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(54) PROCESS FOR PREPARING SILVER HALIDE EMULSION.

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Description

This invention relates to a light-sensitive silver halide photographic emulsion, more particularly to a method for sensitizing a silver halide emulsion including silver halide grains mainly comprising silver iodobromide, and a silver halide photographic emulsion sensitized by the aforementioned method.

Heretofore, as silver halides for photography, there has been utilized a variety of silver halides such as silver chloride, silver bromide, silver chlorobromide, silver iodobromide and silver chloroiodobromide, but as silver halides for high-sensitive photography, the silver iodobromide has been used to obtain high-sensitive emulsions.

In recent years, requirements for the silver halide emulsions for high-sensitive photography have been getting increasingly strict, and with regard to photographic performances such as high sensitivity, excellent graininess, high sharpness, low fog density and sufficiently high optical density, better performances are increasingly desired.

Further, the exhaustion of silver resources is now feared, and the development of a light-sensitive material low in silver content is strongly demanded. The above-mentioned requirements can almost be satisfied by preparing a high-sensitive silver halide emulsion with reduced photographic fog, though the above requirements are considered to be irrelevant to fogging. Therefore, it is no exaggeration to say that the development of a silver iodobromide silver halide emulsion which has little tendency to photographic fog but high sensitivity is the largest problem in the art.

The most orthodox method for obtaining photographic performances such as high sensitivity and low fog mentioned above is to improve the quantum efficiency of the silver halide. For this purpose, use is made of knowledge of, e.g., solid state physics. Researches, in which the quantum efficiency is calculated theoretically and the influence of grain size distribution is studied, are described, for example, on page 91 of "Interactions between Light and Materials for Photographic Applications" contributed in a preliminary text for lectures at Tokyo Symposium regarding the advancement of photography in 1980. According to the above research, it is predicted that preparing a monodispersed emulsion of a narrow grain size distribution would improve the quantum efficiency. Further, to establish a high sensitivity in a chemical sensitization process, i.e. in the sensitization of a silver halide emulsion while maintaining low photographic fog, the monodispersed emulsion can be theoretically presumed to be advantageous.

However, there are actually few examples in which a simple system or a mixture system of the monodispersed emulsions is employed, and examples of negative-type high sensitive emulsions are especially scarce. This is because it is extensively known in the art that even if the monodispersed emulsion is prepared in a usual manner and the normal chemical sensitization is tried, the sensitization cannot be achieved, and what is worse, give poorer results than in the case of a polydispersed emulsion such as is generally used.

To manufacture the monodispersed emulsion on an industrial scale, it is necessary to have strict control of pAg and pH, regulation of a theoretically determined feed rate of silver ions and halogen ions into a reaction system, and sufficient stirring, as decribed in Japanese Patent Provisional Publication No. 48521/1970. The silver halide emulsion manufactured under such conditions comprises the so-called regular crystal grains having faces (100) and faces (111) in various ratios, and these grains have any configuration of cube, octahedron and tetradecahedron.

On the other hand, in the technical field of manufacturing the emulsion grains, it has been known that since octahedral, tetradecahedral or platelike crystals having the faces (111) are usually prepared under conditions of low silver concentration, silver nuclei which will become latent nuclei or fog nuclei are advantageously small.

However, in the technical field of chemical sensitization, it has been also known that the chemical sensitization reaction depends greatly on crystal habit. For example, in a usual manner, sulphur sensitization nuclei are disadvantageously produced in larger quantities on the faces (111) than on the faces (100), therefore the latent image formed is scattered and efficiency is bad, which leads to a poor sensitization efficiency. Accordingly, it has been considered in the art that silver halide grains having (111) faces, as mentioned above, are disadvantageous and difficult to use in practice.

The characteristics of octahedral grains are described in, e.g., "Journal of Photographic Science", Volume 14, pages 181 to 184 (1966), and Volume 16, pages 102 to 113 (1968), "Photographische Korrespondenz), Volume 106, pages 149 to 160 (1970) and "Nippon Shashin Gakkai Journal", Volume 42, pages 112 to 121 (1979). It can be supposed from these reports that the chemical sensitization of the tetradecahedral grains is predominantly advanced on the faces (111), and that tetradecahedral grains are considered to have the same characteristics as in the octahedral grains. From our research it has been found that tetradecahedral grains have indeed similar properties to those of octahedral grains.

Further, a hydroxyazaindene compound is well known in the art, as a stabilizer for a photographic emulsion because it has the ability to inhibit chemical ripening by a sulphur-containing compound. Therefore, the azaindene compound has been used with the aim of terminating a sulphur sensitization reaction and/or preventing the occurrence of fog in the course of a manufacturing process, a storage step or a development processing. Also, it has been known that this compound increases photographic sensitivity. For example, U.K. Patent No. 1,315,755 describes that the inherent sensitivity of the silver halide is higher than by the conventional method, when in gold-sulphur sensitization of the silver halide emulsion,

the azaindene is added prior to the sulphur sensitization, and at the same time or subsequently a monovalent gold complex salt compound including sulphur is also added, followed by ripening. However, when the sensitization method without the azaindene is applied to the silver halide emulsion, a sufficient effect cannot be obtained.

Furthermore, JP—A—63914/1975 and DE—A—2,419,798 disclose that when a monodispersed silver halide cubic grain emulsion in which the molar percentage of silver bromide is 80% or more, is sulphur sensitized and the hydroxytetrazaindene compound is then added thereto, the sensitivity increases. However, these publications also describe that crystalline grains other than cubes, e.g. octahedral grains and platelike grains substantially surrounded with the faces (111) decrease rather than increase in sensitivity, or even if it increases, it is only a little.

Moreover, in JP—A—77223/1976 and U.S. Patent No. 4,078,937, it is disclosed that if the silver halide grains in a sulphur sensitized silver halide photographic emulsion have an average grain size of 0.5 μm or less, the sensitivity increases on condition that a particular hydroxytetrazaindene compound is added thereto.

Indeed, when a case where the hydroxytetrazaindene compound is added after the sulphur sensitization followed by coating, and a case where no compound is added followed by coating are compared with each other, the former case can sometimes provide the slightly larger sensitivity, as disclosed in the examples of the above-mentioned publications. However, it is now customary in the art to add the hydroxytetrazaindene compound as a stabilizer after chemical ripening, irrespective of the presence or recognition of its sensitization effect. Accordingly, it is not considered that Japanese Patent Provisional Publication No. 77223/1976 and U.S. Patent No. 4,078,937 intend to provide a new sensitization method for preparing the emulsion having a higher sensitivity than the conventional art.

A first object of this invention is to provide a method by which a monodispersed emulsion including silver halide grains of octahedral or tetrahedral crystals having faces (111) is noticeably sensitized, scarcely producing a photographic fog, and a second object of this invention is to provide a silver halide photographic emulsion having a high sensitivity obtained by such a chemical sensitization method.

The invention provides a method for preparing a silver halide emulsion which comprises subjecting the silver halide emulsion including core-shell type silver halide grains substantially composed of silver iodobromide to a gold-sulphur sensitization or gold-selenium sensitization by use of a gold sensitizer and sulphur or selenium sensitizer, characterized in that the silver halide grains are octahedral or tetradecahedral crystals each having faces (111); the coefficient of variation regarding a grain size distribution of the silver halide grains is 0.18 or less; and the sensitization is carried out in the presence of a nitrogen-containing heterocyclic compound capable of forming a complex with silver or a silver ion.

This invention is based on the discovery that when the silver halide grains contained in the silver halide emulsion are monodispersed core-shell type silver iodobromide grains comprising octahedral or tetradecahedral crystals each having (111) faces, and when the ratio between the selenium sensitizer and gold sensitizer or the ratio between the sulphur sensitizer and gold sensitizer is controlled in a certain range in the presence of the nitrogen-containing heterocyclic compound which forms the complex with silver in an amount sufficient to cover the grains, a noticeably high sensitization can be accomplished. This invention removes the disadvantage that when the known gold-sulphur sensitization or gold-selenium sensitization is used for the octahedral or tetradecahedral silver iodobromide grains, the silver sulphide nuclei are easily produced on the faces (111) and many light-sensitive nuclei are formed on one silver iodobromide grain, which fact prevents the increase in the quantum efficiency. In other words, the effect of this invention can be procured by constituting the silver iodobromide grains in the form of the core-shell type in the monodispersed emulsion, and intentionally controlling a light-sensitive nucleus-forming reaction on the (111) faces in the presence of the nitrogen-containing heterocyclic compound capable of producing the complex with silver or a silver ion. When cubic crystals are used in place of the octahedral or tetradecahedral crystals in the present invention, the effect of this invention cannot be obtained, because the cubic silver halide grains allow light-sensitive nuclei to be more easily and selectively formed on the vertices of each cube than on the faces (100) thereof.

When the method of this invention is applied to a monodispersed octahedral or tetradecahedral silver iodobromide emulsion which is not of the core-shell type, the effect of the sensitization is not so great. Further, when the core-shell type monodispersed octahedral or tetradecahedral silver iodobromide emulsion is gold-sulphur sensitized or gold-selenium sensitized in the absence of any nitrogen-containing heterocyclic compound, the effect of the sensitization is also small.

If iodine is added to the silver bromide grains, the quantum efficiency will increase and the gold-sulphur sensitization or gold-selenium sensitization will also increase, but due to the added iodine, lattice defects increase and thus the number of silver ions between lattices also increase. Further, the iodine atoms which are present on the surfaces of the crystals serve to restrain the gold-sulphur sensitization or gold-selenium sensitization reaction.

The fact that a conventional monidispersed octahedral or tetradecahedral silver iodobromide emulsion does not increase its sensitivity much even upon gold-sulphur sensitization or gold-selenium sensitization, according to the estimation of the inventors of this invention, is attributable to the formation of many light-sensitive nuclei on the (111) faces due to the aforesaid crystal habit dependency of the chemical sensitization reaction in the case of octahedral and tetradecahedral silver halide grains. When the nitrogen-

containing heterocyclic compound is not present, the influence of the iodine atoms, on the surfaces, during chemical sensitization can be weakened by using core-shell grains to reduce the content of the silver iodide on the faces, but use of these grains is not effective against the increase in the lattice defects and the augmentation in the silver ions between the lattices and cannot control the crystal habit dependency of the chemical sensitization reaction. It is supposed that the nitrogen-containing heterocyclic compound serves to reduce the amount of the silver ions between the lattices to a level necessary for the chemical sensitization reaction by forming a complex with the silver ion on the surfaces thereby controlling the chemical sensitization reaction so that effective light-sensitive nuclei may be produced in a small amount, but the compound cannot prevent the restraining effect on the chemical sensitization reaction by the iodine atoms on the surfaces. As seen from the foregoing, when the core-shell type octahedral or tetradecahedral silver iodobromide emulsion is gold-sulphur sensitized or gold-selenium sensitized in the presence of a nitrogen-containing heterocyclic compound, good results can be expected, and the degree of sensitization obtained is more remarkable than anticipated, because of a synergistic effect which could not be predicted.

