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(54) Silver halide photographic emulsions.

(57) A silver halide photographic emulsion having a high sensitivity is disclosed, which comprises a dispersion medium and silver halide grains, wherein said silver halide grains contain at least one phase composed of two or more kinds of different silver halides and the phase contains at least 10 mol% silver chloride with microscopically homogeneous distribution.

SILVER HALIDE PHOTOGRAPHIC EMULSIONS

FIELD OF THE INVENTION

This invention relates to a light-sensitive silver halide emulsion useful in the field of photography, and more particularly, to a silver halide photographic emulsion composed of a dispersion medium and silver halide grains containing silver chloride and also to a process of producing the emulsion.

BACKGROUND OF THE INVENTION

Light-sensitive silver halide emulsions containing silver chloride are known to give the specific advantages as shown below. For example, silver chloride is more soluble than other photographically useful silver halides, whereby the development and fixing can be achieved in a shorter time. An emulsion containing silver chloride (silver chloride emulsion) has found to be particularly useful in applications requiring high contrast, such as graphic arts, and in applications requiring quick processing, such as black and white films for camera use, radiographic films, and color print products.

Recently, with the increased propagation of color photographic materials, the color photographic processing thereof is more simplified and quickened and on the other hand, the formation of high quality images and the uniformity of the finished quality have been required.

That is, the simplification and quickening of photographic process, or practically the reduction of the number of processing baths being used, the reduction of replenishing amounts (low replenishing), and the reduction of processing time have strongly been desired at present.

The processing time of color negative photographic materials is very quickened by the C-41 process by Eastman Kodak Corporation but even in the process, it requires 17 minutes and 20 seconds in the wet processing time without including a drying step and also even in the quick process CN-16Q by Fuji Photo Film Co., Ltd., which has recently been introduced into mini-laboratory markets, it required 9 minutes and 50 seconds in processing.

For improving the existing processing systems for color negative photographic films and color photographic papers such that they meet the consumer's requirements, shortening of the processing time has been strongly desired.

A negative photographic film for camera use using silver iodobromide emulsions most effectively utilize the merit of silver iodide contained therein, such as high sensitivity, a double layer effect, etc., but at the same time the existence of silver iodide makes it difficult to shorten the photographic processing. That is, the iodide ions accumulated in the desilvering processing solution cause a fatal fault that the bleach and fix of silver are greatly delayed to obstruct quickening of processing and the reduction of the amounts of replenishers.

On the other hand, a silver chlorobromide emulsion is very useful for quick processing but has the disadvantages that the sensitivity is low, a chemical sensitization and a spectral sensitization are reluctant to apply to the emulsion, the sensitivity obtained by such sensitizations are unstable even when they can be applied, and fog is liable to occur.

Tabular grain silver halide grains (hereinafter, are referred to as "tabular grains") containing parallel twin planes have the following photographic characteristics:

1) The ratio of the surface area to the volume (hereinafter, referred to as "specific surface area") is large and hence a large amount of sensitizing dye can be adsorbed on the surface. Thus, the color sensitized sensitivity thereof is relatively high to the intrinsic sensitivity.

2) When an emulsion containing the tabular grains is coated and dried, the tabular grains dispose in parallel with the surface of the support, thereby the thickness of the coated layer can be reduced to improve the sharpness of images formed.

3) In a radiographic system by the addition of sensitizing dye(s) to tabular grains, the extinction coefficient of the dye(s) can be increased over the extinction coefficient of the indirect transition of silver halide, crossover light can be remarkably reduced, and the deterioration of image quality can be prevented.

4) Light scattering is minimized and images having a high resolving power are obtained.

5) Since the sensitivity to blue light is low, when the tabular grains are used for a green-sensitive emulsion layer or a red-sensitive emulsion layer, a yellow filter can be omitted from the emulsion layers.

Owing to such various advantages, the tabular grains have been used high speed photographic materials.

As to tabular silver bromide grains and tabular silver iodobromide grains, tabular grains having an aspect ratio of at least 8 are disclosed in JP-A-58-113926, JP-A-58-113927, and JP-A-58-113928. (The term "JP-A" as used herein means an "unexamined published Japanese patent application".)

The aspect ratio is shown by the ratio of the diameter of a tabular grain to the thickness thereof. Also, the diameter of the grains means a diameter of a circle having the same area as the projected area of the grain when the grains are observed by a microscope or an electro-microscope. Furthermore, the thickness thereof is shown by the distance between two parallel planes constituting the tabular silver halide grain.

U.S. Patent 4,399,215 describes that tabular silver chlorobromide grains having a silver chloride content of at least 50 mol% or tabular silver chloride grains are obtained by performing the grain formation using ammonia while keeping pAg of the system at the range of from 6.5 to 10 and pH at the range of from 8 to 10 without containing silver bromide and silver iodide in the inside thereof. U.S. Patent 4,400,463 describes that a tabular silver halide emulsion having a silver chloride content of at least 50% is obtained by performing the grain formation in the co-existence of aminoazaindene and a peptizer having a thioether bond. U.S. Patent 4,713,323 describes that tabular silver chloride grains or tabular silver chlorobromide grains are obtained by using a gelatin dispersion medium having a methionine content of less than 30 mole/g. Also, JP-A-58-111936 describes that tabular silver chlorobromide grains having a mean mol ratio of chloride to bromide of at least 2/3 are obtained by double jet while keeping the mol ratio of chloride ions to bromide ions in the reaction vessel at a value of from 1.6/1 to 258/1 and also keeping the total concentration of halogen ions in the reaction vessel at a value of from 0.10 to 0.90 normal.

As described above, tabular silver chlorobromide grains having various silver chloride contents and the production processes of them are described in the aforesaid patents but they do not solve the above-described problems that a silver chlorobromide emulsion is reluctant to increase the sensitivity as compared with a silver iodobromide emulsion and also the sensitivity obtained is unstable as well as fog is liable to form.

On the other hand, various methods for solving these problems are proposed.

For example, there are a method of adding a soluble bromide ion or a soluble iodide ion to a silver halide emulsion after adding thereto sensitizing dye(s) as described in JP-A-48-51627 and JP-B-49-46932 (the term "JP-B" as used herein means an "examined published Japanese patent application"); a method of simultaneously adding a bromide ion and a silver ion to silver halide grains having a high silver chloride content to form the layer containing more than 60 mol% of silver bromide on the surface of the grains and a method of adding halide ions as above to form wholly or partially the layer of silver bromide of from 10 to 50 mol% on the surface of the grains as described in JP-A-58-108533 and JP-A-60-222845; and a method of forming silver halide grains of multiphase structure, such as core-shell type double structure grains or junction structure grains by performing halogen convertion by the addition of bromide ions or by the simultaneous addition of bromide ions and silver ions to silver halide grains having a high silver chloride content as described in JP-B-50-36978 and JP-B-58-24772, U.S. Patent 4,471,050, and West German Patent Application (OLS) 3,229,999.

However, the aforesaid method are all insufficient in the point of sensitivity.

The contents described in the aforesaid patents are that the content of silver bromide is changed in each place of each silver chlorobromide grain (in particular, the inside or outside of the grain or a position on the surface of the grain) to, thereby, obtain good photographic characteristics.

For example, JP-A-58-111935 discloses a photographic emulsion composed of tabular silver halide grains containing 50 mol% silver chloride, which contain at least one of a bromide and an iodide in the central region thereof.

The topograph of the silver chloride content (or silver bromide content) of these tabular silver chlorobromide grains can be determined by using an analytical electron microscopy.

In the case of tabular silver chlorobromide grains, the change in the halogen composition of the main surface of the tabular grain in the width direction can be observed by measuring as it is. Also, it is described in the summary of 1987 Annual Lectures, The Society of Photographic Science and Technology of Japan, by M. Inoue and T. Nagasawa, Observation of the Halogen, Distribution in Silver Halide Grains and Multilayer Structure Grains bv Analytical Electron Microscopy that as to twin or normal crystal silver chlorobromide grains having a low aspect ratio, the topography of the halogen composition can be known by analyzing the very thin cut piece thereof using an analytical electron microscopy.

For example, the result of determining the topography of the silver iodide content in tabular silver iodobromide grains is described in M.A. King, M.H. Lorretto, T.J. Meternaghan, 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 aforesaid report showed that even when tabular silver iodobromide grains were grown with a constant silver iodide content, the silver iodide content was higher in the peripheral portion than in the central portion. In other words, it was shown that in the formation of a silver iodobromide phase, the grains were intended to grow in such a manner that the iodide content would become constant in the silver iodobromide phase but, actually, such phases could not be formed.

On the other hand, Y.T. Tan and R.C. Baetzold presented, as the result of calculating the energy state of silver halide, an expectation that iodine in silver iodobromide crystal grains had a tendency of forming clusters, in The 41st SPSE Annual Conference. The distribution of silver iodide in tabular silver iodobromide grains described above is the change of a silver iodide content in different portions apart from each other at a unit of at least 300 to 1,000 Å but as the expectation by Y.T. Tan and R.C. Baetzold, the more microscopically (100 Å or less) heterogeneous distribution of silver iodide is confirmed in silver iodobromide crystals.

These knowledges were confirmed in tabular silver iodobromide grains and it has been confirmed by the present inventors that they are same in tabular silver chlorobromide grains and also are a common problem in so-called mixed crystal grains composed of two or more kinds of different silver halides.

SUMMARY OF THE INVENTION

The object of this invention is to provide a photographic emulsion composed of negative working silver halide grains giving less fog, having a high sensitivity, having improved graininess, sharpness, and covering power, and being excellent in storage stability and pressure resistance.

It has now been discovered that the aforesaid object can be attained by the present invention as described below.

That is, according to this invention, there is provided a silver halide emulsion comprising a dispersion medium and silver halide grains, wherein the silver halide grains contain at least one phase composed of two or more kinds of different silver halides, and the phase contains at least 10 mol% of silver chloride with microscopically homogeneous distribution.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is transmission type electron microphotographs of 15,000 magnifications showing the crystal structures of conventional silver halide grains wherein the silver chloride distribution of silver chlorobromide is not microscopically homogeneous.

Fig. 2 is a schematic view showing a process of supplying fine silver halide grains from a mixer disposed outside of a reaction vessel as one of the emulsion production processes of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The microscopic silver chloride distribution can be confirmed by a cooling type transmission type electron microscopy as explained in detail below, and the silver chloride-containing phase having the microscopically homogeneous silver chloride distribution disclosed by the present invention have not been obtained before the present invention.

Now, the invention is explained with reference to silver chlorobromide grains having a chlorobromide phase of a microscopically homogeneous silver chloride distribution.

As a means for measuring the silver chloride distribution (or silver bromide distribution) in silver chlorobromide grains, an analytical electron microscopy is well used. For example, the aforesaid M.A. King et al report on The Investigation of Iodide Distribution by Analytical Electron Microscopy described above describes that the size of the probe for electron ray distribution is 50 Å but practically, the diameter of the electron ray spot irradiated onto the surface of a sample is broadened by the elastic scattering of electrons to a diameter of larger than about 300 Å. Accordingly, by the aforesaid method, it is impossible to measure a finer silver chloride distribution.

In JP-A-58-113927, the silver iodide distribution in silver iodobromide was measured by the same manner as above but the size of the electron ray spot used was 0.2 µm.

Therefore, by such measurement methods, it is impossible to clarify the more microscopic (100 Å or less) silver chloride distribution.

The microscopic distribution of silver chloride can be observed by the direct method using a transmission type electron microscopy at low temperature described, e.g., in J.F. Hamilton, Photographic Science and Engineering, Vol. 11, 57 (1967) and Takekimi Shiozawa, Journal of the Society of Photographic Science and Technology of Japan, Vol. 35, No. 4, pp. 213 (1972). That is, silver halide grains taken from a silver halide emulsion under a safe light such that the emulsion is not printed out are placed on a mesh for electron microscopic observation and the grains are observed by a transmission method in a state of cooling the sample with liquid nitrogen or liquid helium for preventing the damage (printout, etc.) by electron beams.

In this case, sharper transmitted images are obtained as the accelerating voltage of the electron microscope is higher, but the voltage is preferably 200 kvolts until the grain thickness of 0.25 µm and is preferably 1,000 kvolts for the grain thickness of larger than 0.25 µm. Since as the acceleration voltage is higher, the damage of the grains by the irradiation of electron beam is larger, it is preferred to cool the sample with liquid helium than by liquid nitrogen.

The photographing magnification for the electron microscopy can be properly selected according to the size of grains being used as the sample but is usually from 20,000 to 40,000 magnifications.

When the transmission type electron microphotograph of tabular silver chlorobromide grains is taken as described above, a very fine annular ring-form striped pattern is observed at the portion of a silver chlorobromide phase. An example thereof is shown in Fig. 1 which is transmission type election microphotographs of tabular silver chlorobromide grains containing 35 mol% silver chloride. As shown in Fig. 1, a very fine annular ring-form striped pattern are clearly seen. It can be seen that the interval of the striped pattern is very fine as an order of 100 Å or less, which shows very microscopic heterogeneity. It can be clarified by various methods that the very fine striped pattern shows the heterogeneity of a silver chloride distribution but it can be more directly concluded from the fact that when the tabular grains are annealed under a condition capable of transferring chlorine ions in silver halide crystals (e.g., for 3 hours at 250° C), the striped pattern completely disappears.

The annular ring-form striped pattern showing the heterogeneity of the silver iodide distribution in tabular silver iodide grains is clearly observed in the transmission type electron microphotograph in JP-A-58-113927 described above and also is clearly shown in the transmission type electron photograph by the King et al investigation described above. Also, Japanese Patent Application No. 63-7852 described a transmission type electron microphotograph showing the heterogeneity of the silver iodide distribution of tabular silver iodobromide grains having a silver iodide content of 10 mol%.

The annular ring-form striped pattern described above, which shows the microscopic heterogeneity of silver chloride in tabular silver halide grains containing silver chloride such as tabular silver chlorobromide grains has never been observed and has first been discovered by the inventors of the present invention.

From the facts described above, it is clear that the silver chlorobromide grains, which are prepared for obtaining substantially homogeneous silver chloride distribution, have a very microscopic heterogeneous distribution of silver chloride completely against the intension of the production thereof and neither the technique of homogenizing the silver chloride distribution nor the production process for obtaining such silver chlorobromide grains has been disclosed.

As described above, the silver halide grains having the "microscopically homogeneous silver chloride distribution" in this invention can be clearly distinguished from conventional grains by observing the transmitted images of images using cooling type transmission type electron microphotography. That is, in tabular silver halide grains containing silver chloride for use in this invention, there are at most two microscopic lines caused by the microscopic heterogeneity of silver chloride in an interval of 0.2 µm, preferably one microscopic line and more preferably none. The lines constituting an annular ring-form striped pattern showing the microscopic heterogeneity occur in the form of perpendicularly crossing the growing direction of the grains and these lines distribute concentrically from the center as the result thereof.

For example, in the case of the tabular grains shown in Fig. 1, the lines constituting the annular ring-form striped patterns showing the heterogeneity of silver chloride perpendicularly cross the growing direction of the tabular grain, therefor the direction of the lines is parallel to the edge of the grain, the direction perpendicularly crossing the direction of the lines directs to the center of the grain, and the aforesaid lines distribute concentrically around the center of the grain.

As a matter of course, when the content of silver chloride is rapidly changed during the growth of the grains, the boundary line thereof is observed as the line described above by the aforesaid observation method and such a change of the silver chloride content forms a simple line only and such a line can be clearly distinguished from the plural lines caused by the microscopic heterogeneity of silver chloride. Furthermore, the silver chloride contents at both the sides of the line can be clearly confirmed by measuring them using the aforesaid analytical electron microscopy. The line formed by such a change of a silver chloride content is completely different from the line caused by the microscopic heterogeneity of silver chloride and shows a "macroscopic silver chloride distribution".

Also, when the silver chloride content is gradually changed during the growth of silver halide grains, the aforesaid line showing the macroscopic change of a silver chloride content is not observed since, in this case, there is no abrupt change of a silver chloride content and hence if there exist at least 3 lines within an interval of 0.2 µm, it means that there exists a microscopic heterogeneity of a silver chloride content.

Thus, the silver halide grains of this invention having the microscopically homogeneous silver chloride distribution are silver grains having at most 2 lines showing the microscopic silver chloride distribution within an interval of 0.2 µm in the direction of perpendicularly crossing the line in the transmitted image of the grain obtained by using a cooling type transmission electron microscopy and the silver halide grain has preferably one such line and more preferably has no such line. Also, silver halide grains in the emulsion of this invention include the aforesaid grains in a proportion of at least 40%, preferably at least 60%, and more preferably at least 80%.

Conventional silver halide grains which are called to be silver halide grains containing homogeneous silver chloride are those prepared by simply adding silver nitrate and a mixture of halides having a constant composition (constant iodide content) to a reaction vessel by a double jet method at the growth of the grains and in such silver halide grains, the macroscopic silver chloride distribution is surely constant but the microscopic silver chloride distribution is not homogeneous. In this invention, the aforesaid silver halide grains are called as grains having a "constant halogen composition" and are clearly distin guished from the silver halide grains of this invention having the "microscopically homogeneous silver chloride distribution".

