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(54) **PROCESS FOR PREPARING SILVER HALIDE EMULSION.**

(57) A process for preparing a silver halide emulsion containing core/shell type silver halide grains, which comprises using silver halide grains of octahedral or tetradecahedral crystals having a (1 1 1) face substantially comprising silver bromoiodide and having a variation coefficient of particle size distribution of 0.18 or less, and subjecting them to gold-sulfur sensitization or gold-selenium sensitization in the presence of a nitrogen-containing heterocyclic compound capable of forming a complex with silver or its ion. This emulsion shows a remarkably high photographic sensitivity and less reciprocity law failure in high illuminance region, and undergoes less fogging, thus being suitable as a silver halide photographic light-sensitive material.

EP 0 097 720 A1

SPECIFICATION

Method for preparing silver halide emulsion

(Technical Field)

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.

(Background of the Technology)

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 photograph have been getting strict increasingly, and with regard to photographic performances such as high sensitivity, excellent

graininess, high sharpness, low fog density and sufficiently high optical density, a heightened level has increasingly been desired.

Further, the exhaustion of silver resources is now feared, and the development of a light-sensitive material low in a silver content is strongly demanded. The above-mentioned requirements can almost be satisfied by a technique of preparing a high-sensitive silver halide emulsion reduced in a photographic fog, though the above requirements are considered to be irrelevant to the fog. Therefore, it is no exaggeration to say that the development of the silver iodobromide silver halide emulsion which is low in the photographic fog and high in the sensitivity is the largest task 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, the knowledge of solid physics and the like are positively taken into account. Researches, in which the quantum efficiency is calculated theoretically and the influence of a grain size distribution is studied, are described, for example, on page 91 of "Interactions between Light and Materials for Photographic Applications" contributed in a prelimirary text for lectures at Tokyo Symposium regarding the advancement of photography in 1980. According to the researches above, it is predicted that preparing a monodispersed emulsion of a narrow grain size distribution would be effective to improve the quantum efficiency. Further, for the purpose of establishing a high sensitivity in a process called a chemical sensitization, i.e in the sensitization of a silver halide emulsion while the low photographic fog remains, the monodispersed emulsion can be theoretically presumed to be advantageous.

However, there are actually less examples each in which a simple system or a mixture system of the monodispersed emulsions is employed, and especially examples of negative-type high sensitive emulsions are scarcely present. This fact is because it is extensively known in the art that even if the monodispersed emulsion is prepared in a usually prevalent manner and the normal chemical sensitization is tried, the sensitization cannot be achieved, and what is worse, poorer results than in the case of a polydispersed emulsion generally used are brought about.

In order to manufacture the monodispersed emulsion on an industrial scale, there are required a strict control of a pAg and pH, a regulation of a theoretically determined feed rate of silver ions and halogen ions into a reaction system, and a sufficient stirring condition, as described 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 platy crystals having the faces (111) are usually prepared under the condition of a low silver concentration, silver nuclei which will become latent unclei or fog nuclei are advantageously small.

However, in the tehnical field of the chemical sensitization, it has been also known that the chemical sensitization reaction depends greatly on a 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 formation of a latent image is scattering and an efficiency is bad, which leads to a poor sensitization efficiency. Accordingly, it has been considered in the art that the silver halide grains having the faces (111), as mentioned above, are disadvantageous and difficult to be put to practical use.

With regard to such characteristics of the octahedral grains, one can learn them from "Journal of Photographic Science", Volume 14, pages 181 to 184 (1966), and Volume 16, pages 102 to 113 (1968), "Photographiche 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 above that the chemical sensitization of the tetradecahedral grains is predominantly advanced on the faces (111), and the tetradecahedral grains are considered to have the same characteristics as in the octahedral grains. According to researches by the present inventors it has been found that the tetradecahedral grains have indeed the similar properties to those of the octahedral grains.

Further, a hydroxyazaindene compound has been well known as a stabilizer for a photographic emulsion in the art, because of having a property to inhibit a 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 the fog in the course of a manufacturing process, a storage step or a development processing. Also, it has been known that this compound has an effect to increase a 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 the gold-sulphur sensitization method 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 further added, followed by ripening. However, in the case that the above sensitization method is merely applied to the silver halide emulsion, a sufficient effect cannot be obtained.

Furthermore, Japanese Patent Provisional Publication No. 63914/1975 and German Patent Application (OLS) No. 2,419,798 describe that when a monodispersed silver halide cubic grain emulsion, in which a molar percentage of contained silver bromide is 80 % or more, is sulphur sensitized and the hydroxytetrazaindene compound is then added thereto, a sensitivity increases. However, these publications also describe that crystalline grains other than cubes, e.g. octahedral grains and platy grains substantially surrounded with the faces (111) rather decrease in the sensitivity, or even if it increases, its degree is only a little.

Moreover, in Japanese Patent Provisional Publication No. 77223/1976 and U.S. Patent No. 4,078,937, it is described 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 kind of hydroxytetrazaindene compound is added thereto.

Indeed, when a case where the hydroxytetrazaindene compound is added after the sulphur sensitization followed by coating and another 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 examples of the above-mentioned publications. However, it is now ordinarily carried out in the art to add the hydroxytetrazaindene compound as a stabilizer after

chemical ripening, irrespective of a 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.

(Disclosure of the Invention)

A first object of this invention is to provide a method by which a monodispersed emulsion including silver halide grains of octahedral or tetradecahedral 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.

Other objects and features of this invention will be understood from the following description.