A feature of this invention is that the reaction of forming the nuclei for the chemical sensitization is controlled by taking the above-mentioned technical constitution and the combination effect of the gold-sulphur or gold-selenium sensitization is obtained more remarkably than in the conventional one. In contrast, according to the sensitization method disclosed in JP—A—63914/1975 and DE—A—2,419,798, the nitrogen-containing heterocyclic compound is added at the end of the sulphur sensitization in order to control silver ions on and near the surfaces of the silver halide grains and to thereby improve the efficiency of latent image formation. Therefore, this invention is different from these in technique.

Further, JP—A—77223/1976 and U.S. Patent No. 4,078,937 disclose a method in which a specific hydroxytetrazaindene compound is added to an emulsion of a sulphur sensitized silver halide the average grain size of which is not in excess of 0.5 μm, in order to increase the sensitivity of the silver halide emulsion. However, the above publications disclose neither the particular combination of features nor the effects of this invention anywhere, and, in all the examples of the publications, the hydroxytetrazaindene compound is added after chemical ripening. Probably for this reason, the effect of the sensitization by the above method depends on the average grain size, and the particular crystal habit of the silver halide grains is not selected. Accordingly, the inventions disclosed in these publications are different from this invention in technique.

US—A—3,317,322 discloses the use of core-shell type grains in silver halide emulsions. The specification of U.K. Patent No. 1,315,755 discloses a method in which after the azaindene compound has been added, a monovalent gold complex salt compound including sulphur is added to carry out a gold-sulphur sensitization, but it does not refer to the crystal structure of the silver halide grains, the core-shell structure or the like anywhere. Therefore, this invention is not anticipated by the instant literature.

With regard to the silver halide grains of octahedral or tetradecahedral crystals used in this invention, the silver halide composition preferably comprises substantially silver iodobromide including 0.5 to 15 mol% of silver iodide, but it may include silver chloride in an amount that the object of the invention is still achieved.

The morphology of the silver halide grains is octahedral substantially formed with faces (111), or tetradecahedral formed with the faces (111) and faces (100). There is no limit to the diameters of these grains.

On the surfaces of the tetradecahedral silver halide grains used in this invention, the ratio between the faces (111) and faces (100) is not limited to a specific range, but the percentage of the faces (111) is generally at least 5% of the whole surface area of the grains. The greater the percentage of (111) faces, the greater the sensitization effect according to the method of this invention, and so the percentage of the faces (111) is preferably 40% or more. Also, with regard to the emulsion, the greater the percentage of silver halide grains with the required features of the whole silver halide grains contained in the emulsion, the greater the effect of this invention. Therefore, the percentage of the silver halide grains with the required features is preferably 50% or more, more preferably 70% or more. The emulsion in which the silver halide grains substantially comprise the silver halide grains with the required features is most preferred.

In this invention, a so-called monodispersed emulsion is employed in which coefficient of variation of the grain size distribution of the silver halide grains contained in the silver halide emulsion is 0.18 or less.

The method is based on the concept that gold-selenium sensitization or gold-sulphur sensitization is controlled by covering the silver halide surfaces with the nitrogen-containing heterocyclic compound capable of forming a complex with silver or a silver ion, but it seems that when a polydispersed emulsion is used, the distribution of a grain surface area is large, and it is thus difficult to efficiently cover the grain surfaces.

The uniformity of the size of the silver halide grains included in the silver halide emulsion can be represented by a value obtained by dividing the standard deviation S of a grain size distribution by the average grain size (diameter) $\bar{r}$, i.e. the coefficient of variation of the grain diameter distribution, as shown by the following formula (1):

$$\text{Coefficient of varation} = \frac{S}{\bar{r}} \qquad (1)$$

$$S = \sqrt{\frac{\Sigma(\bar{r} - r_i)^2 n_i}{\Sigma n_i}} \quad (2)$$

The average grain diameter referred to here means an average value of diameters obtained by converting projected images of the silver halide grains into circular images having the same areas, and it can be defined as r by the following formula, when each grain diameter is r_i and the number of the grains of radius r_i is n_i.

$$\bar{r} = \frac{\Sigma n_i r_i}{\Sigma n_i} \quad (3)$$

The grain diameter r_i can be measured in various ways usually used in the art for the aforesaid purpose. Typical methods are described in Loveland, "Analytical Method of Grain Diameter", A.S.T.M. Symposium on Light Microscopy, pages 94 to 122 (1955), and Mies and James, "Theory Of Photographic Process", 3rd Edition, Volume 2, McMillan Co., Ltd. (1966).

In the following description, the emulsion with a coefficient of variation of 0.18 or less will be referred to as a monodispersed emulsion.

The silver halide emulsion can be prepared by the use of methods described in, for example, P. Glafkides, "Chimie et Physique Photographique", Paul Montel Co., Ltd. (1967); G. F. Duffin, "Photographic Emulsion Chemistry", The Focal Press (1966); and V. L. Zelikman, "Making and Coating Photographic Emulsion", The Focal Press (1964). That is to say, the silver halide emulsion may be prepared by an acidic method, a neutral method or an ammonia method, and the soluble silver salt may be reacted with a soluble halogen salt to an injection mixing process, a simultaneous mixing process or a combination thereof.

An example of the aforesaid simultaneous mixing process is a method of constantly maintaining a pAg in a liquid phase in which the silver halide is produced, i.e. the so-called controlled double-jet method.

The core-shell type silver halide grains have a grain structure comprising two or more layers which differ in the content of silver iodide, and it is preferred that a portion nearer the surface has a smaller silver iodide content, as compared with an inner portion of the grain. The surface-near portion referred to above means an outer portion of the grain which ranges from 0.001 to 0.1 μm in thickness from the surface. The difference between the respective silver iodide contents in the outer portion and the inner layers is preferably 5 mol % or more.

In this invention, the lower the silver iodide content in the outer portion is, the better, and it is preferred that the outer portion substantially comprises silver bromide. An emulsion including such silver halide grains can provide a high sensitization efficiency and is especially suitable for obtaining a surface latent image type emulsion.

In the core-shell type silver halide grains, the transition from the layer having the higher silver iodide content to the layer having the lower content thereof may be bounded by a sharp or gradual transition.

The distribution of the silver iodide in the aforementioned silver halide grains can be detected by a variety of physical measurements, for example, by measuring luminescence at low temperature, as described in Annual Congress Lecture Summary Bulletin in 1981 published by Nippon Shashin Gakkai.

In preferred examples of the silver halide grains, the outer portion of each grain includes 0 to 4 mol % of silver iodide and the inner portion includes 2 to 15 mol % of silver iodide. In this invention, the silver halide composition other than the aforementioned silver iodide is mainly silver bromide, but silver chloride may be employed so long as it does not impair the effect of this invention, and this limit is typically less than approximately 1 mol %.

The silver halide emulsion may include a mixture of octahedral and tetradecahedral grains.

The core-shell type silver halide grains included in the silver halide emulsion can be prepared by covering, with a shell, a core comprising a monodispersed silver halide grain.

Monodispersed cores of appropriate size can be manufactured by the double-jet method, while maintaining pAg at a constant level. For example, the monodispersed silver halide emulsion can be prepared by a method disclosed in JP—A—48521/1979. For example, the emulsion is manufactured by adding an aqueous potassium iodide-gelatin solution and an aqueous ammoniacal silver nitrate solution to an aqueous gelatin solution including silver halide seed crystals, with an addition rate varied as a function of time. In this case, by suitably selecting the variation in the addition rate, pH, pAg, temperature and the like, it is possible to obtain high-grade monodispersed silver halide grains.

Manufacturing methods of the above-mentioned core-shell type silver halide are described in, for example, DE—C—1,169,290, U.K. Patent No. 1,027,146, JP—A—154232/1982 and J—A—1417/1976.

In the manufacturing processes of the silver halide grains, there may coexist, for example, a cadmium salt, zinc salt, lead salt, thallium salt, iridium salt, any one of their complex salts, rhodium salt or its complex salt.

The nitrogen-containing heterocyclic compounds used in this invention, may be, e.g., a pyrazole ring, pyrimidine ring, 1,2,4-triazole ring, 1,2,3-triazole ring, 1,3,4-thiadiazole ring, 1,2,3-thiadiazole ring, 1,2,4-thiadiazole ring, 1,2,5-thiadiazole ring, 1,2,3,4-tetrazole ring, pyridazine ring, 1,2,3-triazine ring, 1,2,4-

triazine ring, 1,3,5-triazine ring, benzotriazole ring, benzimidazole ring, benzothiazole ring, quinoline ring, benzoxazole ring, benzoselenazole ring, naphthothiazole ring, naphthoimidazole ring, rhodanine ring, thiohydantoin ring, oxazole ring, thiazole ring, oxadiazole ring, selenadiazole ring, naphthoxazole ring, oxazolidinedione ring, triazolotriazole ring, azaindene ring (e.g., diazaindene ring, triazaindene ring, tetrazaindene ring and pentazaindene ring), phthalazine ring and indazole ring.

Preferred nitrogen-containing heterocyclic compounds have an azaindene ring, and azaindene compounds having hydroxy groups as substituent groups, e.g. hydroxytriazaindene, tetrahydroxy-azaindene and hydroxypentazaindene compounds are particularly preferred.

The heterocyclic rings may have substituent groups other than hydroxy. Examples of the other substituent groups include an alkyl group, alkylthio group, amino group, hydroxyamino group, alkylamino group, dialkylamino group, arylamino group, carboxy group, alkoxycarbonyl group, halogen atom, acylamino group, cyano group and mercapto group.