As the composition of the silver halide grains having the microscopically homogeneous silver chloride distribution in this invention, silver chlorobromide, silver iodochloride, or silver iodochlorobromide may be used but silver chlorobromide or silver iodochlorobromide is preferred.

The position of the phase containing silver chloride in the silver halide grain may be at the central portion, over the whole grain, or at outside portion(s). Also, the phase containing silver chloride may be one or plural. In general, the phase containing silver chloride frequently forms a layer structure on account of the grain growing mechanism but may form specific portion(s). For example, by utilizing the difference in property between the edges and corners of the silver halide grain, the silver chloride phase can be formed in the edge portions or corner portions only. Also, by further forming a shell outside the silver halide grain having such edge portions or corner portions silver halide grains having the silver chloride phase at specific points without forming an annular structure in the grain can be formed.

Practically, after forming nuclei, growing of the grains can be performed by the following constitution as an example.

	First Coating Layer	Second Coating Layer	Third Coating Layer
1	Homogeneous* AgBrCl	-	-
2	AgBr	Homogeneous AgBrCl	-
3	Homogeneous AgBrCl	AgBr	-
4	Homogeneous AgBrCl	Homogeneous AgBrCl	-
5	AgBr	Homogeneous AgBrCl	AgBr
6	AgBr	Heterogeneous AgBrCl	Homogeneous AgBrCl
7	Homogeneous AgBrCl	AgBr	Homogeneous AgBrCl
8	Heterogeneous AgBrCl	AgBr	Homogeneous AgBrCl
9	Heterogeneous AgBrCl	Homogeneous AgBrCl	AgBr
10	Homogeneous AgBrCl	Heterogeneous AgBrCl	AgBr

(*): The term "homogeneous" means the "microscopically homogeneous" defined in this invention.

Furthermore, in the case of silver iodochlorobromide for the coating layer, silver iodide may be incorporated in silver chlorobromide (AgBrCl) in each layer and the coating layer containing silver iodide may be the first coating layer, the second coating layer, and/or the third coating layer.

The ratio of the homogeneous silver chloride-containing phase in one silver halide grain in this invention is generally from 5 to 99 mol%, preferably from 20 to 99 mol%, and more preferably from 50 to 99 mol%.

The silver chloride content in the silver chloride-containing phase of this invention is at least 10 mol% and preferably not more than 90 mol%, and more preferably from 20 mol% to 80 mol%. As described above, in the case of using a silver chlorobromide emulsion, it is difficult to obtain a high sensitivity and also fog is liable to occur, which is more remarkable as the silver chloride content is higher. Accordingly, if the silver chloride content is less than 10%, even when the microscopic heterogeneity of silver chloride exists, the difference in silver chloride content (i.e., the silver chloride distribution) is substantially negligible and thus so much inconvenience does not occur. On the other hand, if the silver chloride content of the outermost layer containing silver chloride is 10 mol% or higher, the sensitivity of conventional silver halide grains having the microscopically heterogeneous distribution of silver chloride is low even when a chemical sensitization is applied thereto and in particular, in the case of applying thereto sulfur and gold sensitizations, fog is liable to occur and the sensitivity is reluctant to be increased. In other words, in the conventional silver halide grains having "a constant silver chloride content but a microscopic heterogeneous silver chloride distribution, the chemical sensitization is obstructed. Accordingly, in such conventional silver halide grains, a quick processing property which is a feature of silver chlorobromide cannot be attained. However, when the silver halide grains having the "microscopically homogeneous" silver chloride distribution of this invention exists in the outermost layer, there is no disturbance action to the chemical sensitization and the merits of containing silver chloride are all attained, thereby silver chloride containing grains (e.g., silver chlorobromide grains and silver chloroiodobromide grains) showing a high development speed and a high fixing speed, which have never been attained by conventional silver chloride-containing grains, and having a high sensitivity, low fog, good graininess, and high sharpness can be obtained.

The reason why the surface of the silver halide grains having a heterogeneous silver chloride distribution disturbs the chemical sensitization thereof and the surface of the silver halide grains having the microscopically homogeneous silver chloride distribution does not disturb the chemical sensitization thereof is considered to be that since in the heterogeneous silver chloride distribution, the lattice constant on the surface of the grain crystals is not constant, the composition and the sizes of the chemical sensitizing nuclei formed thereon become varied, thereby the optimum chemical sensitization conditions cannot be obtained and on the other hand, in the case of the surface of silver halide grains having the microscopically homogeneous silver chloride distribution, the composition and the sizes of the chemical sensitization nuclei become uniform, thereby the optimum chemical sensitization can be performed. However, the real detailed reason must need further investigations.

Also, when silver halide containing silver chloride exists in the inside of the silver halide grain, the sensitivity thereof is increased if the phase is "microscopically homogeneous". That is, it is considered that if the distribution of silver chloride contained in the inside of silver halide grains is heterogeneous, the grains have many traps of electrons generated by light and the effective concentration of photoelectrons cannot be made. This matter also, however, needs further investigations.

Various means for increasing the sensitivity of silver chlorobromide grains (in particular, high silver chloride content) are proposed in JP-A-48-51627, JP-B-49-46932, JP-A-58-108533, JP-A-60-222845, JP-B-50-36978, JP-B-24772, U.S. Patent 4,471,050, and West German Patent Application (OLS) No. 3,229,999 as described above. In these techniques, by making the distribution of silver chloride in the silver chlorobromide grains (or silver chloroiodobromide grains) which becomes a host or core "microscopically homogeneous", silver halide grains having a higher sensitivity and showing lower fog than conventional silver halide grains having a heterogeneous silver chloride distribution can be obtained. Furthermore, in these techniques, it is necessary for obtaining silver halide grains having high sensitivity and forming low fog that the silver chloride distribution of the outside phase of that silver halide grains is "microscopically homogeneous" as described above. The reason that the microscopic homogeneity of the silver chloride distribution in the silver halide grains containing silver chloride is important is considered to be in that the electrons generated by light are liable to move as compared to the case of heterogeneity and the concentration principle of latent images can be effectively realized.

The total silver chloride content in the silver halide grain of this invention is preferably from 10 to 90 mol%, more preferably at least 20 mol%, and most preferably at least 30 mol%.

There is no particular restriction on the size of the silver halide grains having the completely homogeneous silver chloride distribution of this invention but the size thereof is preferably at least 0.3 µm, more preferably from 0.8 to 5 µm.

The form of the silver halide grains of this invention may be a regular crystal form (normal crystal grains) such as cubic, octahedral, dodecahedral, tetradecahedral, tetracosahedral (trisoctahedron, tetrahexahedron, icositetrahedron), hexatetracontahedral, etc., an irregular-crystal form such as spherical and potato-like, or various forms having at least one twin plane, in particular, tabular grains having parallel twin planes, e.g., hexagonal tabular grains and triangular tabular grains each having two or three twin planes.

Also, there is no particular restriction on the size of the tabular silver halide grains having the microscopically homogeneous silver chloride distribution of this invention but the size thereof is preferably from 0.5 to 5 µm and more preferably at least 1.0 µm, as the diameter of a circle corresponding to the mean projected area of the grains.

The size distribution of the tabular silver halide grains in this invention may be a mono-dispersion or a poly-dispersion but it is preferred that the silver halide grains are monodispersed grains in the form and the grain size. That is, the silver halide emulsion wherein the tabular silver halide grains having a hexagonal form with the ratio of the length of the longest side to the length of the shortest side of at most 2 and having two parallel planes as the outer surfaces account for at least 70% of the total projected area of the total silver halide grains, and further the hexagonal tabular silver halide grains are mono-dispersed grains, as described in JP-A-63-151618, is preferred in this invention. The term "monodispersed" grains or emulsion means that the coefficient of variation of the grain sizes is at most 20%, and preferably at most 15%.

The tabular grains of this invention are composed of parallel main surfaces each composed of a (111) plane and the aspect ratio thereof is at least 2, preferably from 3 to 20, and more preferably from 3 to 15. The grain sizes are at least 0.4 µm, and preferably from 0.4 to 4 µm.

The silver halide photographic emulsion of the present invention preferably contains the tabular silver halide grains accounting for at least 50 % of the total projected area of silver halide grains containd in the emulsion, the mean aspect ratio of the tabular silver halide grains being at least 3.

The mean aspect ratio (γ) in this invention is defined as follows:

$$\gamma = \left(\sum_{i=1}^{N} \frac{D_i}{t_i} \right) \Big/ N$$

In the above equation, when the tabular silver halide grains are oriented on a plane such that the two parallel main surfaces of the grain are parallel to the plane, D_i is the diameter of a circle having the same area as the projected area of the (i)th silver halide grain; t_i is the thickness of the (i)th grain in the direction perpendicular to the two parallel main surfaces; and N is a number of the tabular grains necessary and sufficient for giving a mean aspect ratio of silver halide grains and N is generally more than 600.

The tabular silver halide grains in the emulsion of the present invention preferably have the mean aspect ratio of from 3 to 20 and more preferably from 3 to 15.

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

The production process of the silver halide grains of this invention is composed of nuclear formation and grain growth.

1. Nuclear Formation

The silver halide grains which become nuclei of silver halide grains of this invention can be prepared by using the method described P. Glafkides, Chimie et Phisique Photographique (published by Paul Montel Co., 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, the emulsion composed of the silver halide grains can be prepared by an acid method, a neutralization method, an ammonia method, etc., and as a method of reacting a soluble silver salt and a soluble halide, a single jet method, a double jet method, or a combination of them may be employed.

A so-called reverse mixing method of forming silver halide grains in the existence of excessive silver ions can also be used. As one system of the double jet method, a so-called controlled double jet method of keeping a pAg constant in a liquid phase of forming silver halide grains can also be used. According to the method, a silver halide emulsion containing silver halide grains having a regular crystal form and substantially uniform grain sizes can be obtained.

A mixture of two or more kinds of silver halide emulsions each formed separately can be used.

At the preparation of the nuclei of silver halide grains, it is preferred that the halogen composition is constant, and a double jet method or a controlled double jet method is preferably employed.

The pAg at the preparation of the nuclei depends upon the reaction temperature and the kind of a silver halide solvent employed but is preferably from 5 to 10. Also, a silver halide solvent is preferably used and in this case, the time for forming silver halide grains can be shortened. For example, a conventional silver halide solvent such as ammonia, thioether, etc., can be used.

The form of the nuclei may be tabular, spherical, or twin system and also may be octahedral, cubic, tetradecahedral, or a mixed system of them.

Also, the nuclei may be a poly-dispersed or mono-dispersed system but is preferably a mono-dispersed system. The term "mono-dispersed" in the aforesaid case is same as defined hereinbefore.

Also, for obtaining silver halide grains having uniform grain sizes, it is preferred to quickly grow the silver halide grains but to an extent that the critical supersaturation is not attained, by using a method of changing the addition rates of an aqueous silver nitrate solution and an aqueous alkali halides solution according to the growing speed of the silver halide grains as described in British Patent 1,535,016 and JP-B-48-36890 and JP-B-52-16364 or a method of changing the concentrations of the aqueous solutions as described in U.S. Patent 4,242,445 and JP-A-55-158124.

Since in these methods, each silver halide grain is uniformly coated without causing regeneration of nuclei, they can also be preferably used in the case of forming coating layer as will be explained below.

The aforesaid nucleus formation is carried out by adding an aqueous silver salt solution and an aqueous halide solution to a reaction vessel containing an aqueous solution of a dispersion medium while fully stirring the dispersion medium.

In the nucleus formation step or the physical ripening step of silver halide grains, a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt or the complex salt thereof, a rhodium salt or the complex salt thereof, or an iron salt or the complex salt thereof may coexist.

2. Growing

After finishing the nucleus formation, an aqueous silver salt solution and an aqueous alkali halide solution are added to the reaction vessel for growing the nuclei thus formed such that new nuclei are not formed. In a conventional method, an aqueous silver salt solution and an aqueous halide solution are added to the reaction vessel with fully stirring. In this case, when silver halide grains of a single halogen composition (e.g., silver bromide and silver chloride) is grown, the silver halide phase is completely homogeneous and no microscopic heterogeneity is observed using a transmission type electron microscopy. In the case of a single halide composition, a heterogeneous growth of the silver halide grains cannot occur in principle and hence in the growth of pure silver bromide or pure silver chloride, there is not heterogeneity described above regardless of the preparation conditions. However, in the growth of silver halide having plural halide compositions (so-called mixed crystals), the heterogeneous growth in halide compositions becomes a serious problem. The heterogeneous distribution of silver chloride is clearly confirmed by a transmission type electron microscopy as described above already.

On the other hand, various investigation have been made for obtaining a homogeneous growth of silver halide grains. It is known that the growing speed of silver halide grains is greatly influenced by the silver ion concentration, halide concentration, and the equilibrium solubility in the reaction solution. Accordingly, if the concentrations (silver ion concentration and halide ion concentration) in the reaction solution are heterogeneous, it is considered that the growing speed differs by each concentration so that a heterogeneous growth occurs. For improving the deviation of the local concentration, various techniques are proposed in, for example, U.S. Patent 3,415,650, British Patent 1,323,464, and U.S. Patent 3,692,283. In these methods, a rotary cylindrical mixer with bulging sides, which has slits on the sides and is filled with an aqueous colloid solution (the mixer is preferably partitioned by a disc-like partition on into an upper chamber and a lower chamber) is equipped to a reaction vessel filled with an aqueous colloid solution such that the rotary shaft of the mixer becomes vertical, an aqueous halide solution and an aqueous silver salt solution are supplied into the mixer rotated at high speed through supply conduits from openings formed at the upper and lower parts of the mixer, respectively, to rapidly mixing them and cause the reaction (when the mixer is partitioned into two chamber by a disc-like partition, an aqueous halide solution and an aqueous silver salt solution separately supplied into the upper and lower chambers and each diluted with the aqueous colloid solution filling each chamber and rapidly mixed near the outlet slit of the mixer to cause the reaction of the components), and the silver halide grains formed are discharged through the slits into the aqueous colloid solution in the reaction vessel by the centrifugal force generated by the rotation of the mixer to grow silver halide grains. However, by these methods, the problem of causing the heterogeneity of the silver chloride distribution cannot be solved and the annular ring-form striped pattern showing the heterogeneous distribution of silver chloride is clearly observed by a cooling type transmission electron microscopy.

On the other hand, a technique of improving the local eviation of the concentration to prevent the occurrence of heterogeneous growth is disclosed in JP-B-55-10545. In the method, an aqueous halide solution and an aqueous silver salt solution are separately supplied to a mixer filled with an aqueous colloid solution, said mixer being equipped in a reaction vessel filled with an aqueous colloid solution, from the lower portions thereof through supply conduits, the reaction solutions are supplied and abruptly mixed by lower stirring blades (turbine blades) equipped to the mixer to grow silver halide grains, and the silver halide grains thus formed are immediately discharged into the aqueous colloid solution in the reaction vessel through upper outlet portion of the mixer by means of upper stirring blades equipped to the upper portion of the lower stirring blades. However, by the method, the problem of causing the heterogeneity of the silver chloride distribution cannot be solved either and the formation of the annular ring-form striped pattern showing the heterogeneous distribution of silver chloride is clearly confirmed.

As the result of various investigations, the inventor has been discovered that by adding silver ions and halide ions (chloride ions and bromide ions and/or iodide ions) in the form of fine silver halide grains instead of supplying as aqueous solutions to a reaction vessel in the growth of silver halide grains containing silver chloride, an annular ring-form striped pattern is completely vanished and the microscopically homogeneous silver chloride distribution is obtained. This cannot be attained by conventional techniques and the aforesaid technique for obtaining the microscopically homogeneous silver chloride distribution is an astonishing technique.

Practical methods are as follows.

(1) Method of adding a fine grain silver halide emulsion containing silver chloride, said emulsion being previously prepared.

A silver halide emulsion containing fine silver halide grains (silver chlorobromide grains, silver chloroiodobromide grains, or silver iodochloride grains) having the same silver chloride content as the silver chloride content of desired silver halide grains is previously prepared and the fine grain silver halide emulsion is supplied to the reaction vessel to grow tabular grains without supplying an aqueous silver salt solution and an aqueous halide solution to the reaction vessel.

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

A mixer having a strong and efficient stirring means is disposed outside the reaction vessel, an aqueous silver salt solution, an aqueous halide solution, and an aqueous protective colloid solution are supplied to the mixer followed by quickly mixing them to form very fine silver halide grains, and the fine grains are immediately supplied to the reaction vessel. In this case, an aqueous silver salt solution and an aqueous halide solution are not supplied to the reaction vessel as well as the method (1) described above.

U.S. Patent 2,146,938 discloses a method of forming a coarse grain silver halide emulsion by mixing fine silver halide grains having no absorbed materials with coarse silver halide grains having no adsorbed materials or by slowly adding a fine grain silver halide emulsion to a coarse grain silver halide emulsion. However, in the method, silver iodobromide only is formed.

