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(54) Silver halide emulsion.

(57) There is disclosed a silver halide emulsion comprising monodispersed silver halide grains in which a selenium sensitization and a sulfur sensitization are carried out simultaneously or separately in the presence of a nitrogen-containing heterocyclic compound capable of forming a complex with silver.

The silver halide emulsion of this invention does not cause photographic fog and can attain high sensitivity of a photographic material.

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Silver halide emulsion

BACKGROUND OF THE INVENTION

This invention relates to a silver halide emulsion, more particularly to a silver halide emulsion having a high sensitivity and an improved fogging property.

With respect to a light-sensitive silver halide photographic material, particularly a light-sensitive silver halide color photographic material, there has recently been a strong desire for high sensitivity capable of copying with wide range of conditions for photography in a dark place, accurate photographing of even a rapidly moving object and so on. Thus, there have been developed the sulfur sensitization technique, the selenium sensitization technique and so on which are useful as chemical ripening methods for enhancement of the sensitivity of a silver halide emulsion which has hitherto been used for the above-mentioned light-sensitive material. Of the above-mentioned sensitization techniques, the selenium sensitization technique has been paid attention to as one which is suitable for higher sensitization.

As the selenium sensitization technique mentioned above, there are described in the each specification or

Publicaition, for example, U.S. Patents No. 1,574,944, No. 1,602,592, No. 1,623,499, No. 2,642,361, No. 2,739,060, No. 3,297,446, No. 3,420,670, No. 3,320,069, No. 3,658,540, No. 3,408,196, No. 3,408,197, No. 3,442,653 and No. 3,591,385; U.K. Patents No. 255,846 and No. 861,984; West German Patents No. 1,033,510 and No. 1,547,762; French Patents No. 2,093,038 and No. 2,093,209; and Japanese Patent Publications No. 34491/1977, No. 34492/1977, No. 295/1978, No. 36009/1977, No. 38408/1977 and No. 22090/1982. The conventional selenium sensitization is useful for sensitization of a photographic material, particularly for improving the sensitivity in the toe portion of the characteristiv curve. However, this method has disadvantages in that it is accompanied by occurrence of fog, and by increase of fog during the storage of a photographic material.

A method for removing the above-mentioned problems in the selenium sensitization is described in, for example, Japanese Patent Publication No. 20970/1974, in which there has been disclosed a selenium sensitization method of a monodispersed silver halide emulsion. However, this method can not achieve sufficiently high sensitivity and will cause a problem of environmental pollution due to the toxicity of a mercury compound which is added for the purpose of preventing fog.

It is therefore an object of this invention to provide a silver halide emulsion of which the sensitivity has sufficiently been enhanced by selenium sensitization and which which has been improved in photographic fogging property and stability during storage, and does not cause any problem such as environmental pollution.

SUMMARY OF THE INVENTION

The present inventors have found that the above object

can be accomplished by a silver halide emulsion having monodispersed silver halide grains which have been selenium sensitized and sulfur sensitized simultaneously or separately in the presence of a nitrogen-containing heterocyclic compound capable of forming a complex with silver.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be described in further detail below.

In the present invention, the above-mentioned silver halide grains which are selenium sensitized and sulfur sensitized simultaneously or separately in the presence of a nitrogen-containing heterocyclic compound are monodispersed silver halide grains.

The monodispersed silver halide grains in this invention refer to those which exhibit a variation coefficient of a grain size distribution of 0.18 or less when the emulsion is observed with an electron microscope photograph. Namely, when the standard deviation S of the grain size distribution is divided by the average grain size $\bar{r}$, its value (variation coefficient) is 0.18 or less. The standard deviation S is calculated by the following formula:

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

The average grain size herein mentioned refers to an average value of diameters in the case of spherical silver halide grains or an average value of diameters of circular images calculated to be of the same area from the projected images in the case of cubic or other shapes than spheres, and $\bar{r}$ may be defined by the following

formula, when individual grain sizes having such a meaning are represented by r_i and their numbers by n_i:

$$\bar{r} = \frac{\Sigma n_i r_i}{\Sigma n_i}$$

The above grain sizes can be measured according to various methods generally employed in the related field of art for the above purpose. Representative methods are written in Rubland, "Grain Size Analytical Method", A.S. T.M. Symposium on light microscopy, 1955, pp. 94 - 122 or "Theory of Photographic Process" by Mieth & James, 3rd. edition, Chap. 2, published by Macmillan Co. (1966). This grain size can be measured by the use of the projected area of grains or approximate diameter values. When the grains are substantially of uniform shapes, the grain size distribution can be expressed considerably accurately as diameter or projected area.

The relation of the grain size distribution can be determined according to the method described in the essay by Triberi and Smith in "Empirical relation between the sensitometry distribution and grain size distribution in photographic emulsions", The Photographic Journal vol. LXXIX (1949), pp. 330 - 338.

The silver halide grains according to this invention mean the grains having the variation coefficient of 0.18 or less as mentioned above, preferable monodispersed silver halide grains in the present invention are 0.15 or less. As the composition of the silver halide grains, there may be employed widely used materials such as silver chloride, silver bromide, silver chlorobromide, silver iodobromide, silver chloroiodobromide and the like, and preferably silver iodobromide which is suitable for high sensitization. As the shape of the silver halide grains,

normal crystals such as hexahedron, octahedron and tetradecahedron are preferable, and normal crystals of octahedron crystal and tetradecahedron crystal are most preferable.

The silver halide emulsion having monodispersed silver halide grains according to this invention can be prepared by the use of methods described in P. Glafkides, "Chemie et Physique Photographique", published by Paul Montel Co., Ltd. (1967); G.F. Duffin, "Photographic Emulsion Chemistry", published by The Focal Press (1966); and V.L. Zelikman et al., "Making and Coating Photographic Emulsion", published by The Focal Press (1964). That is to say, the silver halide emulsion may be prepared by any of an acidic method, a neutral method and an ammoniacal 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.

The emulsion having monodispersed silver halide grains according to this invention obtained by the above-mentioned preparing method is, in accordance with this invention as mentioned above, selenium sensitized and sulfur sensitized in the presence of the nitrogen-containing heterocyclic compound which is capable of forming a complex with silver.

In the nitrogen-containing heterocyclic compounds used in the present invention, examples of 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, benzoselena-

zole 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 such as diazaindene ring, triazaindene ring, tetrazaindene ring, and pentazaindene ring, phthalazine ring and indazole ring.

Preferred compounds among the above are the compounds having the azaindene ring, and more preferably, the azaindene compounds having hydroxy groups as substituent groups such as hydroxytriazaindene, hydroxytetrazaindene and hydroxypentazaindene compounds.

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

Examples of the nitrogen-containing compounds according to 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-tetrazainene

(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-toluene sulfonate

(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-thioxazolidinedione

(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-aminoxadiazole
(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 emulsion, composition, ripening condition and the like, but the compound is added in an amount of 10 mg to 1000 mg, preferably 50 mg to 200 mg per mole of silver halide, and is preferably 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 addition of said 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. Said compound may be present at a time of the selenium sensitization and sulfur sensitization, but it is preferred that the compound is added thereto at the time of on or before the addition of a selenium sensitizer and sulfur sensitizer. Namely, the

compound may be added during the chemical ripening by the selenium sensitizer and sulfur sensitizer, but the addition before the chemical ripening is most preferable.

Next, the monodispersed silver halide grains according to this invention are selenium sensitized and sulfur sensitized in the presence of the above-mentioned nitrogen-containing heterocyclic compound. Examples of the selenium sensitizer used in the present invention include aliphatic isoselenocyanates such as allyl isoselenocyanate, selenoureas, selenoketones, selenoamides, selenocaboxylic acids, selenocarboxylates, selenophosphates, selenides such as diethylselenide, diethyldiselenide and the like, which are described concretely in U.S. Patents No. 1,574,944, No. 1,602,592 and No. 1,623,499.

In this invention, while there can widely been employed the selenium sensitizers as described in each of the above publications, a labile type selenium compound may by used more preferably than a non-labile type selenium compound such as selenious acid and a selenocyanic acid salt.

The term "labile" has a meaning well-known to the art and "a labile substance" is specifically an appellation for a substance which forms a silver salt when added to an aqueous solution of silver nitrate. For instance, a labile sulfur or selenium compound forms silver sulfate or silver selenide, respectively, when added to an aqueous silver nitrate.

The selenium sensitizer usen in this invention also includes wide range of a labile selenium sensitizer, and the descriptions in U.S. Patents. No. 1,623,499, No. 1,574,944 and No. 1,602,592 may be referred thereto.