Examples of the nitrogen-containing compounds used in this invention are as follows:

N—1 2,4-Dihydroxy-6-methyl-1,3a,7-triazaindene
N—2 2,5-Dimethyl-7-hydroxy-1,4,7a-triazaindene
N—3 5-Amino-7-hydroxy-2-methyl-1,4,7a-triazaindene
N—4 4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene
N—5 4-Hydroxy-1,3,3a,7-tetrazaindene
N—6 4-Hydroxy-6-phenyl-1,3,3a,7-tetrazaindene
N—7 4-Methyl-6-hydroxy-1,3,3a,7-tetrazaindene
N—8 2,6-Dimethyl-4-hydroxy-1,3,3a,7-tetrazaindene
N—9 4-Hydroxy-5-ethyl-6-methyl-1,3,3a,7-tetrazaindene
N—10 2,6-Dimethyl-4-hydroxy-5-ethyl-1,3,3a,7-tetrazaindene
N—11 4-Hydroxy-5,6-dimethyl-1,3,3a,7-tetrazaindene
N—12 2,5,6-Trimethyl-4-hydroxy-1,3,3a,7-tetrazaindene
N—13 2-Methyl-4-hydroxy-6-phenyl-1,3,3a,7-tetrazaindene
N—14 4-Hydroxy-6-methyl-1,2,3a,7-tetrazaindene
N—15 4-Hydroxy-6-ethyl-1,2,3a,7-tetrazaindene
N—16 4-Hydroxy-6-phenyl-1,2,3a,7-tetrazaindene
N—17 4-Hydroxy-1,2,3a,7-tetrazaindene
N—18 4-Methyl-6-hydroxy-1,2,3a,7-tetrazaindene
N—19 7-Hydroxy-5-methyl-1,2,3,4,6-pentazaindene
N—20 5-Hydroxy-7-methyl-1,2,3,4,6-pentazaindene
N—21 5,7-Dihydroxy-1,2,3,4,6-pentazaindene
N—22 7-Hydroxy-5-methyl-2-phenyl-1,2,3,4,6-pentazaindene
N—23 5-Dimethylamino-7-hydroxy-2-phenyl-1,2,3,4,6-pentazaindene
N—24 1-Phenyl-5-mercapto-1,2,3,4-tetrazole
N—25 6-Aminopurine
N—26 Benzotriazole
N—27 6-Nitrobenzimidazole
N—28 3-Ethyl-2-methylbenzothiazolium-p-toluenesulfonate
N—29 1-Methylquinoline
N—30 Benzothiazole
N—31 Benzoxazole
N—32 Benzoselenazole
N—33 Benzimidazole
N—34 Naphthothiazole
N—35 Naphthoselenazole
N—36 Naphthoimidazole
N—37 Rhodanine
N—38 2-Thiohydantoin
N—39 2-Thio-2,4-oxazolidinedione
N—40 3-Benzyl-2-mercaptobenzimidazole
N—41 2-Mercapto-1-methylbenzothiazole
N—42 5-(m-Nitrophenyl)tetrazole
N—43 2,4-Dimethylthiazole
N—44 1-Methyl-5-ethoxybenzothiazole
N—45 2-Methyl-β-naphthothiazole
N—46 1-Ethyl-5-mercaptotetrazole
N—47 5-Methylbenzotriazole
N—48 5-Phenyltetrazole
N—49 1-Methyl-2-mercapto-5-benzoylamino-1,3,5-triazole
N—50 1-Benzoyl-2-mercapto-5-acetylamino-1,3,5-triazole
N—51 2-Mercapto-3-aryl-4-methyl-6-hydroxypyrimidine

N—52 2,4-Dimethyloxazole
N—53 1-Methyl-5-phenoxybenzoxazole
N—54 2-Ethyl-β-naphthoxazole
N—55 2-Mercapto-5-aminothiadiazole
N—56 2-Mercapto-5-aminoxazole
N—57 2-Mercapto-5-aminoselenadiazole

The amount of nitrogen-containing heterocyclic compound to be added varies extensively with the size of the silver halide grains, composition, ripening condition and the like, but the compound is required to be added in such an amount as to enable the formation of from 3/10 to 10 molecular layers on the surface of each silver halide grain. This amount can be adjusted by the control of an adsorption equilibrium condition in accordance with a variation of a pH and/or temperature at the time of ripening.

The nitrogen-containing heterocyclic compound can be used together with a sensitizing dye at the time of the gold-sulphur sensitization or gold-selenium sensitization of this invention. In this case, the nitrogen-containing heterocyclic compound and the sensitizing dye are added in a total amount such as to enable the formation of from 3/10 to 10 molecular layers on the surface of each silver halide grain, but it is preferred that the amount of the sensitizing dye does not exceed 70% of the amount required to form a single molecular layer on the surface of the silver halide grain.

The amount of the nitrogen-containing heterocyclic compound necessary for the formation of the single molecular layer can be determined by a drawn adsorption isotherm, but, for example, when the silver iodobromide emulsion grains comprising octahedral grains of 0.65 μm in diameter are covered with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, the required amount is approximately 210 mg/Ag mol. Therefore, an area occupied by this compound is approximately 30nm^2 per molecule. For other grains different in diameter, the amount of the compound may be found by an appropriate calculation, taking the value of the above example as a standard.

The nitrogen-containing heterocyclic compounds used in this invention are preferably colorless.

The addition of the nitrogen-containing heterocyclic compound to the emulsion can be carried out in the form of a solution where it is dissolved in a suitable solvent (e.g., water or an aqueous alkaline solution) which has no harmful influence on the photographic emulsion. The compound may exist in the emulsion at the time of the gold-sulphur sensitization or gold-selenium sensitization, and it is preferred that the compound is added thereto at the time of or before the addition of a sulphur sensitizer or selenium sensitizer. The addition of the gold sensitizer may be carried out in the course of or at the end of the ripening for the sulphur or selenium sensitization.

The complex referred to here means a combination of two or more compounds or ions.

In this invention, known types of sulphur sensitizers can be used. Examples include thiosulfate, allythiocarbamidothiourea, allylisothiocyanate, cystine, p-toluenethiosulfonate and rhodanine. Sulphur sensitizers which are disclosed in U.S. Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313 and 3,656,955, German Patent No. 1,422,869, JP—A—24937/1981 and JP—A—45016/1980 may also be used. The amount of sulphur sensitizer is such that it effectively increases the sensitivity of the emulsion. This amount varies over a fairly extensive range under various conditions such as the amount of nitrogen-containing heterocyclic compound used, the pH, the temperature and the size of the silver halide grains, but about 10^{-7} to about 10^{-1} mol per mol of the silver halide is generally preferable.

In place of the sulphur sensitizers, selenium sensitizers may be used, which include aliphatic isoselenocyanates such as allyisoselenocyanate, selenoureas, selenoketones, selenoamides, selenocarboxylic acids, selenoesters, selenophosphates, and selenides such as diethylselenide and diethyl diselenide. These examples are disclosed in U.S. Patents Nos. 1,574,944, 1,602,592 and 1,623,499.

The amount of the selenium sensitizer, as in the case of the sulphur sensitizer, varies over an extensive range, but approximately 10^{-7} to 10^{-1} mol per mol of the silver halide is generally preferable.

As the gold sensitizers used in this invention, a variety of gold compounds inclusive of ones having oxidation numbers of +1 and +3 can be employed. Typical examples of the gold sensitizers include chloroaurate, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate and pyridyltrichlorogold.

The amount of the gold sensitizer is typically within the range of from about 10^{-7} to 10^{-1} mol per mol of the silver halide, though varying with various conditions.

When the gold sensitizer is used together with the sulphur sensitizer or selenium sensitizer, gold nuclei and silver sulphide-gold nuclei or silver selenide-gold nuclei are produced as light-sensitive nuclei. However, the number of these nuclei and especially the composition of the silver gold sulphide or silver gold selenide nuclei greatly influence the electron trap and development characteristics. The proportion of gold sensitizer with respect to sulphur or selenium sensitizer has a great influence on the sensitization effect. Therefore, to effectively increase the sensitivity of the emulsion in compliance with ripening conditions, the proportion of the gold sensitizer with respect to the sulphur sensitizer or selenium sensitizer must be such that the ratio of gold atoms to sulphur atoms in the sulphur sensitizer which are capable of forming silver sulphide with silver ions or selenium atoms in the selenium sensitizer which are capable of forming silver selenide with the silver ions is within the range of 1:2 to 1:200.

For example, when sodium thiosulfate and sodium chloroaurate are used as the sulphur sensitizer and the gold sensitizer respectively, the ratio of the latter to the former is within the range of 1:2 to 1:200.

The emulsion which undergoes the gold-sulphur sensitization or gold-selenium sensitization preferably has a pAg of 7.5 to 10.0 and a pH of 5.0 to 9.0.

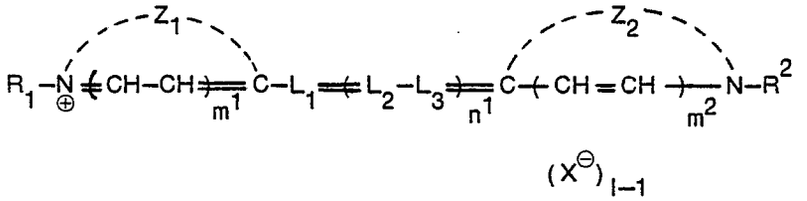
The sensitization step can also be used with a sensitization process based on another noble metal such as platinum, palladium, iridum or rhodium, or a salt thereof.

It is also possible to employ a reduction sensitization. Usable reducing agents are not particularly limited, but include stannous chloride, thiourea dioxide, hydrazine derivatives and silane compounds.

It is preferred that reduction sensitization is carried out while the silver halide grains grow or after the sulphur and gold sensitization has been completed.

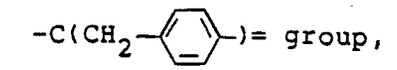
The sensitizing process can also perform a noticeable spectrophotometric sensitization by using the sensitizing dye on the occasion of the gold-sulphur sensitization or gold-selenium sensitization of this invention. The sensitizing dyes referred to above mean dyes which can expand the light-sensitive region of the silver halide for an electromagnetic wave into the outside of an inherent light-sensitive wave range. Particular sensitizing dyes useful in this invention include cyanine dyes, merocyanine dyes, hemicyanine dyes, oxonol dyes, hemioxonol dyes and conjugate merocyanine dyes. These dyes are disclosed in, for example, F. M. Hamer, "The Cyanine Dye and Related Compounds" and C. T. H. James, "The Theory of the Photographic Process, Fourth Edition", pages 194 to 234.

Among the above recited sensitizing dyes, those which are represented by the following general formula (I) are particularly preferable in this invention:

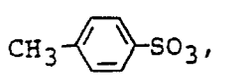


(I)

wherein R_1 and R_2 are groups selected from alkyl groups (e.g., a methyl group, ethyl group, propyl group, pentyl group, chloroethyl group, hydroxyethyl group, methoxyethyl group, acetoxyethyl group, carboxymethyl group, carboxyethyl group, ethoxycarbonylmethyl group, sulfoethyl group, sulfopropyl group, sulfobutyl group, β-hydroxy-γ-sulfopropyl group, propyl sulphate group, allyl group, benzyl group and phenethyl group) and aryl group (e.g., a phenyl group, carboxyphenyl group, sulfonyl group and the like); L_1, L_2 and L_3 each are methylene groups (e.g., a —CH= group, —C(CH_3)= group, —C(C_2H_5)= group, —C(CH_2COOH)= group,



