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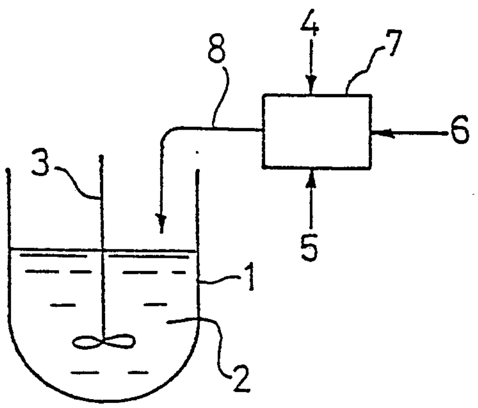
(54) SILVER HALIDE PHOTOGRAPHIC MATERIAL AND PROCESS FOR ITS PREPARATION.

(57) A photographic material prepared by using a silver halide emulsion containing silver halide grains wherein a halide distribution is microscopically completely uniform and/or which comprise a core part not containing reduced silver formed upon formation of the grains and a shell part different from the core part in a halide composition, and a process for its preparation are disclosed. This material has excellent properties with respect to sensitivity, gradation, graininess, sharpness, resolving power, covering power, preservability, latent image stability and pressure effect.

Fig. 3



TITLE MODIFIED
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SPECIFICATION

SILVER HALIDE PHOTOGRAPHIC MATERIAL 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 photographic light-sensitive material using a silver halide emulsion containing silver halide grains wherein the microscopic halide distribution in the inside of each silver halide mixed crystal is completely homogeneous and/or the inside of the silver halide crystals does not have reduced silver formed at the formation of the silver halide grains.

BACKGROUND ART

Recently, the requirement for the improvement of the performance of silver halide photographic materials is becoming severe and severe and, in particular, the increase of the sensitivity while restraining the reduction of graininess and sharpness as low as possible and the increase of the development speed have been desired.

For meeting these requirements, the development of a so-called core/shell type emulsion having different halide composition between the inside and the surface layer of the silver halide grains has been performed. In a silver iodobromide emulsion, it is disclosed that the inside (core) of the grains is composed of silver iodobromide having a high silver iodide content and the surface (shell) thereof is composed of silver iodobromide having a less silver iodide content or pure silver bromide. These techniques are disclosed, e.g., in JP-A-57-15432, JP-A-60-14331, JP-A-60-138538, JP-A-60-147727, JP-A-61-245151, and JP-A-61-14363 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). Also, the core/shell emulsion wherein the surface of the grains is composed of silver chloride or silver chlorobromide is disclosed in JP-A-58-9137, JP-A-58-9537, JP-A-59-48755, JP-A-61-215540, and JP-A-62-69621. Furthermore, the core/shell emulsion wherein the silver iodide content of the surface of the grains is higher than the inside thereof is disclosed in JP-A-56-78831 and JP-A-62-19843.

By these core/shell emulsions, the increase of light absorption, the increase of the latent image forming efficiency by the formation of the layer structure of core and shell, and the improvement of the development speed are attained but, on the other hand, it has been confirmed that in these grains, a microscopic heterogeneous distribution of halide in the grains exists, which disturbs the movement of electrons generated by light exposure to reduce the latent image forming efficiency, and the improvement thereof has been required.

In general, silver halide grains are produced by reacting an aqueous silver salt solution and an aqueous halide solution in an aqueous colloid solution in a reaction vessel. For the purpose, a single jet method wherein an aqueous solution of a protective colloid such as gelatin and an aqueous halide solution are placed in a vessel and an aqueous silver salt solution is added thereto with stirring for a certain period of time and a double jet method wherein an aqueous gelatin solution is placed in a reaction vessel and an aqueous halide solution and an aqueous silver salt solution are added thereto for a certain period of time are known. The comparison of both the methods shows that in the double jet method, silver halide grains having a narrow grain size distribution is obtained and further the halide composition can be freely changed with the growth of the grains.

Also, it is known that the growing speed of silver halide grains is greatly influenced by the silver ion (or halogen ion) concentration of the reaction solution, the concentration of a silver halide solvent, the distance between the grains, the grain sizes, etc. In particular, the heterogeneity of the concentration of silver ions or halogen ions formed by an aqueous silver salt solution and an aqueous halide solution being added to a reaction vessel causes a difference in growing speed of silver halide grains by the concentration of each solution, which results in causing the heterogeneity of the silver halide emulsion obtained. Thus, for homogenizing the concentration of the silver ions or the halogen ions in the reaction vessel, it is required to quickly and uniformly mixing an aqueous silver salt solution and an aqueous halide solution being supplied to an aqueous colloid solution to cause the reaction. 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 a 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 the aqueous colloid solution filled in each room and are quickly mixed with each other at the vicinities 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 (the term "JP-B" as used herein means an "examined Japanese patent publication"). 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 portions 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 positions. 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 stage 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 emulsions) in a reaction vessel from the bottom of 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 of performing 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 of the aqueous silver salt solution and the aqueous halide solution. Accordingly, as described above, it is in principle impossible to homogenize 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.

The object of this invention is to provide a silver halide photographic material giving less fog, having high sensitivity, having improved graininess, sharpness, and covering power, and having excellent storage stability and pressure resistance by completely homogenize the microscopic halide distribution in the inside (core) of silver halide grains and/or homogenizing reduced silver in the grains in a so-called core/shell emulsion differing in halide composition between the surface (shell) of the grains and the inside (core) of the grains, and also to provide a process of producing the photographic light-sensitive material.

DISCLOSURE OF THE INVENTION

The aforesaid object of this invention has been attained by the invention shown below.

(1) A silver halide photographic material having on a support at least one silver halide emulsion layer, characterized in that the inside of the light-sensitive silver halide grains contained in the silver halide emulsion layer is composed of at least one phase containing at least two kinds of silver halides, the

halide composition thereof is completely homogeneous, and the surface of the silver halide grains has a different halide composition from the inside of silver halide grains adjacent to the surface.

(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 silver halide grains nucleus-formed and/or crystal-grown in a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains by adding previously prepared silver halide of fine size into the reaction vessel, said silver halide grains having silver halide of a different halide composition from that of the silver halide grains at the outside of the silver halide grains.

(3) A process of producing the silver halide photographic material described in the above (2), which comprises mixing an aqueous solution of a water-soluble silver salt and an aqueous solution of a water-soluble halide in a mixer disposed outside a reaction vessel for causing a nucleus formation and/or a crystal growth of light-sensitive silver halide grains to form silver halide having fine grain sizes, supplying the silver halide into the reaction vessel immediately after the formation

thereof to perform the nucleus formation and/or the crystal growth of light-sensitive silver halide grains, and further forming silver halide having a different composition from the grains at the outside of the silver halide grains.

The feature of the silver halide grains of this invention is that the grains have a so-called core/shell structure and the core portion has a completely homogeneous halide distribution.

The shell portion must be differed in halogen composition from the core portion adjacent to the shell portion and it is unnecessary that the halide composition of the shell portion is completely homogeneous. Also, the halide composition thereof may be a single composition or a so-called mixed crystal.

An example of the silver halide emulsion grains having "completely homogeneous halide distribution" in this invention is explained on tabular silver iodobromide grains having a silver iodobromide phase.

The term "completely homogeneous silver iodide distribution" means a more microscopic distribution which is completely different from a conventional silver iodide distribution. Hitherto, as a means for measuring the silver iodide distribution in silver iodobromide grains, an Analytical Electron Microscopy is frequently used. For example, the result of the topography on the content of silver iodide in tabular silver iodobromide grains is described 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 Köln, 1986. The size of the probe for electron ray irradiation used in the investigation is 50 Å but actually, the electron beam is broadened by the elastic scattering of electron and the diameter of the spot of the electron beam irradiated onto the surface of 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 beam 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 low temperature described, for example, in J.H. Hamilton, Photographic Science and Engineering, Vol. 11, page 57, 1967 and Takekimi Shiozawa, 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. 5. The tabular grains shown in the figure are grains composed of tabular silver bromide grain as the core and silver iodobromide containing 10 mol% 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 that 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 intension for the production thereof and neither the technique for homogenizing the distribution nor the production process for such silver halide grain has been disclosed. This invention discloses the core/shell emulsion having the core portion wherein the microscopic distribution of silver iodide is completely homogeneous and the production process thereof.