Preferable examples of the selenium sensitizers used in this invention include colloidal selenium metals, aliphatic isoselenocyanates and the like, and particularly useful selenium sensitizers include compounds having aliphatic groups as substituent groups such as methylselenourea, ethylselenourea, propylselenourea, isopropylselenourea, butylselenourea, selenoketones e.g. selenoacetone and selenoacetophenone, selenoamides and selenocarboxylic acids; as well as compounds which are substituted by aromatic groups or heterocyclic groups such as phenylselenourea, benzothiazolylselenourea, pyridylselenourea and the like. In this invention, in addition to the labile organic selenium compounds as mentioned above, there may also be employed other useful selenium sensitizers having labile selenium atom. Examples of the useful selenium sensitizers include tetramethylselenourea, N-(β-carboxyethyl)-N',N'-dimethylselenourea, selenoacetamide, diethylselenide, 2-selenopropionic acid, 3-selenobutyric acid, methyl-3-selenobutyrate and tri-p-tolylselenophosphate.

Among each kind of selenium sensitizers, particularly preferably employed is selenourea derivatives. An amont of these selenium sensitizers varies under various conditions such as a kind of used selenium sensitizer, a characteristics of the silver halide and ripening conditions, but generally 2.0×10^{-3} to 10 mg, preferably 2.0×10^{-2} to 1.0 mg, more preferably 0.1 to 0.5 mg per mole of the silver halide.

The monodispersed silver halide grains according to this invention are carried out the sulfur sensitization together with the above selenium sensitization.

In this invention, known types of sulfur sensitizers can be used in the above sulfur sensitization. Examples of the sulfur sensitizer include thiosulfate, allylthio-

carbamidothiourea, allylisothiocyanate, cystin, p-toluenethiosulfonate and rhodanine. Besides, there can be employed sulfur sensitizers which are disclosed in U.S. Patents No. 1,574,944, No. 2,410,689, No. 2,278,947, No. 2,728,668, No. 3,501,313 and No. 3,656,955; West German Patent No. 1,422,869; and Japanese Provisional Patent Publications No. 24937/1981 and No. 45016/1980. An amount of the sulfur 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 0.01 to 100 mg, preferably 0.1 to 10 mg per mole of silver halide is used, as a standard. The above selenium sensitizer and sulfur sensitizer are added as aqueous solutions at a time during the chemical ripening of the emulsion having monodispersed silver halide grains in accordance with the present invention. These sensitizers may be added individually, but simultaneous addition of the both sensitizers is preferable. Thus, silver halide emulsion (hereinafter referred to as the emulsion of this invention) having monodispersed silver halide grains which are selenium sensitized and sulfur sensitized in the presence of the nitrogen-containing heterocyclic compounds which are capable of forming a complex with silver.

In this invention, effective sensitization can be obtained by further carrying out a gold sensitization.

As the gold sensitizers used in this invention, a variety of gold compounds inclusive of ones having oxidation numbers of +1 or +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.

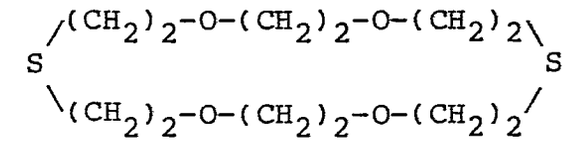
An amount of the gold sensitizer is prefrably within the range of about 0.01 to 10 mg, preferably 1.5×10^{-2} to 4 mg per mole of silver halide as a standard, though varying with various conditions.

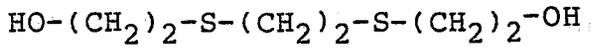
The gold sensitizer may be added to the emulsion of this invention as an aqueous solution. The gold sensitizer is preferably added simultaneously with the addition of the selenium sensitizer and the sulfur sensitizer, but may be added individually.

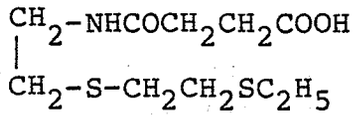
In this invention, the selenium sensitization and sulfur sensitization and the gold sensitization may preferably be carried out in the presence of a solvent for silver halide.

The solvents for silver halide used in this invention include (a) organic thioethers as described in U.S. Patents No. 3,271,157, No. 3,531,289 and No. 3,574,628; and Japanese Provisional Patent Publications No. 1019/1979 and No. 158917/1979; (b) thiourea derivatives as described in Japanese Provisional Patent Publications No. 82408/1978, No. 77737/1980 and No. 2982/1980; (c) solvents for a silver halide having a thiocarbonyl group sandwiched between an oxygen atom or a sulfur atom and a nitrogen atom as described in Japanese Provisional Patent Publication No. 144319/1978; (d) imidazoles as described in Japanese Provisional Patent Publication No. 100717/1979; (e) sulfites; (f) thiocyanates and the like. Specific compounds will be given below:

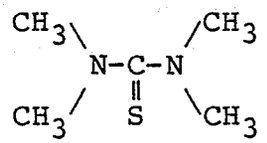
(a)







(b)



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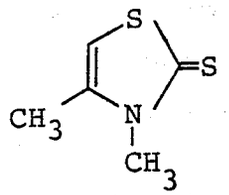
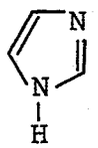


(d)



(e) K_2SO_3

(f) NH_4SCN

KSCN

An amount of the solvent for silver halide used for the emulsion of this invention may, in the case of, for example, a thiocyanate, range from 10 to 1000 mg, preferably 50 to 200 mg per mole of silver halide. The solvent for the silver halide may be added to the emulsion so as to present when the selenium sensitization and the sulfur sensitization is carried out, but the addition before the chemical ripening is preferable as the same in the aforesaid nitrogen-containing heterocyclic compound according to this invention.

In this invention, it is further possible to employ a reduction seneitization 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 the silver halide grains grow or after the selenium sensitization, sulfur sensitization and gold sensitization have been completed.

As described in detail above, the emulsion having the monodispersed silver halide grains of this invention which is selenium sensitized and sulfur sensitized in the presence of the aforesaid nitrogen-containing heterocyclic compound, or further gold sensitized and sensitized in the presence of the solvents for silver halide is endowed extremely high sensitivity and reduced the occurrence of photographic fog. In the thus highly sensitized emulsion of this invention, when it constitutes an emulsion layer of a light-sensitive material, the monodispersed silver halide grains can be used by mixing together with other silver halide grains. In these emulsion layer, the silver halide grains according to this invention may preferably contain 70 % by weight or more based on the total silver halide grains of the layer.

The silver halide emulsion of this invention can be carried out a spectral sensitization by adding sensitizing dyes. The addition of the sensitizing dyes can be carried out at the beginning of a chemical ripening (which is also called a second ripening) of the silver halide emulsion, or during the growth of the ripening, or after the completion of the ripening, or at a suitable time prior to the coating operation of the emulsion.

Adding the sensitizing dyes to the aforesaid photographic emulsion can be accomplished by a variety of manners which have heretofore been suggested. For example, a

manner described in U.S. Patent No. 3,469,987 may be employed in which the sensitizing dyes are first dissolved in a volatile organic solvent, the resulting solution is dispersed in a hydrophilic colloid, and the thus prepared dispersion is added to the emulsion.

With regard to the solvents for the sensitizing dyes, water-soluble organic solvents such as methyl alcohol, ethyl alcohol and acetone can be preferably used. An amount of each sensitizing dye is within the range of 1×10^{-5} mole to 2.5×10^{-2} mole, preferably 1.0×10^{-4} mole to 1.0×10^{-3} mole per mole of the silver halide.

For the purpose of preventing the occurrence of a photographic fog during a manufacturing process, a storage or a developing treatment, and stabilizing photographic properties, a variety of compounds may be added to the silver halide grains at the time of after the completion of the chemical ripening.

Antifoggants and stabilizers which can be used for the aforesaid purposes include many known compounds, for example, azoles such as benzothiazolium salts, nitroindazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazols, mercaptothiazoles, mercaptobenzimidazols, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (particularly 1-phenyl-5-mercaptotetrazole), mercaptopyrimidines, mercaptotriazines, thioketo compounds such as oxazolinethione, and also benzenethiosulfinic acid, benzenesulfinic acid, benzenesulfonamide, hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives and ascorbic acid derivatives. These additives are preferebly added on the chemical ripening or before the coating process.

As a binder employed for the silver halide emulsion of this invention, a variety of hydrophilic colloid can be

employed in addition to gelatins. The gelatins include not only a gelatin but also gelatin derivatives. As the gelatin derivatives, there may be included a reaction product of the gelatin and an acid anhydride, a reaction product of the gelatin and an isocyanate, or a reaction product of the gelatin and a compound having an active halogen atom, and the like. The above-mentioned acid anhydrides used in these reactions with the gelatin include, for example, maleic anhydride, phthalic anhydride, benzoic anhydride, acetic anhydride, isatoic anhydride, succinic anhydride and the like, and the above-mentioned isocyanate compounds include, for example, phenyl isocyanate, p-bromophenyl isocyanate, p-chlorophenyl isocyanate, p-tolyl isocyanate, p-nitrophenyl isocyanate, naphthyl isocyanate and the like.