The object of this invention is accomplished by a method for preparing a silver halide emulsion which comprises subjecting the silver halide emulsion including core-shell type silver halide grains to a gold-sulphur sensitization or gold-selenium sensitization by use of a gold sensitizer and sulphur sensitizer or selenium sensitizer, characterized in that the silver halide grains are octahedral or tetradecahedral crystals each having faces (111); a silver halide constituting the grains is substantially composed of silver iodobromide; the coefficient of variation regarding a grain size distribution of the silver halide grains is 0.18 or less; and the gold-sulphur sensitization or gold-selenium 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 the monodispersed core-shell type silver iodobromide grains comprising the octahedral or tetradecadedral crystals each having the faces (111), 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 of an amount enough to cover the grains, the noticeably high sensitization is accomplished. The effect of this invention can be obtained by removing 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 faces (111) in the presence of the nitrogen-containing heterocyclic compound capable of producing the complex with silver or a silver ion. However, 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 vertexes of each cube than on the faces (100) thereof, without any special attention thereto.

When the method of this invention is applied to the

monodispersed octahedral or tetradecahedral silver iodobromide emulsion which is not of the core-shell type, the effet 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 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 conventional monodispersed octahedral or tetradecahedral silver iodobromide emulsion does not increase so much in the sensitivity even by means of the gold-sulphur sensitization or gold-selenium sensitization, but this fact, according to the estimation of the inventors of this invention, would be attributable to the above-mentioned functions and the formation of many light-sensitive nuclei on the faces (111) due to the aforesaid crystal habit dependency of the chemical sensitization reaction in the cases of the octahedral and tetradecahedral silver halide grains. In the case that the nitrogen-containing heterocyclic compound is not present, the influence of the iodine atoms, on the surfaces, on the chemical sensitization reaction can be weakened by giving the core-shell configulation to reduce the content of the silver iodide on the faces, but such a configulation 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 in 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 and to control the chemical sensitization reaction so that effective light-sensitive nuclei may be produced in a small amount, but the compound cannot prevent the function of restraining 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 the nitrogen-containing heterocyclic compound, good results can be expected, and the degree of the obtained sensitization is more remarkable than anticipated, which would be atributed to a synergistic effect other than predicted by the inventors.

The 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. On the contrary, according to the sensitization method disclosed in Japanese Patent Provisional Publication No. 63914/1975 and West German Patent Application (OLS) No. 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 a latent image formation. Therefore, this invention is different from the disclosed ones in technique.

Further, Japanese Patent Provisional Publication No.

77223/1976 and U.S. Patent No. 4,078,937 disclose a method in which a specific hydroxytetrazatindene 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 constitution nor effects of this invention anywhere, and, especially in all the examples of the publications, the hydroxyeterazaindene compound is added aftrer chemical ripening. Probably for this, the effect of the sensitization by the above method depends on the average grain size, and the crtsytal habit of the silver halide grains is not selected. Accordingly, the inventions of the publications are different from this invention in technique.

Additionally, the specification of U.K. Patent No. 1,315,755 discloses a method in which after the azaindene compound has been added as mentioned above, a monovalent gold complex salt compound including sulphur is added in order to carry out a gold-sulphur sensitization, but it does no refer to the crystal habit of the silver halide grains, the core-shell structure and the like anywhere. Therefore, this invention cannot be anticipated by the instant literature.

This invention will be described in the concrete, as follows:

With regard to the silver halide grains of the octahedral or tetradecahedral crystals of 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 within such a range as not to harm the effect of this invention.

The morphology of the silver halide grains is an

octahedron which is substantially formed with faces (111), or a tetradecahedron formed with the faces (111) and faces (100). Diameters of these grains are not to be limited.

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 at least 5 % of the whole surface area of the grains. The greater the percentage of the faces (111) is, the greater the sensitization effect according to the method of this invention is, and so the percentage of the faces (111) is preferably 40 % or more. Also, with regard to the emulsion of this invention, the greater the percentage occupied by the silver halide grains of this invention out of the whole silver halide grains contained in the emulsion is, the greater the effect of this invention is. Therefore, the percentage of the silver halide grains of this invention is preferably 50 % or more, more preferably 70 % or more. The emulsion in which the silver halide grains substantially comprise the silver halide grains of this invention is most preferred.

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

The method according to this invention is based on the concept that the gold-selenium sensitization reaction or gold-sulphur sensitization reaction 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 scatter of a grain surface area is large among the grains, 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 with a value obtained by dividing a standard deviation S of a grain size distribution by an average grain size (diameter) $\bar{r}$, i.e. the coefficient (hereinafter referred to as the disperse degree) of variation of the grain diameter distribution, as shown by the following formula (1):

$$\text{Disperse Degree} = \frac{S}{\bar{r}} \qquad (1)$$

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

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 is n_i.

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

The grain diameter mentioned above can be measured in various manners usually used in the art for the aforesaid purpose. The typical manners above 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 of 0.18 or less in the disperse degree will be referred to as a monodispersed emulsion.

The silver halide emulsion according to this invention can be prepared by the use of methods described in, for example, P. Glafkides, "Chimie et Phyeique 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 any of an acidic method, a neutral method and an ammonia method, and as a manner of allowing a soluble silver salt to react with a soluble halogen salt, an injection mixing process, a simultaneous mixing process or a combination thereof may be employed.

As one example of the aforesaid simultaneous mixing process, there may be used 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 each of this invention have a grain structure comprising two or more layers different in the content of silver iodide, and it is preferred that a portion of the two or more layers and near the surface thereof is smaller in the silver iodide content, as compared with a more inside portion thereof than the above portion. 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. A difference betwen the respective silver iodide contents in the surface-near portion and the more inside portion of the layers is preferably 5 mol % or more.