As described above, the silver halide grains having "the completely homogeneous halide 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 of this invention, there exist at most two microscopic lines caused by the microscopic heterogeneity of silver iodide of, for example, aforesaid silver iodobromide at an interval of 0.2 µm in the direction crossing the lines, preferably there exists one such a 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 occurring the form of crossing the growing direction of the grains, which results in concentrically distribution these lines from the center of the grain. For example, in the case of the tabular grains shown in Fig. 5, 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 grain.

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

Conventional silver halide grains which are called silver halide grains containing, for example, homogeneous silver iodide are prepared by simply adding silver nitrate and a mixture of halides having a definite composition (a definite content of silver 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" are clearly distinguished from the grains of this invention showing "the complete homogeneity".

The above explanation is on the example of silver iodobromide core grains but the problems on the microscopic halide composition are same on all silver halide mixed crystals such as silver chlorobromide, silver chloroiodide, silver chloroiodide, etc.

The homogeneity of the microscopic halide distribution of silver halide mixed crystals can be further measured by utilizing X-ray diffraction.

It is well known for a person skilled in the art to determine the halogen composition using an X-ray diffractometer. This principle is explained briefly below.

By measuring a Bragg angle in X-ray diffraction, a lattice constant a can be determined by the following Bragg's formula:

$$2d_{hkl}\sin\theta_{hkl} = \lambda$$

λ : Wave length of X-ray
θ_{hkl} : Bragg angle from (hkl)plane

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+\ell^2}}$$

d_{hkl} : Spacing from (hkl)plane
$\underline{a}$: Lattice constant

Now, in the 1st Chapter of T.H. James, The Theory of the Photographic Process, 4th edition, MaCmillan Co. Ltd., New York, the reaction of lattice constants a for halogen compositions on silver iodobromide, silver chlorobromide, and silver iodochloride is shown. As shown in the book, if the lattice constant (halogen composition) differs, the positions of the diffraction peaks differ. Accordingly, in the silver halide grains having excellent homogeneity of the halogen composition distribution, the dispersion of lattice constants is less and the half value width of the diffraction profile become narrow. For the measurement of the diffraction profile, the K_α line having a high intensity and showing good monochromaticity is more preferably used than the K_β line. In addition, since the K_α line is double lines, it is possible to determine the half value width from a simple profile obtained by using a Rachinger's method.

As the sample, powdered particles obtained by removing gelatin from a silver halide emulsion are used or a coated silver halide emulsion film immersed in a 50% glycerol solution for 20 minutes to remove the pressure of gelatin applied to the surface of grains in the dry film according to the method by G.C. Farnell, R.J. Jenkins, and L.R. Solman, Journal of Photographic Science, Vol. 24, page 1 (1976) can be used.

For correctly determining the angle of a diffraction profile, a method of mixing a Si powder or NaCl powder the diffraction angle of which is known with the sample is used. Furthermore, it is known that for measuring the diffraction angle and the line width of the diffraction profile with good accuracy, a diffraction profile of a large diffraction angle from a high index plane is preferably used. Accordingly, in this patent, the diffraction profile of a (420) plane was measured in the range of the diffraction angle (twice the Bragg angle) of from 71° to 77° by the K_α line of a copper target.

In addition, for the X-ray diffraction measurement, the coated emulsion film give better measurement accuracy than the powder and hence the measurement was performed on the coated emulsion film in the examples described below.

Now, the half value width of the diffraction profile of the system causing no strain by an external stress as the form of the samples described in this patent is not determined by the halogen composition distribution only but includes furthermore, a half value width by an optical system of a diffractometer and a half value width by the sizes of the crystallites of the sample. Accordingly, for obtaining the half value width originated in the distribution of halogen composition, it is necessary to subtract the contribution of the half value widths by the aforesaid two matters.

The half value width by an optical system of a diffractometer can be obtained as the half value width of the diffraction profile of single crystals of at least 25 µm in grain sizes having no strain (having no dispersion of lattice constant). The use of α-quartz of from 25 to 44 µm (500 mesh on, 350 mesh under) annealed at 800°C as such a sample is described in X-Sen Kaisetsu no Tebiki (Manual of X-Ray Diffraction), revised edition, Chapter 2, Paragraph 8, by Rigaku Denki K.K. Si particles, Si single crystal wafers, etc., can be also used. Since the half value width by an optical system has a diffraction angle reliance, it is necessary to obtain half value widths on several diffraction profiles. By applying, if necessary, an extrapolation or an interpolation, the half value width by an optical system on the diffraction angles of the system being measured is obtained.

On the other hand, the half value width by the sizes of crystallites is shown by the following formula.

$$\beta = \frac{K\lambda}{D\cos\theta} \times \frac{180}{\pi}$$

β: Half value width (°) by the sizes of crystallites

K: Constant (generally 0.9)

D: Size (Å) of crystallite

λ: Wavelength (Å) of X-ray

θ: Bragg angle

By subtracting the half value width by an optical system and the half value width by the sizes of crystallites thus obtained from the half value width of the diffraction profile measured, the half value width by the distribution of halogen composition is obtained. The half value width by an optical system of mixed crystal grains and the half value width by the sizes of crystallites being measured are equivalent to the half value width of the diffraction profile of silver halide grains having a homogeneous distribution of halogen composition (definite lattice constant) and having the same size of crystallite as the size of the grain to be measured. In general, when there is no strain by an external stress, in grains having no lattice defect, the size of the grain (the length of the side, the diameter corresponding to the sphere having the same volume, etc.) coincides with the size of the crystallite. On the aforesaid matter, it is reported by F.W. Willets, British Journal of Applied Physics, Vol. 16, page 323 (1965) that the size of the crystallite of AgBr obtained by the diffraction line width corresponds to the size of the grain although the measurement is not by a diffractometer but by a photographic method. In the report, 1.44 is selected as a Scherrer constant by a photographic method not using the half value width but using the standard deviation of profile.

In our measurement system wherein a diffractometer is used, it has been found that the size of the crystallite obtained from the half value width from which the half value width by an optical system using obtained by Si single crystals is subtracted coincides well with the size of the grain in AgBr grains prepared by a balanced double jet method.

In other words, the half value width of mixed crystal emulsion grains by an optical system and the half value width by the sizes of the crystallites can be obtained as the half value width of the diffraction profile of AgBr grains, AgCl grains or AgI grains having the same grain size as the size of the mixed crystal emulsion grains.

The half value width by the halogen composition distribution only of mixed crystal emulsion grains is obtained by subtracting the half value width of the diffraction profile of AgBr grains, AgCl grains, or AgI grains having the same grain size as the grains to be measured from the half value width of the diffraction file measured.

The preferred half value width of the profile of the X-ray diffraction of silver halide emulsion grains having a homogeneous microscopic halogen composition by the aforesaid method is shown in Fig. 1 on silver chlorobromide and in Fig. 2, on silver iodobromide. In Fig. 1 and Fig. 2, the homogeneity of the grains of each halogen composition is shown by the value obtained by subtracting the half value width of pure silver chloride or pure silver bromide having the same grain size as the aforesaid grains from the half value width of the X-ray diffraction of each grain. The grains of this invention have the half value width of not more than the half value width shown by curve A, and preferably not more than the half value width shown by curve B. The halide compositions of the core portion and the shell portion can be measured by an X-ray diffraction method.

Examples of applying an X-ray diffraction method to silver halide grains are stated in H. Hilsh, Journal of Photographic Science, Vol. 10, page 129 infra (1962). When the lattice constant is determined by the halogen composition, the peak of diffraction appears at the diffraction angle satisfying the Bragg's condition ($2d \sin\theta = n\lambda$).