As the hydrophilic colloids used to prepare the silver halide emulsion, besides the above-mentioned derivative gelatins and conventional gelatins for photography, there can be used, if desired, colloidal albumin, agar, gum arabic, dextran, alginic acid, cellulose derivatives such as cellulose acetates in which hydrolysis has been accomplished until an acetyl content gets to a level of 19 to 26 %, polyacrylamide, imido groups-containing polyacrylamides, casein, vinyl alcohol polymers containing urethane carboxyl groups or a cyanoacetyl groups such as vinyl alcohol-vinyl cyanoacetate copolymer, polyvinyl alcohol-polyvinyl pyrrolidones, hydrolized polyvinyl acetates, polymers obtained by polymerization of proteins or acyl saturated proteins with monomers having vinyl groups, polyvinylpyridines, polyvinylamines, polyaminoethyl methacrylates, polyethylene imines and the like.

For various purposes such as coating aid, antistatic, slide improvement, emulsion dispersion, adhesion prevention and improvement of photographic properties (e.g., development acceleration, high contrast and sensitiza-

tion), a variety of known surface active agents may be included in the silver halide emulsion of this invention.

Namely, these surface active agents are described, for example, in U.S. Patents No. 2,240,472, No. 2,831,766, No. 3,158,484, No. 3,210,191, No. 3,294,540 and No. 3,507,660; U.K. Patents No. 1,012,495, No. 1,022,878, No. 1,179,290 and No. 1,198,450; U.S. Patents No. 2,739,891, No. 2,823,123, No. 1,179,290, No. 1,198,450, No. 2,739,891, No. 3,068,101, No. 3,415,649, No. 3,666,478 and No. 3,756,828; U.K. Patent No. 1,397,218; U.S. Patents No. 3,113,816, No. 3,411,413, No. 3,473,174, No. 3,345,974, No. 3,726,683 and No. 3,843,368; Belgian Patent No. 731,126; U.K. Patents No. 1,138,514, No. 1,159,825 and No. 1,374,780; U.S. Patents No. 2,271,623, No. 2,288,226, No. 2,944,900, No. 3,235,919, No. 3,671,247, No. 3,772,021, No. 3,589,906, No. 3,666,478 and No. 3,754,924; West German Patent Application (OLS) No. 1,961,683; Japanese Provisonal Patent Publications No. 117414/1975 and No. 59025/1975; and Japanese Patent Publications No. 378/1965, No. 379/1965 and No. 13822/1968. There can be used nonionic surface active agents, for example, saponin (steroid series), alkyleneoxide derivatives such as polyethylene glycol, condensates of polyethylene glycol/polypropylene glycol, polyethylene glycol alkyl- or alkylaryl-ether polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkyleneglycol alkylamines or amides and polyethylene oxide additives of silicones, glycidol derivatives such as alkenyl succinic acid polyglyceride and alkylphenol polyglyceride, fatty acid esters of polyvalent alcohols, alkylesters of sugar, urethanes or ethers of the sugar, etc.; anionic surface active agents having an acidic group (e.g. a carboxy group, sulfo group, phospho group, sulfuric ester group, phosphoric ester group) such as triterpenoid seires saponin, alkylcarboxylic acid salts, alkylnaphthalene sulfonic acid salts, alkylsulfuric

esters, alkyl phosphoric esters, N-acyl-N-alkyltaurines, sulfosuccinic acid esters, sulfoalkyl polyoxyethylene alkylphenyl ethers and polyoxyethylene alkylphosphoric acid esters; amphoteric surface active agents such as amino acids, aminoalkyl sulfonic acids, aminoalkylsulfuric acid ester or phosphoric acid esters, alkylbetaines, amineimides and amineoxides; and cationic surface active agents such as alkylamine salts, aliphatic or aromatic quaternary ammonium salts, heterocyclic (e.g. pyridinium, imidazolium) quaternary ammonium salts, and sulfonium compounds containing aliphatic or heterocyclic ring or sulfonium salts.

In the silver halide emulsion of this invention, they may include, as development accelerators, in addition to the above-mentioned surfactants, imidazoles, thioethers and selenoethers discribed in West German Patent Applications (OLS) No. 2,002,871, No. 2,445,611 and No. 2,360,878; and U.K. Patent No. 1,352,196.

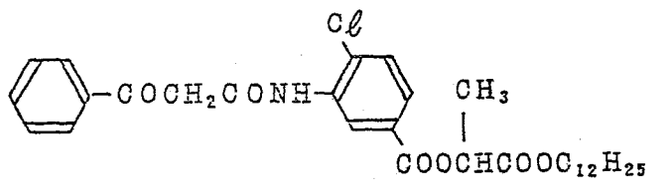
In the case that the silver halide emulsion of this invention is used as a color light-sensitive material, usual techniques and materials for the color light-sensitive material can be employed. That is to say, a yellow coupler, a magenta coupler and a cyan coupler are each combinedly added to the blue-sensitive silver halide emulsion, the green-sensitive silver halide emulsion and the red-sensitive silver halide emulsion. It is preferred that these couplers have hydrophobic groups called as ballast groups and are non-diffusible. Each coupler may be either tetraequivalent or diequivalent to a silver ion. Further, a colored coupler having an effect of a color correction or a coupler (so-called DIR coupler) for giving off development restrainers during the development process may be included in the emulsion.

Furthermore, the coupler above may be a coupler by the

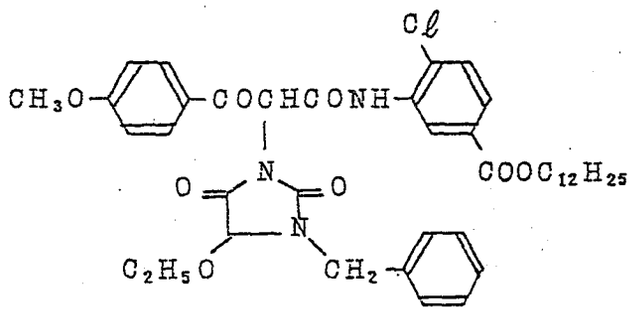
use of which a product of a coupling reaction will become colorless.

As yellow couplers, known open chain ketomethylene couplers can be employed. Among them, benzoylaceto-anilide and pivaloylacetoanilide series compounds are advantageous. Examples of these usable yellow couplers are disclosed in U.S. Patents No. 2,875,057, No. 3,265,506, No. 3,408,194, No. 3,551,155, No. 3,582,322, No. 3,725,072 and No. 3,891,445; West German Patent No. 1,547,868; West German Patent Applications (OLS) No. 2,213,461, No. 2,219,917, No. 2,261,361, No. 2,414,006 and No. 2,263,875. Particularly prefreable yellow couplers are as follows:

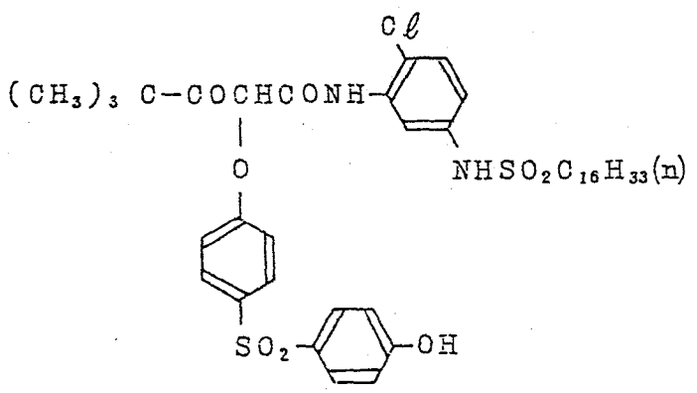
(1)



(2)

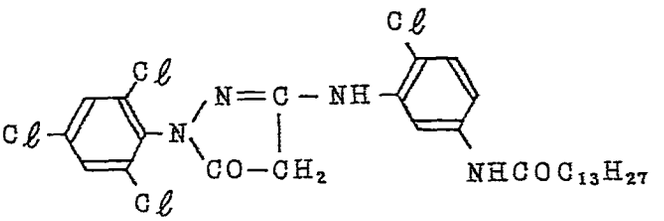


(3)

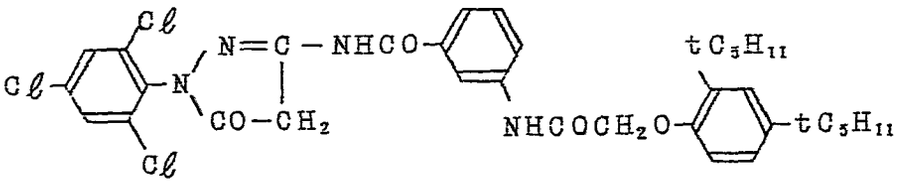


As magenta color forming couplers, there can be employed pyrazolone compounds, indazolone compounds and cyano-acetyl compounds. Particulary, the pyrazolone compounds are advantageous. Examples of the usable megenta color forming couplers are disclosed in U.S. Patents No. 2,600,788, No. 3,062,653, No. 3,408,194 and No. 3,519,429; Japanese Provisional Patent Publications No. 111631/1974, No. 28236/1981 and No. 94752/1982; and Japanese Patent Publication No. 27930/1973. Particularly preferable couplers include following compounds.