In U.S. Patents 3,317,322 and 3,206,313, there is disclosed a method of preparing a silver halide emulsion having a high inside sensitivity by mixing an emulsion of chemically sensitized silver halide grains forming cores having a mean grain size of at least 0.8 µm with an emulsion of silver halide grains having a mean grain size of not more than 0.4 µm, said emulsion being not chemically sensitized, followed by ripening to form shell. These patents, however, relates to a silver bromide emulsion and a silver iodobromide emulsion having a low silver iodide content and are different from the present invention relating to silver halide grains containing silver chloride.

JP-A-58-111936 describes "In placing of introducing a silver salt and a halide in the form of aqueous solution thereof, a silver salt and a halide can be introduced in the form of fine silver halide grains suspended in a dispersion medium at the beginning or at the growing stage. The grain sizes are such that they are easily Ostwald ripening onto a larger grain nuclei which exist at the introduction of the fine grains to the reaction vessel. Silver bromide grains, silver chloride grains and/or mixed silver halide grains can be introduced." However, the aforesaid description is a general description about the growth of silver halide grains and does not teach the specific production process and specific embodiments necessary for preparing the microscopically homogeneous silver halide grains as defined in the present invention.

Then, each method is described in detail.

Re. Method (1):

In the method, silver halide grains becoming nuclei or core are previously placed in a reaction vessel containing an aqueous colloid solution and thereafter a previously prepared silver halide emulsion of fine grain sizes is added thereto, whereby the fine grains are dissolved by so-called Ostwald ripening and the dissolved grains are deposited on the nuclei or cores to grow silver halide grains. The halide composition of the fine grain emulsion has the same silver chloride content as the silver chloride content of the desired silver halide grains and is silver chlorobromide, silver chloroiodobromide, or silver iodochloride. The mean grain size is preferably not more than 0.1 µm, and more preferably from 0.001 to 0.06 µm.

In this invention, the dissolving rate of the fine silver halide grains is important and it is pre ferred to use a silver halide solvent for increasing the dissolving rate. As the silver halide solvent, there are water-soluble bromides, water-soluble chlorides, thiocyanates, ammonia, thioethers, thioureas, etc.

Specific examples of the silver halide solvent are thiocyanates described in U.S. Patents 2,222,264, 2,448,534 and 3,320,069, ammonia, thioether compounds described in U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439, and 4,276,347, thione compounds described in JP-A-53-144319, JP-A-53-82408, and JP-A-55-77737, amine compounds described in JP-A-54-100717, thiourea derivatives described in JP-A-55-2982, imidazoles described in JP-A-54-100717, and substituted mercaptotetrazoles described in JP-A-57-202531.

The temperature for growing silver halide grains is at least 50°, preferably at least 60°, and more preferably at least 70° C.

Also, the fine grain emulsion in the crystal growing may be added at a stretch or in divided portions but a method of supplying at a constant flow rate is preferred, and a method of increasing the addition rate is more preferred. In the latter case, the extent of increasing the addition rate is determined by the concentration of the co-existing colloid, the solubility of the silver halide crystals, the sizes of the fine silver halide grains, the extent of stirring of the reaction vessel, the size and the concentration of the silver halide crystals existing at the time, the hydrogen ion concentration (pH) of the aqueous solution in the reaction vessel, the silver ion concentration (pAg) of the aqueous solution, etc., but simply, the extent can be determined by an ordinary experimental method.

Re. Method (2):

As described above, in the crystal growing method of this invention, the silver ions and halide ions (including chlorine ions) necessary for growing the silver halide crystals are not supplied by the addition of the aqueous solutions thereof but these ions are supplied as fine silver halide grains and the Ostwald ripening is caused by utilizing the high solubility of the fine grains to perform the growth of silver halide grains. The rate-determining step of the system is not the growing step of the silver halide grains but is how fast the fine grains are dissolved to supply silver ions and halide ions in the reaction vessel. When the emulsion of the fine silver halide grains are previously prepared as in the method (1), the sizes of the fine grains are preferably as small as possible but, on the other hand, as the sizes of silver halide grains are smaller, the solubility thereof becomes higher, the silver halide grains become very unstable, and the grains themselves immediately cause Ostwald ripening to increase the grain sizes.

In T.H. James, The Theory of the Photographic Process, 4th edition, a Lippman emulsion cited as an emulsion of fine silver halide grains and is described therein that the mean grain size is 0.05 µm. It may be possible to obtain fine silver halide grains having a mean grain size of 0.05 µm or less, but even when such fine silver halide grains are obtained, they are unstable and the grain sizes are easily increased by Ostwald ripening. When adsorbable materials are adsorbed thereto, the occurrence of Ostwald ripening can be prevented to some extent but the dissolving rate of the fine grains is reduced by the adsorption, which is against the intension of this invention.

In this invention, this problem is solved by the following three techniques.

(a) After forming fine silver halide grains in a mixer, the fine grains are immediately added to a reaction vessel.

As described in the method (1), after previously forming fine silver halide grains to provide a fine grain silver halide emulsion, the fine grain emulsion is dissolved again and the dissolved fine grain emulsion is added to the reaction vessel containing silver halide grains becoming nuclei in the existence of a silver halide solvent to cause the growth of the silver halide grains. However, very fine silver halide grains once formed cause Ostwald ripening in the grain growing step, a washing step, a re dispersing step, and a re-dissolving step and the grain sizes are increased. On the other hand, in the present method, by disposing a mixer at a place very near the reaction vessel, shortening the residence time of the added solutions in the mixer, and immediately adding the fine silver halide grains formed to the reaction vessel, the occurrence of Ostwald ripening is prevented.

Practically, the residence time t of the solutions added to the mixer is shown by the following equiation;

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

V: Volume (ml) of the reaction chamber of the mixer.
a: Adding amount (ml/min.) of aqueous silver nitrate solution.
b: Adding amount (ml/min.) of aqueous halide solution.
c: Adding amount (ml/min.) of aqueous protective colloid solution.

In the production process of this invention, t is not longer than 10 minutes, preferably no longer than 5 minutes, more preferably not longer than 1 minute, and most preferably from 2 to 20 seconds.

The fine silver halide grains formed in the mixer are thus immediately added to the reaction vessel without increasing the grain sizes.

(b) Strong and efficient stirring is applied in the mixer.

In T.H. James, The Theory of the Photographic Process, page 93, there is described "Another mode with Ostwald ripening is coalescence. In coalescence ripening, crystals which are far apart from each other are directly brought into contact with each other and adhere to each other to form larger crystals, thereby the grain sizes suddenly change. Both the Ostwald ripening and the coalescence ripening occur not only after the end of deposition but also during deposition.". Coalescence ripening described above is liable to occur when the grain sizes are very small and in particular, is liable to occur when stirring is insufficient. In the extreme case, coarse massive grains are sometimes formed.

In this invention, since a closed type mixer as shown in Fig. 2 is used, the stirring blades in the reaction chamber thereof can be rotated at high rotation number, mixing by strong and efficient stirring, which has never been practiced by conventional open type reaction vessel (i.e., in an open type vessel, when stirring blades are rotated at high rotation number, the solution in the vessel is scattered away by the centrifugal force to cause foaming problem and hence such high stirring cannot be practiced), and thus the occurrence of the aforesaid coalescence ripening can be prevented, thereby fine grains having very fine grain sizes can be obtained. In this invention, the rotation number of the stirring blades is from 1,000 to 10,000 r.p.m., preferably at least 2000 r.p.m., and more preferably at least 3000 r.p.m.

(c) Introduction of an aqueous protective colloid solution into the mixer.

The occurrence of the aforesaid coalescence ripening can be remarkably prevented by the protective colloid for fine silver halide grains. In this invention, the addition of an aqueous protective colloid solution to the mixer is performed by the following method.

i) An aqueous protective colloid is singly added to the mixer.

The concentration of the protective colloid is from 0.2 to 10% by weight, and preferably from 0.5 to 5% by weight and the flow rate of the aqueous protective colloid solution is from 20 to 300%, preferably at least 50%, and more preferably at least 100% of the sum of the flow rate of an aqueous silver nitrate solution and an aqueous halide solution.

ii) A protective colloid is contained in an aqueous halide solution.

The concentration of the protective colloid in this case is from 0.2 to 10% by weight, and preferably from 0.5 to 5% by weight.

iii) A protective colloid is contained in an aqueous silver nitrate solution.

The concentration of the protective colloid is from 0.2 to 10% by weight, and preferably from 0.5 to 5% by weight. When gelatin is used as the protective colloid, gelatin silver is formed by silver ions and gelatin and gelatin silver causes photodecomposition and thermal decomposition to form silver colloid. Thus, it is better to mix the silver nitrate solution and the protective colloid solution directly before use.

The aforesaid methods i), ii), and iii) may be used solely or as combination thereof, or three methods may be used at the same time.

As the protective colloid for use in this invention, gelatin is usually used but other hydrophilic colloids can be used. Practical examples thereof are described in Research Disclosure, Vol. 176, No. 17643 (December, 1978), Paragraph IX.

The grain sizes of the fine silver halide grains obtained by the aforesaid techniques (a) to (c) can be confirmed by placing the grains on a mesh and measuring them by a transmission type electron microphotography of from 20,000 to 40,000 magnifications. The grain sizes of the fine silver halide grains of this invention are from 0.001 to 0.06 µm, preferably from 0.005 to 0.03 µm, and more preferably not more than 0.01 µm.

As described above, silver halide grains of very fine grain sizes having a high dissolving rate can be supplied to a reaction vessel and hence a high growing rate of silver halide grains contained in the reaction vessel can be obtained.

By using the aforesaid method of this invention, the use of a silver halide solvent is not inevitable in this invention but for obtaining far higher growing rate of the silver halide grains or for other purposes, a silver halide solvent may be, if necessary, used. The silver halide solvent is as described above in the method (1).

According to the method of this invention, the feeding rates of silver ions and halide ions to the reaction vessel can be freely controlled. These ions may be added to a constant rate but it is better to increasing the adding rate thereof. These methods are described in U.S. Patent 3,650,757 and JP-B-52-16364. Other methods are described in the method (1).

Furthermore, according to the method of this invention, the halogen composition during the growth of the silver halide grains can be freely controlled. For example, it is possible, during the growth of the silver halide grains, to keep the silver chloride content at a constant value, continuously increase or decrease the silver chloride content, or change the silver chloride content at a certain time.

The reaction temperature in the mixer is preferably from 0 to 60 °C, more preferably not higher than 50°C, and most preferably not higher than 40 °C. When the reaction temperature is lower than about 30°C, gelatin is usually liable to coagulate and hence in such a case, it is preferred to use gelatin having a low molecular weight (preferably 1,000 to 30,000 in number average molecular weight).

Low molecular weight gelatin which is used in the aforesaid case of this invention can be usually prepared as follows. Ordinary gelatin having an average molecular weight of about 100,000 is dissolved in water and a gelatin decomposing enzyme is added thereto to enzyme-decompose the gelatin molecules. The details of the method is described in R.J. Cox, Photographic Gelatin II, pages 233-251 and pages 335-346, Academic Press, London, 1976. In this case, since the bonded positions being decomposed by enzyme are definite positions, a low molecular weight gelatin having a relatively narrow molecular weight distribution is preferably obtained. In this case, the longer the enzyme decomposition time is, the lower the molecular weight becomes. In other method of obtaining low-molecular weight gelatin, high molecular weight gelatin is heated under the condition of low pH (pH 1 to 3) or high pH (pH 10 to 12) to hydrolyze the gelatin.

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

The production process for obtaining the tabular grains of this invention relates to the growth of tabular grains, and for the formation of nuclei, conventional technique is used.

The nuclei formation for tabular silver halide grains is composed of a tabular grain nucleus formation step and a ripening step. That is, as described in JP-A-63-151618, when tabular grain nuclei are formed, other fine grains (in particular, octahedral grains and single twin grains) are simultaneously formed and by further performing ripening, other grains than the tabular grain nuclei are vanished and nuclei only becoming tabular grains can be obtained. Accordingly, in the formation of tabular grains, the nucleus formation process includes a tabular grain nuclei forming process and a ripening process.

1. Nucleus formation:

As shown in JP-A-63-151618, the nuclear formation in the case that the nuclei are silver bromide or silver iodobromide is performed by adding an aqueous solution of a water-soluble silver salt and an aqueous solution of alkali halide(s) to an aqueous solution containing a dispersion medium while keeping pBr at from 1.0 to 2.5. A tabular silver halide grain has at least one parallel twin plane in the inside thereof and the formation of the twin plane(s) is the so-called nucleus formation process. Accordingly, the nucleus forming condition is determined by the frequency of forming the twin planes and depends upon various saturation factors (the temperature at the nucleus formation, the concentration of gelatin, the addition rates of an aqueous silver salt solution and an aqueous alkali halide solution, Br^- concentration, the rotation number of stirring, the iodine content of an aqueous alkali halide solution being added, the amount of a silver halide solvent, pH, concentration of inorganic salts, etc.), which are illustrated in the figure in JP-A-63-92942.

By controlling the nucleus forming conditions, the form of nucleus grains (the number of twin planes per grain) and the grain number (determining the grain sizes after growing) can be changed. In particular, when the nucleus formation is carried out at a temperature of from 15°C to 39°C and a gelatin concentration of from 0.05 to 1.6% by weight, nuclei having fine grains and a uniform grain size distribution can be formed.

In the case of performing the formation of nuclei for tabular silver chlorobromide grains, a silver salt, a chloride, and a bromide are simultaneously introduced into a reaction vessel containing an aqueous solution of a dispersion medium and in this case, the mol ratio of the chloride ion/bromide ion in the reaction vessel may be maintained at from 1.6/1 to 258/1 and the total concentration of the halogen ions in the reaction vessel may be maintained at from 0.10 to 0.90 normal as shown in JP-A-58-111936.

U.S. Patent 4,399,215 describes that tabular silver chlorobromide grains having a silver chloride content of at least 50 mol% or tabular silver chloride grains can be obtained by performing the grain formation using ammonia without containing silver bromide and silver iodide in the inside thereof, while keeping pAg at the range of from 6.5 to 10 and pH at the range of from 8 to 10.

U.S. Patent 4,400,463 describes that a tabular grain silver halide emulsion having a silver chloride content of at least 50 mol% is obtained by performing the grain formation in the co-existence of aminoazaindene and a peptizer having a thioether bond.

Also, U.S. Patent 4,713,323 describes that tabular grains of silver chloride or silver chlorobromide is obtained by using gelatin having a methionine content of not more than 30 µmol/g.

2. Ripening:

As shown in JP-A-58-151618, fine tabular grain nuclei are formed in the nucleus formation and at the same time a large number of other fine grains (in particular, octahedral grains and single twin grains) are formed. Thus, before entering the grain growing process, it is necessary to vanish other grains than the tabular grain nuclei to obtain the grains only becoming tabular grains. For enabling the aforesaid matter, ripening is performed. Practical method for ripening is described in JP-A-58-151618.

3. Grain Growth:

After finishing the nucleus formation, the same treatment as the grain growing in the aforesaid production of silver halide grains is performed and, thereby, tabular silver halide grains can be also grown.

Then, silver halide photographic materials using the silver halide emulsions of this invention are explained.

As the magenta couplers for use in this invention, there are oil-protect type indazolone series or cyanoacetyl series magenta couplers, preferably 5-pyrazolone series magenta couplers and pyrazoloazole series magenta couplers such as pyrazolotriazole series couplers. The 5-pyrazolone series couplers having an arylamino group or an acylamino group at the 3-position thereof are preferred from the viewpoint of the hue of the colored dyes and the coloring density. Typical examples thereof are described in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896, and 3,936,015. Preferred releasing groups for the 2-equivalent 5-pyrazolone series magenta couplers include nitrogen atom-releasing groups described in U.S. Patent 4,310,619 and arylthio groups described in U.S. Patent 4,351,897. Also, 5-pyrazolone series magenta couplers having a ballast group described in European Patent 73,636 given high coloring density.

Pyrazoloazole series magenta couplers include pyrazolobenzimidazoles described in U.S. Patent 2,369,879, preferably pyrazolo[5,1-c][1,2,4]triazoles described in U.S. Patent 3,725,067, pyrazolotetrazoles described in Research Disclosure, No. 24220 (June, 1984), and pyrazolopyrazoles described in Research Disclosure, No. 24230 (June, 1984). The aforesaid couplers may be polymer couplers.

From the viewpoints of less yellow side adsorption and high light fastness of colored dyes, imidazo[1,2-b]pyrazoles described in U.S. Patent 4,500,630 are preferred and pyrazolo[1,5-b][1,2,4]triazoles described in U.S. Patent 4,540,654 are particularly preferred.

Other examples of the magenta couplers which can be preferably used in this invention are pyrazolo triazole couplers having a branched alkyl group directly bonded to the 2-, 3-, or 6-position of the pyrazolotriazole ring as described in JP-A-61-65245, pyrazoloazole couplers having a sulfonamido group in the molecule as described in J P-A-61-65246, pyrazoloazole couplers having an alkoxyphenylsulfonamide ballast group as described in JP-A-61-147254, and pyrazolotriazole couplers having an alkoxy group or an aryloxy group at the 6-position as described in European Patent (unexamined published) Application 226,849.