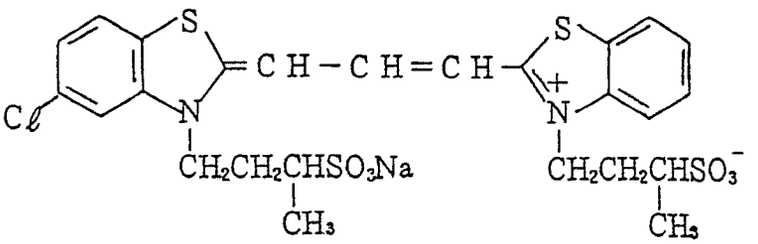
—C(C_6H_5)= group and —C(C_6H_4COOH)= group); Z_1 and Z_2 each represent atoms or atomic groups necessary for the completion of a five-membered or six-membered heterocyclic nucleus, for example, a thiazoline nucleus (e.g., thiazoline, 4-methylthiazoline, 4-phenylthiazoline or the like), oxazoline nucleus (e.g., oxazoline, 4-methyloxazoline or the like), selenazoline nucleus (e.g., selenazoline, 4-methylselenazoline or the like), thiazole nucleus (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole or the like), selenazole nucleus (e.g., selenazole, 4-methylselenazole or the like), oxazole nucleus (e.g., oxazole, 4-methyloxazole, 4,5-dimethyloxazole, 5-ethyloxazole, 5-phenyloxazole or the like), benzothiazole nucleus (e.g., benzothiazole, 4-chlorobenzothiazole, 5-methylbenzothiazole, 6-menthoxybenzothiazole, 5,6-dimethoxybenzothiazole, 5-hydroxybenzothiazole, 5-carboxyethylbenzothiazole, 6-sulphobenzothiazole or the like), benzoaxazole nucleus (e.g., benzoxazole, 5-chlorobenzoxazole, 6-methylbenzoxazole, 5-hydroxybenzoxazole, 4,5-dimethylbenzoxazole or the like), benzoselenazole nucleus (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole or the like), benzimidazole nucleus (e.g., benzimidazole, 3-ethylbenzimidazole or 1-phenyl-5,6-dichlorobenzimidazole or the like), indolenine nucleus (e.g., 3,3-dimethylindolenine, 3,3-diethylindolenine, 3,3,7-trimethylindolenine or the like), naphthothiazole nucleus (e.g., naphto(2,1-d)-thiazole, naphtho(1,2-d)thiazole, 5-methoxynaphtho(2,3-d)-thiazole or the like), naphthoxazole nucleus (e.g., naphtho(2,1-d)oxazole or naphtho(1,2-d)oxazole), naphthoselenazole nucleus (e.g.; naphtho(2,1-d)selenazole, naphtho(1,2-d)selenazole or the like), thienothiazole nucleus, pyridine nucleus (e.g., 2-pyridine, 5-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine or the like), quinoline nucleus (e.g., 2-quinoline, 3-methyl-2-quinoline, 6-chloro-2-quinoline, 8-hydroxy-2-quinoline, 4-quinoline, 6-methoxy-4-quinoline, 1-isoquinoline, 3,4-dihydro-1-isoquinoline, 3-isoquinoline or the like); m^1 and m^2 each represent 0 or 1; n^1 represents 0, 1 or 2; X represents an acidic anion group (e.g., Cl, Br, I, ClO_4,



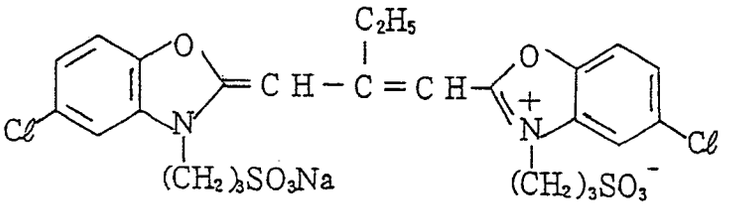
CH_3SO_4 and $C_2H_5SO_4$); and l represents 1 or 2, but when the compound forms an inner salt, l represents 1.

Typical examples of the sensitizing dyes represented by the aforesaid general formula (I) used in this invention are as follows:

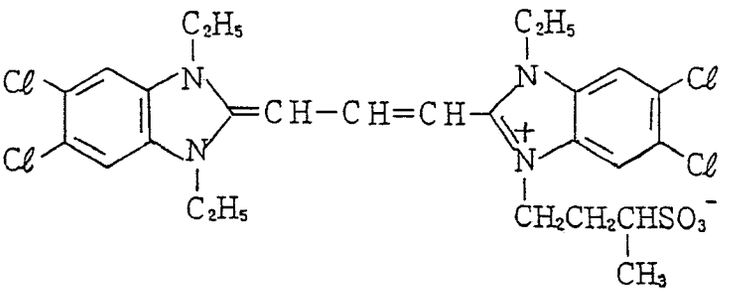
D − 1



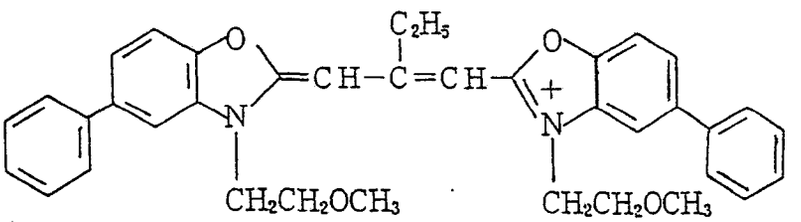
D − 2



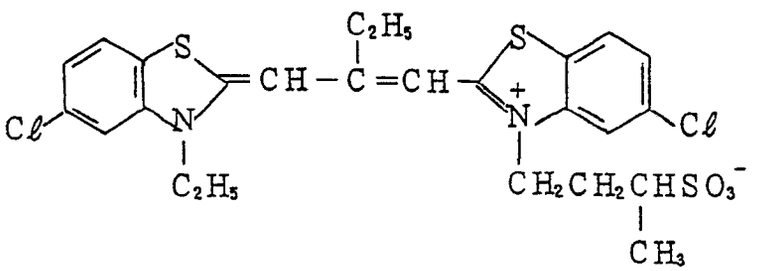
D − 3



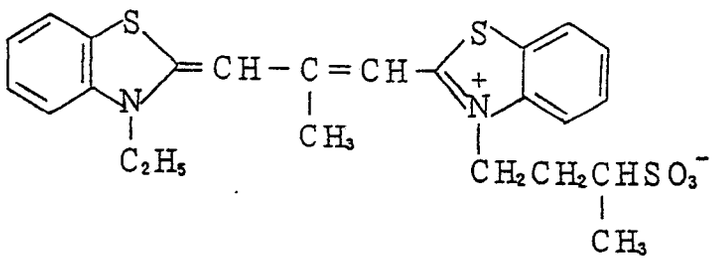
D − 4



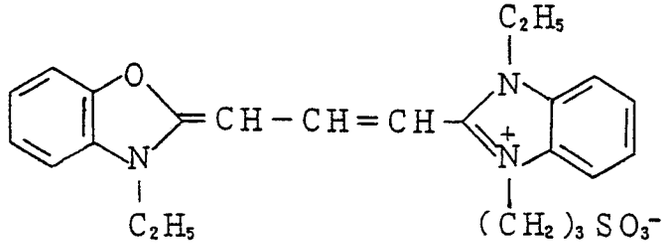
D − 5



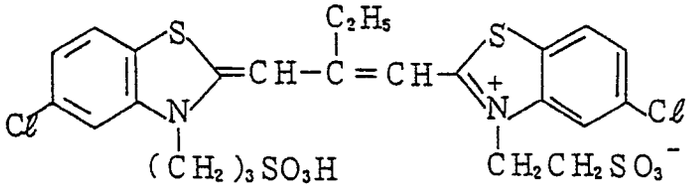
D − 6



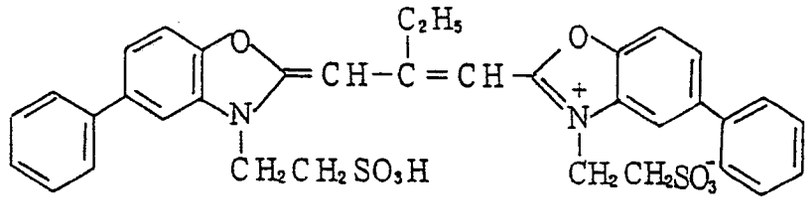
D − 7



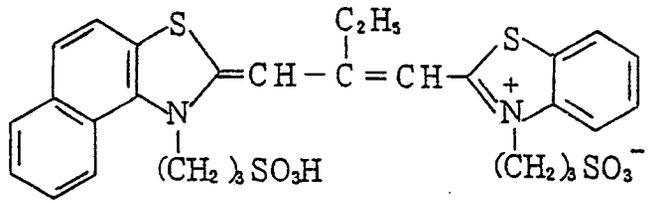
D − 8



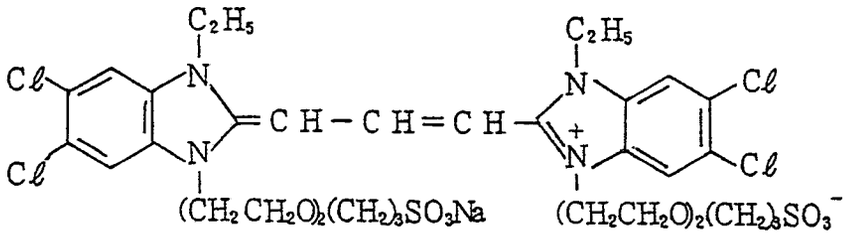
D − 9



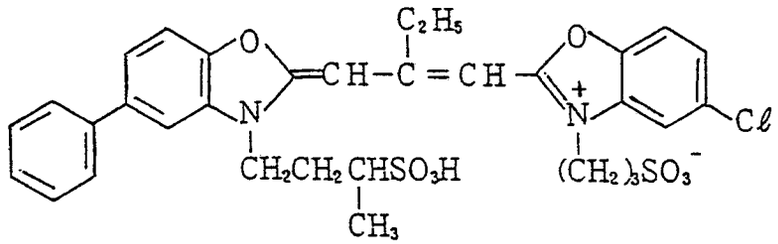
D − 10



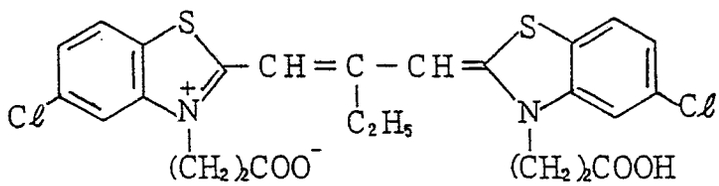
D − 11



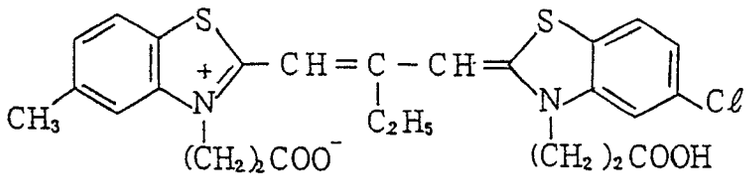
D − 12



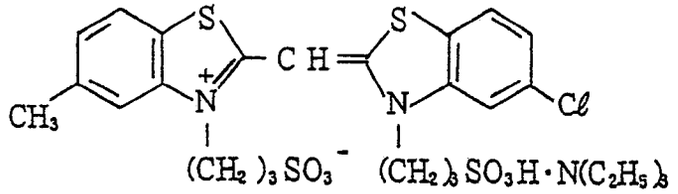
D − 13



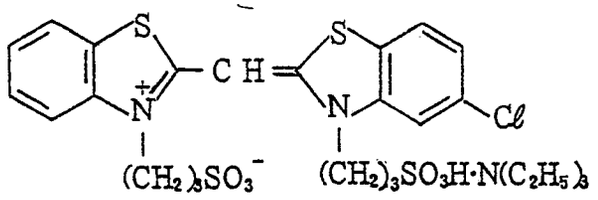
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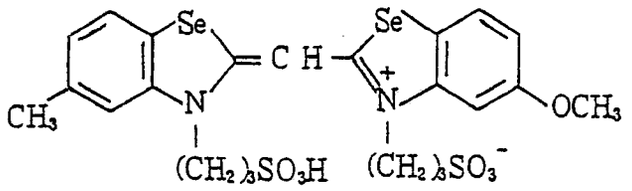
D - 15