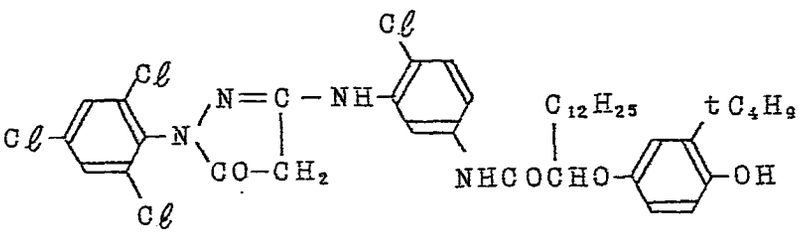
(1)



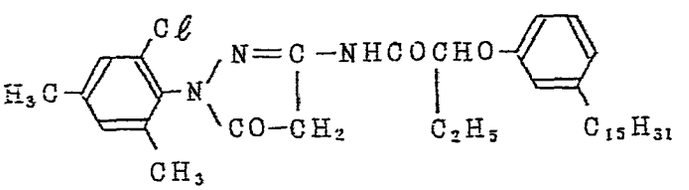
(2)



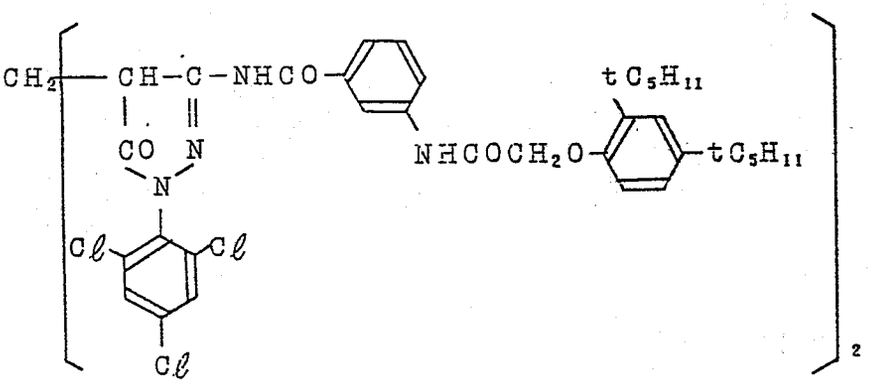
(3)



(4)



(5)



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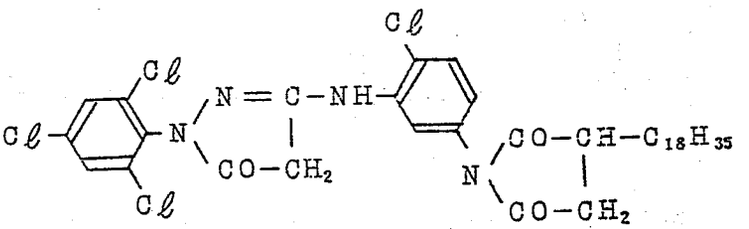

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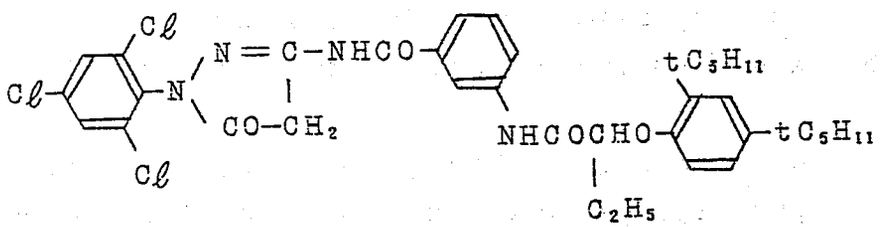
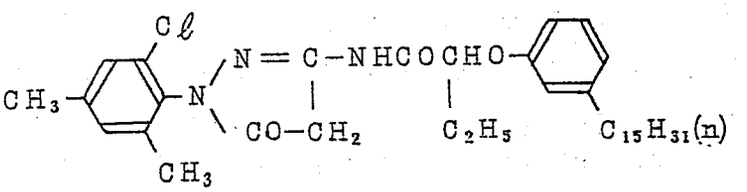
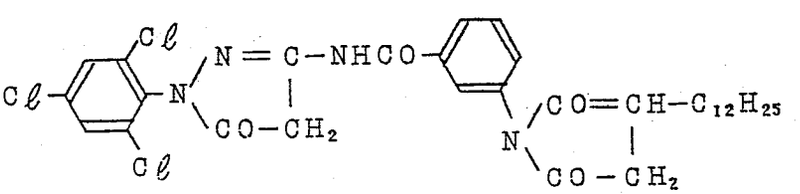


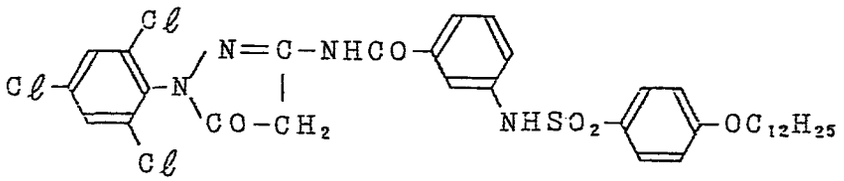
(8)



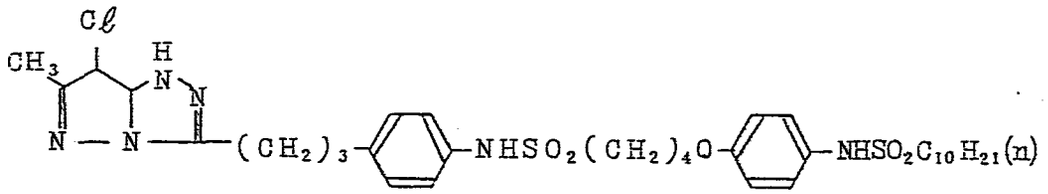
(9)



(10)



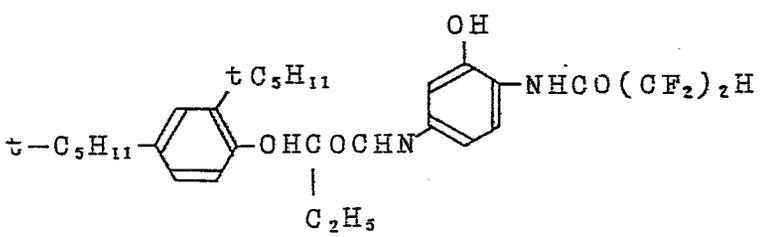
(11)



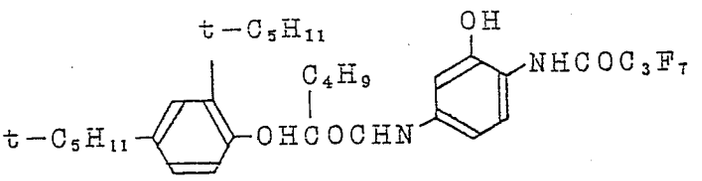
(12) Polymer coupler latex in which the above-mentioned magenta coupler (2) is impregnated into the latex which comprises the copolymer of 1-(2,4,6-trichlorophenyl)-3-(3-acrylamidobenzamide)-4-pyrazoryl-5-oxo-2-pyrazoline and n-butyl acrylate in the ratio of 20 : 80.

As cyan color forming couplers, there can be employed phenol type compounds, naphthol type compounds and the like. Examples of the cyan color forming couplers are those described in U.S. Patents No. 2,423,730, No. 2,474,293 and No. 2,895,826; Japanese Provisional Patent Publication No. 117422/1975; and Japanese Patent Registration No. 127513. Particularly preferable cyan color forming couplers include following compounds.

