol/mol-Ag), sodium thiosulfate (1.2 x 10^{-5} mol/mol-Ag), chloroauric acid (1.6 x 10^{-5} mol/mol-Ag), and potassium thiocyanate (2.5 x 10^{-4} mol/mol-Ag). Then, after adding thereto the following compounds, the emulsion was coated on a triacetyl cellulose film support having subbing layer together with a protective layer by a simultaneous extrusion method.

(1) Emulsion Layer

- Emulsion: shown in Table 3.
- Coupler:



- Tricresyl Phosphate
- Sensitizing Dye: 5-Chloro-5'-phenyl-9-ethyl-3,3'-(3-sulfopropyl)-oxacarbocyanine sodium
- Stabilizer: 4-Hydroxy-6-methyl-1,3,3a,7-tetraazindene
- Antifoggant: 1-(m-Sulfophenyl)-5-mercapto-tetrazole
- Coating Aid: Sodium dodecylbenzene-sulfonate

(2) Protective Layer:

- 2,4-Dichloro-6-hydroxy-s-triazine sodium salt
- Gelatin

Each of the samples was sensitometerically exposed for 1/100 second through a yellow filter and subjected to the following color development process.

The density of each sample thus processed was measured using a green filter. The results of the photographic performances are shown in Table 3. The sensitivity was shown by the reciprocal of the exposure amount giving a density of fog +0.5 with that of Sample 301 being 100.

The following processing steps were carried out at 38°C.

1. Color Development 2 min. 45 sec.

2.	Bleaching	6 min. 30 sec.
3.	Washing	3 min. 15 sec.
4.	Fixing	6 min. 30 sec.
5.	Washing	3 min. 15 sec.
6.	Stabilization	3 min. 15 sec.

The composition of the processing solution used for each step was as follows.

Color Developer:

Sodium Nitrilotriacetate	1.0 g
Sodium Sulfite	4.0 g
Sodium Carbonate	30.0 g
Potassium Bromide	1.4 g
Hydroxylamine Sulfate	2.4 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline Sulfate	4.5 g
Water to make	1 liter

Bleaching Solution:

Ammonium Bromide	160.0 g
Aqueous Ammonia (28%)	25.0 ml
Ethylenediaminetetraacetic Acid Sodium Salt	130 g
Glacial Acetic Acid	14 ml
Water to make	1 liter

Fixing Solution:

Sodium Tetrapolyphosphate	2.0 g

Sodium Sulfite	4.0 g
Ammonium Thiosulfate (70%)	175.0 ml
Sodium Hydrogenesulfite	4.6 g
Water to make	1 liter

Stabilization Solution:

Formalin	8.0 ml
Water to make	1 liter

Table 3

Sample		Emulsion	pH at Grain Formation		Photographic Performance	
			Core	Shell	Fog	Sensitivity
301	Comparison	3 - A	6.5	5.8	0.12	100
302	"	3 - B	6.5	5.8	0.12	120
303	"	3 - C	8.0	5.8	0.16	110
304	"	3 - D	10.0	8.0	0.25	107
305	Invention	3 - E	8.0	5.8	0.12	148
306	"	3 - F	10.0	8.0	0.14	159

As shown in Table 3, Samples 305 and 306 of this invention showed low fog and high sensitivity. Furthermore, the samples of this invention showed high gradation as compared with Comparison Samples 301, 303, and 304.

Example 4

By following the same procedure as Example 5 in Japanese Patent Application No. 63-7853 while using the emulsion in Example 2 of the present specification and the emulsion in Example 3 of the present specification in place of the emulsions of Layer 5 and Layer 16, respectively, of Example 5, it was confirmed that a photographic light-sensitive material having high sensitivity and giving low fog was obtained.

Example 5

Silver Chlorobromide Fine Grain Emulsion 5-A:

To 1.3 liters of an aqueous solution of 2.3% by weight gelatin containing 0.01M of potassium bromide and 0.05M of sodium chloride were added 600 ml of an aqueous solution containing 1.2M of silver nitrate and 600 ml of an aqueous halide solution containing 0.72M of potassium bromide and 1.0M of sodium chloride with stirring by a double jet method over a period of 25 minutes. During the additions, the gelatin solution in the reaction vessel was kept at 35°C.

Thereafter, the emulsion formed was washed by an ordinary flocculation method and after dissolving therein 30 g of gelatin, the pH thereof was adjusted to 6.5. The mean grain size of the silver chlorobromide fine grains (silver chloride content 40 mol%) obtained was 0.09 µm.