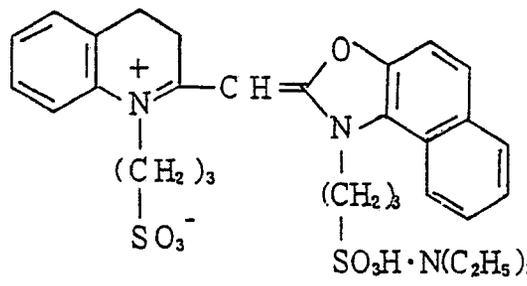
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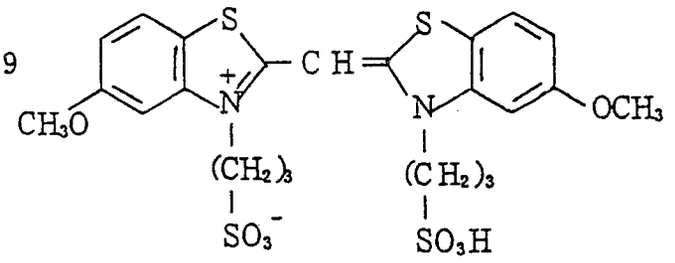
D - 17



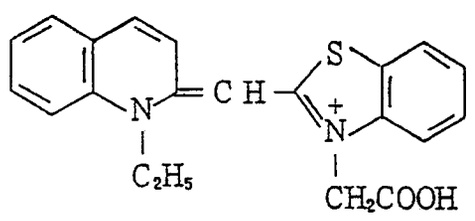
D - 18



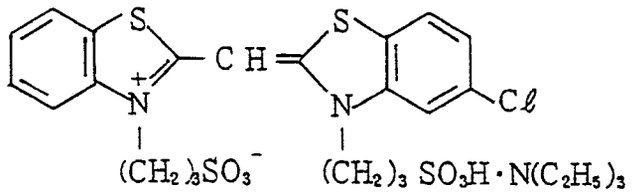
D - 19



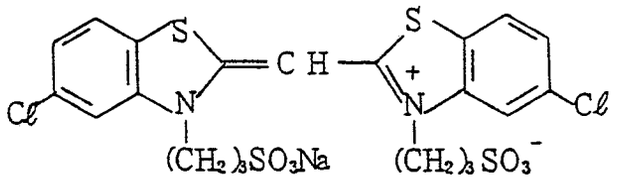
D - 20



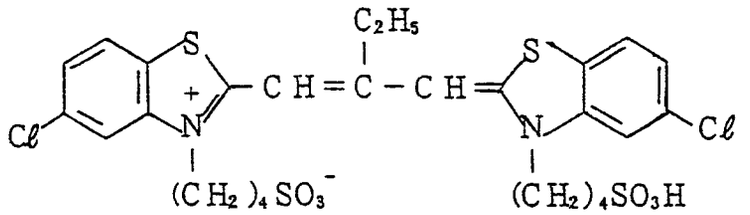
D – 21



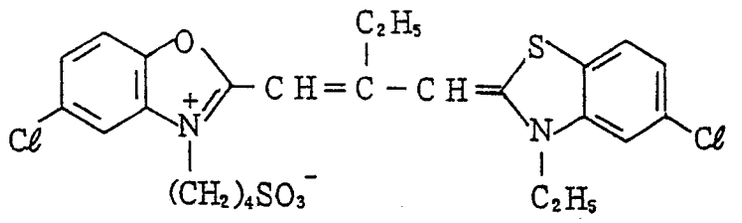
D – 22



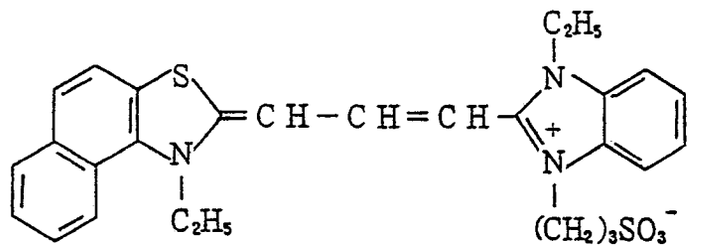
D – 23



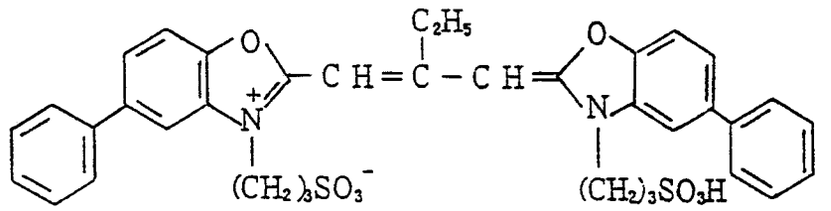
D – 24



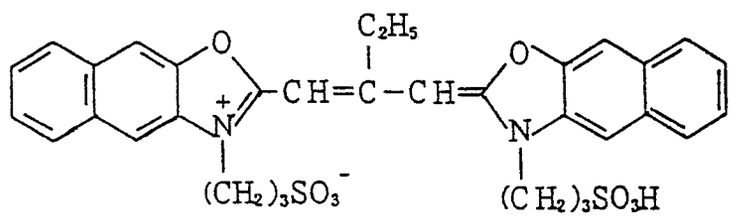
D – 25



D – 26



D – 27



With regard to a processing procedure for the silver halide emulsion prepared by the method of this invention, a particular limitation is not made and any procedure is applicable. For example, typically after color development, bleach-fix processing is carried out, followed, if desired, by washing and then

stabilization; or after color development, bleaching and fixing are carried out separately, followed, if desired, by washing and then stabilization.

The silver halide photographic emulsion manufactured by the method of this invention can suitably be applied to many silver halide photographic light-sensitive materials, because it has a particularly high photographic sensitivity, less failure at high intensity and less photographic fog.

The aforementioned silver halide photographic emulsion can be applied effectively to a variety of the light-sensitive materials for use in black-and-white photography, X-ray photography, color photography, infrared photography, microphotography, silver dye bleach, reversal process and diffusion transfer process.

This invention will be particularly described in the following Examples.

Example 1

An octahedral monodispersed emulsion including grains was prepared by a double jet method, in which pAg and pH were controlled, according to the procedure disclosed in JP—A—48521/1979 (the thus prepared emulsion will hereinafter be referred to as Emulsion (1)). Each of the above grains had an average diameter of 0.9 μm and comprised a core of silver iodide and a shell thereon of silver bromide having an average thickness of 0.016 μm. With regard to the silver halide grains of Emulsion (1), the degree of dispersion of their grain size distribution was 0.15. After usual desalting, this emulsion was divided into 9 portions, and a predetermined amount of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (hereinafter briefly referred to as Compound (I)) was added thereto, as shown in Table 1. In this case, if desired, a pH of each portion was adjusted to a predetermined level with an aqueous potassium hydroxide solution.

The thus prepared respective emulsions were subjected to a sulphur sensitization or gold-sulphur sensitization at a ripening temperature of 55°C, with the ripening temperature adjusted so as to reduce as low a fog as possible and to obtain as high a sensitivity as possible. After completion of the ripening, Compound (I) above was added to every emulsion so that the concentration of Compound (I) might become equal (1.4 g/mol AgX) in every emulsion. Further, usual photographic additives such as a spreading agent, a thickening agent and a hardening agent were added to each emulsion, and undercoated polyethylene terephthalate film bases were coated with the emulsion so that the Ag amount might be 50 mg/dm^2, followed by drying to prepare Samples 1 to 9.

The sensitometry of these samples was performed as follows: With regard to exposure, a 1/50 second exposure was carried out through an optical wedge by the use of a tungsten lamp (color temperature 5,400°K) and a 10^{-6} second exposure was done by the use of a Zenon flash. Development was performed at a temperature of 20°C for a period of 10 minutes with the following developing solution:

Sulfuric acid-p-methylaminophenol	2.5 g
Ascorbic acid	10.0 g
Sodium metaborate·dihydrate	44 g
Potassium bromide	1.0 g
Water	q.s. to 1 liter

Results are set forth in Table 1. Sensitivities each mean a reciprocal number of an exposure necessary to obtain a fog density of +0.1 and are represented with relative sensitivities, taking a value of Samples 1 and 6 as 100.

TABLE 1

	Compound (I) added amount mg/mol AgX	Sodium thiosulfate (pentahydrate) added amount mg/mol AgX	Chloroauric acid (tetrahydrate) added amount mg/mol AgX	pH	Fog	Relative sensitivity	
						$\frac{1}{50}$ s exposure	10^{-6} s exposure
1 (Control)	—	3.5	0.85	6.0	0.01	100	100
2 (This invention)	210	14	3.36	6.5	0.01	200	520
3 (This invention)	210	14	1.13	6.5	0.02	398	1200
4 (This invention)	210	14	0.56	6.5	0.02	500	1580
5 (This invention)	850	28	0.85	5.5	0.03	630	2510
6 (Control)	—	1.0	—	5.5	0.01	100	100
7 (Control)	155	1.0	—	5.5	0.01	16	50
8 (Control)	—	1.0	0.4	5.5	0.02	158	63
9 (This Invention)	155	1.0	0.4	5.5	0.02	794	3160

As is clear from the comparison between Samples 1 to 5 in Table 1 above, the samples prepared by the method of this invention increased in the sensitivities, and particularly in the case of a short-time exposure, the augmentation was noticeable.

Further, as understood from the comparison between Samples 6 and 7, when the sulphur sensitization was only carried out and Compound (I) was added, desensitization adversely occurred rather than sensitization. On the contrary, the comparison between Samples 6, 8 and 9 indicates that when the gold sensitization was employed together with the sulphur sensitization and when Compound (I) was present, a remarkable sensitization effect was obtained.

Example 2

Emulsion (1) prepared in Example 1 was divided into 2 portions, and to these emulsions, a panchromatic sensitizing ew dye, anhydro-2,2'-di-(3-sulfopropyl)-5,5'-dichloro-9-ethylthiacarbocyanine hydroxide, was added in an amount of 140 mg/mol AgX as a methanolic solution. Then, 5 minutes after the addition, 210 mg/mol AgX of Compound (I) was added to either emulsion and the pH was adjusted to 6.5. These emulsions were subjected to a gold-sulphur sensitization at a ripening temperature of 53°C, with the ripening temperature adjusted so as to reduce as low a fog as possible and to obtain as high a sensitivity as possible. After completion of the ripening, Compound (I) was further added so that the concentration of Compound (I) might become constant (1.4 g/mol AgX) in every emulsion.