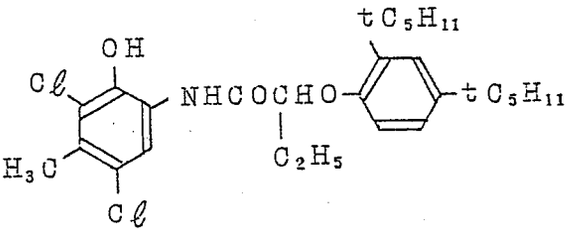
(1)



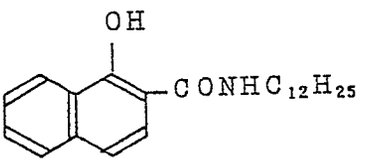
(2)



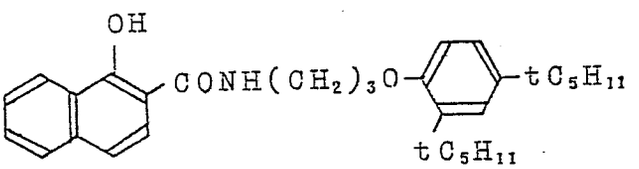
(3)



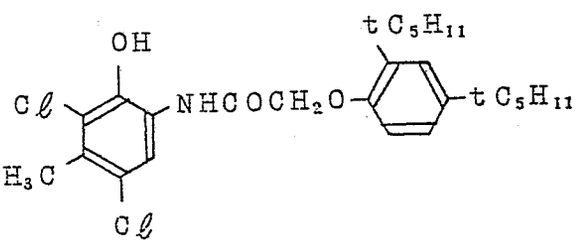
(4)



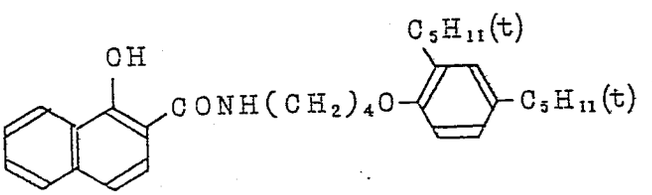
(5)



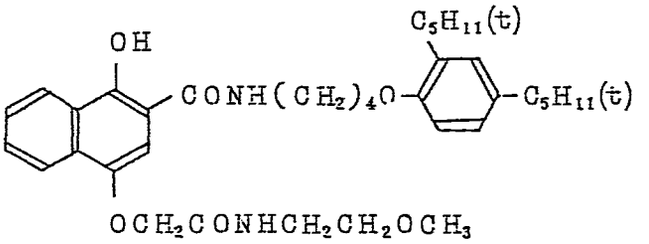
(6)



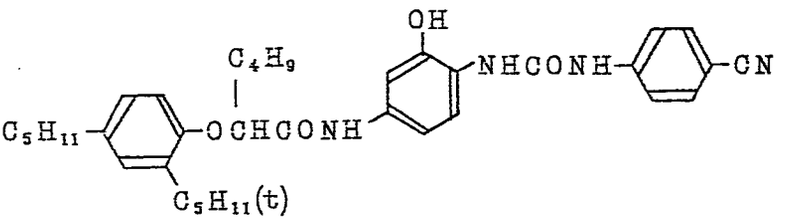
(7)



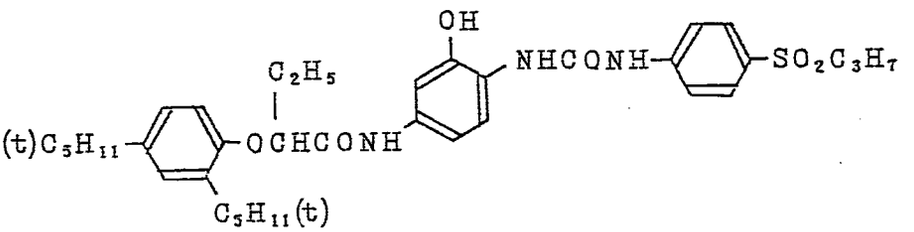
(8)



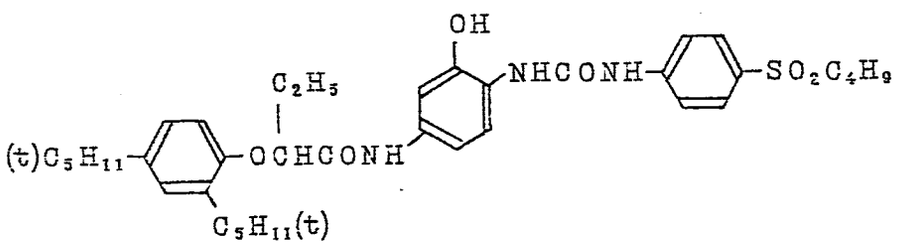
(9)



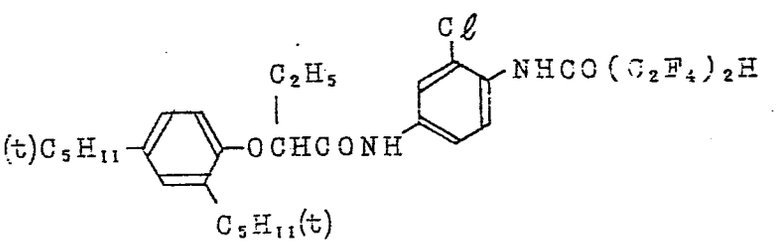
(10)



(11)



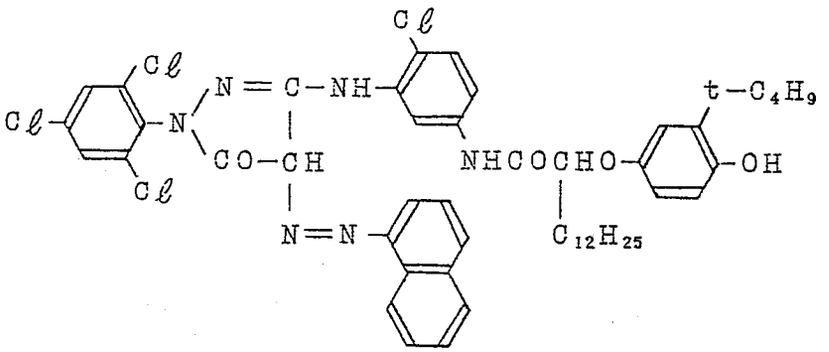
(12)



As colored magenta couplers, examples thereof are described in U.S. patents No. 2,801,171 and No.

3,519,429; and Japanese Patent Publication No. 27930/1973. Paticularly preferable colored magenta couplers include following compounds.

(1)



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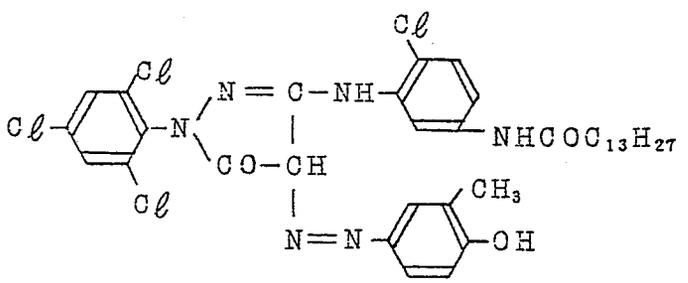
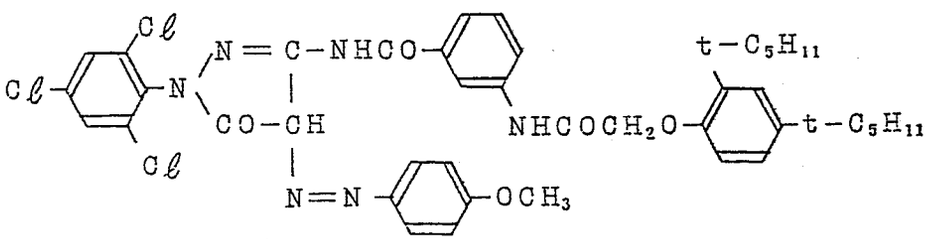
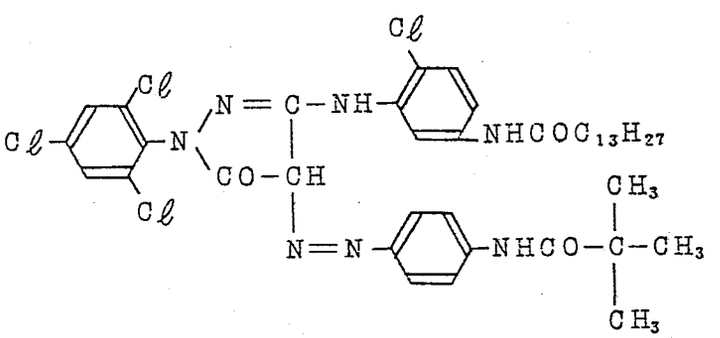


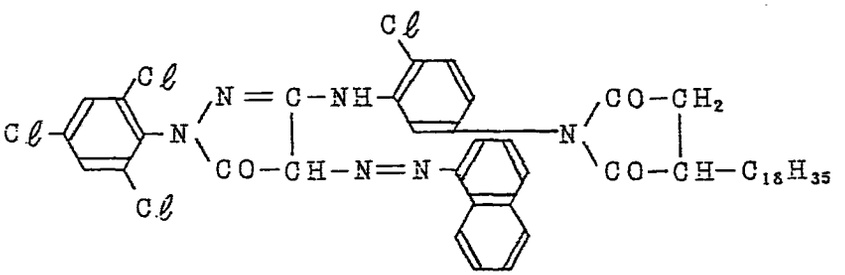
(3)



(4)

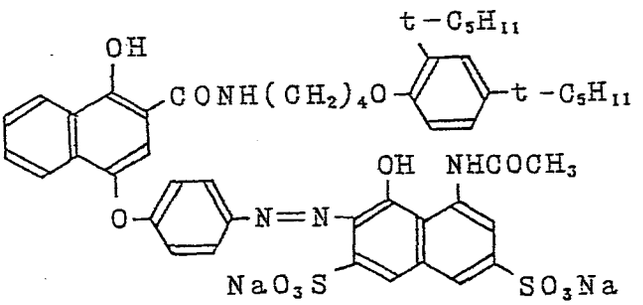


(5)

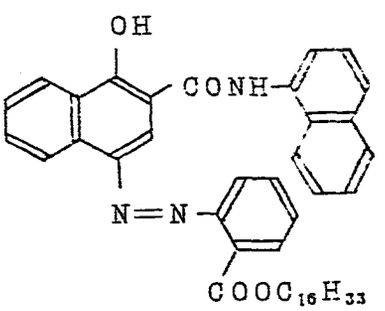


As colored cyan couplers, examples thereof are described in U.S. patent No. 1,084,480; and Japanese Patent Publication No. 32461/1980. Particularly preferable colored cyan couplers include following compounds.