Silver Chlorobromide Octahedral Grain Emulsion 5-B [Comparison Example]

To 1.2 liters of an aqueous solution of 3.0% by weight gelatin containing 0.065M of potassium bromide and 0.3M of sodium chloride was added 80 ml of a methanol solution of 0.1%, 3,4-dimethyl-4-thiazoline-2-thione with stirring and after keeping the reaction vessel at 75°C, 50 cc of an aqueous solution of 0.3M of silver nitrate and 50 cc of an aqueous halide solution containing 0.18M of potassium bromide and 0.8M of sodium chloride by a double jet method over a period of 3 minutes. Thus, chlorobromide grains having a mean grain size of 0.3 µm and containing 40 mol% silver chloride were obtained to perform nucleus formation.

Thereafter, 800 cc of an aqueous solution containing 150 g of silver nitrate and 800 cc of an aqueous solution containing 63 g of potassium bromide and 43 g of sodium chloride were simultaneously added to the emulsion by a double jet method over a period of 100 minutes at 75°C. Thereafter, the emulsion was washed with water by an ordinary flocculation method at 35°C and after adding thereto 70 g of gelatin, pH and pAg thereof were adjusted to 6.2 and 7.8, respectively. In addition, the pH of the system in the reaction vessel during the formation of the grains was adjusted to 4.5. The grains formed were silver chlorobromide octahedral grains having a mean grain size of 1.5 µm and containing 40 mol% silver chloride.

Silver Chlorobromide Octahedral Grain Emulsion 5-C [Comparison Emulsion]

By following the same procedure as the nucleus formation in the case of preparing Emulsion 5-B, silver chlorobromide nucleus grains having a mean grain size of 0.3 µm were obtained and then fine grain emulsion 5-A (silver chloride content 40 mol%) dissolved at 75°C were added to the reaction vessel by a pump. The fine grain emulsion was added over a period of 100 minutes such that the amount thereof became 150 g calculated as silver nitrate. In this case, 20 g of sodium chloride was previously dissolved in the fine grain emulsion. Thereafter, the emulsion was washed with water as in the case of Emulsion 5-B and pH and pAg thereof were adjusted to 6.5 and 7.8, respectively at 40°C. The pH in the reaction vessel during the formation of the grains was adjusted to 4.5.

The grains obtained were silver chlorobromide octahedral grains having a mean grain size of 1.5 µm and a silver chloride content of 40 mol%.

Silver Chlorobromide Octahedral Grain Emulsions 5-D and E [Comparison Emulsion]

By following the same procedure as the preparation of silver chlorobromide octahedral grain emulsion 5-B except that the pH in the reaction vessel during the grain formation was changed as shown in Table 5, Emulsions 5-D and E were prepared. In this case, the addition rates of the aqueous silver nitrate solution and the aqueous halide solution at the nucleus formation were controlled such that the grain size thereof became same as that of Emulsion 5-B.

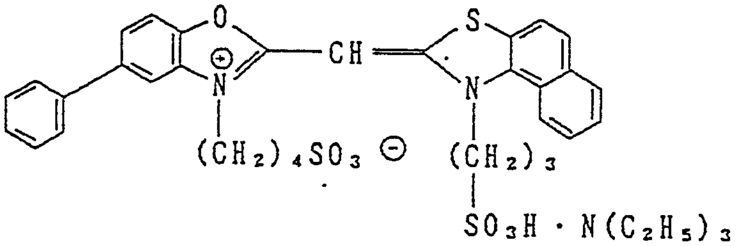
Silver Chlorobromide Octahedral Grain Emulsions 5-F and G [Invention]

By following the same procedure as the preparation of silver chlorobromide octahedral grain emulsion 5-C except that the pH in the reaction vessel was changed as shown in Table 5, Emulsions 5-F and G were prepared. The grain sizes were adjusted such that they became same as above by controlling the addition rate of the fine grain emulsion.