It is preferred that the color couplers for use in this invention are non-diffusible by having a ballast group or by being polymerized. Also, 2-equivalent color couplers having a releasing group at the coupling active position can reduce the amount of coated silver as compared with 4-equivalent color coupler having a hydrogen atom at the coupling active position.

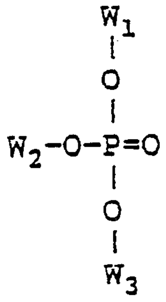
Typical examples of the yellow couplers for use in this invention are oil-protect type acylacetamide type cyan couplers. Specific examples thereof are described in U.S. Patents 2,240,710, 2,875,057, and 3,265,506.

In this invention 2-equivalent yellow couplers are preferably used and typical examples thereof are oxygen atom-releasing type yellow couplers described in U.S. Patents 3,408,194, 3,447,928, 3,933,501, 4,022,620, etc., and nitrogen atom-releasing type yellow couplers described in JP-B-58-10739, U.S. Patents 4,401,752 and 4,326,024, Research Disclosure, No. 18053 (April, 1979), British Patent 1,425,020, West German Patent Applications (OLS) Nos. 2,219,917, 2,261,361, 2,329,587, 2,433,812, etc. In these couplers, α-pivaloylacetanilide series yellow couplers are excellent in fastness, in particular, light fastness of the colored dyes formed, while α-benzoylacetanilide series yellow couplers give high coloring density.

Cyan couplers for use in this invention include oil-protect type naphtholic and phenolic couplers. The naphtholic cyan couplers include naphtholic couplers described in U.S. Patent 2,474,293 and, preferably oxygen atom-releasing type 2-equivalent naphtholic couplers described in U.S. Patents 4,052,212, 4,146,396, 4,228,233 and 4,296,200. Also, specific examples of the phenolic cyan couplers are described in U.S. Patents 2,369,929, 2,801,171, 2,772,162, and 2,895,826. Cyan couplers having high fastness to moisture and heat are preferably used in this invention, and typical examples thereof are the phenolic cyan couplers having an alkyl group of two or more carbon atoms at the meta-position of the phenol nucleus described in U.S. Patent 3,772,002, the 2,5-diacylamino substituted phenolic cyan couplers described in U.S. Patents 2,772,162, 3,758,308, 4,126,396, 4,334,011 and 4,327,173, West German Patent Application (OLS) No. 3,329,729, and JP-A-59-166956, and the phenolic cyan couplers having a phenylureido group at the 2-position and an acylamino group at the 5-position thereof described in U.S. Patents 3,446,622, 4,333,999, 4,451,559 and 4,427,767.

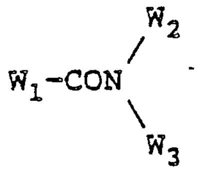
The magenta couplers and other color couplers for use in this invention can be introduced into silver halide emulsions by various dispersion methods. For example, a solid dispersion method, an alkali dispersion method, and preferably a polymer dispersion method or an oil-in-water dispersion method can be used. In the oil-in-water dispersion method, the coupler is dispersed in a high-boiling organic solvent and can be incorporated in a silver halide emulsion as the dispersion.

In the aforesaid case, the high-boiling organic solvent shown by following formula (A) to (E) can be preferably used in this invention:



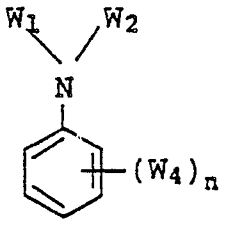
$$W_2-O-\overset{\displaystyle W_1-O}{\underset{\displaystyle O-W_3}{P}}=O \qquad (A)$$

W_1-COO-W_2 (B)



$$W_1\text{-CON}\begin{matrix} W_2 \\ W_3 \end{matrix}$$

(C)



(D)

W_1-O-W_2 (E)

In the above formulae, W_1, W_2, and W_3 each represents a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, aryl, or heterocyclic group; W_4 represents W_1, -OW_1 or -S-W_1; n represents an integer of from 1 to 5, when n is 2 or more, plural W_4s may be the same or different; and in formula (E), W_1 and W_2 may form a condensed ring.

The silver halide emulsions of this invention are usually chemically sensitized. For the chemical sensitization, a conventional method can be applied and the details thereof are described at line 18 of the left lower column to line 16 of the right lower column on page 12 of JP-A-62-215272.

Also, the silver halide emulsions of this invention are usually spectrally sensitized. For the spectral sensitization, ordinary methine dyes can be used and the details thereof are described, e.g., at line 3 up of the right upper column of page 22 to page 38 of JP-A-56-215272 and Attached sheet B of the Amendment dated March 16, 1987 of the JP-A-56-215272.

The silver halide photographic emulsions of this invention can contain various kinds of compounds for inhibiting the formation of for during the production, storage, and photographic processing of photographic light-sensitive materials or for stabilizing the photographic performance thereof. That is, there are many compounds known as antifoggants or stabilizers, e.g., azoles such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzo thiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (in particular, 1-phenyl-5-mercaptotetrazole, etc.), mercaptopyrimidines, mercaptotriazines, etc.; thioketo compounds such as oxazolinethione, etc.; azaindenes such as triazaindenes, tetraazaindenes (in particular, 4-hydroxy-substituted [1,3,3a,7]tetraazaindene), pentaazaindenes, etc.; benzenethiosulfonic acid, benzenesulfinic acid, and benzenesulfonic acid amide.

As the support for use in this invention, there are transparent supports such as polyethylene terephthalate films and cellulose triacetate films and reflective supports described below. In this invention, reflective supports are preferably used and examples thereof are barayta-coated papers, polyethylene-coatd papers, polypropylene series synthetic papers, vinyl chloride resin films containing a white pigment, transparent supports (e.g., glass plates, polyethylene terephthalate films, cellulose triacetate films, cellulose nitrate films, polyamide films, polycarbonate films, and polystyrene films) having thereon a reflective layer or containing therein reflective substances. They maybe properly selected according the purposes.

The color photographic light-sensitive material of this invention can further have a subbing layer, interlayers, protective layers, etc., in addition to the aforesaid emulsion layers.

As the protective colloid for the photographic emulsions of this invention, gelatin is advantageously used but other hydrophilic colloids can be used.

As gelatin, limed gelatin, acid-treated gelatin and deionized gelatin as well as enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, No. 16, 30(1966) can be used and also the hydrolyzed products and enzyme deposition products of gelatin can be also used.

The photographic light-sensitive materials of this invention may further contain hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives, ascorbic acid derivatives, etc., as color fog inhibitors and specific examples thereof are described in U.S. Patents 2,360,290, 2,336,327, 2,418,613, 2,675,314, 2,701,197, 2,704,713, 2,728,659, 2,732,300, and 2,735,765, JP-A-50-92988, JP-A-50-92989, JP-A-50-93928, JP-A-50-110337, and JP-A-52-146235, and JP-B-50-23813.

The color photographic light-sensitive materials of this invention can further contain, if necessary, various photographic additives such as stabilizers, antifoggants, surface active agents, couplers, filter dyes, irradiation inhibiting dyes, developing agents, etc.

Colored dyes are usually deteriorated by the actions of light, heat and humidity as well as are deteriorated and faded by fungi. Cyan images are particularly severely deteriorated by fungi and hence the use of antifungal agents is preferred. Specific examples of the antifungal agent are 2-thiazolylbenzimidazoles described in JP-A-57-157244. The antifungal agent may be incorporated in the photographic light-sensitive materials or may be added thereto from outside in photographic processing steps. That is, if an antifungal agent can exist in the photographic light-sensitive materials , the agent may be added in any optional step.

A color developer being used for developing the color photographic materials of this invention is preferably an alkaline aqueous solution containing an aromatic primary amino color developing agent. As the color developing agent, aminophenol series compounds are useful but p-phenylenediamine series compounds are preferably used. Specific examples thereof are 3-methyl-4 amino-N,N-diethylaniline, 3-methyl-4-amino-N- ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-β-methoxyethylaniline and the sulfates, hydrochlorides, or p-toluenesulfonates thereof. They may be used singly or as a combination of them.

The color developers generally contain pH buffers such as carbonates, borates or phosphates of an alkali metal and development inhibitors or antifoggants such as bromides, iodides, benzimidazoles, benzothiazoles, and mercapto compounds. Also, if necessary, the color developers may contain various preservatives such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazines, phenylsemicarbazides, triethanolamine, catecholsulfonic acids, triethylenediamine(1,4-diazobicyclo[2,2,2]octane)s; organic solvents such as ethylene glycol, polyethylene glycol, etc.; development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts, amines, etc.; dye forming couplers, competing couplers, fogging agents such as sodium boron hydride, etc.; auxiliary developing agents such as 1-phenyl-3-pyrazolidone, etc.; tackifiers; various chelating agents such as aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid, phosphonocarboxylic acid, etc. (for example, ethylenediaminetetraacetic acid, nitrilotri acetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylene phosphonic acid, ethylenediamine-N,N,N,N-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxy phenylacetic acid) and the salts thereof).

Also, in the case of applying reversal processing, a color development is ordinary applied after performing a black and white development.

For the black and white developer, known black and white developing agents such as dihydroxybenzenes (e.g., hydroquinone, etc.), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone, etc.), and minophenols (e.g., N-methyl-p-aminophenol, etc.), can be used solely or as a combination thereof.

The amount of the replenisher for the color developer or the black and white developer depends upon the kind of the color photographic light-sensitive material being processed but is generally less than about 3 liters per square meters of the light-sensitive material and also can be reduced below 500 ml by reducing the bromide ion concentration in the replenisher. In the case of reducing the amount of the replenisher, it is preferred to prevent the evaporation and air-oxidation of the liquid by reducing the open area of the processing tank. Also, by using a means of restraining the accumulation of bromide ions in the developer.

After color development, the photographic emulsion layers are usually bleached and the bleach process may be performed simultaneously with or separately from a fix process. Furthermore, for quickening the photographic processing, after the blix process, a bleach process may be employed. Also, before the blix process, a fix process may be employed.

As the bleaching agent, compounds of multivalent metals such as iron(III), cobalt(IV), chromium(IV), and copper(II), peracids, quinones, nitro compounds, etc., can be used. Typical examples of the bleaching agents are ferricyanides, bichromates, organic complex salts of iron(III) or cobalt(III), complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraretic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, glycol ether diaminetetraacetic acid, etc., or complex salts of citric acid, tartaric acid, malic acid, etc., persulfates, bromates, permanganates, nitrobenzenes, etc., can be used. In these compounds, aminopoly carboxylic acid iron(III) salts such as ethylenediaminetetraacetic acid iron(III) salt, etc., and persulfates are preferred from the viewpoints of quick processing and prevention of environmental pollution. Furthermore, aminopolycarboxylic acid iron(III) complex salt is particularly useful in both the bleach solution and monobath blix solution.

For the bleach solution, blix solution, or a pre-bath, a bleach accelerator can be, if necessary, used.

Specific examples of the useful bleach accelerator are the compounds having a mercapto group or a disulfide groups described in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53 28426, Research Disclosure, No. 17129 (July, 1978); thiazolidine derivatives described in JP-A-50-140129; thiourea derivatives described in JP-B-45-8506, JP-A-52-20832 and JP-A-53-32735, and U.S. Patent 3,706,561; iodides described in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds described in West German Patents 966,410 and 2,748,430; polyamine compounds described in JP-B-45-8836; other compounds described in JP-A-49-42434, JP-A-49-59644, JP-A-53- 94927, JP-A-54-35727, JP-A-55-26505, and JP-A-58-163940; and bromide ions.

Of these compounds, the compounds having a mercapto group or a disulfide group are preferred from the viewpoint of giving a large acceleration effect and the compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630 are particularly preferred.

Furthermore, the compounds described in U.S. Patent 4,552,834 are also preferred. These bleach accelerator may be incorporated in the photographic light-sensitive material.

As a fixing agent, there are thiosulfates, thiocyanates thioether series compounds, thioureas, and a large amount of iodide but the use of a thiosulfate is general and in particular, ammonium thiosulfate is most widely used.

As a preservative for a blix solution, sulfites, hydrogensulfites, or cabonyl-hydrogensulfite addition product are preferably used.

The silver halide color photographic materials of this invention are generally subjected to a wash step and/or a stabilization step after the de-silvering process. The amount of the wash water for the wash step can be selected in a wide range according to the characteristics of the light-sensitive materials (e.g., those by the materials used, such as couplers, etc.), the use thereof, the temperature of wash water, the number of wash tanks (stage number), the replenishing system such as a countercurrent system or regular system), and other various condition. In this case, the relation of the number of wash tanks and the amount of wash water in a multistage countercurrent system can be obtained by the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, 248-253(1955, May).

By the multistage countercurrent system described in the aforesaid literature, the amount of wash water can be greatly reduced but in this case, the increase of the residence time of water in the wash tanks causes the growth of bacteria and a problem that floats formed attach to the light-sensitive materials occurs. As a means for solving the problem in processing of the color photographic light-sensitive materials of this invention, a method of reducing calcium ions and magnesium ions described in JP-A-62-2888838 can be very efficiently used. Also, chlorine series antibacterial agents such as isothiazolone compounds described in JP-A-57-8542, cyabenzoazoles, chlorinated sodium isocyanularate, etc.; benzotriazole; and the antibacterial agents described in Hiroshi Horiguchi, Bookin Boobai Zai no Kagaku (Chemistry of Antibacterial and Antifungal Agents), Biseibutsu no Mekkin, Sakkin, Boobai Gijutsu (Antibacterial and Antifungal Techniques to Microorganisms), edited by Eisei Gijutsu Kai, and Bookin Boobai Zai Jiten (Antibacterial and Antifungal Agent Handbook), edited by Nippon Bookin Boobai Gakkai can be also used.

The pH of the wash water in the processing process of the photographic light-sensitive materials of this invention is from 4 to 9, and preferably from 5 to 8. The temperature of the wash water and the time for washing can be variously selected according to the characteristics and the uses of the light sensitive materials being processed but generally are from 20 seconds to 10 minutes at from 15 to 45°, and preferably from 30 seconds to 5 minutes at from 25 to 40° C.

Furthermore, for the photographic light-sensitive materials of this invention, a stabilization can be directly applied in place of the aforesaid wash. For such a stabilization, the methods described in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345 can be all employed.

Also, as the case may be, a stabilization process is applied after the aforesaid wash process. The stabilization bath may contain a chelating agent and an antifungal agent. The overflow liquid of wash water and/or the stabilization solution upon replenishment can be reused in the de-silvering steps and other steps.

The silver halide color photographic materials of this invention may contain a color developing agent for simplification and quickening of processing. For incorporating a color developing agent, it is preferred to use various precursors for color developing agents. Specific examples thereof are indoaniline compounds described in U.S. Patent 3,342,597, Schiff base type compounds described in U.S. Patent 3,342,599 and Research Disclosure No. 14850 and ibid., No. 15159, aldol compounds described ibid., No. 13924, metal complexes described in U.S. Patent 3,719,492, and urethane series compounds described in JP-A-53-135628.

The color photographic materials of this invention may contain, if necessary, various 1-phenyl-3-pyrazolidones for accelerating color development. Typical examples thereof are described in JP-A-56-

64339, JP-A-57-144547, and JP-A-58-115438.

The various processing solutions in this invention are used at temperature of from 10 to 50° C. Usually a temperature of from 33 to 38° C is standard but a higher temperature may be employed for accelerating processing and shortening the processing times or a lower temperature may be employed for improving the image quality and improving the stability of the processing solutions. Also, for saving silver of the light-sensitive materials, a processing process using a cobalt intensification or a hydrogen peroxide intensification described in West German patent 2,226,770 and U.S. Patent 3,674,499 may be employed.

If necessary, heaters, heat sensors, liquid level sensors, circulation pumps, filters, floating lids, squeezers, etc., may be equipped to various processing tanks.

As described above, according to this invention, there is provided a silver halide emulsion composed of silver halide grains having a mixed silver halide phase containing a silver chloride content having a microscopically homogeneous silver chloride distribution, having excellent characteristics in sensitivity, gradation, graininess, sharpness, resolving powder, covering power, storage stability, latent image stability, and pressure resistance, and showing high developing speed and fixing speed, thereby capable of performing quick processing.

Then, the invention is further explained by the following examples.

Example 1

Fine Grain Silver Chlorobromide Emulsion 1-A

To 1.3 liter of an aqueous solution of 2.3% by weight gelatin containing 0.01M of potassium bromide and 0.05M of sodium chloride were added 600 ml of an aqueous solution 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 over a period of 25 minutes. During the addition, the aqueous gelatin solution in the reaction vessel was kept at 35° C. Thereafter, the emulsion obtained was washed by an ordinary flocculation, 30 g of gelatin was dissolved therein, and then, the pH thereof was adjusted to 6.5. The mean grain size of the fine silver chlorobromide grains (silver chloride content 40 mol%) was 0.09 µm.