The measurement method of X-ray diffraction is described in detail in Kiso Bunseki Kagaku Koza (Fundamental Analytical Chemistry Course) 24, "X-Ray Analysis", published by Kyoritsu Shuppan and X-Sen Kaisetsu no Tebiki (Manual of X-Ray Diffraction), by Rigaku Denki K.K. In the standard measurement method, Cu is used as the target and the diffraction curve of the (220) plane of a silver halide is obtained using the K_β line of Cu as the X-ray source (tube voltage 40 KV, tube current 60 mA). For increasing the resolving power of the measurement device, it is necessary to properly select the width of slits (divergent slit, light-receiving slit, etc.), the time constant of the device, the scanning speed of a goniometer, and the recording speed and confirm the measurement accuracy using a standard sample such as silicon, etc..

When the curve of diffraction intensity to diffraction angle of the (220) plane of a silver halide is obtained using the Kβ line of Cu, there are a case that the diffraction peaks corresponding to the core portion and the shell portion are detected as clearly separated states and a case that the peaks overlap each other and are not separated as clear two peaks.

A method resolving the diffraction curve composed of two diffraction components is well known and described, e.g., in Jikken Butsurigaku Koza 11 Koshi Kekkan (Experimental Physics Course 11 Lattice Defect), published by Kyoritsu Shuppan.

It is also useful to analyze the diffraction curve using a curve analyzer made by Du Pont by assuming the curve as a Gauss' function or as a Lorenz' function.

In the silver halide grains for use in this invention, the aforesaid peaks corresponding to the core portion and the shell portion may be or may not be clearly separated.

In the case of an emulsion wherein two kinds of grains having no clear layer structure and having each different halogen composition co-exist, two peaks appear by the aforesaid X-ray diffraction.

Such an emulsion can not show the excellent photographic performance obtained in this invention.

Whether a silver halide emulsion is the emulsion of this invention or the aforesaid emulsion wherein two kinds of silver halide grains having no clear layer structure can be determined by using an EPMA method (Electron-Probe Micron Analyzer method) in addition to the X-ray diffraction method.

In the method, a sample wherein emulsion grains are dispersed well such that they are not bought into contact with each other and is irradiated by an electron beam. An elemental analysis of a very fine portion can be carried out by an X-ray analysis by an electron ray excitation.

By obtaining the characteristic X-ray intensities of silver and a halogen emitted from each grain by the aforesaid method, the halogen composition of each grain can be determined.

By confirming the halogen composition on at least 50 grains by the EPMA method, whether the emulsion is the emulsion of this invention or is not the emulsion of this invention can be determined.

It is preferred that in the emulsion of this invention, the distribution of the halogen composition in the grains, in particular, the halogen composition distribution in the core portions in the grains is more homogeneous. When the distribution of the halogen composition in the grains (e.g., the distribution of the silver iodide content in silver iodobromide or the distribution of the silver bromide content in silver chlorobromide) is measured by the EPMA method, the relative standard deviation of the halogen content is less than preferably 50%, more preferably less than 35%, and particularly preferably less than 20%.

When overlapping of the diffraction peaks corresponding to the core portion and the shell portion is severe or the halide composition of the shell portion can not be determined since the ratio of the shell portion to the grain is very small and the diffraction peak corresponding to the shell portion is weak, the halide composition in the surface of the grain is measured.

The halide composition in the surface of the grain is measured by a surface analysis method in XPS (X-ray Photoelectron Spectroscopy) (it is said that the depth being measured is about 50 Å).

The principle of the XPS method which is used for the analysis of the halogen content near the surface of silver halide grains is described in Junichi Aihara, et al, Denshi no Bunko (Spectrum of Electron), Kyoritsu Library 16, published by Kyoritsu Shuppan, 1978.

In the standard measurement method of XPS, Mg-Kα is used as X-ray for excitation and the intensities of the photoelectrons of halogen and silver (Ag) (usually, Cl-2p, Br-3d, I-$3d_{5/2}$, and Ag-$3d_{5/2}$) emitted from silver halide grains in a suitable sample form.

For example, the content of iodine can be obtained from the calibration curve of the intensity ratio of the photoelectrons of iodine (I) and silver (Ag) (i.e., intensity (I)/intensity (Ag)) prepared using several kinds of standard samples having a known iodine content. For a silver halide emulsion, the measurement of XPS must be carried out after decomposing gelatin adsorbed on the surfaces of the silver halide grains with a proteolytic enzyme, etc., followed by removal.

The embodiments of the silver halide grains of this invention are as follows.

(1) When the halide compositions of the core portion (when there are cores of two or more layers, the core portion adjacent to the shell portion) and the shell portion are composed of same halide, it is desirable that the difference between both the halide compositions is at least 5 mol%, preferably at least 10 mol%, and more preferably at least 20 mol%. That is, in the case of, for example, silver chlorobromide containing silver chloride, the difference in the silver chloride content between the

core portion and the shell portion is as described above. Also, the kind of halides differs between the core portion and the shell portion, it is desirable that the content of the different halide is at least 3 mol%, preferably at least 6 mol%, and more preferably at least 10 mol%. That is, when, for example, the shell is composed of AgBr and the core is composed of AgBrCl, the content of silver chloride in the core is as above.

(2) The mol ratio of the core portion to the shell portion may be optional but the mol ratio of the shell is preferably not more than 50 mol%, more preferably not more than 30 mol%, and far more preferably not more than 10 mol%.

(3) The microscopic halide composition of the core portion is completely homogeneous but the microscopic halide composition of the shell portion may be completely homogeneous or may be heterogeneous.

(4) The core portion may be a single layer structure or a multilayer structure of two or more layers.

Then, the production process of the silver halide core grains wherein the microscopic halide composition of the inside of the silver halide mixed crystals of the present invention is completely homogeneous and/or the inside of the silver halide crystals does not have reduced silver formed at the formation of the grains is explained.

A silver halide of fine size previously prepared is added to a reaction vessel for forming the nuclei of the grains and/or causing the formation of the crystals, whereby the nucleus formation and/or the crystal growth of the silver halide core grains is carried out in the reaction vessel.

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. 3.

In Fig. 3, 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 silver salt solution, an aqueous halides solution, and an aqueous protective colloid solution 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 solutions 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. 4. 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 nuclei and/or the 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 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. In this case, however, since the fine grains have a high solubility, the fine grains cause so-called Ostwalt ripening 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, 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 immediated 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 into the mixer, and thus by immediately adding the fine grain formed to the reaction vessel, the occurrence of the Ostwald ripening is prevented. Practically, the residence time (t) of the solutions added to the reaction vessel 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 minutes, 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 a coalescence. In coalescence ripening, crystals which were far apart are directly brought into contact with each other and adhered to each other to form larger crystals, and hence the grain sizes change suddenly. Both of Ostwalt 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 as shown in Fig. 4 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 an 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 coalescence 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 gelatin 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 used simultaneously.

(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").

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 grain growth except for pAg control 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 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, 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 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 0.1 µm, preferably not larger than 0.06 µm, and more preferably not larger than 0.03 µm.

The halide composition of the core grain 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 halide distribution, that is, having the "complete homogeneity" is obtained.

Furthermore, the process of this invention is also very effective in the production of core grains composed of pure silver bromide or pure silver chloride. According to a conventional production process, the existence of the local distributions of silver ions and halogen ions in a reaction vessel is unavoidable and the silver halide grains in the reaction vessel are brought into a state different from other homogeneous portions by passing the local heterogeneous portions, whereby the growth of the grains becomes heterogeneous as well as in a high concentration portion of, for example, silver ions, reduced silver or fogged silver is formed. Accordingly, in the case of silver bromide or silver chloride, a heterogeneous distribution of halide does not surely exist but other heterogeneity described above occurs. This problem can be completely solved by the process of this invention. Therefore, the core grains obtained by the process of this invention include a silver halide of a single composition. Also, it is preferred that such reduced silver is not distributed in the core grains.