To these emulsions were added 1-phenyl-5-mercaptotetrazole (hereinafter referred to as Compound (II)) and the following coupler dispersing solution, as well as usually used photographic additives such as a spreading agent and a hardening agent. And, triacetate bases were coated with the respective emulsions so that the amount of the silver might be 20 mg/dm^2, followed by drying in order to prepare Sample 12 and 13.

The coupler dispersing solution was prepared as follows: In a mixture of 100 ml of tricresyl phosphate and 50 ml of ethyl acetate was completely dissolved 80 g of 1-hydroxy-N-[γ-(2,4-di-tert-amylphenoxy-propyl)]-2-naphtho- amide, and 2 g of sorbitan monolaurate was further added thereto. The resultant solution was added to 1 kg of a 10% by weight aqueous gelatin solution including 2.5 g of dodecylbenzene-sulfonate, and a high-speed agitation and ultrasonic agitation followed for emulsification and dispersion, thereby preparing the desired coupler dispersing solution.

The above samples were subjected to the same wedge exposure as in Example 1, and were then color developed at a temperature of 38°C for a period of 3 minutes with a color developing solution having the following composition:

Composition of the color developing solution

4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.80 g
Anhydrous sodium sulfite	0.14 g
Hydroxyamine·$\frac{1}{2}$ sulfate	1.98 g
Sulfuric acid	0.74 g
Anhydrous potassium carbonate	28.85 g
Anhydrous potassium hydrogencarbonate	3.46 g
Anhydrous potassium sulfite	5.10 g
Potassium bromide	1.16 g
Sodium chloride	0.14 g
Trisodium nitrilotriacetic acid (monohydrate)	1.20 g
Potassium hydroxide	1.48 g
Water	q.s. to 1 liter

Results are set forth in Table 2 below. As is clear from Table 2, the sample, which was prepared under conditions that the nitrogen-containing heterocyclic compound and the sensitizing dye were together present at the time of the gold-sulphur sensitization of this invention, had also a remarkably high sensitivity.

TABLE 2

	Compound (I) added amount mg/mol AgX	Sodium thiosulfate (pentahydrate) added amount mg/mol AgX	Chloroauric acid (tetrahydrate) added amount mg/mol AgX	pH	Fog	Relative sensitivity	
						1/50 s exposure	10^{-6} s exposure
10 (Control)	—	3.5	0.85	6.0	0.02	100	100
11 (This invention)	210	14	1.70	6.5	0.02	625	1120

Example 3

As in Example 1, a tetradecahedral monodispersed emulsion (hereinafter referred to as Emulsion (2)) including grains of 0.9 μm in average diameter was prepared by a double jet method in which a pAg and pH were controlled. Each of the grains above comprised a core of silver iodobromide containing 2 mole % of silver iodide and a shell thereon of silver bromide having an average thickness of 0.016 μm. With regard to the silver halide grains of Emulsion (2), the degree of dispersion of their grain size distribution was 0.14. After usual desalting, this emulsion was divided into 3 portions. One of them was processed as a control, and Compound (I) was added to each of the remainder in an amount shown in Table 3. Afterward, a pH of each emulsion was adjusted to a predetermined level.

The thus prepared emulsions were subjected to gold-sulphur sensitization which seemed to be most suitable. After completion of the ripening, Compound (I) was further added thereto so that the content of the compound might be constant (1.4 g/mol AgX) in every emulsion. These emulsions were evaluated in the same manner as in Example 1. Results are set forth in Table 3 below:

TABLE 3

	Compound (I) added amount mg/mol AgX	Sodium thiosulfate (pentahydrate) added amount mg/mol AgX	Chloroauric acid (tetrahydrate) added amount mg/mol AgX	pH	Fog	Relative sensitivity	
						1/50 s exposure	10^{-6} s exposure
12 (Control)	—	4.0	0.75	6.0	0.03	100	100
13 (This invention)	210	14	0.50	6.0	0.02	410	1250
14 (This invention)	850	28	0.76	5.5	0.02	505	1460

As understood from Table 3, also in the case of the silver halide grains of the tetradecahedral crystals, the samples prepared in accordance with this invention were remarkably high in sensitivities.

Reference Examples

In Example 1, in place of Emulsion (1), an emulsion (hereinafter referred to as Emulsion (3); degree of dispersion 0.15) and another emulsion (hereinafter referred to as Emulsion (4); degree of dispersion 0.14) were used. Emulsion (3) above comprised core-shell type silver iodobromide grains (core ... silver iodobromide including 2 mol % of silver iodide; shell ... silver bromide of 0.02 μm in average thickness) of 0.65 μm in average diameter, and Emulsion (4) above comprised twinned crystal silver iodobromide grains (including 2 mol % of silver iodide) having irregular shapes which had heretofore been used generally on products. The same chemical sensitization as in Example 1 was then carried out to prepare Samples 15 to 17 in which Emulsion (3) was used, and Samples 18 to 20 in which Emulsion (4) was used. These samples were evaluated in the same manner as in Example 1. Results obtained are set forth in Table 4 below:

TABLE 4

	Compound (I) added amount mg/mol AgX	Sodium thiosulfate (pentahydrate) added amount mg/mol AgX	Chloroauric acid (tetrahydrate) added amount mg/mol AgX	pH	Fog	Relative sensitivity
						1/60 s exposure
15 (Cubic grains control)	—	5.66	0.51	6.0	0.04	100
16 (Cubic grains control)	210	28.3	0.75	6.5	0.01	45
17 (Cubic grains control)	850	45.3	0.97	5.5	0.01	30
18 (Twinned crystal grains control)	—	7.1	1.3	6.0	0.03	100
19 (Twinned crystal grains control)	210	17.5	0.8	6.5	0.01	64
20 (Twinned crystal grains control)	850	32.0	1.0	5.5	0.01	83

In the case of Reference Example described above, 10 to 50 mg/AgX mol of ammonium thiocyanate was added, because when sodium thiosulfate and chloroauric acid alone were used as sensitizers, the sensitization rate was very bad.

As is clear from Table 4, when the emulsion comprising the cubic grains and irregular-shape twinned crystal grains was subjected to the chemical ripening in the presence of hydroxytetrazaindene, desensitization rather occurred.

Example 4

In place of sodium thiosulfate, 1,1-diphenylthiourea (Sensitizer A) and N-ethyl-N'-4-thiazolylthiourea (Sensitizer B), as sulphur sensitizers, were used in Emulsion (1) obtained in Example 1, and a comparative experiment was carried out in the same manner as in Example 1. Results are set forth in Table 5 below.

TABLE 5

	Compound (I) added amount mg/mol AgX	Sodium thiosulfate (pentahydrate) added amount mg/mol AgX	Chloroauric acid (tetrahydrate) added amount mg/mol AgX	pH	Fog	Relative sensitivity	
						1/50 s exposure	10^{-6} s exposure
21 (Sensitizer A Control)	—	1.4	0.4	8.0	0.02	100	100
22 (Sensitizer A This invention)	160	1.4	0.4	8.0	0.03	450	1350
23 (Sensitizer B control)	—	0.6	0.15	6.0	0.01	100	100
24 (Sensitizer B This invention)	160	0.6	0.15	6.0	0.02	317	1030

As is clear from Table 5, it can be understood that sensitization effect did not depend on the kind of sulphur sensitizer, and even a thiourea derivative sensitizer provided the same sensitization effect as in sodium thiosulfate.

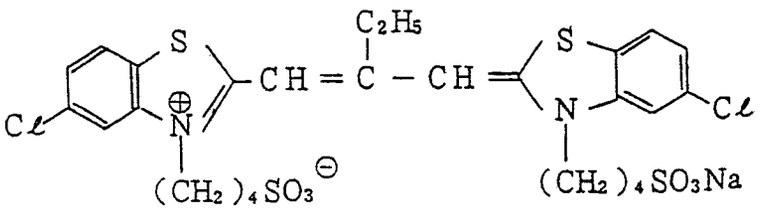
Example 5

Following the procedure of Example 1, two core-shell type octahedral silver iodobromide emulsions (in each of both the emulsions, the content of AgI was 8 mol %; the average diameter of the grains was 0.65 μm; the cores were made from silver iodobromide; the shells were made from silver bromide; and the thickness of each shell was 0.016 μm) of 0.20 and 0.10 in degree of dispersion were prepared. To the respective emulsions were added 50 mg/mol agX of the following sensitizing dye A, 40 mg/mol AgX of the following other sensitizing dye B, 90 mg/mol AgX of Compound (I), sodium thiosulfate, chloroauric acid and 50 mg/mol AgX of ammonium thiocyanate, and the same chemical sensitization as in Example 1 and a spectral sensitization were carried out (either control emulsion included no Compound (I) and was subjected to sensitization ripening).

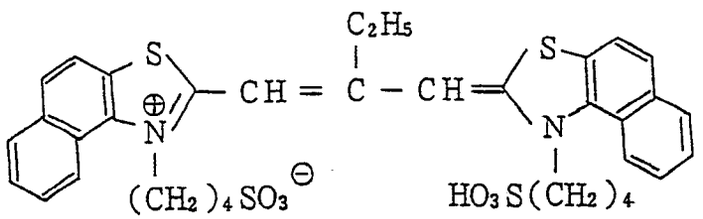
To the thus prepared emulsions were further added the following stabilizer and color coupler dispersing solution, a usually used hardening agent and coating aid. Triacetate film base supports were then coated with the two emulsions respectively, followed by drying in order to prepare Samples 26 and 28

(Sensitizing dye)

〔A〕



〔B〕



(Coupler)

1-Hydroxy-2-[δ-(2,4-di-tert-amylphenoxy)-n-butyl]naphthoamide

(Stabilizer)

(a) Compound (I)

(b) Compound (II)

Sensitometry was carried out for the aforementioned samples in the same manner as in Example 2. Results obtained are set forth in Table 6 below:

TABLE 6

	Degree of dispersion		Compound (I) added amount mg/mol AgX	Sodium thiosulfate (pentahydrate) added amount mg/mol AgX	Chloroauric acid (tetrahydrate) added amount mg/mol AgX	Fog	Relative sensitivity ($\frac{1}{50}$ s exposure)
26	0.20	Control	110	5.3	2.8	0.04	100
28	0.10	This invention	110	5.3	2.8	0.03	209

Table 6 indicates that when the emulsion which was low in the degree of dispersion, i.e. good in mono-dispersibility was subjected to gold-sulphur sensitization in the presence of the nitrogen-containing heterocyclic compound of this invention, the obtained sensitization effect was outstandingly great.