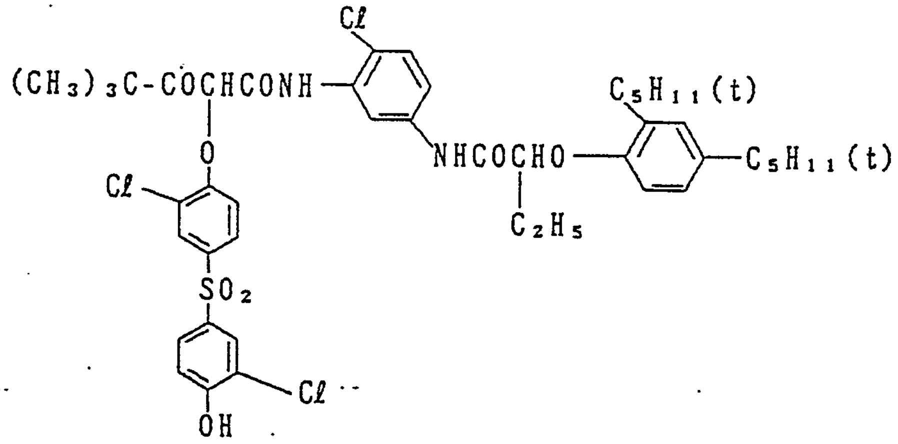
After adding to each of Emulsions 5-B to G thus obtained Blue-sensitive sensitizing dye (a) shown below (150 mg/mol-Ag), sodium thiosulfate (1.2 x 10^{-5} mol/mol-Ag) was added thereto and the emulsion was most advantageously post ripened. Then, after adding thereto, in succession, yellow coupler (b) shown below, color image stabilizer (c), a stabilizer, 4-hydroxy-6-methyl-1,3,3a,7-

tetraazaindene, an antifoggant, 1-[3-(3-methylureido)-phenyl]-5-mercaptotetrazole, a hardening agent, 2,4-dichloro-6-hydroxy-s-triazine sodium, and a coating aid, sodium dodecylbenzenesulfonate, the emulsion was coated on a paper support having polypropylene layer laminated on both the surfaces thereof together with a gelatin protective layer.

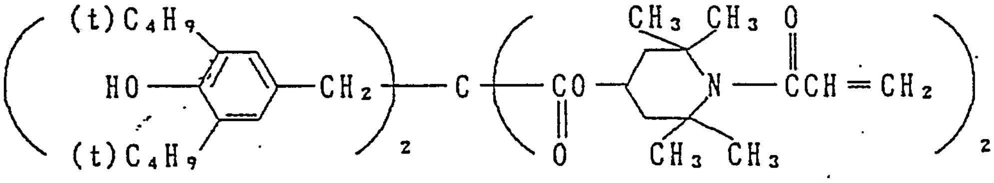
Blue-Sensitive Sensitizing Dye (a):



Yellow Coupler (b):



Color Image Stabilizer (c):



Each of the samples was exposed under an optical wedge, processed according to the following steps, and the results shown in Table 5 were obtained.

In this case, the relative sensitivity was shown by the relative value of the reciprocal of the exposure amount necessary for giving the density of fog value +0.5 with that of Sample 501 in development time of 3 minutes 30 seconds being defined as 100.

Color Developer: 33°C Development

2 min. 30 sec. and 3 min. 30 sec.

Water	800 cc
Diethylenetriaminepentaacetic Acid	1.0 g
Sodium Sulfite	0.2 g
N,N-Diethylhydroxylamine	4.2 g
Potassium Bromide	0.01 g
Sodium Chloride	1.5 g
Triethanolamine	8.0 g

Potassium Carbonate		30 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate		4.5 g
4,4'-Diaminostilbene series Fluorescent Whitening Agent (Whitex 4, made by Sumitomo Chemical Company, Ltd.)		2.0 g
Water to make		1000 cc
pH adjusted with KOH		10.25
Blix Solution	35°C	45 sec.
Ammonium thiosulfate (54 wt.%)		150 ml
Na_2SO_3		15 g
$NH_4[Fe(III)(EDTA)]$		55 g
EDTA·2Na		4 g
Glacial Acetic Acid		8.61 g
Water to make		1000 ml
	(pH 5.4)	
Rinse Solution	35°C	90 sec.
$EDTA\cdot 2Na\cdot 2H_2O$		0.4 g
Water to make		1000 ml
	(pH 7.0)	

Table 5

Sample	Emulsion	pH*	Photographic Performance			
			Relative Sensitivity		Fog	
			2'30"	3'30"	2'30"	3'30"
501 Comp.	5 - B	4.5	75	100	0.03	0.04
502 "	5 - C	4.5	67	79	0.01	0.01
503 "	5 - D	8	79	107	0.07	0.11
504 "	5 - E	9.5	83	112	0.10	0.14
504 Inv.	5 - F	8	93	107	0.02	0.03
506 "	5 - G	9.5	100	115	0.03	0.04

*: pH during the grain formation.

Comp.: Comparison sample. Inv.: Invention Sample.