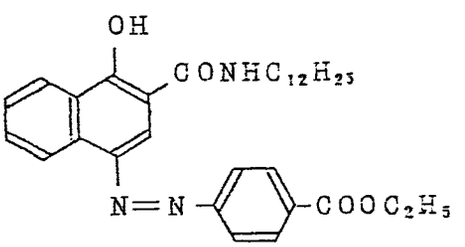
(1)



(2)



(3)



The above-mentioned various coulers may be included in a combination of two or more couplers in a single layer, or the same coupler may be included in more than two different layer.

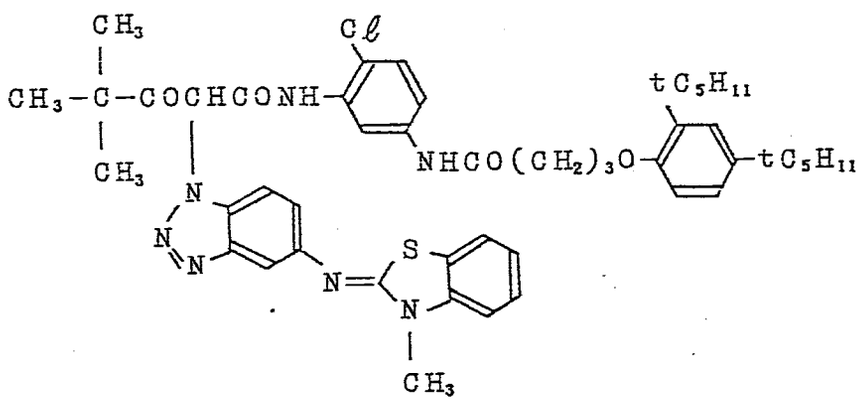
Incorporation of the coupler into a silver halide emulsion layer can be carried out in a known way, for instance, in the way described in U.S. Patent No. 2,322,027. For instance, the coupler is dissolved in an appropriate organic solvent, and then dispersed in a hydrophilic colloidal solution. Examples of the appropriate organic solvent include a phthalic acid alkyl ester such as dibutyl phthalate and dioctyl phthalate, a phosphoric acid ester such as diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and dioctyl butyl phosphate, a citric acid ester such as tributyl acetylcitrate, a benzoic acid ester such as octyl benzoate and an alkyl amide such as diethyllaurylamide. Examples of other types of the appropriate organic solvent include organic solvent having the boiling point in the range of about 30 ^{o}C to 150 ^{o}C, for instance, a lower alkyl acetate such as ethyl acetate and butyl acetate, ethyl propionate, sec-butyl alcohol, methyl isobutyl ketone, β-ethoxyethyl acetate and methyl cellosolve acetate. The above-mentioned high-boiling point solvent and low-boiling point solvent may be employed in combination.

If a coupler contains an acidic group such as carboxylic acid or sulfonic acid, it can be incorporated into a hydrophilic colloidal solution in the form of an aqueous alkaline solution.

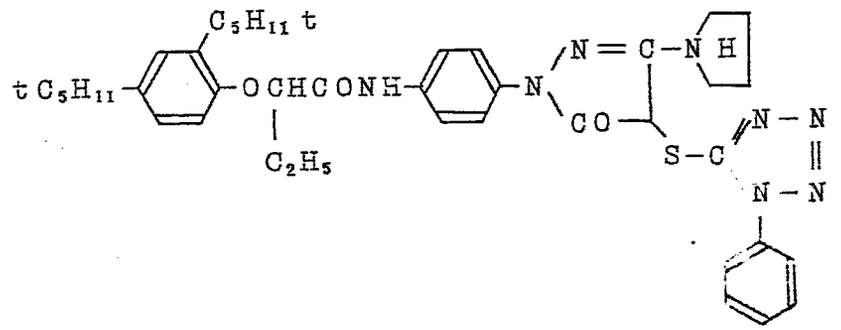
The coupler is incorporated into an emulsion layer generally in an amount from 2×10^{-3} to 5×10^{-1} mole, preferably from 1×10^{-2} to 5×10^{-1} mole per mole of silver in the silver halide emulsion layer.

Furthermore, the light-sensitive material according to this invention may contain a DIR compound. Examples of the DIR compounds are those described in U.S. Patents No. 2,327,554, No. 3,227,554 and No. 3,615,506; Japanese Provisional Patent Publications No. 82424/1977, No. 145135/1979 and No. 151944/1982; and Japanese Patent Publication No. 16141/1976. Particularly preferable DIR compound include following compounds.

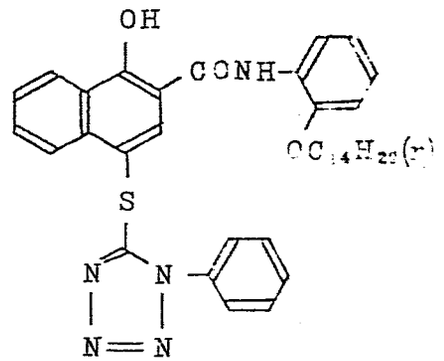
(1)



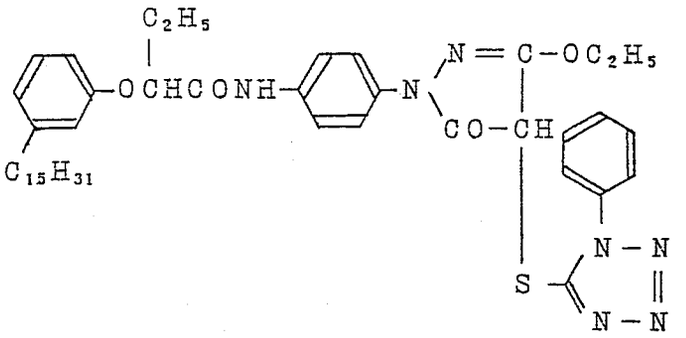
(2)



(3)



(4)



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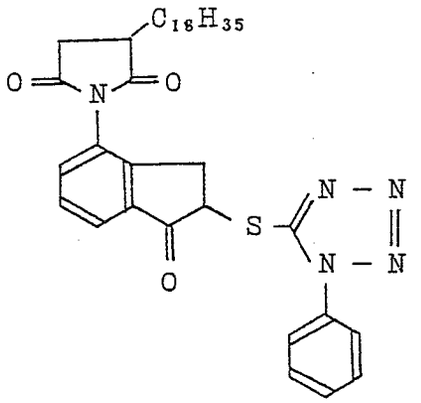

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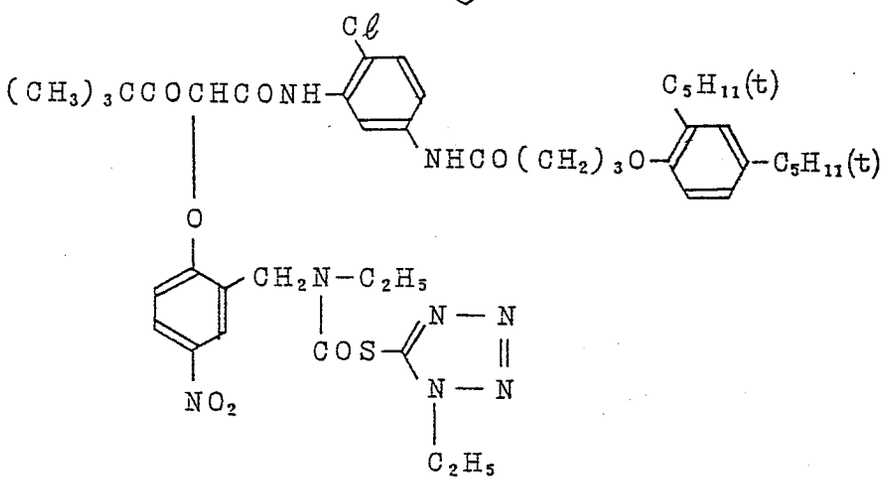