Example 6

Following the procedure of Example 1, an emulsion (hereinafter referred to as Emulsion (5)) and another emulsion (hereinafter referred to as Emulsion (6)) were prepared. Emulsion (5) above was a silver iodobromide emulsion (the content of silver iodide was 6 mol % and the degree of dispersion was 0.12) comprising a silver halide of octahedral crystals having an average diameter of 0.65 μm, with the silver iodide distributed uniformly in the silver halide; Emulsion (6) above was a silver iodobromide emulsion (the content of silver iodide was 8 mol % and the degree of dispersion was 0.12) comprising a silver halide of octahedral crystals having an average diameter of 0.65 μm, with the cores of the crystals coated with the silver bromide shells of 0.016 μm in thickness.

To each of Emulsions (5) and (6) above was added 220 mg/mol AgX of Compound (I), and they were then subjected to the type of sensitizations of a sulphur sensitization and gold-sulphur sensitization in the same manner as in Example 1. As the chemical sensitizers, there were employed 5.7 mg/mol AgX of sodium thiosulfate (pentahydrate), 0.62 mg/mol AgX of chloroauric acid (tetrahydrate) and 50 mg/mol AgX of ammonium thiocyanate. Next, a variety of photographic additives was respectively added to each emulsion in the same manner as in Example 1 in order to prepare Samples 29 to 32, and evaluation was carried out for them like Example 1, obtained results being set forth in Table 7. Sensitivities are represented with relative sensitivities, taking, as a standard (100), a sensitivity obtained by subjecting, to a $\frac{1}{50}$ second exposure, the sample which was prepared only by the sulphur sensitization of Emulsion 5.

TABLE 7

Sample No.	Emulsion	Chemical sensitizations	Sensitivity	
			$\frac{1}{50}$ s exposure	10^{-6} s exposure
29	Emulsion (5)	Sulphur sensitization	100	35
30	"	Gold-sulphur sensitization	250	180
31	Emulsion (6)	Sulphur sensitization	410	210
32	"	Gold-sulphur sensitization	2590	2360

As be definite from Table 7, the case (Sample 32) of this invention, in which the core-shell type emulsion was subjected to gold-sulphur sensitization, can only obtain a noticeable sensitization effect.

Example 7

The following emulsions (7), (8), (9) and (10) were prepared by the double jet method, as in Example 1.

Emulsion (7):

An emulsion of silver iodobromide poly-dispersed twinned crystals having an average diameter of 0.65 μm (the degree of dispersion 0.34, and the content of silver iodide 8 mole %)

Emulsions (8), (9) and (10):

They all were mono-dispersed core-shell type silver iodobromide emulsions (each of which comprised core-shell type silver halide grains, an average diameter thereof being 0.65 μm, the content of silver iodide therein being 8 mol %, shells of the grains having a thickness of 0.016 μm and being made from silver bromide), and Emulsions (8), (9) and (10) comprised cubic crystals, octahedral crystals and tetradecahedral crystals, respectively.

To Emulsions (8), (9) and (10) above were respectively added 14 mg/mol AgX of sodium thiosulfate (pentahydrate) and 1.13 mg/mol AgX of chloroauric acid (tetrahydrate) at the same time, and a gold-sulphur sensitization was carried out as in Example 1. However, 220 mg/mol AgX of Compound (I) was added at different times of addition time (1) (5 minutes before the addition of the chemical sensitizer), addition time (2) (30 minutes after the addition of the chemical sensitizer), and addition time (3) (after the completion of the chemical sensitization). Further, various photographic additives were added to the respective emulsions in the same manner as in Example 1 in order to prepare Samples 33 to 44, and evaluation was carried out as in Example 1. Results obtained are set forth in Table 8 below. The relative sensitivities in the table are represented with relative values, taking, as 100, sensitivities obtained by

subjecting, to a 1/50 second exposure, the samples which were prepared by adding Compound (I) to the respective emulsions at addition time (3) above and by carrying out the chemical sensitization.

TABLE 8

Sample No.	Emulsion	Addition time time of Compound (I)	Relative sensitivity 1/50 s exposure	
33	Emulsion (7)	(1)	87	Control
34	"	(2)	96	"
35	"	(3)	100	"
36	Emulsion (8)	(1)	48	Control
37	"	(2)	60	"
38	"	(3)	100	"
39	Emulsion (9)	(1)	794	This invention
40	"	(2)	303	"
41	"	(3)	100	Control
42	Emulsion (10)	(1)	497	This invention
43	"	(2)	251	"
44	"	(3)	100	Control

When Samples 39 and 40 are compared with Sample 41 and when Samples 42 and 43 are done with Sample 44, it will be found that Compound (I) cannot enhance the effect of this invention even if the compound is added after the completion of the chemical sensitization. Further, as seen from the results of Samples 33 to 38, the emulsion comprising the silver halide grains of the octahedral crystals and the emulsion comprising the silver halide grains of the tetrahedral crystals according to this invention inversely exhibit the greater sensitization effect, when Compound (I) is added after the completion of the chemical sensitization. Therefore, it should be noted that the addition time of Composition (I) is unpredictable.

Example 8

Following the procedure of Example 1, a monodispersed emulsion was prepared by the double jet method in which a pAg and pH were controlled, which monidispersed emulsion was composed of tetradecahedral grains having an average diameter of 0.9 μm and having a degree of disperse of 0.15, each of the grains comprising a cover of silver iodobromide including 10 mol% of silver iodide and a shell thereon of silver bromide having an average thickness of 0.016 μm. After desalting, the thus prepared emulsion was divided into 9 portions, and 3 portions of them were treated as controls; to the remainder were added compounds in amounts shown in Table 9 and their pH and pAg were adjusted to predetermined levels. The thus prepared emulsions were subjected to gold-sulphur sensitization and dye sensitization as in Example 2. The same photographic additives as in Example 2 were then added thereto, followed by coating and drying in order to prepare Samples 45 to 53. These samples were evaluated as in Example 2, and results obtained are set forth in Table 9 below:

TABLE 9

Sample No.		Nitrogen-containing heterocyclic compound added amount (mg/mol AgX)	Sodium thiosulfate (pentahydrate) added amount (mg/mol AgX)	Chloroauric acid (tetrahydrate) added amount (mg/mol AgX)	Sensitizing dye added amount (mol/mol AgX)	Fog	Relative sensitivity	
							1/50 s exposure	10^{-6} s exposure
45	Control	—	3.5	0.85	(A) 5×10^{-5}	0.04	100	100
46	This invention	Compound (I) 80 Compound (II) 1.4	3.8	0.90	"	0.02	800	1200
47	"	Compound (I) 80 Compound (III) 2.0	4.0	0.90	"	0.02	750	1250
48	Control	—	6.0	1.20	(B) 2×10^{-5} (C) 3×10^{-5} (D) 2×10^{-5}	0.05	100	100
49	This invention	Compound (I) 80 Compound (II) 2.6	6.0	1.20	"	0.01	650	1050
50	"	Compound (I) 80 Compound (III) 2.6	6.0	1.20	"	0.01	700	1050
51	Control	—	4.0	1.00	(E) 4×10^{-5} (F) 1×10^{-5}	0.08	10	100
52	This invention	Compound (I) 80 Compound (II) 1.8	4.3	1.00	"	0.02	650	1350
53	This invention	Compound (I) 80 Compound (III)	4.3	1.00	(E) 4×10^{-5} (F) 1×10^{-5}	0.03	650	1400

Note: (1) Compound (III) was 2-mercaptobenzothiazole.
(2) Sensitizing dyes were as follows:

0 097 720

Sensitizing dyes

(A): 3,3'-Di-(3-sulfopropyl)-4,5,4',5'-dibenzothiacyanine hydroxide

(B): 5,5'-Dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)oxacarbocyanine hydroxide

(C): 5,5'-Diphenyl-9-ethyl-3,3'-di-(3-sulfopropyl)oxacarbocyanine hydroxide

(D): 9-Ethyl-3,3'-di-(3-sulfopropyl)-5,6,5',6'-di-benzoxacarbocyanine hydroxide

(E): Anhydro-5,5'-dichloro-3,3'-di-sulfopropyl-9-ethylthiacarbocyanine hydroxide

(F): Anhydro-9-ethyl-3,3'-di-(3-sulfopropyl)-4,5,4',5'-dibenzothiacarbocyanine hydroxide

As is clear from Table 9, with regard to the samples obtained by this invention, the occurrence of their photographic fog was less and their sensitivities were higher. Further, it was found that the comparative samples each were greater in a high intensity sensitivity failure, whereas the samples according to this invention were improved in this point.

Example 9

In Example 2, in place of Compound (I), benzotriazole was added. The obtained sensitization effect was good similarly to that of Example 2.

Example 10

In Example 2, in place of Compound (I), benzothiazole was added. The obtained sensitization effect was good similarly to that of Example 2.

Example 11

In Example 2, in place of Compound (I), benzimidazole was added. The obtained sensitization effect was good similarly to that of Example 2.

Claims

1. A method for preparing a silver halide emulsion which comprises subjecting the silver halide emulsion including core-shell type silver halide grains substantially composed of silver iodobromide to gold-sulphur sensitization or gold-selenium sensitization by use of a gold sensitizer and sulphur sensitizer or selenium sensitizer, characterised in that said silver halide grains are octahedral crystals of tetradecahedral crystals each having (111) faces; the coefficient of variation regarding the grain size distribution of said silver halide grains is 0.18 or less; and the sensitization is carried out in the presence of a nitrogen-containing heterocyclic compound capable of forming a complex with silver or a silver ion.

2. The method for preparing a silver halide emulsion according to claim 1 wherein the amount of said nitrogen-containing heterocyclic compound is an amount necessary to cover the surfaces of said silver halide grains therewith with a thickness 3/10 to 10 times as much as a single molecular layer thereof.

3. The method for preparing a silver halide emulsion according to claim 1 or 2 wherein the ratio of gold atoms in said gold sensitizer to sulphur atoms in said sulphur sensitizer which are capable of forming silver sulphide with silver ions or to selenium atoms in said selenium sensitizer which are capable of forming silver selenium with silver ions is within the range of 1:200 to 1:2.

4. The method for preparing a silver halide emulsion according to claim 1, 2 or 3 wherein said nitrogen-containing heterocyclic compound includes at least one selected from the group consisting of an azaindene ring, triazole ring, tetrazole ring, thiazole ring, benzothiazole ring, naphthothiazole ring, oxazole ring, benzoxazole ring, thiadiazole ring, oxadiazole ring and selenazole ring.

5. The method for preparing a silver halide emulsion according to claim 4 wherein said nitrogen-containing heterocyclic compound includes an azaindene ring.

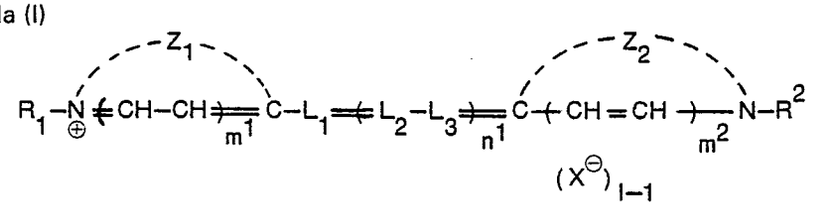
6. The method for preparing a silver halide emulsion according to claim 5 wherein said azaindene compound is a hydroxyazaindene compound having 3 to 5 nitrogen atoms on said azaindene ring.