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, 3,320,069, etc.), ammonia, thioether compounds (e.g., 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).

There is no particular restriction on the grain size of the completely homogeneous silver halide emulsion grains thus obtained but the grain size is preferably at least 0.3 µm, more preferably at least 0.8 µm, and particularly preferably at least 1.4 µm.

The form of the silver halide grains by this invention may be a regular crystal form (normal crystal grains) such as hexahedron, octahedron, dodecahedron, tetradecahedron, tetracosahedron, and octatetraconsahedron, may be an irregular crystal form such as sphere or potato form, or may be various forms having one or more twin crystal plane, in particular, hexagonal tabular grains or triangular tabular twin grains having two or three parallel thin planes.

Then, the process of forming the shell of this invention is explained. In succession to the formation of the core described above, the shell is formed and for producing the shell, Method A or Method B can be applied. Details of these methods are as described above.

Also, for the formation of the shell in this invention, conventional method of forming silver halide grains can be used. That is, an aqueous silver salt solution and an aqueous halide solution are added with stirring efficiently to the reaction vessel containing an aqueous solution containing the core silver halide grains and a protective colloid.

Practical processes for producing the shell are described in P. Glafkides, Chimie et Phisique Photographique, (published by Paul Montel, 1967), G.F. Duffin, Photographic Emulsion Chemistry, (published by The

Focal Press, 1966), and V.L. Zelikman et al, Making and Coating Photographic Emulsion (published by The Focal Press, 1964).

That is, an acid process, a neutralization process, an ammonia process, etc., can be used and also, as a system for reacting a soluble silver salt and soluble halides, a single jet process, a double jet process, or a combination thereof can be used. A process of forming the shell in the existence of excessive silver ions (so-called reverse mixing process) can be also used. As one of the double jet processes, a so-called controlled double jet process of keeping constant pAg in the liquid phase of forming the silver halide grains can be used.

In the step of forming or physical ripening the core/shell emulsion grains of this invention, a cadmium salt, a zinc salt, a lead slat, a thallium salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, or an iron salt or a complex iron salt thereof may coexist.

Also, it is preferred to quickly grow the grains in the range of not over the crytical supersaturation using a process of changing the addition rates of an aqueous silver nitrate solution and an aqueous alkali halide solution according to the rate of the grain growth as described in British Patent 1,535,016 and JP-B-48-36890 and JP-B-52-16364 or a process of changing the concentration of aqueous solution(s) as described in U.S. Patent 4,242,445 and JP-A-55-158124. These processes are preferably used since the re-formation of nuclei does not occur and the core silver halide grains are homogeneously covered.

In the core/shell type silver halide grains of this invention, 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 octahedron. 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 formed at the edge portions, corner portions or plane portions of the host crystals with a different composition from that of the host crystal. The host crystals on which the junction crystals are formed may be homogeneous in regard to the halogen composition or may have a core/shell type structure.

In the case of the junction structure, the combination of silver halides each other can be as a matter of course employed but a combination of a silver salt compound having no rock salt structure, such as silver rhodanide, silver carbonate, etc., and silver halide can be employed for the junction structure. Also, a non silver salt compound such as PbO can be used if possible.

In the case of the silver iodobromide grains having the aforesaid structure, in for example, core/shell type grains, the silver iodide content may be higher in the core portion and lower in the shell portion or conversely, the silver iodide content may be lower in the core portion and higher in the shell portion. 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 be also 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 nuclei 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 silver halide emulsion of this invention is usually spectrally sensitized.

As the spectral sensitizing dye for use in this invention, methine dyes are usually used and the dyes include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes. To these dyes can be applied nuclei which are usually 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, benzindaizolenine 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- or 6-membered heterocyclic nuclei such as pyrazolin-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.

The amount of the sensitizing dye being added during the preparation of the silver halide emulsion depends upon the kind of the additive and the amount of the silver halide but may be an ordinary amount of a sensitizing dye added in conventional method.

That is, the amount of the sensitizing dye is preferably from 0.001 to 100 mmols, and more preferably from 0.01 to 10 mmols.

The sensitizing dye is added after chemical ripening or before chemical ripening. It is more preferred for the silver halide grains of this invention to add the sensitizing dye thereto during chemical ripening or before chemical ripening (e.g., at the formation of grains or at physical ripening).

Together with the sensitizing dye, a dye having no spectral sensitizing action by itself or a material which does not substantially absorb visible light and shows a supersensitizing action may exist in the silver halide emulsion in this invention. For example, the emulsion may contain aminostyryl compounds (e.g., those described in U.S. Patents 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensates (e.g., those described in U.S. Patent 3,743,510), cadmium salts, azaindene compounds, etc. Furthermore, combinations described in U.S. Patents 3,615,613, 3,615,641, 3,617,295, and 3,635,721 are particularly useful.

The silver halide emulsion of this invention is usually chemically sensitized. For the chemical sensitization, the methods described, e.g., in H. Frieser, Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden, pages 675-734 (1968) can be used.

That is, a sulfur sensitizing method using active gelatin or a sulfur-containing compound capable of reacting with silver (e.g., thiosulfates, thioureas, mercapto compounds, and rhodanines); a reduction sensitizing method using a reducing agent (e.g., stannous salts, amines, hydrazine derivatives, formamidinesulfinic acid, and silane compounds); and a noble metal sensitizing method using a noble metal compound (e.g., gold complex salts and complex salts of metals belonging to group VIII of the periodic table, such as Pt, Ir, Pd, etc.) can be used solely or as a combination thereof.

The photographic emulsions for use in this invention can contain various compounds for inhibiting the occurrence of fog during the production, storage, and photographic processing of the photographic materials or stabilizing the photographic performance thereof. That is, there are many compounds known as antifoggants or stabilizers such as azoles, e.g., benzothiazolium salts, nitroindazoles, triazoles, benzotriazoles, and benzimidazoles (in particular, nitro- or halogen-substituted products); heterocyclic mercapto compounds, e.g., mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, mercaptotetrazoles (in particular, 1-phenyl-5-mercaptotetrazole), and mercaptopyrimidines; the aforesaid heterocyclic mercapto compounds having a water soluble group such as carboxy group and sulfon group; thioketo compounds, e.g., oxazolinethione; azaindenes, e.g., tetraazaindenes (in particular, 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes); benzenethiosulfonic acids; and benzenesulfinic acids.

The antifoggant or the stabilizer is usually added to the silver halide emulsion after chemical sensitization but the addition time can be preferably selected from the times during chemical ripening and before the initiation of chemical ripening. That is, the addition may be carried out during the addition of a silver salt solution, at a step from the addition of the silver salt solution to the initiation of chemical ripening, or during chemical ripening (i.e., at chemical ripening, preferably within 50% of the time from the initiation, and more preferably within 20% of the time) in the step of forming the silver halide emulsion grains.

The silver halide emulsion of this invention can be used for photographic light-sensitive material having one or two layers, or any optional layer structure.

A silver halide multilayer color photographic material using the emulsions of this invention has a multilayer structure having laminated emulsion layers containing a binder and silver halide grains for separately recording blue light, green light, and red light, and each emulsion layer is composed of at least two layers, i.e., a high speed layer and a low speed layer. Particularly practical layer structures are as follows:

(1) BH/BL/GH/GL/RH/RL/S,

(2) BH/BM/BL/GH/GM/GL/RH/RM/RL/S,

(3) BH/BL/GH/RH/GL/RL/S described in U.S. Patent 4,184,876, and

(4) BH/GH/RH/BL/GL/RL/S described in RD-22534, JP-A 59-177551 and JP-A-59-177552.

Wherein B represents a blue-sensitive layer, G a green-sensitive layer, R a red-sensitive layer, H a highest speed layer, M a middle speed layer, L a low speed layer, and S a support. In the aforesaid layer structures, protective layer(s), a filter layer, intermediate layer(s), an antihalation layer, subbing layer(s), etc., are omitted. In the aforesaid layer structures, the structures (1), (2) and (4) are preferred.