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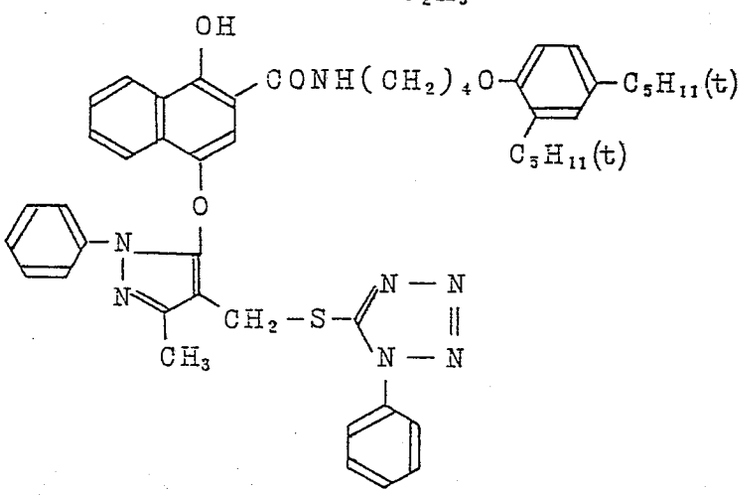
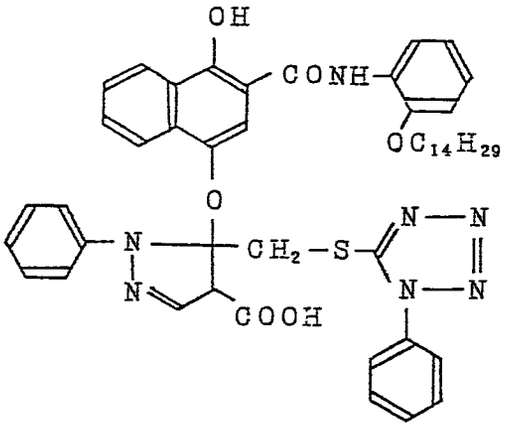
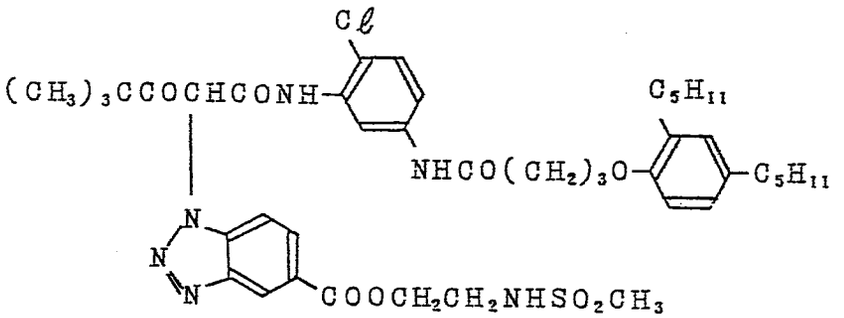


(8)

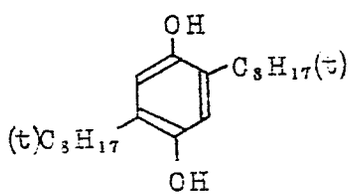


(9)

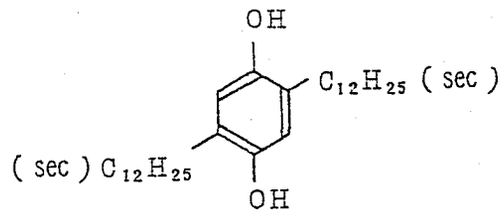


Moreover, as stain preventive agents efectively usable in the emulsion of this invention, examples thereof are described in U.S. Patent No. 2,728,659; and Japanese Provisional Patent Publication No. 2123/1971. Particularly preferable stain preventive agents include following compounds.

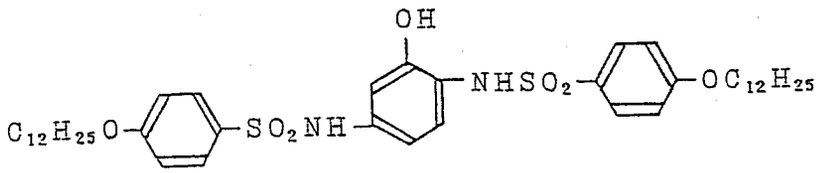
(1)



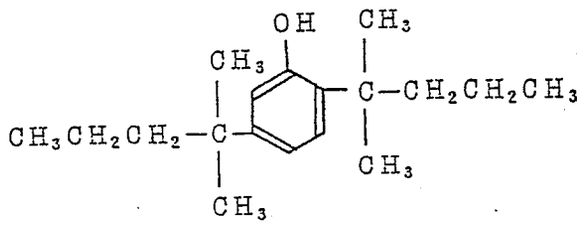
(2)



(3)



(4)



As antistatic agents to be used in the emulsion of this invention, there may be effectively employed diacetyl cellulose, styrene-perfluoroalkyllithium maleate copolymer, an alkali salt of a reaction product between styrene-maleic anhydride copolymer and p-aminobenzenesulfonic acid. Illustrative of matting agents are polymethyl methacrylate, polystyrene and alkali-soluble polymers. Further, it is also possible to use a colloidal silicon oxide. Also, as latexes to be added for improvement of the film properties, there may be employed copolymers of acrylic acid ester, vinyl ester, etc. with other monomers having ethylenic groups. Gelatin plasticizers may be exemplified by glycerine and glycol type compounds, and thickeners may include styrene-sodium maleate copolymer, alkyl vinyl ether-maleic acid copolymer and the like.

As the support for the light-sensitive material by the

use of the emulsion of this invention as prepared above, there may be employed, for example, baryta paper, polyethylene-coated paper, polypropylene synthetic paper, glass paper, cellulocse acetate, cellulose nitrate, polyvinyl acetal, polypropylene, polyester film such as of polyethyleneterephthalate, polystyrene, etc. These supports may be chosen suitably depending on the purpose of use of the respective light-sensitive silver halide photogaphic material.

These supports may be applied with subbing treatment, if necessary.

The light-sensitive material prepared by the use of the emulsion of this invention may be subjected to light exposure and then developed according to the known method conventionally used.

The black-and-white developer is an alkaline solution containing developing agents such as hydroxy benzenes, aminophenols or aminobenzenes, and it may further contain alkali metal salts such as a sulfite, a carbonate, a bisulfite, a bromide and an iodide. When said light-sensitive material is for color photography, it may be developed by a color developing process which is commonly used. In a reversal process, it is firstly developed by a developer for a black-and-white negative and then subjected to white color exposure, or subjected to treatment in a bath containing an antifoggant, and further developed for color development in an alkaline developing solution containing color developing agents.

There is no particular restriction to the method for treatment, and any method may be applied. As a typical example, there may be mentioned, a system in which bleach-fix treatment is conducted after the color development and further washing and stabilizing

treatments are carried out as the case requires, or a system in which the bleaching and the fixing are separately caried out after the color development, and further washing and stabilizing treatments are carried out as the case require.

The aforementioned silver halide photographic emulsion can particularly preferably be used for color photography and can suitably be applied to many light-sensitive material because it has a noticeably high photographic sensitivity and a less photographic fog. For example, the light-sensitive material according to this invention can be applied effectively to a variety use in a black-and-white generic photography, X-ray photography, color photography, infrared photography, microphotography, silver dye bleach, reversal process and diffusion transfer process.

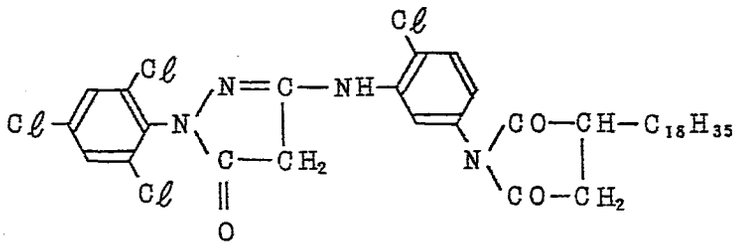
This invention is illustrated in detail by referring to the following Examples, by which the embodiments of this invention are not limited.

Example 1

To a green-sinsitive high sensitivity silver iodobromide gelatin emulsion comprising silver halide grains of mono-dispersed cubic crystals each having a grain size of 1.6 μ, and a silver iodide content of 2 mole % and a variation coefficient of a grain size distribution of 12 %, various kinds of sensitizers are added in amounts as shown in the following Table 1 per mole of silver halide in the presence of a hydroxy tetrazaindene compound as a nitrogen-containing heterocyclic compound according to this invention and ammonium thiocyanate as a solvent for silver halide, and then subjected to a chemical ripening at 55 ^{o}C for 50 minutes. After completion of the chemical ripening, to the aforesaid emulsion were added a

magenta coupler dispersion as shown below and a film hardner, and the thus prepared emulsions were applied onto cellulose triacetate base supports and were dried.

(Magenta coupler)



Next, the samples were subjected to 1/50 second's Wedge exposure through a green filter (produced by Tokyo Shibaura Denki K. K.) by the use of a KS-1 type photo-sensitometer (produced by Konishiroku Photo Industry Co., Ltd.), and a color negative development was carried out in accrdance with the undermentioned conditions.