Octahedral Grain Silver Chlorobromide Emulsion 1-B

(Comparison Emulsion)

To 1.2 liter of an aqueous solution of 3.0% by weight gelatin containing 0.065M of potassium bromide and 0.3M of sodium chloride in a reaction vessel kept at 75° C was added 80 ml of an methanol solution of 0.1% 3,4-dimethyl-4-thiazoline-2-thione with stirring. Then, 50 ml of an aqueous solution of 0.3M of silver nitrate and 50 ml of an aqueous solution containing 0.18M of potassium bromide and 0.8M of sodium chloride were added thereto by a double jet method over a period of 3 minutes to complete the nuclear formation, whereby silver chlorobromide grains (silver chloride content 40 mol%) having a mean grain size of 0.3 µm were obtaind.

To the reaction vessel kept at 75 C, 800 ml of an aqueous solution containing 150 g of silver nitrate and 800 ml of an aqueous solution containing 63 g of potassium bromide and 43 g of sodium chloride were further added by a double jet method over 100 minutes.

Thereafter the resulting emulsion was cooled to 35° C, washed by an ordinary flocculation method, and after adding thereto 70 g of gelatin, the pH and pAg thereof were adjusted to 6.2 and 7.8, respectively. The grains formed were octahedral silver chlorobromide grains having a mean grain size of 1.5 µm and a silver chloride content of 40 mol%.

Octahedral Grain Silver Chlorobromide Emulsion 1-C

(The Invention)

After following the same procedure as the case of preparing Emulsion 1-B to provide a silver halide emulsion of silver chlorobromide grains having a mean grain size of 0.3 µm in a reaction vessel, the fine grain emulsion 1-A (having a silver chloride content of 40 mol%) dissolved at 75° C was added to the reaction vessel by a pump. The addition rate was such that the fine grain emulsion was added in an amount as calculated as silver nitrate of 150 g 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 as in the preparation of Emulsion 1 B and the pH and pAg thereof were adjusted to 6.5 and 7.8, respectively at 40° C.

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

Octahedral Grain Silver Chlorobromide Emulsion 1-D

(The Invention)

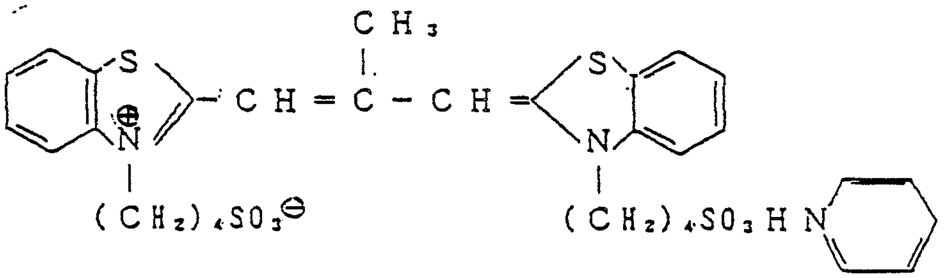
After following the same procedure as the case of the nucleus formation in Emulsion 1-B to provide a silver chlorobromide grains having a mean grain size of 0.3 µm, the growth of the feed crystals was performed as follows. As shown in Fig. 2, 800 ml of an aqueous solution containing 150 g of silver nitrate, 800 ml of an aqueous solution containing 63 g of potassium bromide and 43 g of sodium chloride, and 800 ml of an aqueous solution of 10% by weight gelatin were added to a mixer having strong and efficient stirring blades disposed near the reaction vessel by a triple jet method over a period of 100 minutes. The very fine grains (mean grain size of 0.02 µm) thus formed were immediately introduced into the reaction vessel continuously. During the step, the temperature of the mixer was kept at 25° C and the temperature of the reaction vessel was kept at 75° C.

Thereafter, the emulsion was washed with water as in Emulsion 1-B, and the pH and pAg thereof were adjusted to 6.5 and 7.8, respectively at 40° C.

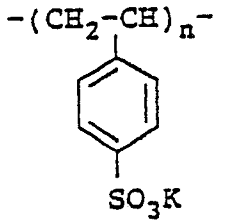
The grains thus obtained were octahedral silver chloride grains having a mean grain size of 1.5 µm and a silver chloride content of 40 mol%.

Then 150 mg/mol-Ag of Sensitizing Dye 1 shown below was added to each emulsion at 60° C and after 10 minutes, each of Emulsions 1-B, 1-C, and 1-D was most suitably chemically sensitized by sodium thiosulfate, potassium chloroaurate, and potassium thiocyanate.

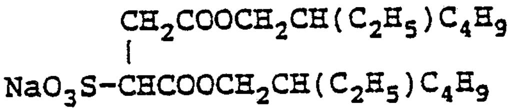
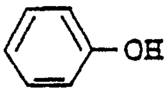
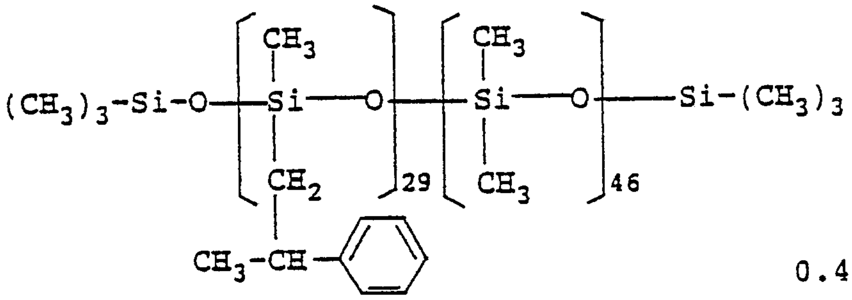
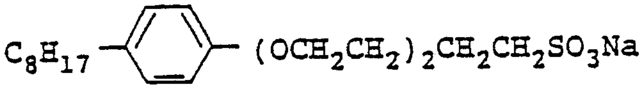
Sensitizing Dye 1:



Then, after dissolving 100 g of each of Emulsions 1-B, 1-C, and 1-D (each containing 0.08 mol of Ag) at 40° C, following component (1) to (3) were added thereto successively with stirring.

(1)	4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	3%	2 ml
(2)	$C_{17}H_{35}-O-(CH_2CHO)_{25}-H$	2%	2.2 ml
(3)	 n=ca.3000	2%	1.6 ml

Then, a coating composition for a surface protective layer was prepared by successively adding the following components (1) to (5) with stirring at 40° C.

(1)	Aqueous 14% gelatin solution		56.8 g
(2)	Polymethyl methacrylate fine particles (mean particle size 3.0 μm)		3.9 g
(3)	Emulsion:		
	Gelatin	10%	4.24 g
	 $NaO_3S-\underset{}{\overset{CH_2COOCH_2CH(C_2H_5)C_4H_9}{\overset{\vert}{C}}}HCOOCH_2CH(C_2H_5)C_4H_9$		10.6 mg
		72%	0.02 ml
			0.424 g
(4)	Water		68.8 ml
(5)		4.3%	3 ml

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

After applying a wedge exposure to the sample for 1/10 second at 200 lux by a light source of a color temperature of 2854° K, the sample was developed by following developer D-1 for 7 minutes at 20° C, fixed by the following fix solution F-1, washed, and dried.

[Developer D-1]	
Metol	2 g
Sodium sulfite	100 g
Hydroquinone	5 g
Borax·$5H_2O$	1.53 g
Water to make	1 liter
[Fix Solution F-1]	
Ammonium Thiosulfate	200.0 g
Sodium Sulfite (anhydrous)	20.0 g
Boric Acid	8.0 g
Ethylenediaminetetraacetic Acid Di-sodium	0.1 g
Aluminum Sulfate	15.0 g
Sulfuric Acid	2.0 g
Glacial Acetic Acid	22.0 g
Water to make	1 liter
(pH adjusted to 4.2)	

The results of the sensitometry are shown in Table 1.

Table 1

Emulsion	Relative Sensitivity	Fog
1-B	100	0.15
1-C	150	0.15
1-D	165	0.14
(*) Emulsion 1-B: Comparison Emulsion Emulsions 1-C and 1-D: Emulsion of the Invention		

As shown in Table 1, it can be seen that the emulsions of this invention show a high sensitivity as compared with the comparison emulsion.

EXAMPLE 2

Fine Grain Silver Chlorobromide Emulsion 2-A

To 1.2 liters of an aqueous solution of 1.5% by weight gelatin containing 0.01M of potassium bromide and 0.06M 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 0.6M of potassium bromide and 1.2M of sodium chloride with stirring well by a double jet method over a period of 20 minutes. During the additions, the solution in the vessel was kept at 35 °C.

Thereafter, the emulsion was washed by an ordinary flocculation method and after dissolving 20 g of gelatin in the emulsion, the pH thereof was adjusted to 6.5. The mean size of the fine silver chlorobromide grains (silver chloride content of 50 mol%) thus obtained was 0.08 µm.

Octahedral Silver Chlorobromide Emulsion 2-B

(Comparison Emulsion)

To 1.1 liters of an aqueous solution of 3.5% by weight gelatin containing 0.03M of potassium bromide was added 40 ml of a solution of 5% 3,6-dithioctane-1,8-diol with stirring, and then an aqueous solution containing 100 g of silver nitrate and an aqueous solution containing 70 g of potassium bromide were simultaneously added thereto by a double jet method at 70 °C to provide octahedral silver bromide grains having a mean grain size of 0.8 µm. Then, after lowering the temperature to 65 °C, 60 ml of an aqueous solution of 20% sodium chloride was added thereto using the above-prepared grains as cores and thereafter, an aqueous solution of 100 g of silver nitrate and an aqueous solution containing 35 g of potassium bromide and 22.2 g of sodium chloride were immediately added thereto by a double jet method over a period of 70 minutes.

Thereafter, the emulsion was cooled to 35 °C, washed by an ordinary flocculation method, and the pH and pAg thereof were adjusted to 6.2 and 8.1, respectively at 40 °C. The silver halide grains were octahedral grains having a mean grain size of 1.0 µm, wherein the core was silver bromide and the shell was silver chlorobromide containing 50 mol% silver chloride.

Octahedral Silver Chlorobromide Emulsion 2-C

(Emulsion of the Invention)

After forming octahedral silver bromide grains having a mean grain size of 0.8 µm by following the same procedure as the case of Emulsion 2-B, 60 ml of an aqueous solution of 20% sodium chloride was added thereto at 65 °C and the dissolved fine grain emulsion 2-A (silver chloride content of 50 mol%) was immediately added to the reaction vessel by a pump. The fine grain emulsion was added over a period of 70 minutes such that the amount thereof became 100 g as silver nitrate calculated. In this case, 5.0 g of sodium chloride was previously dissolved in the fine grain emulsion. The emulsion was washed as in the case of Emulsion 2-B and then the pH and pAg were adjusted to 6.2 and 8.1, respectively at 40 °C.

The grains formed were octahedral grains having a mean grain size of 1.0 µm, wherein the core was silver bromide and the shell was silver chlorobromide having a silver chloride content of 50 mol%.

Octahedral Silver Chlorobromide Emulsion 2-D

(Emulsion of the Invention)

The same procedure as the case of preparing Emulsion 2-C except the following matters was followed.

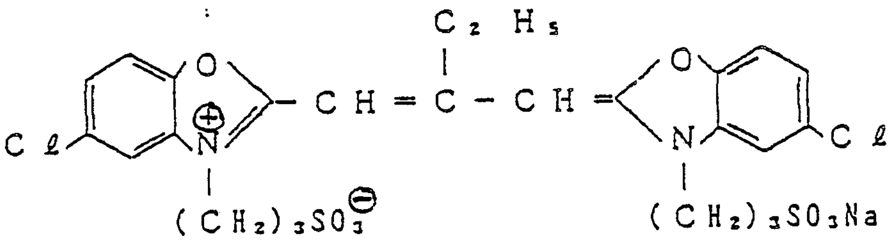
In this case, after forming the silver bromide cores, the grain growth was performed as follows. That is, an aqueous solution containing 100 g of silver nitrate, an aqueous solution containing 35 g of potassium bromide and 22.2 g of sodium chloride, and an aqueous solution of 3% by weight gelatin (bone gelatin, mean molecular weight 100,000) were added to a mixer having a strong and efficient stirring means disposed near the reaction vessel as shown in Fig. 2 by a triple jet method over a period of 70 minutes. The very fine grains (mean grain size 0.01 µm, silver chlorobromide containing a silver chloride content of 50 mol%) were immediately and continuously added to the reaction vessel containing the core grains from the mixer. The temperature of the mixer was kept at 25 °C. Thereafter, the emulsion formed was washed as in the case of Emulsion 2-C and the pH and pAg thereof were adjusted to 6.2 and 8.1, respectively at

40° C.

The grains obtained were octahedral grains having a mean grain size of 1.0 µm, wherein the core was silver bromide and the shell was silver chlorobromide containing 50 mol% silver chloride.

After most suitably sensitizing each of Emulsions 2-B, 2-C, and 2-D thus obtained with sodium thiosulfate, chloroauric acid, and potassium thiocyanate at 60° C, following Sensitizing Dye 2 was added such that the amount became 50 mg/mon-Ag.

Sensitizing Dye 2:



Thereafter, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added (in the case of Emulsion 2-C, the addition amount was adjusted so that the total addition amount became same as that of other emulsion) and then the emulsion was coated on a polyethylene phthalate film support at a silver coverage of 2 g/m^2.

After exposing each sample by a light source of 5400° K for 1/10 second using a filter cutting light of wavelength shorter than 500 n.m. (minus blue exposure), the sample was developed by Developer D-2 shown below (20° C, 4 minutes), fixed by Fix Solution F-1 used in Example 1, washed and dried.

[Developer D-2]	
1-Phenyl-3-pyrazolidone	0.5 g
Hydroquinone	20.0 g
Ethylenediaminetetraacetic Acid Di-sodium	2.0 g
Potassium Sulfite	60.0 g
Boric Acid	4.0 g
Potassium Carbonate	20.0 g
Sodium Bromide	5.0 g
Diethylene Glycol	30.0 g
Water to make	1 liter
(pH adjusted to 10.0)	

The results of sensitometry are shown in Table 2.

Table 1

Emulsion	Relative Sensitivity	Fog
2-B	100	0.07
2-C	150	0.07
2-D	160	0.07

EXAMPLE 3

Each of multilayer color photographic materials (Samples 301 to 303) having the layers of the following compositions on a cellulose triacetate film support having subbing layer was prepared.

Composition of Layers

The coating amount was shown by a g/m^2 unit of silver with respect to silver halide and colloid silver, by a g/m^2 unit with respect to coupler, additives, and gelatin, and a mol number per mol of silver halide in the same layer with respect to sensitizing dye. The chemical structures the chemical names of the compounds used are shown later.

Layer 1 : Antihalation layer	
Black Colloid Silver	0.2
Gelatin	1.3
Colored Coupler C-1	0.06
Ultraviolet Absorbent UV-1	0.1
Ultraviolet Absorbent UV-2	0.2
Dispersion Oil Oil-1	0.01
Dispersion Oil Oil-2	0.01

Layer 2 : Interlayer	
Fine Grain Silver Chloride (mean grain size 0.07 µm)	0.15
Gelatin	1.0
Colored Coupler C-2	0.02
Dispersion Oil Oil-1	0.1

Layer 3 : First Red-sensitive Emulsion Layer	
Emulsion (mean grain size 0.4 µm; AgBrCl (silver chloride 35 mol%))	1.0-silver
Sensitizing Dye I	1.5×10^{-4}
Sensitizing Dye II	3.5×10^{-4}
Sensitizing Dye III	1.5×10^{-5}
Coupler C-3	0.48
Coupler C-4	0.48
Coupler C-8	0.08
Coupler C-2	0.08
Dispersion Oil Oil-1	0.30
Dispersion Oil Oil-3	0.04

Layer 4 : Second Red-sensitive Emulsion Layer	
Emulsion (1) - shown in Table 3	1.0-silver
Gelatin	1.0
Sensitizing Dye I	1×10^{-4}
Sensitizing Dye II	3×10^{-4}
Sensitizing Dye III	1×10^{-5}
Coupler C-6	0.05
Coupler C-7	0.1
Dispersion Oil Oil-1	0.01
Dispersion Oil Oil-2	0.05

Layer 5 : Interlayer	
Gelatin	1.0
Compound Cpd-A	0.03
Dispersion Oil Oil-1	0.05

Layer 6 : First Green-sensitive Emulsion Layer	
Emulsion (mean grain size 0.4 µm; AgBrCl (silver chloride 35 mol%))	0.8-silver
Sensitizing Dye IV	5×10^{-4}
Sensitizing Dye V	2×10^{-4}
Coupler C-9	0.50
Coupler C-1	0.06
Coupler C-10	0.03
Coupler C-5	0.02
Dispersion Oil Oil-1	0.4

Layer 7 : Second Green-sensitive Emulsion Layer	
Emulsion (2) - shown in Table 3	0.85-silver
Gelatin	1.0
Sensitizing Dye IV	3.5×10^{-4}
Sensitizing Dye V	1.4×10^{-4}
Coupler C-11	0.01
Coupler C-12	0.03
Coupler C-13	0.20
Coupler C-1	0.02
Coupler C-15	0.02
Dispersion Oil Oil-1	0.20
Dispersion Oil Oil-2	0.05

Layer 8 : Yellow Filter Layer	
Gelatin	1.2
Yellow Colloid Silver	0.08
Compound Cpd-B	0.1
Dispersion Oil Oil-1	0.3

Layer 9 : First Blue-sensitive Emulsion Layer	
Emulsion (3) (mean grain size 0.4 µm; AgBrCl (silver chloride 45 mol%))	0.4-silver
Gelatin	1.0
Sensitizing Dye VI	2×10^{-4}
Coupler C-14	0.9
Coupler C-5	0.07
Dispersion Oil Oil-1	0.2

Layer 10 : Second Blue-sensitive Emulsion Layer	
Emulsion (3) - shown in Table 3	0.5-silver
Gelatin	0.6
Sensitizing Dye VI	1×10^{-4}
Coupler C-14	0.25
Dispersion Oil Oil-1	0.07

Layer 11 : First Protective Layer	
Gelatin	0.8
Ultraviolet Absorbent UV-1	0.1
Ultraviolet Absorbent UV-2	0.2
Dispersion Oil Oil-1	0.01
Dispersion Oil Oil-2	0.01

Layer 12 : Second Protective Layer	
Fine Grain Silver Chloride (mean grain size 0.7 µm)	0.5
Gelatin	0.45
Polymethyl Methacrylate Particles (diameter 1.5 µm)	0.2
Hardening Agent H-1	0.4
Formaldehyde scavenger S-1	0.5
Formaldehyde scavenger S-2	0.5

For each layer was further used a surface active agent in addition to the aforesaid components. Thus, Samples 301 to 303 were prepared.