Also, the layer structures of

(5) BH/BL/CL/GH/GL/RH/RL/S and

(6) BH/BL/GH/GL/CL/RH/RL/S described in JP-A-61-34541

are preferred.

Wherein CL is an interlayer effect providing layer and others are same as above.

Also, the disposition of the high speed layer and the low speed layer in a same color sensitive layer may be reversed.

The silver halide emulsion of this invention can be applied to color photographic materials as described above but can be also applied other light-sensitive materials having one or more layers, such as X-ray light-sensitive materials, black and white light-sensitive materials for camera use, light-sensitive materials for photomechanical process, photographic papers, etc.

There are no particular restriction on various additives for the silver halide emulsions of this invention, such as binders, chemical sensitizers, spectral sensitizers, stabilizers, gelatin hardening agents, surface active agents, antistatic agents, polymer latexes, matting agents, color couplers, ultraviolet absorbents, fading inhibitors, dyes, etc., as well as supports for the photographic materials using these emulsions, coating methods, exposure methods, development processing methods, etc., and the descriptions of e.g., Research Disclosure, Vol. 176, Item 17616 (RD-17643), ibid., Vol. 187, Item 18716 (RD-18716), and ibid., Vol. 225, Item 22534 (RD-22534) can be referred to.

The descriptions of these research disclosures are shown in the following table

	Additives	RD17643	RD18716	RD22534
1	Chemical Sensitizer	Page 23	Page 648, right column	Page 24
2	Sensitivity Increasing Agent		do	
3	Spectral Sensitizer, Super Color Sensitizer	Pages 23-24	Page 648, right column-page 649, right column	Pages 24-28
4	Whitening Agent	Page 24		
5	Antifoggant, Stabilizer	Pages 24-25	Page 649, right column	Pages 24, and 31
6	Light Absorbent, Filter Dye, Ultraviolet Absorbent	Pages 25-26	Page 649, right column-page 650, left column	
7	Stain Inhibitor	Page 35, right column	Page 650, left-right column	
8	Dye Image Stabilizer	Page 25		Page 32
9	Hardening Agent	Page 26	Page 651, left column	Page 28
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	
14	Color Coupler	Page 25	Page 649	Page 31

As a gelatin hardening agent, active halogen compounds (2,4-dichloro-6-hydroxy-1,3,5-triazine and the sodium salts thereof) and active vinyl compounds (1,3-bisvinylsulfonyl-2-propanol, 1,2-bis(vinylsulfonylacetamido)ethane and vinylic polymer having a vinylsulfonyl group at the side chain) are preferred since they harden quickly a hydrophilic colloid such as gelatin to give stable photographic characteristics. N-carbamoylpyridinium salts [(1-morpholinocarbonyl-3-pyridinio)methanesulfonate, etc.] and haloamidinium salts [1-(1-chloro-1-pyridinomethylene)pyrrolidinium 2-naphthalenesulfonate, etc.] are excellent in hardening speed.

The color photographic materials using the silver halide photographic emulsions of this invention can be processed by the ordinary processes described in Research Disclosure, No. 17643, pages 28-29 and ibid., No. 18716, page 651, left column to right column.

After developing and bleach-fixing or fixing the color photographic materials using the silver halide photographic emulsions of this invention, washing or stabilization is usually applied.

The washing is generally performed by a countercurrent washing process using two or more baths for saving water. As the stabilization process, a typical example is a multistage countercurrent stabilization process as described in JP-A-57-8543 in place of a washing step.

BRIEF EXPLANATION OF THE DRAWINGS

Fig. 1 and Fig. 2 are X-ray diffraction curves showing the homogeneity of silver halide grains, wherein the axis of ordinate shows the half value width of an X-ray diffraction profile and the axis of abscissa shows the halogen composition of silver halide grains.

Fig. 3 shows schematically 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 protective colloid

7: Mixer

Fig. 4 shows the details of the mixer in this invention.

4, 5, 6, and 7 have the same significance as in Fig. 4.

8: Introduction system to the reaction vessel

9: Stirring blade

10: Reaction chamber

Fig. 5 is a transmission type electron microphotograph showing the crystal structure of conventional tabular silver halide grains having not completely homogeneous iodine distribution of silver iodobromide phase.

BEST MODE FOR PRACTICING THE INVENTION

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

Example 1

Silver iodobromide fine grain emulsion 1-A:

To 2.6 liters of a 2.0% by weight gelatin solution containing 0.126M of potassium bromide were added 1,200 ml of a solution of 1.2M of silver nitrate and 1,200 ml of an aqueous halide solution containing 0.9M of potassium bromide and 0.3M of potassium iodide by a double jet method with stirring over a period of 15 minutes. During the addition thereof, the gelatin solution was kept at 35°C. Thereafter, the emulsion thus obtained was washed by an ordinary flocculation method and after adding thereto 30 g of gelatin and dissolving it therein, pH and pAg of the emulsion were adjusted to 6.5 and 8.6, respectively. The mean grain size of the silver iodobromide fine grains obtained (silver iodide content 25% by weight) was 0.05 µm.

Silver iodobromide octahedral core emulsion 1-B (This invention):

To 1.2 liters of an aqueous solution of 1.5% by weight gelatin containing 0.05M of potassium bromide was added 60 ml of 0.5% 3,6-dithiaoctane-1,8-diol with stirring at 75°C in a reaction vessel and an emulsion obtained by adding 270 ml of water to 100 g of the silver iodobromide fine grain emulsion 1-A (containing silver corresponding to 10 g as silver nitrate) to perform nucleus formation. The mean grain size of the silver iodobromide octahedral nucleus grains was 0.4 µm.

Then, successively 1,000 g of the fine grain emulsion 1-A (containing silver corresponding to 100 g of silver nitrate) was continuously added to the reaction vessel over a period of 100 minutes. Thereafter, the emulsion was cooled to 35°C, washed with water by an ordinary flocculation method, 70 g of gelatin was added thereto, and pH and pAg thereof were adjusted to 6.2 and 8.8, respectively.

The core emulsion grains obtained were an octahedral silver iodobromide emulsion having a mean diameter corresponding the projected area of 1.2 µm (having an iodide content of 25 mol%).

Silver iodobromide octahedral core emulsion 1-C (this invention):

To 1.2 liters of an aqueous solution of 1.5% by weight gelatin containing 0.05M of potassium bromide was added 20 ml of 0.5% 3,6-dithiaoctane-1,8-diol with stirring at 75°C in a reaction vessel. To a mixer disposed near the reaction vessel were added 100 ml of an aqueous solution of 0.59M of silver nitrate, 100 ml of an aqueous solution containing 0.44M of potassium bromide and 0.148M of potassium iodide, and 300 ml of an aqueous solution of 2% by weight gelatin over a period of 5 minutes by a triple jet method. The temperature of the mixer was 20°C and the rotation number of the stirring blade of the mixer was 6000 r.p.m. The mean grain size of the fine grains confirmed by a direct method transmission type electron microscope of 20,000 magnifications was 0.01 µm.

The fine grains formed in the mixer were continuously introduced into the reaction vessel kept at 75°C. The mean grain size of the silver iodobromide octahedral nucleus grains (silver iodide content 25 mol%) obtained was 0.4 µm.

Then, in succession, 600 ml of an aqueous solution of 1M of silver nitrate, 600 ml of an aqueous solution containing 0.75M of potassium bromide and 0.25M of potassium iodide, and 800 ml of an aqueous solution of 2% by weight gelatin were added to the mixer by a triple jet method at 75°C. The grain size of the fine grains thus formed in the mixer was 0.02 µm and the fine grains were continuously added to the reaction vessel. In this case, the mixer was kept at 20°C. The emulsion formed in the reaction vessel was washed with water and pH and pAg thereof were controlled as in the case of Emulsion 1-B. The core emulsion grains obtained was an octahedral silver iodobromide emulsion (silver iodide content 25 mol%) having a mean diameter corresponding to the circle of the projected area of 1.2 µm.