In this invention, the lower the silver iodide content in the surface-near portion is, the more desirable, and it is preferred that the surface-near portion substantially comprises silver bromide. The emulsion including such

silver halide grains can provide a high sensitization efficiency and is suitable especially for obtaining a surface latent image type emulsion.

In the core-shell type silver halide grains of this invention, the transition from the layer having the higher silver iodide content to the layer having the lower content thereof may be bounded in a sharp state or in an indefinite and dim state.

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 Congres Lecture Summary Bulletin in 1981 published by Nippon Shashin Gakkai.

In preferred examples of the silver halide grains according to this invention, the surface-near portion of each grain includes 0 to 4 mol % of silver iodide and the more inside portion includes 2 to 15 mol % of silver iodide. In this invention, a 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 its limit is less than approximately 1 mol %.

The silver halide emulsion according to this invention may include a mixture of the octahedral and tetradecahedral grains.

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

The monodispersed silver halide grains for the cores

having a desired size can be manufactured by the double-jet method, while maintaining a pAg at a constant level. For example, the monodispersed silver halide emulsion can be prepared by a method disclosed in Japanese Patent Provisional Publication No. 48521/1979. As one 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 time function of the addition rate, pH, pAg, temperature and the like, it is possible to obtain the high-grade monodispersed silver halide grains.

With regard to the manufacturing methods of the above-mentioned core-shell type silver halide grains, for example, West German Patent No. 1,169,290, U. K. Patent No. 1,027,146, Japanese Patent Provisional Publication No. 154232/1982 and Japanese Patent Publication No. 1417/1976 can be referred to.

In the manufacturing processes of the silver halide grains of this invention, 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.

In the nitrogen-containing heterocyclic compounds used in this invention, examples of nitrogen-containing heterocyclic rings include 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 the azaindene rings among the above rings, and azaindene compounds having hydroxy groups as substituent groups, e.g. hydroxytriazaindene, tetrahydroxyazaindene and hydroxypentazaindene compounds are more preferable.

The heteroyclic rings may have substituent groups other than the hydroxy group. 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, but they are not to be limited to the examples below:

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-methylbenzothiazoliump-toluenesulfonate

N-29 1-Methylquinoline

N-30 Benzothiazole

N-31 Benzoxazole

N-32 Benzoselenazole

N-23 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

An amount of the nitrogen-containing heterocyclic compound to be added varies extensively in compliance 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 a single molecular layer 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 such a total amount as to enable the formation of from the single molecular layer 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 an amount to permit forming the 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 comprisin octahedral grains of 0.65 μm in diameter are covered with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, its necessary amount is approximately 210 mg/Ag mol. Therefore, an area occupied by this compound is approximately 30 $\mathring{A}^2$ per molecule. For other grains different in diameter, the amount of the compound may be found by an area proportion 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 into 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 above 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. Their examples include thiosulfate, allythiocarbamidothiourea, allylisothiocyanate, cystine, p-toluenethiosulfonate and rhodanine. Besides, there can be employed 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, and Japanese Patent Provisional Publication Nos. 24937/1981 and 45016/1980. The amount of the 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 the used nitrogen-containing heterocyclic compound, a pH, a 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 preferable, as a standard.

In place of the sulphur sensitizers, this invention allows using selenium sensitizers, 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. Patent 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 preferable, as a standard.

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 preferalby within the range of from about 10^{-7} to 10^{-1} mol per mol of the silver halide as a standard, 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 excert a great influence on an electron trap character or development character. A proportion of the gold sensitizer with respect to the sulphur sensitizer or selenium sensitizer has a great influence on a sensitization effect. Therefore, for the purpose of effectively increasing 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 number of gold atoms with respect to the number of sulphur atoms capable of forming silver sulphide with silver ions out of the sulphur atoms included in the sulphur sensitizer or the number of selenium atoms capable of forming silver selenide with the silver ions out of the selenium atoms included in the selenium sensitizer 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 latter is added within the range of 1/2 to 1/200 with respect to the former.

The emulsion which will undergo the gold-sulphur sensitization or gold-selenium sensitization in this invention has preferably a pAg of 7.5 to 10.0 and a pH of 5.0 to 9.0

In the sensitization step of this invention, there can also be together used a sensitization process based on another noble metal such as platinum, palladium, iridum or rhodium, or a salt thereof.

In this invention, it is further possible to employ a reduction sensitization together. Usable reducing agents are not particularly limited, but their examples include known stannous chloride, thiourea dioxide, hydrazine derivatives and silane compounds.

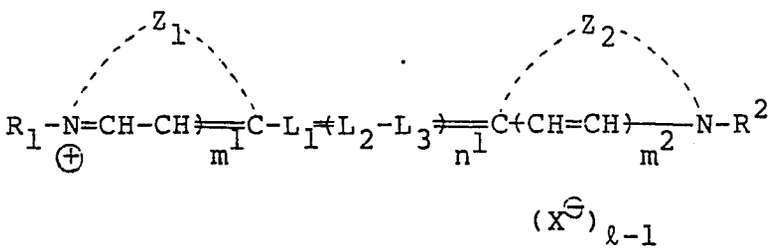
It is preferred that the reduction sensitization is carried out while the silver halide grains grow or after the sulphur sensitization and gold sensitization have been completed.

The sensitizing process of this invention 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. The concrete 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.