Table 3

	Sample 301	Sample 302	Sample 303
Layer 4 [Emulsion (1)]	1-B	1-C	1-D
Layer 7 [Emulsion (2)]	1-B	1-C	1-D
Layer 10 [Emulsion (3)]	1-B	1-C	1-D

In addition, each emulsion was most suitably chemically sensitized for fitting each emulsion layer.

After applying light exposure to each sample using a tungsten light source the color temperature of which was adjusted to 4800° C by a filter for 1/100 second at 25 CMS, each sample was processed by the following process at 38° C.

Color Development	2 min. 15 sec.
Bleach	6 min. 30 sec.
Wash	2 min. 10 sec.
Fix	4 min. 20 sec.
Wash	3 min. 15 sec.
Stabilization	1 min. 05 sec.

The compositions of the processing solutions used for the process were as follows.

Color Developer	
Diethylenetriaminepenttaacetic Acid	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic Acid	2.0 g
Sodium Sulfite	4.0 g
Potassium Carbonate	30.0 g
Potassium Bromide	1.4 g
Hydroxylamine sulfate	2.4 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline Sulfate	4.5 g
Water to make	1.0 liter
pH	10.0

Bleach Solution	
Ethylenediaminetetraacetic Acid Ferric Ammonium Salt	100.0 g
Ethylenediaminetetraacetic Acid Di-sodium Salt	10.0 g
Ammonium Bromide	150.0 g
Ammonium Nitrate	10.0 g
Water to make	1.0 liter
pH	6.0

Fix Solution	
Ethylenediaminetetraacetic Acid Di-sodium Salt	1.0 g
Sodium Sulfite	4.0 g
Aqueous Solution of Ammonium Thiosulfate (70%)	175.0 ml
Sodium Hydrogensulfite	4.6 g
Water to make	1.0 liter
pH	6.6

Stabilization Solution	
Formalin (40%)	2.0 ml
Polyoxyethylene-p-monononyl phenyl ether (mean polymerization degree 10)	0.3 g
Water to make	1.0 liter

On each of the samples 301 to 303 thus processed, the densities were measured by red light, green light, and blue light. The results obtained are shown in Table 4. In the table, the relative sensitivity is shown by antilogarithm of the relative value of the exposure amount necessary for giving a density corresponding to [minimum density + 0.2].

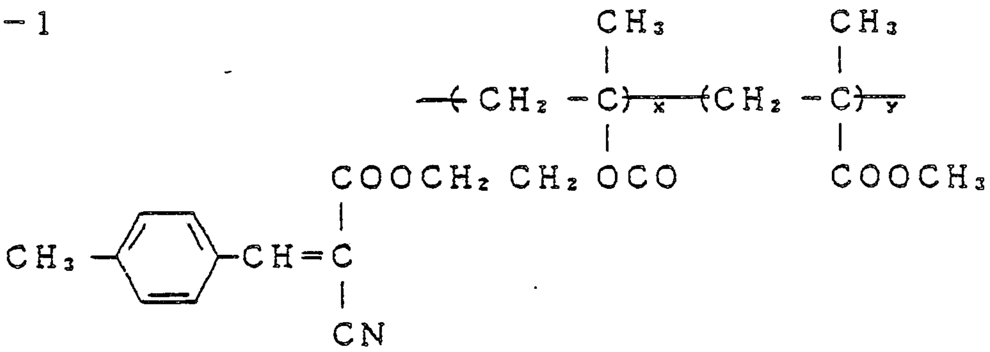
Table 4

Sample No.	Red-Sensitive Layer	Green-Sensitive Layer	Blue-Sensitive Layer
301	100	100	100
302	140	145	145
303	160	155	160
Sample 301: Comparison Sample Samples 302 and 303: Samples of the Invention			

As is clear from Table 4, the emulsions of this invention give remarkably high sensitivity as compared to the comparison emulsion.

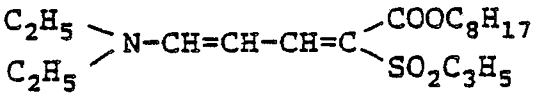
The compound used are shown below.

UV-1



x/y=7/3 (by weight ratio)

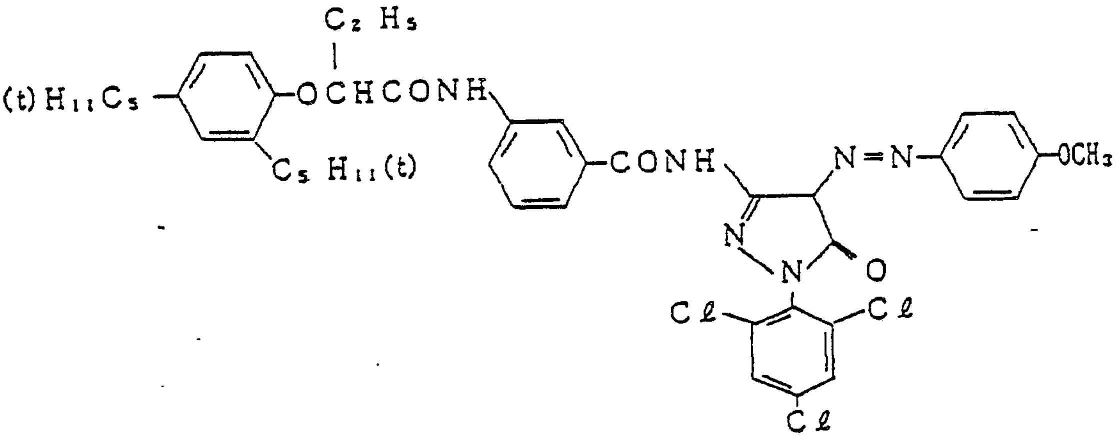
UV-2



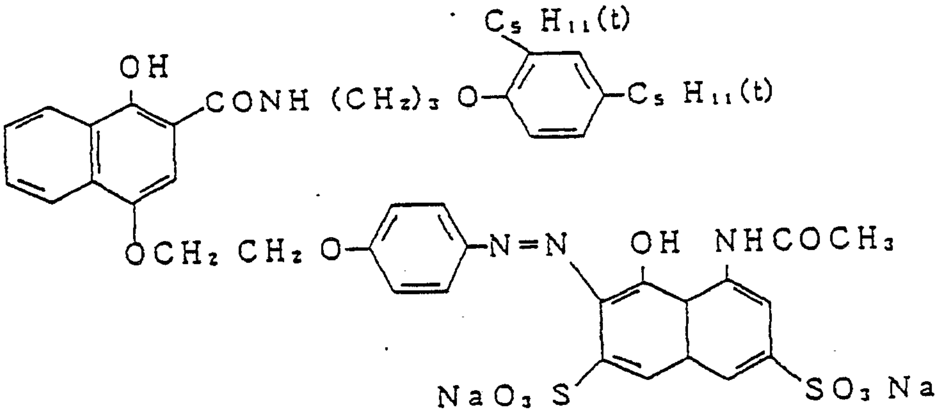
$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>N-CH=CH-CH=C<\begin{matrix}COOC_8H_{17}\\SO_2C_3H_5\end{matrix}$$

Oil-1 Tricresyl Phosphate
Oil-2 Dibutyl Phthalate
Oil-3 Bis(2-ethylhexyl) Phthalate