Silver iodobromide octahedral core emulsion 1-D (Comparison emulsion):

To 1.2 liters of an aqueous solution of 3.0% by weight gelatin containing 0.06M of potassium bromide was added 50 ml of 3,6-dithiaoctane-1,8-diol with stirring at 75°C in a reaction vessel and then 50 cc of an aqueous solution of 0.3M of silver nitrate and 50 cc of an aqueous solution containing 0.063M of potassium iodide and 0.19M of potassium bromide were added to the reaction vessel kept at 75°C by a double jet method over a period of 3 minutes. Thus, silver iodobromide grains having a mean diameter corresponding to the circle of the projected area of 0.4 µm and containing silver iodide content of 25 mol% were obtained to form nuclei.

Then, in succession, 600 ml of an aqueous solution of 1M of silver nitrate and 600 ml of an aqueous solution containing 0.75M of potassium bromide and 0.25M of potassium iodide were added to the reaction vessel by a double jet method. The emulsion thus formed was washed with water and pH and pAg thereof were adjusted as in the case of Emulsion 1-B. The core emulsion grains obtained were an octahedral silver iodobromide emulsion (silver iodide content 25 mol%) having a mean diameter corresponding to the circle having the projected area of 1.2 µm.

For determining the microscopic iodide distribution of Emulsions 1-B, 1-C and 1-D, the X-ray diffraction of the (420) plane was measured using the Kα line described above. In this case, the X-ray diffraction of a pure silver bromide emulsion having the same grain size as above was also measured. The results are shown in Table 1.

Table 1

Half Value Width	Emulsion		
	1-B	1-C	1-D
A Half value width	0.14°	1.13°	0.22°
B Half value width of pure AgBr	0.08°	0.08°	0.08°
(A - B)	0.06°	0.05°	0.14°

The value of (A - B) in Table 1 shows a heterogeneous distribution of iodide and it can be seen that the half value width of emulsion grains 1-B and 1-C is less than 1/2 of the half value width of the comparison emulsion 1-D.

Example 2

Onto the core emulsion obtained in Example 1 was formed a shell of pure AgBr by a double jet method at pAg of 9.0. The content of the shell formed is shown in Table 2 below.

Table 2

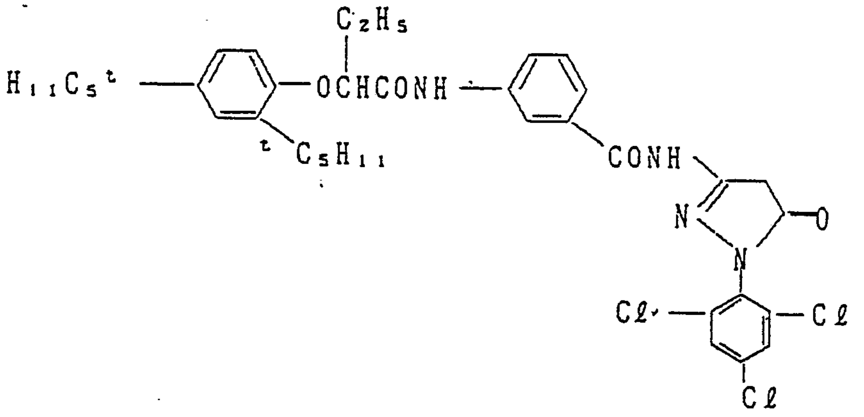
Emulsion	2-A	2-B	2-C	2-D	2-E	2-F
Core Emulsion	1-B (Invention)		1-C (Invention)		1-D (Comparison)	
C/S (mol%)	3/2	9/1	3/2	9/1	3/2	9/1

Each of the emulsions 2-A to 2-F thus obtained was most properly chemically sensitized by sodium thiosulfate, potassium chloroaurate, and potassium thiocyanate and after adding thereto the following compounds, the emulsion was coated on a triacetyl cellulose film support having a subbing layer.

(1) Emulsion Layer:

- Emulsion --- Emulsion shown in Table 3

- Coupler



- Tricresyl Phosphate
- Sensitizing Dye: 5-Chloro-5'-phenyl-4-ethyl-3,3'-(3-sulfopropyl)oxacarbocyanine sodium
- Stabilizer: 4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene
- Coating Aid: Sodium dodecylbenzenesulfonate

(2) Protective Layer

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

Each of these samples was subjected to a sensitometric exposure and subjected to the following color development process.

Then, the density of the processed sample was measured using a green filter. The results of the photographic performance obtained are shown in Table 3.

The following development process was performed at 38°C.

1.	Color Development . .	2 minutes 45 seconds
2.	Bleaching	6 minutes 30 seconds
3.	Washing	3 minutes 15 seconds
4.	Fixing	6 minutes 30 seconds
5.	Washing	3 minutes 15 seconds
6.	Stabilization	3 minutes 15 seconds

The composition of the processing solution used for each step were 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-methyl-aniline 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 g
Sodium Hydrogenesulfite	4.6 g
Water to make	1 liter

Stabilization Solution

Formalin	8.0 ml
Water to make	1 liter

Table 3

Emulsion	C/S (mol ratio)	Relative Sensitivity	Fog	Content
2-A	3/2	160	0.15	Invention
2-C	"	170	0.15	"
2-C	"	100	0.15	Comparison
2-B	9/1	150	0.17	Invention
2-D	"	160	0.18	"
2-F	"	100	0.17	Comparison

As is shown from the results of Table 3, it can be seen that the emulsions of this invention have higher sensitivity than the comparison emulsions.

Example 3

Silver Chlorobromide Fine Grain Emulsion 3-A:

To 1.3 liters of a 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 of 1.2M of silver nitrate and 600 ml of an aqueous solution containing 0.72M of potassium bromide and 1.0M of sodium chloride by a double jet method with stirring over a period of 25 minutes. During the addition, the temperature of 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 30 g of gelatin in the emulsion, pH thereof was adjusted to 6.5. The mean grain size of the silver chlorobromide fine grains (silver chloride content 40%) thus obtained was 0.09 µm.

Silver Chlorobromide Cubic Grain Emulsion 3-B (Comparison Emulsion):

To 1.2 liters of a solution of 3.0% by weight gelatin containing 0.065M of potassium bromide and 0.3M of sodium chloride was added 4.5 ml of a solution of 1% N-N'-dimethylimidazoline-2-thione in a reaction vessel kept at

75°C and 50 cc of an aqueous solution of 0.3M of silver nitrate and 50 cc of an aqueous solution containing 0.18M of potassium bromide and 0.8M of sodium chloride by a double jet method with stirring over a period of 3 minutes.

By the aforesaid process, silver chlorobromide grains having a mean grain size of 0.2 µm and a silver chloride content of 40 mol% were obtained to perform, thus, the nucleus formation. In succession, 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 similarly added thereto by a double jet method at 75°C over a period of 100 minutes. Thereafter, the emulsion was cooled to 35°C, washed by an ordinary flocculation method, and after adding thereto 70 g of gelatin, pH and pAg thereof were adjusted to 6.2 and 7.8, respectively. The grains thus obtained were silver chlorobromide cubic grains having a mean grain size of 1.1 µm and a silver chloride content of 40 mol%.

Silver Chlorobromide Cubic Grain Emulsion 3-C (This Invention):

To 1.0 liter of an aqueous solution of 0.5% by weight gelatin containing 0.065M of potassium bromide and 0.3M of sodium chloride was added 4.5 ml of a solution of

1% N-N'-dimethylimidazoline-2-thione with stirring in a reaction vessel and the fine grain emulsion 3-A described above was added to the reaction vessel at 75°C by a pump. The addition rate was such that the fine grain emulsion corresponding to 5 g calculated as the silver nitrate amount was added over a period of 10 minutes.

Thereafter, in succession, the fine grain emulsion 3-A was added to the reaction vessel at 75°C by a pump. The addition rate was such that the fine grain emulsion of 150 g calculated as the silver nitrate amount was added over a period of 100 minutes.