7. The method for preparing a silver halide emulsion according to any one of claims 1 to 5 wherein the content of silver iodide in said silver iodobromide is from 0.5 to 15 mol %.

8. The method for preparing a silver halide emulsion according to any one of claims 1 to 7 wherein the content of silver iodide is smaller in the shell portion of each core-shell type silver halide grain than in the core portion.

9. The method for preparing a silver halide emulsion according to any one of claims 1 to 8 wherein said silver halide emulsion further includes at least one of sensitizing dyes represented by the following general formula (I):

General Formula (I)



(I)

wherein R_1 and R_2 are each an alkyl group or an aryl group; L_1, L_2 and L_3 each are a methyne group; Z_1 and Z_2 each represent atoms or atomic groups necessary for the completion of a five-membered or six-membered heterocyclic ring; m^1 and m^2 each represent 0 or 1; n^1 represents 0, 1 or 2; X represents an acidic anion group; and l represents 1 or 2, but when the compound forms an inner salt, l represents 1.

10. The method for preparing a silver halide emulsion according to any one of claims 1 to 9 wherein said nitrogen-containing heterocyclic compound is a transparent substance.

Patentansprüche

1. Verfahren zur Herstellung einer Silberhalogenidemulsion unter Gold/Schwefel- oder Gold/Selen-Sensibilisierung einer Silberhalogenidemulsion mit im wesentlichen aus Silberjodbromid bestehenden Silberhalogenidkörnchen vom Kern/Hülle-Typ mit Hilfe eines Goldsensibilisators und eines Schwefelsensibilisators oder Selensensibilisators, dadurch gekennzeichnet, daß es sich bei den Silberhalogenidkörnchen um oktaedrische oder tetradekaedrische Kristalle mit jeweils [111]-flächen handelt, die prozentuale quadratische Streuung bezüglich der Korngrößenverteilung der Silberhalogenidkörnchen 0,18 oder weniger beträgt und die Sensibilisierung in Gegenwart einer zur Bildung eines Komplexes mit Silber oder einem Silberion fähigen stickstoffhaltigen heterocyclischen Verbindung erfolgt.

2. Verfahren zur Herstellung einer Silberhalogenidemulsion nach Anspruch 1, dadurch gekennzeichnet, daß die Menge an der stickstoffhaltigen heterocyclischen Verbindung der zum Abdecken der Oberflächen der Silberhalogenidkörnchen (mit dieser Verbindung) in einer Stärke entsprechend dem $^3/_{10}$-bis 10fachen einer einmolekularen Schicht (dieser Verbindung) erforderlichen Menge entspricht.

3. Verfahren zur Herstellung einer Silberhalogenidemulsion nach Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß das Verhältnis der Goldatome in dem Goldsensibilisator zu den in dem Schwefelsensibilisator enthaltenen und zur Bildung von Silbersulfid mit Silberionen fähigen Schwefelatome oder zu den in dem Selensensibilisator enthaltenen und zur Bildung von Silberselen mit Silberionen fähigen Selenatome im Bereich von 1:200 bis 1:2 liegt.

4. Verfahren zur Herstellung einer Silberhalogenidemulsion nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß es sich bei der stickstoffhaltigen heterocyclischen Verbindung um mindestens eine Verbindung mit einem Azainden-, Triazol-, Tetrazol-, Thiazol-, Benzothiazol-, Naphthothiazol-, Oxazol-, Benzoxazol-, Thiadiazol-, Oxadiazol- oder Selenazolring handelt.

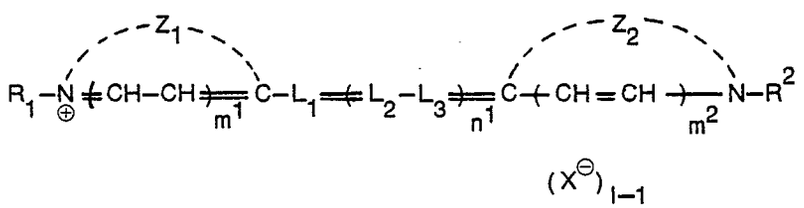
5. Verfahren zur Herstellung einer Silberhalogenidemulsion nach Anspruch 4, dadurch gekennzeichnet, daß es sich bei der stickstoffhaltigen heterocyclischen Verbindung um eine solche mit einem Azaindenring handelt.

6. Verfahren zur Herstellung einer Silberhalogenidemulsion nach Anspruch 5, dadurch gekennzeichnet, daß es sich bei der Azaindenverbindung um eine Hydroxyazaindenverbindung mit 3—5 Stickstoffatomen am Azaindenring handelt.

7. Verfahren zur Herstellung einer Silberhalogenidemulsion nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Gehalt an Silberjodid in dem Silberjodbromid 0,5—15 Mol-% beträgt.

8. Verfahren zur Herstellung einer Silberhalogenidemulsion nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Silberjodidgehalt im Hülleteil jeden Silberhalogenidkorns vom Kern/Hülle-Typ geringer ist als im Kernteil.

9. Verfahren zur Herstellung einer Silberhalogenidemulsion nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Silberhalogenidemulsion zusätzlich mindestens einen Sensibilisierungsfarbstoff der allgemeinen Formel:



(I)

worin bedeuten:

R_1 und R_2 jeweils eine Alkyl- oder Arylgruppe;

L_1, L_2 und L_3 jeweils eine Methingruppe;

Z_1 und Z_2 jeweils diejenigen Atome oder Atomgruppen, die zur Vervollständigung eines 5- oder 6-gliedrigen heterocyclischen Rings erforderlich sind;

m^1 und m^2 jeweils 0 oder 1;

n^1 = 0, 1 oder 2;

X ein Säureanion und

l = 1 oder 2, wobei gilt, daß im Falle, daß die Verbindung ein inneres Salz bildet, l = 1, enthält.

10. Verfahren zur Herstellung einer Silberhalogenidemulsion nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß es sich bei der stickstoffhaltigen heterocyclischen Verbindung um eine durchsichtige Substanz handelt.

Revendications

1. Procédé de préparation d'une émulsion d'halogénure d'argent qui comprend l'étape consistant à soumettre l'émulsion d'halogénure d'argent, comprenant des grains d'halogénure d'argent du type à coquille contrale, essentiellement composé par de l'iodobromure d'argent, à une sensibilisation par or-soufre ou or-sélénium, avec utilisation d'un sensibilisant or et d'un sensibilisant soufre ou d'un sensibilisant sélénium, caractérisé en ce que les grains d'halogénure d'argent sont des cristaux octaédriques ou tétradécaédriques possédant chacun des faces (111); le coefficient de variation concernant la distribution des dimensions des grains d'halogénure d'argent est de 0,18 ou moins; et la sensibilisation est effectuée en présence d'un composé hétérocyclique contenant de l'azote, capable de former un complexe avec l'argent ou avec un ion argent.

2. Procédé de préparation d'une émulsion d'halogénure d'argent selon la revendication 1, caractérisé en ce que la proportion du composé hétérocyclique contenant de l'azote est une proportion nécessaire pour couvrir les surfaces des grains d'halogénure d'argent avec ce composé sur une épaisseur de 3/10 à 10 fois celle d'une couche monomoléculaire de ce composé.

3. Procédé de préparation d'une émulsion d'halogénure d'argent selon la revendication 1 ou 2, caractérisé en ce que le rapport des atomes d'or dans le sensibilisant or aux atomes de soufre dans le sensibilisant soufre, qui sont capables de former du sulfure d'argent avec les ions argent, ou aux atomes de sélénium dans le sensibilisant sélénium qui sont capables de former du séléniure d'argent avec les ions argent, est dans la gamme allant de 1:200 à 1:2.

4. Procédé de préparation d'une émulsion d'halogénure d'argent selon la revendication 1, 2 ou 3, caractérisé en ce que le composé hétérocyclique contenant de l'azote comprend au moins un des membres du groupe constitué par un cycle azaindène, un cycle triazole, un cycle tétrazole, un cycle thiazole, un cycle benzothiazole, un cycle naphtothiazole, un cycle oxazole, un cycle benzoxazole, un cycle thiadiazole, un cycle oxadiazole et un cycle sélénazole.

5. Procédé de préparation d'une émulsion d'halogénure d'argent selon la revendication 4, caractérisé en ce que le composé hétérocyclique contenant de l'azote comprend un cycle azaindène.

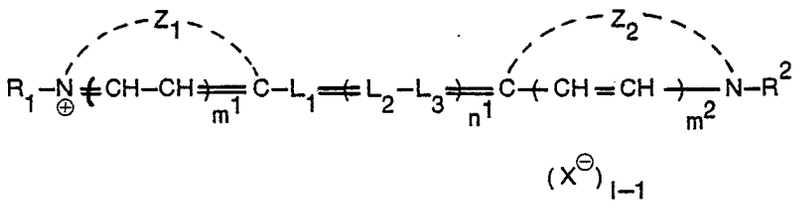
6. Procédé de préparation d'une émulsion d'halogénure d'argent selon la revendication 5, caractérisé en ce que le composé azaindène est un composé hydroxyazaindène comportant 3 à 5 atomes d'azote sur le cycle azaindène.

7. Procédé de préparation d'une émulsion d'halogénure d'argent selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la teneur en iodure d'argent de l'iodobromure d'argent est de 0,5 à 15 moles %.

8. Procédé de préparation d'une émulsion d'halogénure d'argent selon l'une quelconque des revendications 1 à 7, caractérisé en ce que la teneur en iodure d'argent est plus petite dans la partie de coquille de chaque grains d'halogénure d'argent du type à coquille centrale que dans la partie centrale.

9. Procédé de préparation d'une émulsion d'halogénure d'argent selon l'une quelconque des revendications 1 à 8, caractérisé en ce que l'émulsion d'halogénure d'argent comprend en outre au moins un colorant sensibilisant représenté par la formule générale (I) suivante:

Formule générale (I)



(I)

dans laquelle R_1 et R_2 sont chacun un groupe alkyle ou un groupe aryle; L_1, L_2 et L_3 sont chacun un groupe méthyne; Z_1 et Z_2 représentent chacun des atomes ou des groupes atomiques nécessaires pour compléter un anneau hétérocyclique à 5 ou 6 membres; m^1 et m^2 représentent chacun 0 ou 1; n^1 représente 0, 1 ou 2; X représente un anion acide; et l représente 1 ou 2, étant entendu que lorsque le composé forme un sel interne, l représente 1.

10. Procédé de préparation d'une émulsion d'halogénure d'argent selon l'une quelconque des revendications 1 à 9, caractérisé en ce que le composé hétérocyclique contenant de l'azote est une substance transparente.