As is clear from Table 5, Samples 505 and 506 had a high sensitivity as compared to the comparison samples and were suitable for quick processing owing to the small deviation in photographic performance by development time. On the other hand, Comparison Samples 501, 503, and 504 using the emulsions the grain growth of which was carried out by the addition of the aqueous silver nitrate solution and the aqueous halide solution showed large deviation in photographic performance by development time and also Samples 503 and 504 caused severe fog formation.

The feature of this invention of high sensitivity, low fog, and less deviation in photographic performance by development time was almost kept in the high silver chloride cubic grains (silver chloride 99 mol%, silver bromide 1 mol% (existing at the corner)).

[Industrial Applicability]

The photographic light-sensitive materials obtained by the process of this invention has high sensitivity, gives less fog, and show good graininess.

CLAIMS

1. A silver halide photographic material having on a support at least one silver halide emulsion layer, characterized in that the light-sensitive silver halide grains contained in the silver halide emulsion layer are light-sensitive silver halide grains obtained by adding previously prepared silver halide grains having fine grain sizes into a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains to cause the nucleus formation and/or the crystal growth of the grains in the reaction vessel, and the silver halide grains are reduction sensitized.

2. A silver halide photographic material having on a support at least one silver halide emulsion layer, characterized in that the light-sensitive silver halide grains contained in the silver halide emulsion layer are light-sensitive silver halide grains obtained by adding previously prepared silver halide grains having fine grain sizes into a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains under the condition capable of reduction sensitizing the silver halide grains to cause the nucleus formation and/or the crystal growth in the reaction vessel.

3. The silver halide photographic material described in claim 1 or 2, wherein the silver halide

grains having fine grain sizes are formed by mixing an aqueous solution of a water-soluble silver salt and an aqueous solution of water-soluble halide(s) in a mixer disposed outside a reaction vessel of causing the nucleus formation and/or the crystal growth of the light-sensitive silver halide grains, and immediately after the formation, the fine silver halide grains are supplied to the reaction vessel for the nucleus formation and/or the crystal growth of the light-sensitive silver halide grains.

4. The silver halide photographic material described in claim 2 or 3, wherein an oxidizing agent and/or an inhibitor exists in addition to the condition capable of causing the reduction sensitization.

5. The silver halide photographic material described in 2, 3, or 4, wherein the light-sensitive silver halide grains are silver iodobromide having a silver iodide content of from 3 mol% to 40 mol%.

6. The silver halide photographic material described in claim 2, 3, or 4, wherein the halogen composition is silver chlorobromide, silver chloroiodide, or silver chloroiodobromide.

7. A process of producing a silver halide photographic material having on a support at least one silver halide emulsion layer, which comprises producing the light-sensitive silver halide grains contained in the

silver halide emulsion layer by adding previously prepared silver halide grains having fine grain sizes into a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains to cause the nucleus formation and/or the crystal growth in the reaction vessel, said silver halide grains being reduction sensitized.

8. A process of producing a silver halide photographic material having on a support at least one silver halide emulsion layer, which comprises producing the light-sensitive silver halide grains contained in the silver halide emulsion layer by adding previously prepared silver halide grains having fine grain sizes under the condition capable of reduction sensitizing the silver halide grains to a reaction vessel for causing the nucleus formation and/or the crystal growth of the silver halide grains to cause the nucleus formation and/or the crystal growth in the reaction vessel.

9. The process of producing a silver halide photographic material described in claim 7 or 8, wherein the silver halide grains having fine grain sizes are formed by mixing an aqueous solution of a water-soluble silver salt and an aqueous solution of water-soluble halide(s) in a mixer disposed outside the reaction vessel for causing the nucleus formation and/or the crystal

growth of the light-sensitive silver halide grains and after the formation thereof are immediately supplied to the reaction vessel for causing the nucleus formation and/or the crystal growth of the light-sensitive silver halide grains.

10. The process of producing a silver halide photographic material described in claim 8 or 9, wherein an oxidizing agent and/or an inhibitor exists in addition to the condition capable of reduction sensitizing.

11. The process of producing a silver halide photographic material described in claim 8, 9, or 10, wherein the silver halide grains are silver iodobromide having a silver iodide content of from 3 mol% to 40 mol%.

12. The process of producing a silver halide photographic material described in claim 8, 9, or 10, wherein the halogen composition is silver chlorobromide silver chloroiodide, or silver chloroiodobromide.