In this case, 20 g of sodium chloride was previously dissolved in the fine grain emulsion. Thereafter, the emulsion obtained was washed with water as in the case of the emulsion 1-B and pH and pAg thereof were adjusted to 6.5 and 7.8, respectively at 40°C. The grains obtained were silver chlorobromide cubic grains having a mean grain size of 1.1 µm and a silver chloride content of 40 mol%.

Silver Chlorobromide Octahedral Grain Emulsion 3-D (This Invention):

After performing the nucleus formation as in the case of the emulsion 1-C, 800 cc of an aqueous solution containing 150 g of silver nitrate, 800 cc of an aqueous solution containing 63 g of potassium bromide and 43 g of sodium chloride, and 800 cc of an aqueous solution of 10% by weight low-molecular weight gelatin (average molecular weight 20,000) were added to a mixer having a strong and efficient stirring means disposed in the vicinity of the reaction vessel by a triple jet method over a period of 100 minutes. Very fine grains (mean grain size 0.02 μm) formed by stirring the reaction mixture in the mixer were immediately introduced continuously into the reaction vessel from the mixer. During the introduction, the temperature of the mixer was kept at 25°C and the temperature of the reaction vessel at 75°C.

Thereafter, the emulsion was washed with water as in the case of the emulsion 1-B and pH and pAg thereof were adjusted to 6.5 and 7.8, respectively at 40°C. The grains thus obtained were silver chlorobromide cubic grains having a mean grain size of 1.1 μm and a silver chloride content of 40 mol%.

Each of the emulsions 3-B, 3-C, and 3-D was coated on a film base support at a silver coverage of 3 g/m^2 and for determining the microscopic distribution of the halide, the X-ray diffraction of the (420) plane was measured using the Kα line described above. In this case, X-ray diffractions of pure silver chloride and pure silver bromide each having the same mean grain size as above were performed. The results are shown in Table 4.

Table 4

Half Value Width	Emulsion		
	3-B	3-C	3-D
A Half value width	0.22°	0.10°	0.10°
B Half value width of AgBr.AgCl	0.08°	0.08°	0.08°
(A - B)	0.14°	0.02°	0.02°

The value of (A - B) in Table 4 shows a microscopic heterogeneity and the half value widths of the emulsion grains 3-C and 3-D of this invention are very small as compared with that of the comparison emulsion 3-B and are almost near that of silver bromide (silver chloride).

Example 4

The core emulsion obtained in Example 3 was kept at 60°C in the reaction vessel and an aqueous solution of 1M of silver nitrate and an aqueous solution of 1M potassium bromide were added with stirring by a double jet method to form a silver bromide shell. The content of the shell formation is shown in Table 5.

Table 5

Emulsion	4-A	4-B	4-C	4-D	4-E	4-F
Core Emulsion	3-B (Comparison)		3-C (Invention)		3-D (Invention)	
C/S (mol ratio)	7/3	94/6	7/3	94/6	7/3	94/6

Each of the emulsions 4-A to 4-F was most suitably chemically sensitized with sodium thiosulfate, potassium chloroaurate, and potassium thiocyanate and coated on a support as in Example 2 to provide coated samples. The results obtained by performing a sensitometry as in Example 2 are shown in Table 6.

Table 6

Emulsion	C/S (mol ratio)	Relative Sensitivity	Fog	Content
4-A	7/3	100	0.13	Comparison
4-C	"	150	0.13	Invention
4-E	"	160	0.14	"
4-B	94/6	100	0.14	Comparison
4-D	"	140	0.14	Invention
4-F	"	150	0.14	"

From the results of Table 6, it can be seen that the emulsions of this invention show higher sensitivity than the comparison emulsions.

[Industrial Applicability]

The silver halide photographic material containing the silver halide emulsion of this invention thus obtained have a completely homogeneous halide distribution of the silver halide core grains contained in the emulsion and can have the characteristics excellent in sensitivity, gradation, graininess, sharpness, resolving power, covering power, storage stability, latent image stability, and pressure resistance.

CLAIMS

1. A silver halide photographic material having on a support at least one silver halide emulsion layer, characterized in that the inside of the light-sensitive silver halide grains contained in the silver halide emulsion layer is composed of at least one phase containing at least two kinds of silver halides, the halide composition thereof is completely homogeneous, and the surface of the silver halide grains has a different halide composition from the inside of silver halide grains adjacent to the surface.

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 silver halide grains nucleus-formed and/or crystal-grown in a reaction vessel for causing the nucleus formation and/or the crystal growth of the grains by adding previously prepared silver halide of fine size into the reaction vessel, said silver halide grains having silver halide of a different halide composition from that of the silver halide grains at the outside of the silver halide grains.

3. A process of producing the silver halide photographic material described in claim 2, which

comprises mixing an aqueous solution of a water-soluble silver salt and an aqueous solution of a water-soluble halide in a mixer disposed outside a reaction vessel for causing a nucleus formation and/or a crystal growth of light-sensitive silver halide grains to form silver halide having fine grain sizes, supplying the silver halide into the reaction vessel immediately after the formation thereof to perform the nucleus formation and/or the crystal growth of light-sensitive silver halide grains, and further forming silver halide having a different composition from the grains at the outside of the silver halide grains.