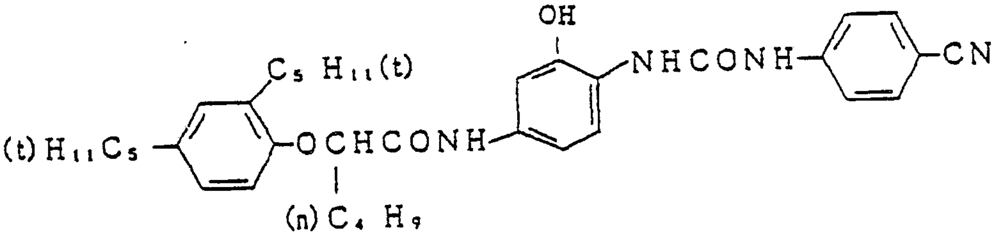
C－1



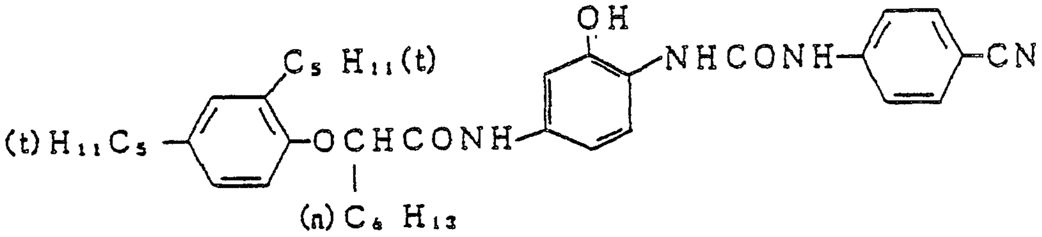
C－2



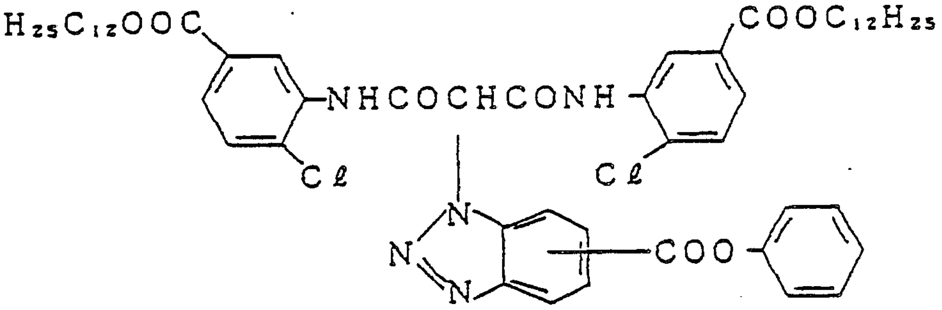
C－3



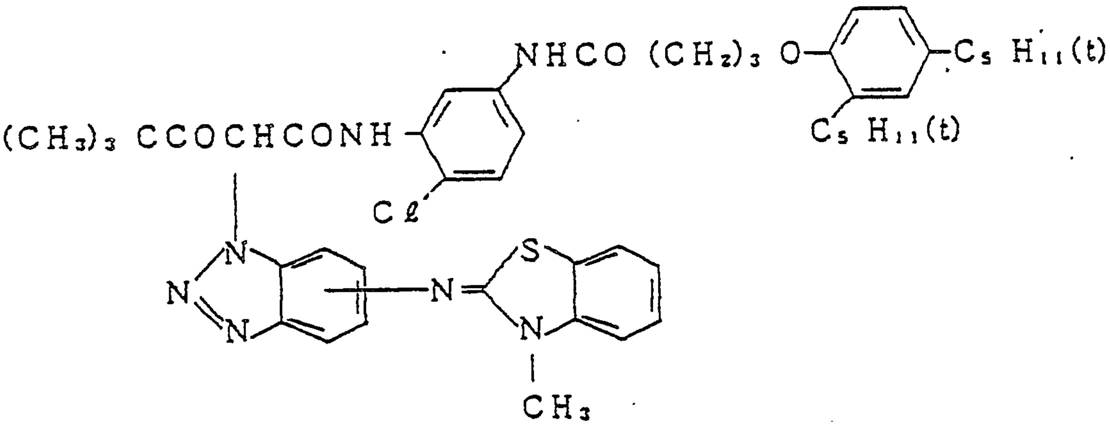
C-4



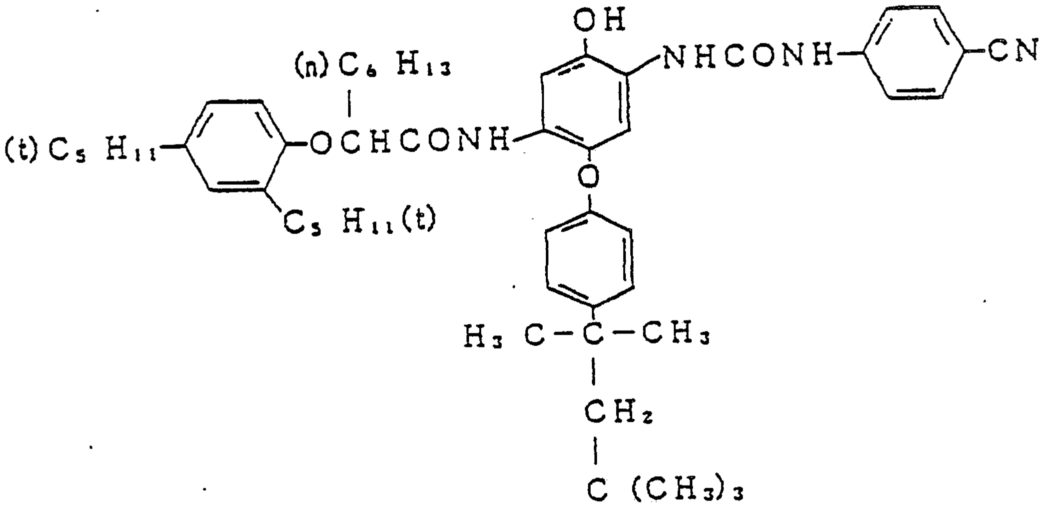
C-5



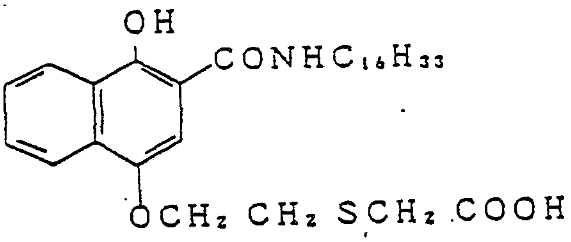
C-15



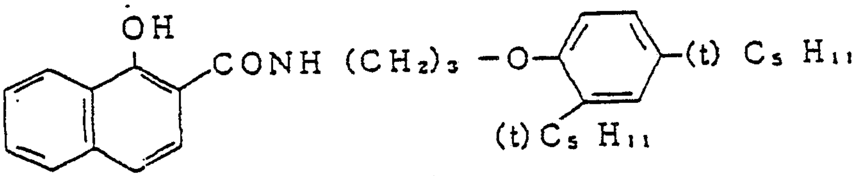
C－6



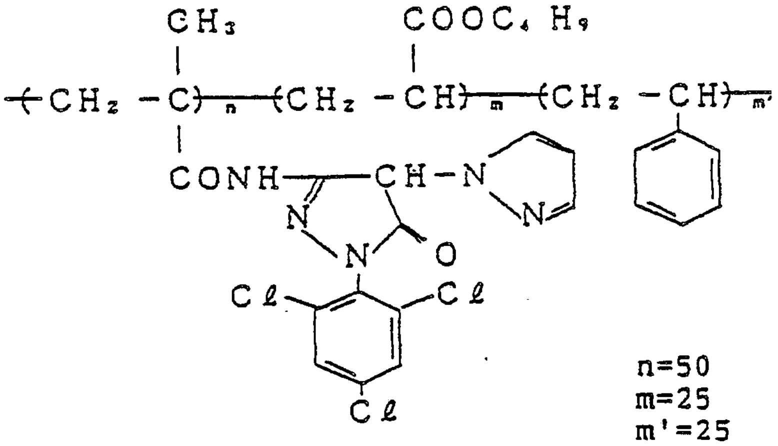
C－7



C－8

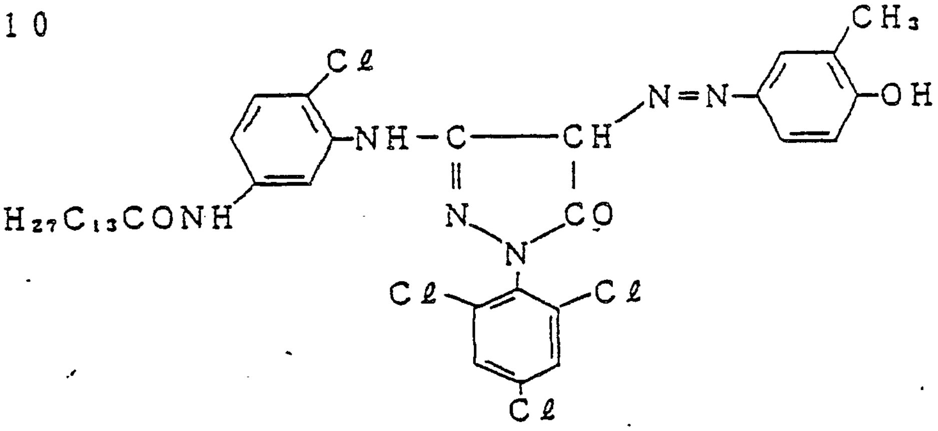


C-9

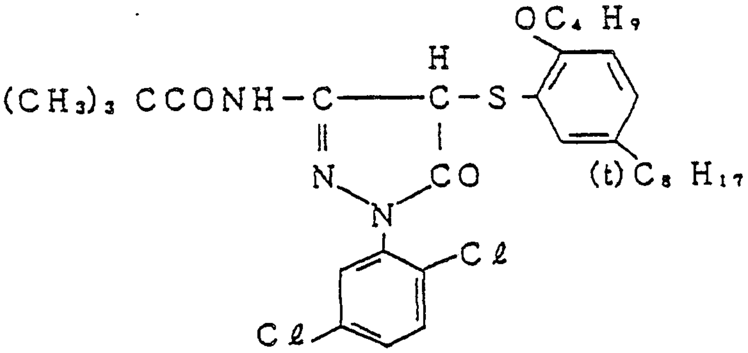


n=50
m=25
m'=25
mol.wt. about 20,000

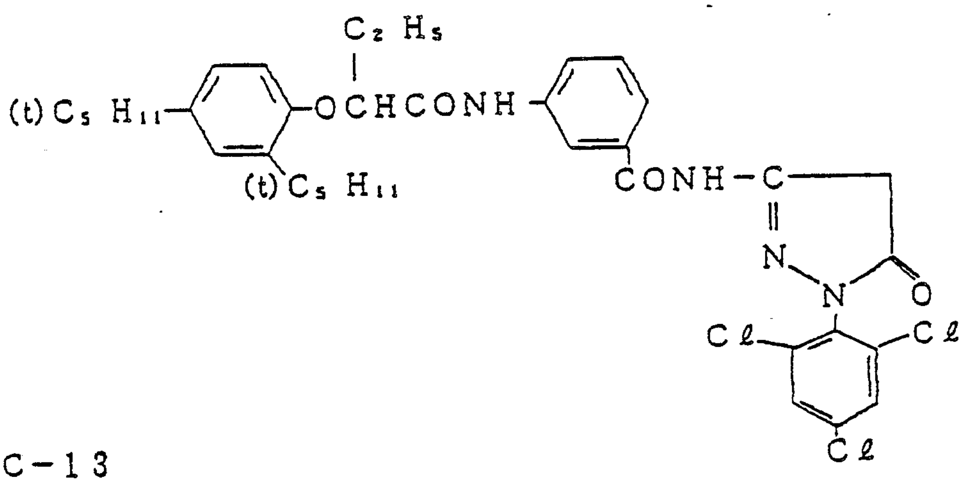
C-10



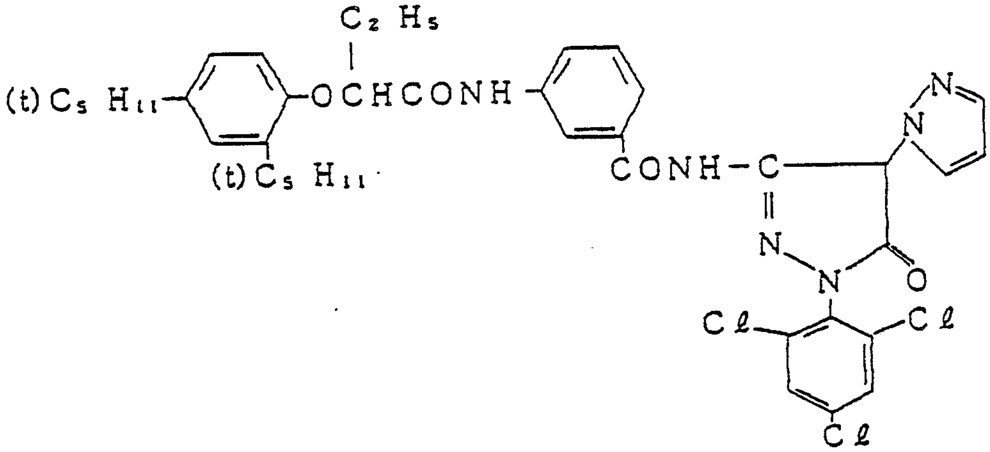
C-11



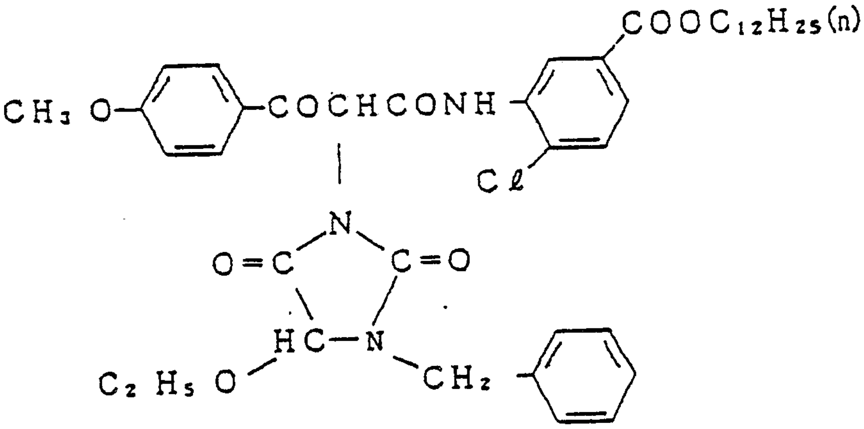
C－１２



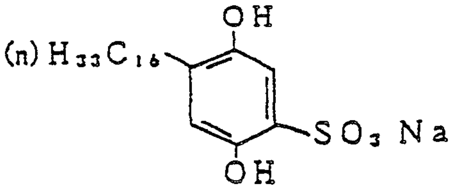
C－１３



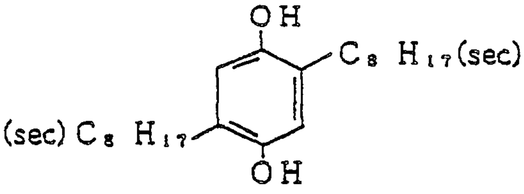
C－１４



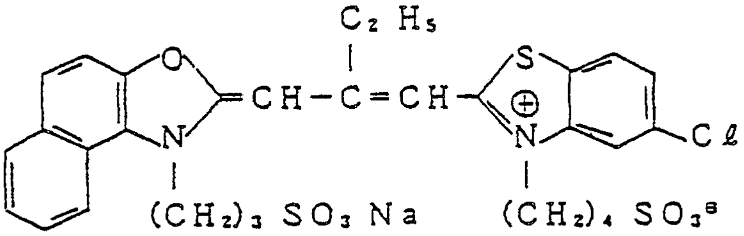
CpdA



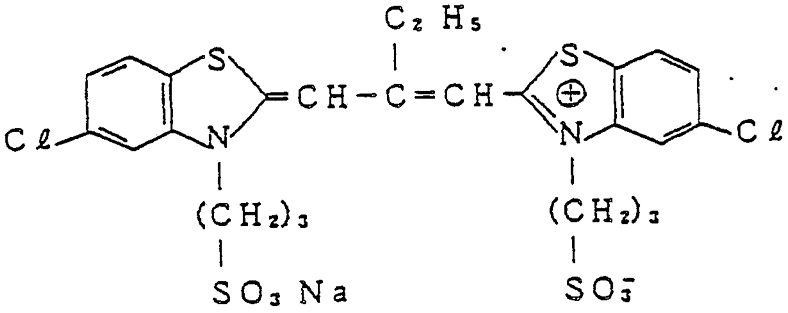
CpdB



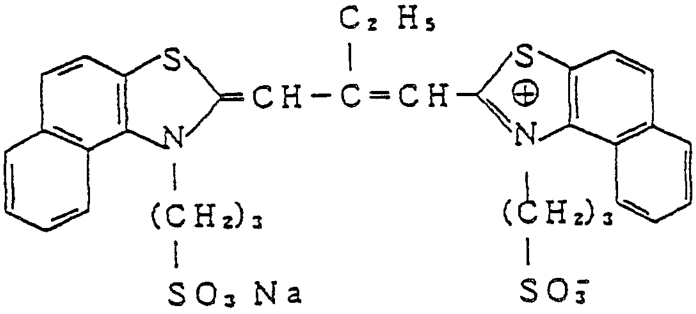
Sensitizing dye I



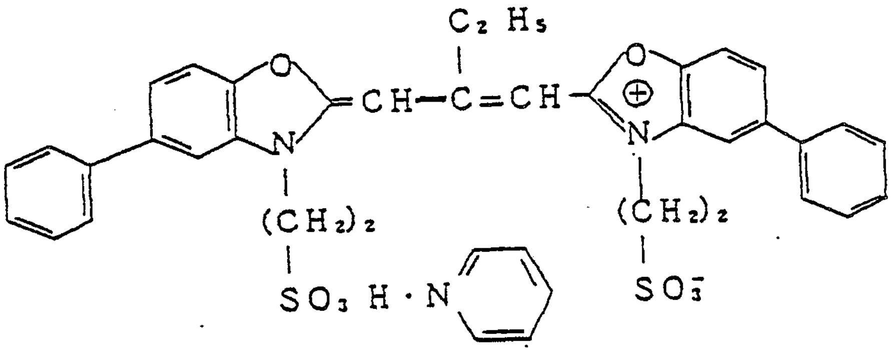
Sensitizing dye II



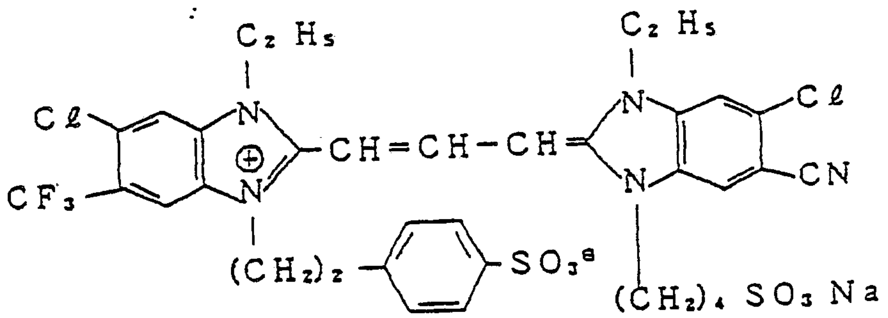
Sensitizing dye III



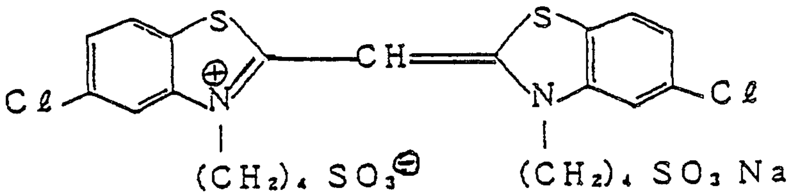
Sensitizing dye IV



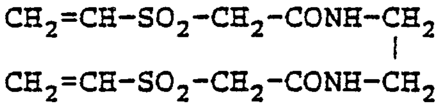
Sensitizing dye V



Sensitizing dye VI

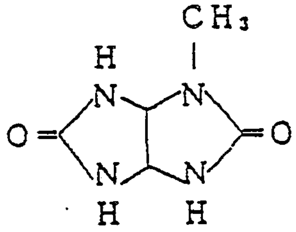


H-1

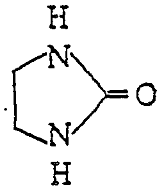


$$\begin{array}{r} CH_2=CH-SO_2-CH_2-CONH-CH_2 \\ | \\ CH_2=CH-SO_2-CH_2-CONH-CH_2 \end{array}$$

S-1



S-2



Example 4

Tabular Silver Bromide Nucleus Grains 4-A

To 1.3 liters of an aqueous solution of 0.8% by weight gelatin containing 0.08M of potassium bromide were added 150 ml of an aqueous solution of 2.0M of silver nitrate and 150 ml of an aqueous solution of 2.0M of potassium bromide with stirring by a double jet method. During the addition, the gelatin solution was kept at 30° C. Thereafter, the temperature of the emulsion was raised to 70° C and after adding thereto 30 g of gelatin, the silver halide grains were ripened for 30 minutes.

The tabular silver bromide grains for nuclei (hereinafter, is referred to as seed crystals) thus formed were washed by an ordinary flocculation method and the pH and pAg thereof were adjusted to 6.0 and 8.5, respectively at 40° C. The diameter of the circle corresponding to the mean projected area of the tabular grains obtained was 0.4 µm.

Tabular Grain Silver Chlorobromide Emulsion (Comparison Emulsion)

After dissolving 1/10 by weight of the aforesaid seed crystals in one liter of an aqueous solution of 3% by weight gelatin, the solution was kept at 75° C. Then, after adding thereto 30 ml of an aqueous solution of 20% sodium chloride and 0.5 g of 3,6-dithioctane-1,8-diol, an aqueous solution containing 150 g of silver nitrate and an aqueous solution containing 63 g of potassium bromide and 31 g of sodium chloride were immediately added thereto by a double jet method over a period of 100 minutes.

Thereafter, the emulsion was cooled to 35° C, washed by an ordinary flocculation method, and the pH and pAg thereof were adjusted to 6.5 and 8.0, respectively at 40° C. The grain obtained were tabular silver chlorobromide grains having a diameter of the circle corresponding to the mean projected area thereof of 2.0 µm and a mean thickness of 0.32 µm, wherein the outside of the core had 60 mol% silver bromide and 40 mol% silver chloride.

Tabular Silver Chlorobromide Emulsion 4-C (Emulsion of the Invention)

After dissolving 1/10 by weight of the seed crystal emulsion 4-A in one liter of an aqueous solution of 3% by weight gelatin, the solution was kept at 75° C. Thereafter, after adding thereto 30 ml of an aqueous solution of 20% sodium chloride and 0.5 g of 3,6-dithioctane-1,8-diol, the dissolved fine grain emulsion 1-A in Example 1 was immediately added thereto by a pump. In this case, the fine grain emulsion was added over a period of 100 minutes so that the amount became 150 g as silver nitrate calculated. In this case, 10.4 g of sodium chloride was previously dissolved in the fine grain emulsion. Thereafter, the emulsion was washed as in the case of Emulsion 4-B and the pH and pAg thereof were adjusted to 6.5 and 8.0, respectively at 40° C. The diameter of the circle corresponding to the mean projected area of the tabular grains was 2.1 µm and the thickness of the tabular grains was 0.31 µm.

Tabular Silver Chlorobromide Emulsion 4-D (Emulsion of the Invention)

The emulsion was prepared by following the same procedure as Emulsion 4-B except the following procedure.

That is, the grain growth was performed as follows. An aqueous solution containing 150 g of silver nitrate, an aqueous solution containing 63 g of potassium bromide and 31 g of sodium chloride, and an aqueous solution of 10% by weight low molecular weight gelatin (mean molecular weight of 10,000) were added to a mixer having strong and efficient stirring means disposed near the reaction vessel as shown in Fig. 2 by a triple jet method over a period of 100 minutes. The very fine grains formed in the mixer (mean grain size 0.02 µm) were immediately introduced into the reaction vessel containing seed crystals from the mixer. During the step, the mixer was kept at 27° C.

Thereafter, the emulsion was washed as in Emulsion 4-B and the pH and pAg thereof were adjusted to 6.5 and 8.0, respectively at 40° C. The diameter of the circle corresponding to the mean projected area of the tabular grains was 2.1 µm and the mean thickness of the grains was 0.32 µm.

Tabular Silver Chlorobromide Emulsion 4-E (Comparison Emulsion)

The emulsion was prepared by following the same procedure as Emulsion 4-B except that the addition of 3,6-dithioctane-1,8-diol was omitted.

The mean circle-corresponding diameter of the tabular grains formed was 2.3 µm and the mean thickness thereof was 0.27 µm.