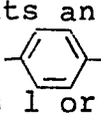
Among the above recited sensitizing dyes, those which are represented by the following general formula (I) are particularly preferable in this invention:

(I)



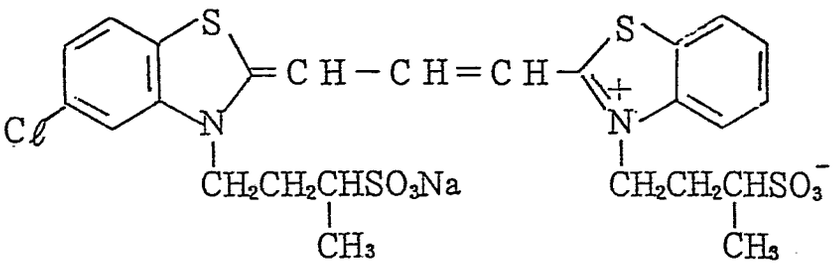
wherein R_1 and R_2 are groups selected from alkyl groups (e.g., a methyl group, ethyl group, propyl group, pentyl group, chloroethyl group, hydroxyethyl group, methoxyethyl group, acetoxyethyl group, carboxymethyl group, carboxyethyl group, ethoxycarbonylmethyl group, sulfoethyl group, sulfopropyl group, sulfobutyl group, ß-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, $-C(CH_2-C_6H_4-)=$ 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-diemthoxybenzothiazole, 5-hydroxybenzothiazole, 5-carboxyethylbenzothiazole, 6-sulphobenzothiazole or the like), benzoxazole 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,

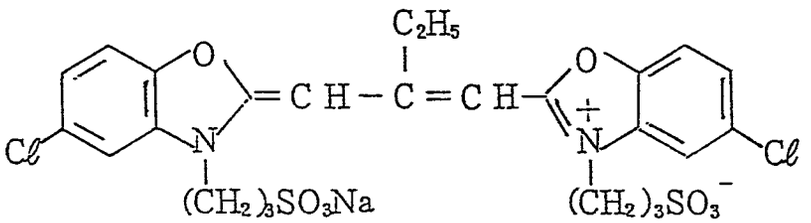
4-quinoline, 6-methoxy-4-quinoline, 1-isoquinoline, 3,4-dihydro-1-isoquinoline, 3-isoquinoline or the like); m^1 and m^2 each represent 0 or 1; n^1 represents 0, 1 or 2; X represents an acidic anion group (e.g., Cℓ, Br, I, $C\ell O_4$, CH_3-  -SO_3, CH_3SO_4 and $C_2H_5SO_4$); and ℓ represents 1 or 2, but when the compound forms an inner salt, the ℓ represents 1.

Typical examples of the sensitizing dyes represented by the aforesaid general formula (I) used in this invention are as follows, but the compounds which are usable in this invention are not to be limited thereto:

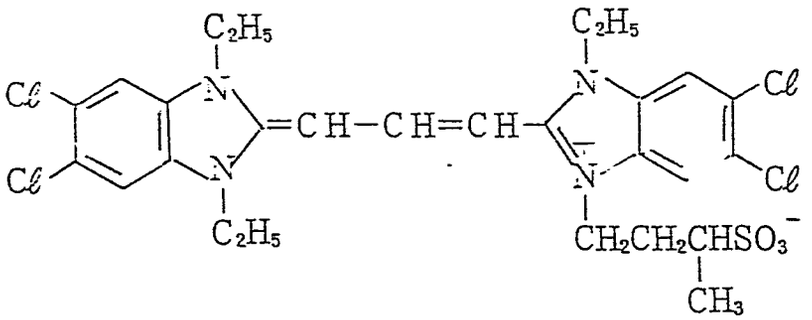
D − 1



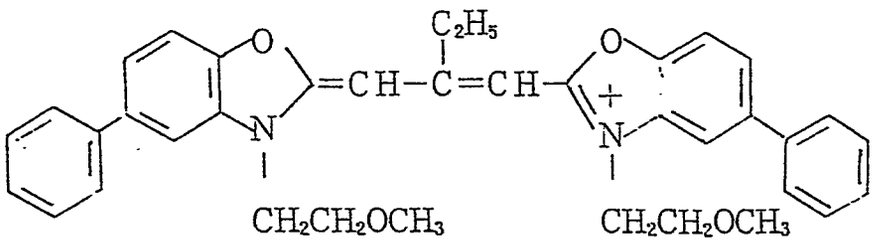
D − 2



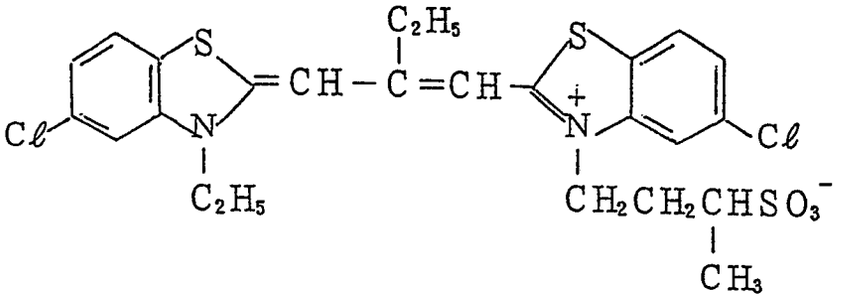
D − 3



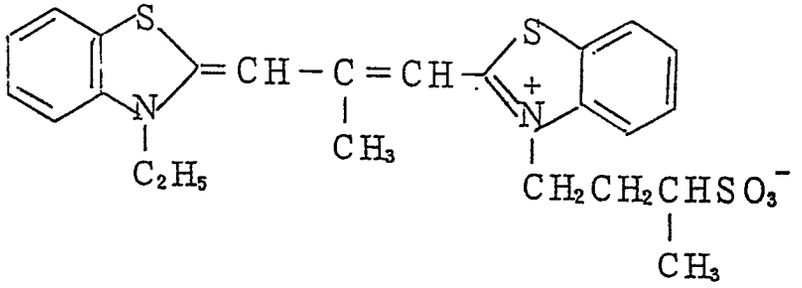
D − 4



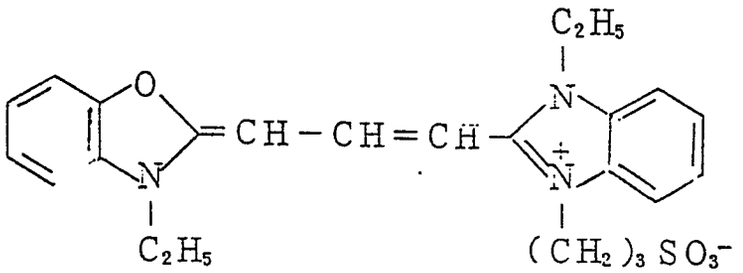
D − 5



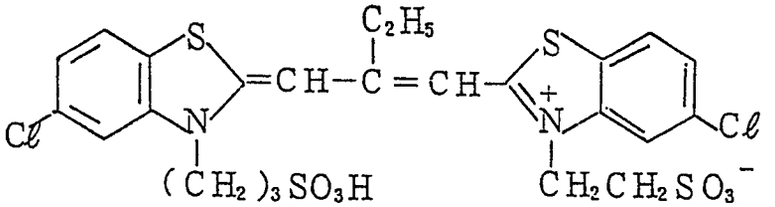
D − 6



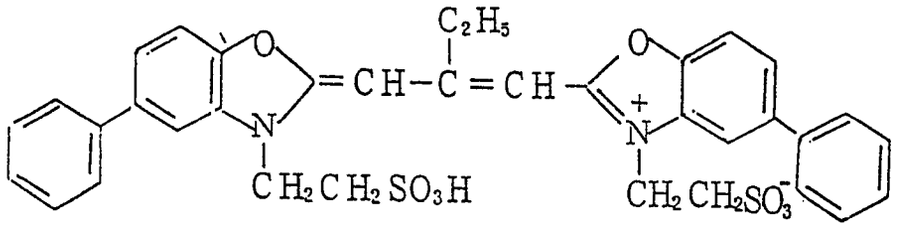
D − 7



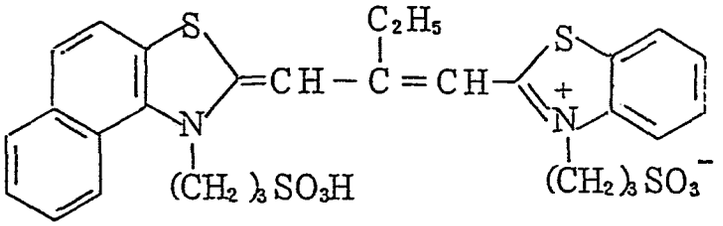
D − 8



D − 9



D − 10



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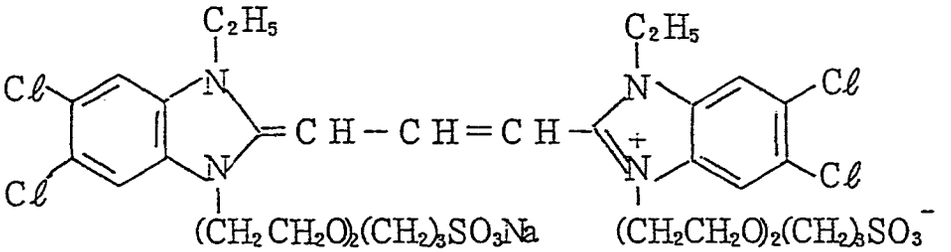

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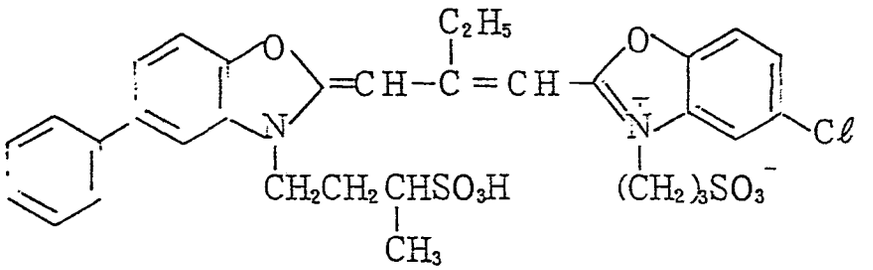

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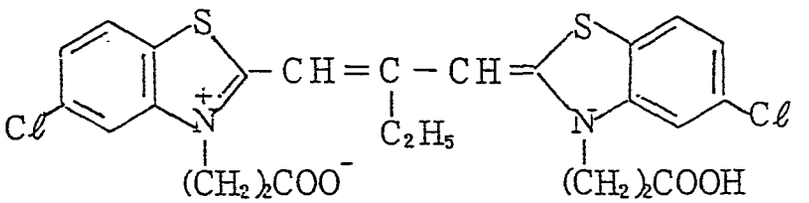
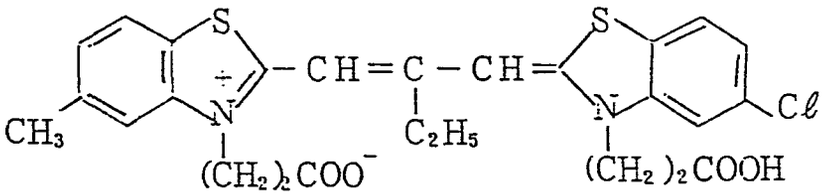