Fig. 1

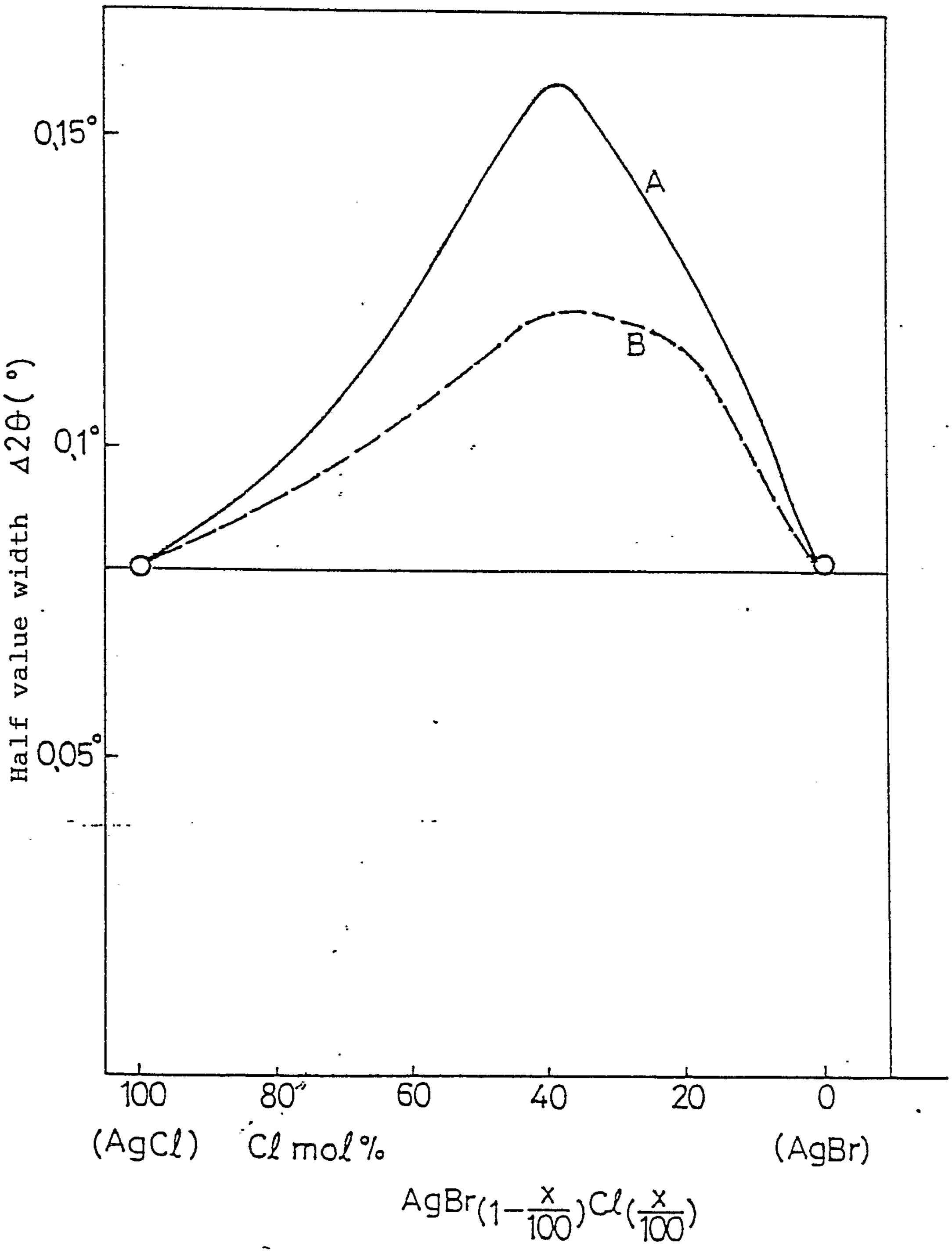

0,15°
0,1°
0,05°
Half value width Δ2θ (°)
A
B
100
80
60
40
20
0
(AgCℓ)
Cℓ mol%
(AgBr)
$AgBr_{(1-\frac{x}{100})}Cℓ_{(\frac{x}{100})}$

Fig. 2

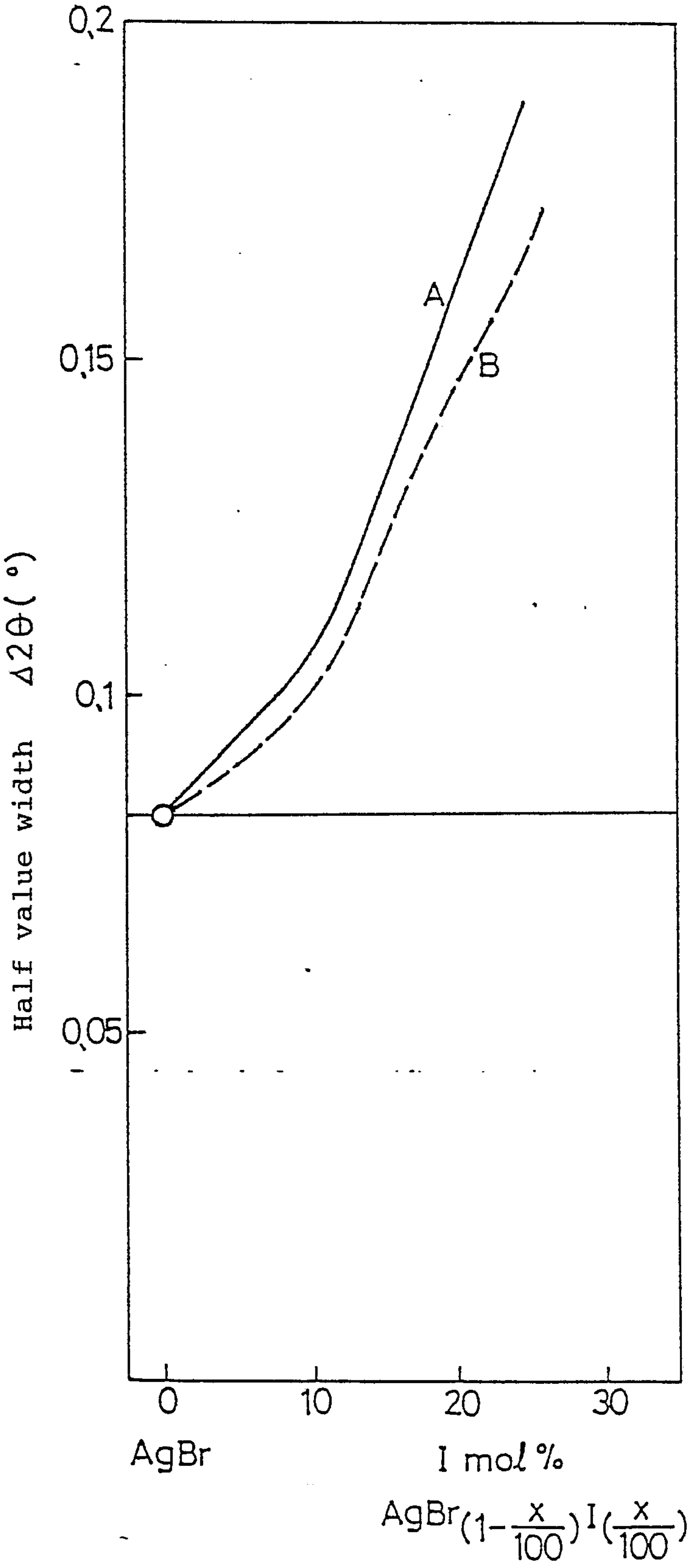

0,2
0,15
0,1
0,05
Half value width Δ2θ(°)
A
B
0
10
20
30
AgBr
I mol %
AgBr(1-x/100)I(x/100)

Fig. 3

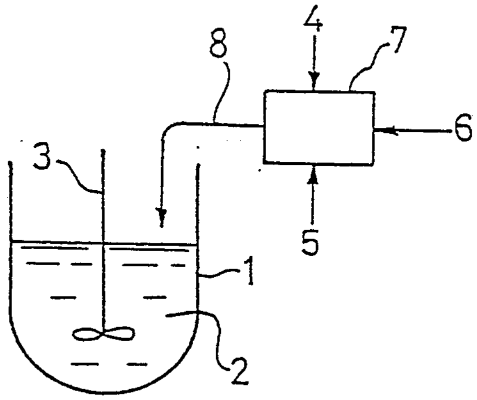


Fig. 4

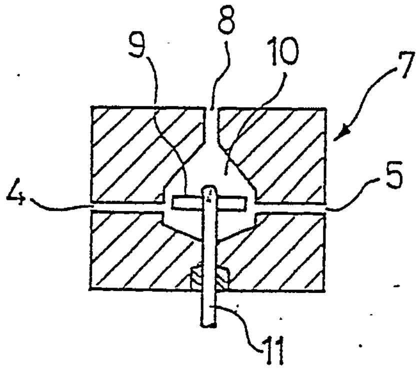
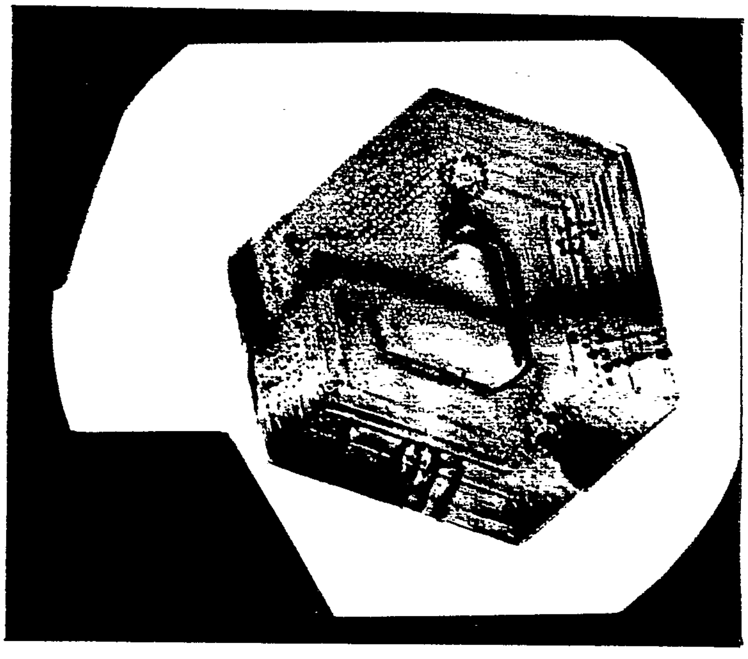


Fig. 5



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/00038

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

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	G03C1/02

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, A0, 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	1-3
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, A0, 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 & LU, A, 84459	1-3

* Special categories of cited documents: [10]

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

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"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