Tabular Silver Chlorobromide Emulsion 4-F (Emulsion of the Invention)

The emulsion was prepared by following the same procedure as Emulsion 4-D except that the addition of 3,6-dithioctane-1,8-diol was omitted.

The mean circle-corresponding diameter of the tabular grains obtained was 2.2 µm and the mean thickness thereof was 0.27 µm.

Tabular Silver Chlorobromide Emulsion 4-G (Reference Example)

The same procedure as Emulsion 4-C except that the addition of 3,6-dithioctane-1,8-diol was omitted was followed.

In this case, the fine grains added were only partially dissolved and the fine grains left after finishing the addition thereof.

Each of Emulsions 4-B, 4-C, 4-D, 4-E, and 4-F thus obtained was sampled and the transmitted images thereof were observed by a transmission type electron microscope of 200 Kvolts in a state being cooled by liquid nitrogen. The results showed that in Emulsions 4-B and 4-E, a clear annular ring-like striped pattern (8 lines in 0.2 µm interval) was observed but in Emulsions 4-C, 4-D, and 4-F of this invention, no such striped pattern was observed. Thus it can be seen that in this invention, tabular silver chlorobromide emulsion having the microscopically homogeneous silver halide distribution was obtained.

The comparison of Emulsion 4-C with Emulsion 4-G shows that in the method of adding the previously prepared fine grain emulsion, the mean size of fine grains 1-A is 0.09 µm and for dissolving the grains, a silver halide solvent is necessary (in this case, the solvent is 3,6-dithioctane-1,8-diol). However, as shown in the example of Emulsion 4-F, in the method of using the mixer, the use of such a silver halide solvent is not required since the sizes of the fine grains are very fine, thereby an emulsion having small thickness of grains and hence having a high aspect ratio and a narrow grain size distribution is obtained. Thus, it can be easily understood that the aforesaid method can give the microscopically homogeneous silver chloride distribution and is an ideal growing method of tabular silver halide grains.

Then, after adding sodium thiosulfate, potassium chloroaurate, and potassium thiocyanate to each of the emulsion 4-B to 4-F (pH 6.5, pAg 8.0), the emulsion was most suitably chemically sensitized at 60° C. After finishing the chemical sensitization, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added to the emulsion, and the emulsion was coated on a polyethylene terephthalate film support at a silver coverage of 3 g/m^2.

Then, after exposing each sample to blue light using a tungsten light source of 2854°K and an interference filter of 419 nm for 1/10 second, the sample was developed and fixed as in Example 2 and then washed and dried.

The results of the sensitometry for the samples thus processed are shown in Table 5.

Table 5

Emulsion	Relative	Fog	Content
4-B	105	0.16	Comparison Emulsion*1
4-C	150	0.16	Emulsion of Invention*2
4-D	160	0.16	Emulsion of Invention*3
4-E	100	0.18	Comparison Emulsion*4
4-F	170	0.16	Emulsion of Invention*5

(*1): Silver halide solvent used.
(*2): Grain growth by the addition of fine grain emulsion.
(*3): Mixer used, silver halide solvent used.
(*4): Silver halide solvent not used.
(*5): Mixer used, silver halide solvent not used.

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

Example 5

Tabular Silver Bromide Core Emulsion 5-A

To one liter of an aqueous solution of 2% by weight gelatin containing 0.09M of potassium bromide were added 100 ml of an aqueous solution of 1.5M of silver nitrate and 100 ml of an aqueous solution of 1.5M of potassium bromide with stirring by a double jet method. During the addition, the reaction solutions were kept at 40° C. Thereafter, the temperature thereof was raised to 75° C and 40 g of gelatin was added thereto. Thereafter, the pBr thereof was adjusted to 2.5 by adding an aqueous solution of 1.0M silver nitrate and thereafter, an aqueous solution of 150 g of silver nitrate was added at an accelerated flow rate (the flow rate at the end thereof was 10 times that of the beginning) over a period of 60 minutes while simultaneously adding thereto an aqueous solution of potassium bromide by a double jet method such that pBr was kept at 2.5.

Thereafter, the emulsion was cooled to 35° C, washed with an ordinary flocculation method, and after adding thereto 60 g of gelatin and dissolving at 40° C, the pH and pAg thereof were adjusted to 6.5 and 8.7, respectively.

The tabular silver bromide grains formed were mono-dispersed tabular grains having a mean circle-corresponding diameter of 2.2 µm, a grain thickness of 0.18 µm and a variation coefficient of the circle-corresponding diameters of 18%.

Tabular Silver Chlorobromide Emulsion 5-B (Comparison Emulsion)

After dissolving Emulsion 5-A containing silver bromide corresponding to 100 g as silver nitrate in one liter of water, the temperature of the solution was raised to 70° C and after adding thereto 50 ml of an aqueous solution of 20% sodium chloride, an aqueous solution containing 50 g of silver nitrate and an aqueous solution containing 17.5 g of potassium bromide and 13 g of sodium chloride were immediately added thereto by a double jet method over a period of 100 minutes.

Thereafter, the emulsion was cooled to 35° C, washed by an ordinary flocculation method, and pH and pAg thereof were adjusted to 6.5 and 8.1 at 40° C.

The grains thus formed were tabular silver chlorobromide grains having a diameter of the circle corresponding to the mean projected area of 2.4 µm and the mean thickness of 0.22 µm, the outside of core being composed of 50 mol% silver bromide and 50 mol% silver chloride.

Tabular Silver Chlorobromide Emulsion 5-C (Emulsion of the Invention)

After dissolving Emulsion 2-A in Example 2 corresponding to 100 g as silver nitrate in one liter of water, the temperature of the solution was raised to 70° C. After adding thereto 50 ml of an aqueous solution of 20% by weight sodium chloride, fine grain emulsion 2-A dissolved at 40° C was immediately added thereto by a pump. The fine grain emulsion was added over a period of 100 minutes such that the amount thereof became 50 g as silver nitrate calculated. In this case, 4.4 g of sodium chloride was previously added to the fine grain emulsion. Thereafter, the emulsion was washed as in Emulsion 4-B and pH and pAg thereof were adjusted to 6.5 and 8.1, respectively, at 40° C.

The diameter of the circle corresponding to the mean projected area of the tabular grains was 2.3 µm and the mean thickness of the grains was 0.24 µm.

Tabular Silver Chlorobromide Emulsion 5-D (Emulsion of the Invention)

The emulsion was prepared by the same manner as Example 4-B except the following procedure.

That is, the grain growth was performed as follows. An aqueous solution containing 50 g of silver nitrate, an aqueous solution containing 35 g of potassium bromide and 13 g of sodium chloride, and an aqueous solution of 3% by weight of gelatin (bone gelatin, mean molecular weight 100,000) were added to a mixer having strong and efficient stirring means disposed near the reaction vessel as shown in Fig. 2 by a triple jet method over a period of 100 minutes.

The very fine grains (mean grain size 0.02 µm, silver bromide 50 mol%, silver chloride 50 mol%) formed in the mixer were immediately introduced into the reaction vessel containing seel grains from the mixer. The temperature of the mixer was kept at 25° C. Thereafter, the emulsion was washed as in Emulsion 4-B and the pH and pAg thereof were adjusted to 6.5 and 8.1, respectively. .

The diameter of the circle corresponding to the mean projected area of the tabular grains formed was 2.4 µm and the mean thickness thereof was 0.22 µm.

Each of the emulsions 5-B, 5-C, and 5-D thus obtained was sampled and the transmitted images were observed by a transmission type electron microscope of 200 Kvolts in a state being cooled by liquid nitrogen as in Example 4. There emulsions were clearly confirmed by the transmitted images of the grains that the core was composed of AgBr and the shell was composed of silver chlorobromide (silver content 50 mol%). In Emulsion 5-B, an annular ring-like striped pattern (8 lines in 0.2 µm interval) was clearly observed but in the grains of the emulsions 5-C and 5-D of this invention, the striped pattern was not observed and it can be seen that by the present invention, a tabular grain silver chlorobromide emulsion having the microscopically homogeneous silver chloride distribution was obtained.

Then, after most suitably chemically sensitizing each of the emulsions 5-B, 5-C, and 5-D with sodium thiosulfate, chloroauric acid, and potassium thiocyanate at 60° C, Sensitizing Dye 2 in Example 2 was added thereto at 200 mg/mol Ag.

Thereafter, after adding thereto 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (in the case of Emulsion 5-B, the addition amount was adjusted such that the total amount became same as the addition amount in other emulsion), the emulsion was coated on a polyethylene terephthalate film support at a silver coverage of 2 g/m^2.

After exposing each sample to a light source of 5400° K using a filter cutting light of wavelengths shorter than 500 nm (minus blue exposure) for 1/10 second, the sample was developed by Developer D-2 for 4 minutes at 20° C, fixed by aforesaid Fixing Solution F-1, washed and dried.

The results of the sensitometry are shown in Table 6.

Table 6

Emulsion	Relative Sensitivity	Fog
5-B	100	0.07
5-C	150	0.07
5-D	160	0.07
Emulsion 5-B: Comparison Emulsion Emulsions 5-C and 5-D: Emulsion of Invention		

As shown in the above table, it can be seen that the emulsions of this invention have a higher sensitivity than the comparison emulsion with same fog.

Example 6

Tabular Silver Chlorobromide Emulsion 6-A (Comparison Emulsion)

To 1.0 liter of an aqueous solution of 3% by weight gelatin containing 0.47M of potassium chloride and 0.01M of potassium bromide were added 13 ml of an aqueous solution of 2M of silver nitrate and 13 ml of an aqueous solution containing 1.7M of potassium bromide and 1.3M of potassium chloride with stirring by a double jet method over a period of 5 minutes. During the addition, the gelatin solution was kept at 55° C. After ripening the emulsion for 20 minutes as it was, the temperature thereof was raised to 70° C and 32 ml of an aqueous solution containing 2M of silver nitrate and 32 ml of an aqueous solution containing 1.2M of potassium bromide and 1.8M of potassium chloride by a double jet method over a period of 80 minutes.

Thereafter, the emulsion was cooled to 35° C, washed by an ordinary flocculation method, and after adding thereto 60 g of gelatin and dissolving at 40° C, the pH and pAg thereof were adjusted to 6.5 and 7.8, respectively.

The tabular silver chlorobromide grains were grains having a mean circular corresponding diameter of 2 µm and a mean grain thickness of 0.2 µm, wherein the silver chloride content of the core was 15 mol% and the silver chloride content of the shell was 40 mol%.

Tabular Silver Chlorobromide Emulsion 6-B (Emulsion of the Invention)

To 1.0 liter of an aqueous solution of 3% by weight gelatin containing 0.47M of potassium chloride and 0.001M of potassium bromide were added 13 ml of an aqueous solution of 2M of silver nitrate and 13 ml of an aqueous solution containing 1.7M of potassium bromide and 1.3M of potassium chloride with stirring by a double jet method over a period of 5 minutes. During the step, the gelatin solution was kept at 55° C. After ripening the emulsion as it was, the temperature was raised to 70° C and the fine grain silver chlorobromide emulsion 1-A (silver chloride content 40 mol%) in Example 1 was added thereto by a pump. The fine grain emulsion 1-A was added over a period of 80 minutes so that the amount became 109 g as silver nitrate calculated. In this case, 23.9 g of potassium chloride was previously added to the fine grain emulsion.

Thereafter, the emulsion was washed as in Emulsion 6-A and the pH and pAg thereof were adjusted to 6.5 and 7.8, respectively at 40° C. The diameter of the circle corresponding to the mean projected area of the tabular grains was 2.2 µm and the mean grain thickness was 0.3 µm.

Tabular Silver Chlorobromide Emulsion 6-C (Emulsion of the Invention)

The emulsion was prepared as in Example 6-B except the following procedure.

In this case, the grain growth was performed as follows. That is, 320 ml of an aqueous solution of 2M of silver nitrate, 320 ml of an aqueous solution containing 1.2M of potassium bromide and 1.8M of potassium chloride, and 500 ml of an aqueous solution of 10% by weight low molecular weight gelatin (mean molecular weight 5,000) were added to a mixer having strong and efficient stirring means disposed near the reaction vessel as shown in Fig. 2 by a triple jet method. The very fine grains (mean grain size 0.01 µm, silver bromide 60 mol%, silver chloride 40 mol%) formed in the mixer were immediately and continuously introduced into the reaction vessel containing seed grains from the mixer. The mixer was kept at 15° C.

Thereafter, the emulsion was washed as in Emulsion 4-A and the pH and pAg thereof were adjusted to 6.5 and 7, respectively. The diameter of the circle corresponding to the mean projected area of the tabular grains was 2.2 µm and the mean grain thickness was 0.3 µm.

Each of Emulsions 6-A, 6-B and 6-C thus obtained was sampled and the transmitted images thereof were observed by a transmission type electron microscope of 200 Kvolts in a state being cooled by liquid nitrogen. The results showed that in Emulsion 6-A, a clear annular ring-like striped pattern (6 lines in 0.2 µm interval) was observed but in Emulsions 6-B and 6-C of this invention, no such striped pattern was observed. Thus it can be seen that in this invention, tabular silver chlorobromide emulsion having the microscopically homogeneous silver halide distribution was obtained.

To each of the emulsions 6-A, 6-B, and 6-C thus obtained was added Sensitizing Dye 1 in Example 1 at 60° C at 250 mg/mol-Ag and after 10 minutes, the emulsion was most suitably chemically sensitized by the addition of sodium thiosulfate and potassium chloroaurate.

After finishing the chemical sensitization, the emulsion coating composition and the coating composition for protective layer were coated as in Example 1 to provide each sample. Each sample was exposed, developed, fixed, washed and dried as in Example 1.

The results of the sensitometry are shown in Table 7.

Table 7

Emulsion	Relative Sensitivity	Fog
6-A	100	0.10
6-B	160	0.08
6-C	180	0.07

Emulsion 6-A: Comparison Emulsion

Emulsions 6-B and 6-C: Emulsion of Invention

As shown in Table 7, the emulsions of this invention have remarkable high sensitivity and low fog as compared to the comparison emulsion. Furthermore, the emulsions of this invention had high gradation as compared with the comparison emulsion.

EXAMPLE 7

Multilayer color photographic materials (Samples 701 to 705) were prepared by following the same procedure as Example 3 except that Emulsions (1), (2), and (3) of Layers 4, 7, and 10 were changed as shown in Table 8.

Table 8

	Sample 701	Sample 702	Sample 703	Sample 704	Sample 705
Layer 4 (Emulsion 1)	4-B	4-D	6-A	6-B	6-C
Layer 7 (Emulsion 2)	4-B	4-D	6-A	6-B	6-C
Layer 10 (Emulsion 3)	4-B	4-D	6-A	6-B	6-C
Samples 701 and 703: Comparison samples Samples 702, 704, and 705:Samples of Invention					

In addition, each emulsion was most suitable chemically sensitized for meeting each emulsion layer.

Each of the sample was exposed and processed as in Example 3 and the densities were measured by red light, green light, and blue light. The results obtained are shown in Table 9.

Table 9

Sample No.	Red-Sensitive Layer	Green-Sensitive Layer	Blue-Sensitive Layer
701	100	100	100
702	130	135	140
703	80	85	80
704	110	120	120
705	120	135	130
Samples 701 and 703: Comparison Samples Samples 702, 704, and 705:Samples of Invention			

As is clear from the above result, the emulsions of this invention have high sensitivity as compared with the comparison emulsions.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide photographic emulsion comprising a dispersion medium and silver halide grains, wherein said silver halide grains contain at least one phase composed of two or more kinds of different silver halides and the phase contains at least 10 mol% silver chloride with microscopically homogeneous distribution.

2. The silver halide photographic emulsion of claim 1, wherein said silver halide grains include tabular grains accounting for at least 50% of the total projected area of said silver halide grains, the mean aspect ratio of the tabular grains being at least 3.

3. The silver halide photographic emulsion of claim 1, wherein said phase contains from 10 to 90 mol% of silver chloride.

4. The silver halide photographic emulsion of claim 3, wherein said phase contains from 20 to 80 mol%

of silver chloride.

5. The silver halide photographic emulsion of claim 1, wherein said phase is contained in the proportion of from 5 to 99 mol% of the silver halide grain.

6. The silver halide photographic emulsion of claim 5, wherein said phase is contained in the proportion of from 20 to 99 mol% of the silver halide grain.

7. The silver halide photographic emulsion of claim 1, wherein said silver halide grains are contained in the proportion of at least 40% based on the total silver halide grains in the emulsion.

8. The silver halide photographic emulsion of claim 1, wherein said phase is silver chlorobromide or silver iodochlorobromide.

9. The silver halide photographic emulsion of claim 1, wherein said silver halide grain is a tabular grain having at most 2 lines showing the microscopic silver chloride distribution within an interval of 0.2 µm in the direction of perpendiculary crossing the line in the transmitted image of the grain obtained by using a cooling type transmission election microscopy.

10. The silver halide photographic emulsion of claim 9, wherein said silver halide grain is a tabular grain having no line showing the microscope silver chloride distribution.

M 1721

F I G. 1

F I G. 2