D − 14



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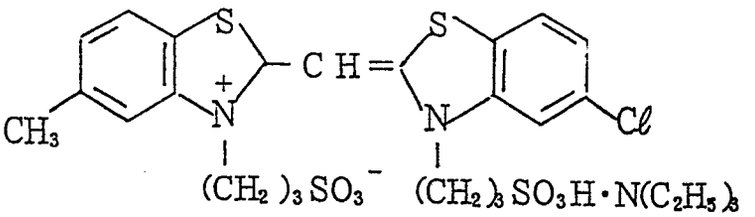
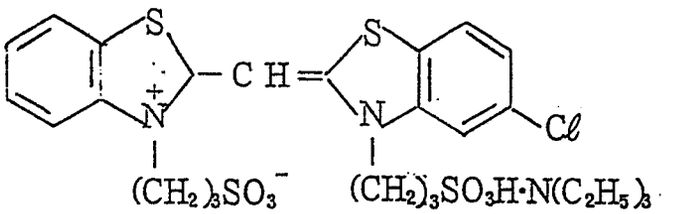
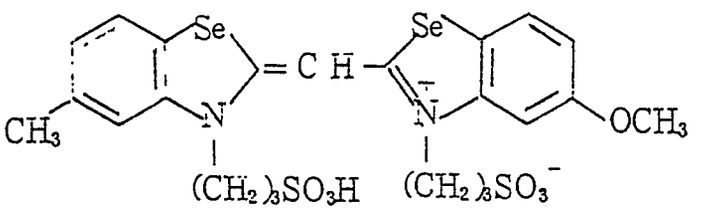


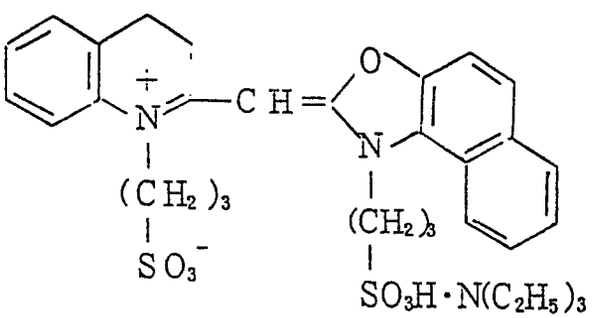
D − 16



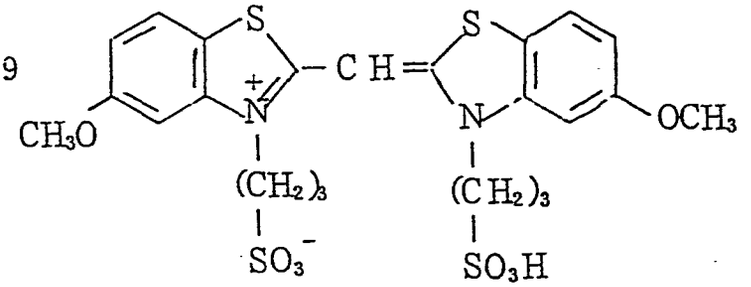
D − 17



D − 18



D − 19



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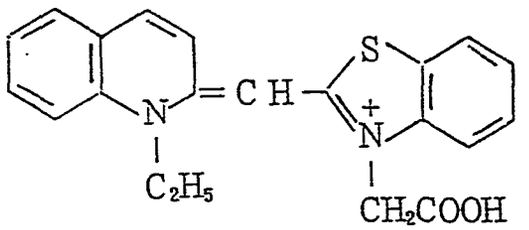
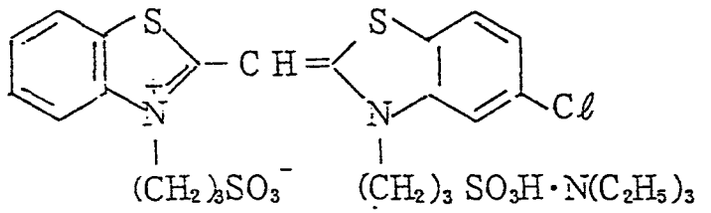
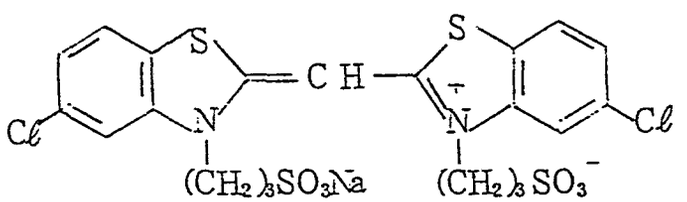