Fig. 1

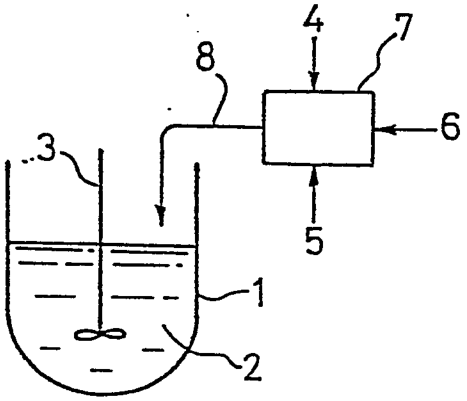


Fig. 2

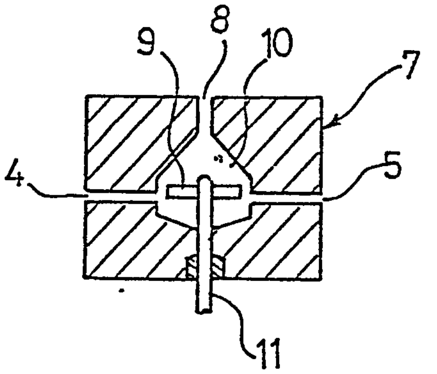
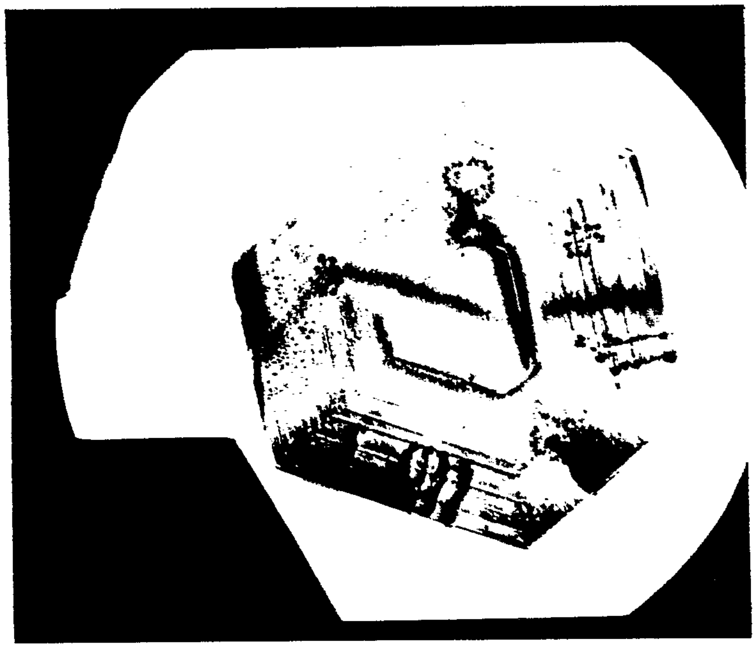


Fig. 3



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/00039

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl^4 G03C1/02, G03C1/08

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	G03C1/02, G03C1/08

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	JP, A, 58-113927 (Eastman Kodak Co.) 7 July 1983 (07. 07. 83) & DE, A1, 3241639 & BE, A1, 894967 & FR, A1, 2516264 & NL, A, 8204390 & GB, A1, 2110830 & SE, AO, 8206425 & AU, A1, 9037782 & NO, A, 823791 & DK, A, 505982 & ZA, A, 828347 & BR, A, 8206561 & PT, A, 75846 & ES, A1, 517309 & US, A, 4434226 & CA, A1, 1175697 & CH, A, 653147 & LU, A, 84461	1-12
X	JP, A, 58-113928 (Eastman Kodak Co.) 7 July 1983 (07. 07. 83) & DE, A1, 3241634 & BE, A1, 894965 & GB, A1, 2109576 & FR, A1, 2516257 & NL, A, 8204388 & SE, AO, 8206424 & AU, A1, 9037682 & NO, A, 823792 & DK, A, 506182 & BR, A, 8206558 & ZA, A, 828344 & PT, A, 75844 & ES, A1, 517316 & US, A, 4434226 & CA, A1, 1175700 & CH, A, 653147	1-12

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search March 17, 1989 (17. 03. 89)	Date of Mailing of this International Search Report April 10, 1989 (10. 04. 89)
International Searching Authority Japanese Patent Office	Signature of Authorized Officer

Form PCT ISA 210 (second sheet) (January 1985)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

& LU, A, 84459

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been establisned in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter not required to be searched by this Authority, namely:

2.☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3.☐ Claim numbers ...., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.