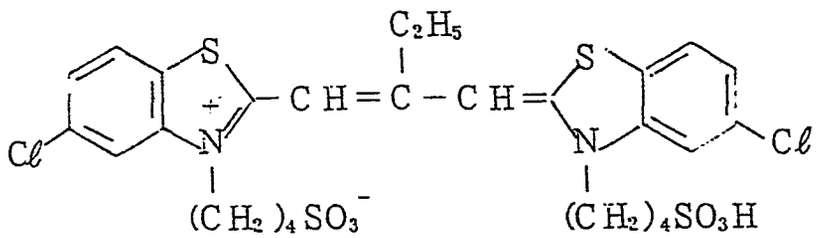
D − 21



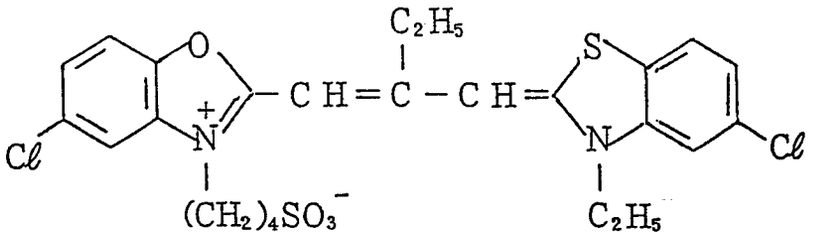
D − 22



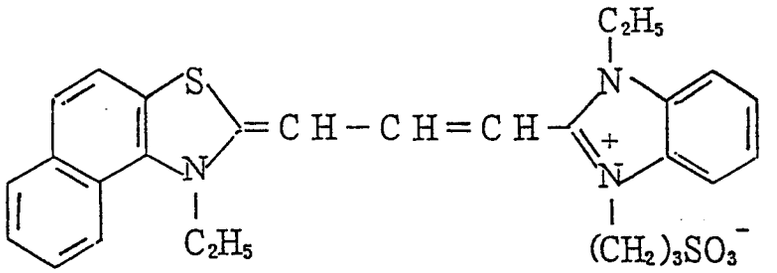
D − 23



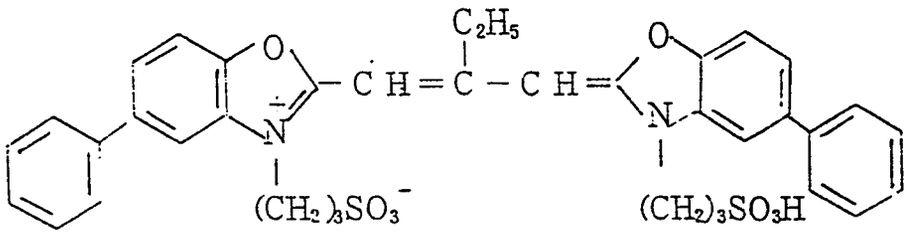
D - 24



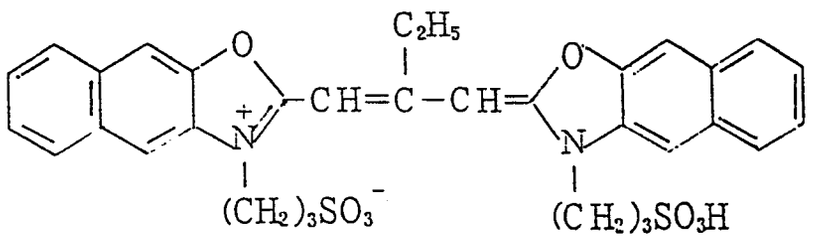
D - 25



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, as its typical examples, there are a system in which after color development, bleach-fix processing is carried out; if desired, followed by washing; and stabilization is then given; and a system in which after color development, bleach and fixation are separately carried out; if desired, followed by washing; and stabilization is then given.

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 noticeably high photographic sensitivity, a less high intensity failure and a less photographic fog.

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

(Best Examples for Implementation of the Invention)

This invention will be described in the concrete in accordance with example, but it is not to be limited to them.

Example 1

An octahedral monodispersed emulsion including grains was prepared by a double jet method, in which a pAg and pH were controlled, according to the procedure disclosed in Japanese Patent Provisional Publication No. 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 iodobromide containing 2 mol % 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 xenon 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 sensitivites, 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	
						1/50 sec. exposure	10^{-6} 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 (")	210	14	1.13	6.5	0.02	398	1200
4 (")	210	14	0.56	6.5	0.02	500	1580
5 (")	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 sensitizingew dye, anhydro-3,3'-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-amylphenoxypropyl)]-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 dodecylbenzenesulfonate, 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-(ß-hydroxyethyl)-aniline sulfate	4.80 g
Anhydrous sodium sulfite	0.14 g
Hydroxyamine·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 sec. exposure	10^{-6} 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 sec. exposure	10^{-6} 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 (")	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 1/50 sec. exposure
15 (Cubic grains control)	-	5.66	0.51	6.0	0.04	100
16 ("")	210	28.3	0.75	6.5	0.01	45
17 (")	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 (")	210	17.5	0.8	6.5	0.01	64
20 (")	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 sec. exposure	10^{-6} 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.

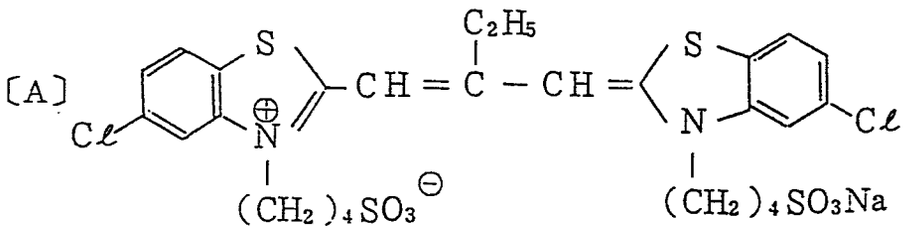
Example 5

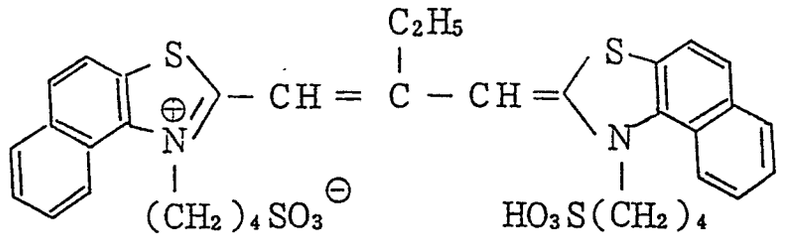
Following the procedure of Example 1, two core-shell type octahedral silver iodobromide emulsions (in each of both the emulsions, the content of AgI was 8 mol %; the average diameter of the grains was 0.65 μm; the cores were made from silver iodobromide; the shells were made from silver bromide; and 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 despersion		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 (1/50 sec. 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 monodispersibility 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 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	
			1/50 sec. exposure	10^{-6} sec. 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 iodo-

bromide 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 sec. 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 monodispersed 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 core 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 (penta-hydrate) added amount (mg/mol AgX)	Chloro-auric acid (tetra-hydrate) added amount (mg/mol AgX)	Sensitizing dye added amount (mol/mol AgX)	Fog	Relative sensitivity	
							1/50 sec. exposure	10^{-6} sec. 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	100	100
52	This invention	Compound (I) 80 Compound (II) 1.8	4.3	1.00	"	0.02	650	1350

Table 9 (cont'd)

Sample No.		Nitrogen-containing heterocyclic compound added amount (mg/mol AgX)	Sodium thiosulfate (penta-hydrate) added amount (mg/mol AgX)	Chloro-auric acid (tetra-hydrate) added amount (mg/mol AgX)	Sensitizing dye added amount (mol/mol AgX)	Fog	Relative sensitivity	
							1/50 sec. exposure	10^{-6} sec. exposure
53	This invention	Compound (I) 80 Compound (III) 2.2	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:

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-sulforpropyl)-5,6,5',6'-dibenzoxacarbocyanine 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 to gold-sulphur sensitization or gold-selenium sensitization by use of a gold sensitizer and sulphur sensitizer or selenium sensitizer, characterized in that said silver halide grains are octahedral crystals or tetradecahedral crystals each having faces (111); the silver halide constituting said grains is substantially composed of silver iodobromide; the coefficient of variation regarding the grain size distribution of said silver halide grains is 0.18 or less; and said gold-sulphur sensitization or gold-selenium 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 wherein the number of gold atoms included in said gold sensitizer with respect to the number of sulphur atoms capable of forming silver sulphide with silver ions out of the sulphur atoms included in said sulphur sensitizer or the number of selenium atoms capable of forming silver selenide with silver ions out of the selenium atoms included in said selenium sensitizer is within the range of 1/200 to 1/2.

4. The method for preparing a silver halide emulsion according to claim 1 wherein said nitrogen-containing

heterocyclic compound includes 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 said azaindene ring.

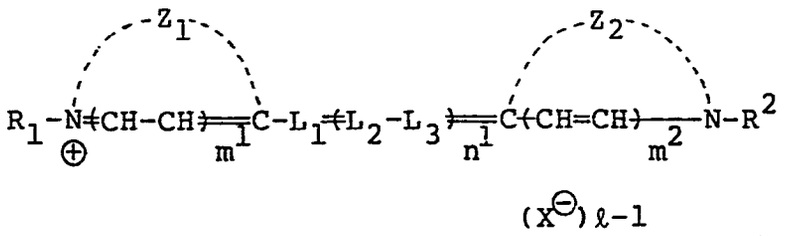
6. The method for preparing a silver halide emulsion according to claim 5 wherein said azaindene compound is a hydroxyazaindene compound having 3 to 5 nitrogen atoms in said azaindene ring.

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

8. The method for preparing a silver halide emulsion according to anyone of claims 1 to 4 wherein the content of silver iodide is smaller in the vicinity of the surface of each core-shell type silver halide grain than in a more inside portion thereof.

9. The method for preparing a silver halide emulsion according to anyone of claims 1 to 5 wherein said silver halide emulsion further includes at least one of sensitizing dyes represented by the following general formula (I):

General Formula (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 represents 1 or 2, but when the compound forms and inner salt, the represents 1.

10. The method for preparing a silver halide emulsion according to claim 1 wherein said nitrogen-containing heterocyclic compound is a transparent substance.

INTERNATIONAL SEARCH REPORT

International Application No. 0097720 PCT/JP82/00471

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

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

Int. Cl.[3] G03C 1/02

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
I P C	G03C 1/00-1/02, 1/06-28

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	GB,A, 1,315,755 (Eastman Kodak Co.), 2. May 1973 (02.05.1973)	1 - 10
Y	JP,A, 50-63914 (Fuji Photo Film Co., Ltd.), 30. May. 1975 (30.5.1975)	1 - 10
Y	JP,A, 51-77223 (Fuji Photo Film Co., Ltd.), 5. July. 1976 (05.07.1976)	1 - 10
Y	JP,A, 54-100717 (Agfa-Gevaert A.G.), 8. August. 1979 (08.08.1979) & DE,A, 2,758,711	1 - 10
Y	US,A, 2,756,148 (Eastman Kodak Co.), 24. July. 1956 (24. 7. 1956)	1 - 10
Y	US,A, 3,317,322 (Eastman Koclak Co.), 2. May. 1967 (02.05.1967)	1 - 10

* Special categories of cited documents: [15]

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

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

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

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

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

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

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

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

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
March 14, 1983 (14.03.83)	March 28, 1983 (28.03.83)
International Searching Authority [1]	Signature of Authorized Officer [20]
Japanese Patent Office	