[Development condition]

Treating process (38 °C)	Processing time
Color developing	2 min. 45 sec.
Bleaching	6 min. 30 sec.
Washing	3 min. 15 sec.
Fixing	6 min. 30 sec.
Washing	3 min. 15 sec.
Stabilization	1 min. 30 sec.

Compositions of the processing solutions used in the respective processing steps were as follows:

[Composition of color developing solution]

4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.8 g
Anhydrous sodium sulfite	0.14 g
Hydroxylamine·1/2 sulfate	1.98 g
Sulfuric acid	0.74 mg

Anhydrous potassium carbonate	28.85 g
Anhydrous soudium hydrogen carbonate	3.46 g
Anhydrous potassium sulfite	5.10 g
Potassium bromide	1.16 g
Sodium chloride	0.14 g
Nitrilotriacetic acid trisodium salt (monohydrate)	1.20 g
Potassium hydroxide	1.48 g

(make up to one liter with addition of water)

[Composition of bleaching solution]

Ferric ammonium ethylenediamine-tetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml

(make up to one liter with addition of water and adjust to pH 6.0 by using an aqueous ammonia solution)

[Composition of fixing solution]

Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.6 g
Sodium metasulfite	2.3 g

(make up to one liter with addition of water and adjust to pH 6.0 by using acetic acid)

[Composition of stabilizing solution]

Formalin (37 % aqueous solution)	1.5 ml
Konidax (Trade name, produced by Konishiroku Photo Industry, Co., Ltd.)	7.5 ml

(make up to one liter with addition of water)

For the resulting dye images, density measurement was carried out through a green filter to obtain green light sensitivities and photographic fogs. Obtained results

are shown in Table 1 below. Each sensitivity was expressed by normalizing an inverse number of exposure necessary to provide an optical density of a fog plus 0.1, and assuming the sensitivity of Sample No. 1 as 100.

Table 1

Sample No.	1	2	3	4	5
N,N-dimethyl-selenourea (0.2 mg/mole of Ag)	O	O	O	O	O
Chloroauric acid (0.18 mg/mole of Ag)	X	X	O	O	O
Sodium thiosulfate (1.0 mg/mole of Ag)	X	O	O	O	O
Nitrogen-containing compound: Example compound (N - 4) (100 mg/mole of Ag)	O	O	O	O	X
Solvent for silver halide: rhodane ammonium (122 mg/mole of Ag)	X	X	X	O	X
Photographic characteristics					
Sensitivity	100	169	191	208	170
Photographic fog	0.14	0.16	0.15	0.17	0.20

As is clear from Table 1 above, it can be understood that, in Samples 2, 3 and 4 according to this invention, sensitivities thereof are high and the occurrence of photographic fog has been reduced, whereas, in Samples 1 and 5 which are outside the present invention, high sensitivity could not be attained or photographic fog was increased if high sensitivity was attained.

Example 2

An emulsion was prepared in the same manner as in Example

1 except that a green-sinsitive high sensitivity silver iodobromide gelatin emulsion comprising silver halide grains of monodispersed octahedral crystals each having a grain size of 1.6 μ, and a silver iodide content of 2 mole % and a variation coefficient of a grain size distribution of 12 % is used. With respect to a Sample which was obtained by applying the resulting emulsion onto a support, a treatment for development was conducted in the same manner as in Example 1. The results ontained by the measurement of the photographic properties are shown in the Table 2 below.

Table 2

Sample No.	6	7	8	9	10
N,N-dimethyl-selenourea (0.2 mg/mole of Ag)	○	○	○	○	○
Chloroauric acid (0.18 mg/mole of Ag)	X	X	○	○	○
Sodium thiosulfate (1.0 mg/mole of Ag)	X	○	○	○	○
Nitrogen-containing compound: Example compound (N - 4) (100 mg/mole of Ag)	○	○	○	○	X
Solvent for silver halide: rhodane ammonium (122 mg/mole of Ag)	X	X	X	○	X
Photographic characteristics					
Sensitivity	100	183	209	212	183
Photographic fog	0.12	0.15	0.13	0.16	0.19

This example was to accomplish the same sensitization as in Example 1 by using a monodispersed emulsion having octahedral crystals in place of the monodispersed emulsion having cubic crystals used in Example 1. As

understood from Table 2, Samples 7, 8 and 9 according to this invention showed the same excellent sensitization effects as in Example 1, and high sensitization could be accomplished.

Example 3

An emulsion was prepared in the same manner as in Example 1 except that a green-sinsitive high sensitivity silver iodobromide gelatin emulsion comprising silver halide grains of monodispersed tetradecahedral crystals each having a grain size of 1.6 μ, and a silver iodide content of 2 mole % and a variation coefficient of a grain size distribution of 12 % is used. With respect to a Sample which was obtained by applying the resulting emulsion onto a support, a treatment for development was conducted in the same manner as in Example 1. The results ontained by the measurement of the photographic properties are shown in the Table 3 below.

Table 3

Sample No.	11	12	13	14	15
N,N-dimethyl-selenourea (0.2 mg/mole of Ag)	○	○	○	○	○
Chloroauric acid (0.18 mg/mole of Ag)	X	X	○	○	○
Sodium thiosulfate (1.0 mg/mole of Ag)	X	○	○	○	○
Nitrogen-containing compound: Example compound (N - 4) (100 mg/mole of Ag)	○	○	○	○	X
Solvent for silver halide: rhodane ammonium (122 mg/mole of Ag)	X	X	X	○	X
Photographic characteristics					
Sensitivity	100	193	215	230	195
Photographic fog	0.10	0.12	0.11	0.13	0.17

This example was to accomplish the same sensitization as in Example 2 by using a monodispersed emulsion having tetradecahedral crystals in place of the monodispersed emulsion having octahedral crystals in Example 2. As understood from Table 3, Samples 12, 13 and 14 according to this invention showed the same excellent sensitization effects as in Example 2, and high sensitization could be accomplished.

The silver halide emulsion having monodispersed silver halide grains which have been selenium sensitized and sulfur sensitized simultaneously or separately in the presence of a nitrogen-containing heterocyclic compound capable of forming a complex with silver does not cause photographic fog and can attain high sensitivity of a photographic material. Additional gold sensitization and

incorporation of a solvent for silver halide would promote the high sensitization according to this invention.

Claims:

1. A silver halide emulsion which comprises monodispersed silver halide grains in which a selenium sensitization and a sulfur sensitization are carried out simultaneously or separately in the presence of a nitrogen-containing heterocyclic compound capable of forming a complex with silver.

2. The silver halide emulsion according to Claim 1, wherein said nitrogen-containing heterocyclic compound includes heterocyclic rings selected from the group consisting of a pyrazole ring, pyrimidine ring, 1,2,4-triazole ring, 1,2,3-triazole 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, phthalazine ring and indazole ring.

3. The silver halide emulsion according to Claim 2, wherein said heterocyclic rings have a substituent group selected from the group consisting of a hydroxy group, an alkyl group, an alkylthio group, an amino group, a hydroxyamino group, an alkylamino group, a dialkylamino group, an arylamino group, a carboxy group, an alkoxycarbonyl group, a halogen atom, an acylamino group, a cyano group and a mercapto group.

4. The silver halide emulsion according to Claim 1, wherein said said nitrogen-containing heterocyclic compound is added in an amount of 10 mg to 1000 mg per

mole of the silver halide.

5. The silver halide emulsion according to Claim 1, wherein said monodispersed silver halide grains have a variation coefficient of a grain size distribution of 0.18 or less.

6. The silver halide emulsion according to Claim 5, wherein said monodispersed silver halide grains have the variation coefficient of the grain size distribution of 0.15 or less.

7. The silver halide emulsion according to Claim 1, wherein said selenium sensitization is carried out in the presence of at least one selenium sensitizer selected from the group consisting of an aliphatic isoselenocyanate, a selenourea, a selenoketone, a selenoamide, a selenocaboxylic acid, a selenocarboxylate, a selenophosphate, a selenide, a colloidal selenium metal, an aliphatic isoselenocyanate, a selenourea having an aliphatic group or an aromatic group, a selenoketone, a selenoamide and a selenocarboxylic acid.

8. The silver halide emulsion according to Claim 7, wherein said selenium sensitizer is added in an amount of 2.0×10^{-3} to 10 mg per mole of the silver halide.

9. The silver halide emulsion according to Claim 8, wherein said selenium sensitizer is added in an amount of 2.0×10^{-2} to 1.0 mg per mole of the silver halide.

10. The silver halide emulsion according to Claim 1, wherein said sulfur sensitization is carried out in the presence of at least one sulfur sensitizer selected from the group consisting of a thiosulfate derivative, a thiourea derivative, allylisothiocyanate, cystin, p-toluenethiosulfonate and rhodanine.

11. The silver halide emulsion according to Claim 10, wherein said sulfur sensitizer is added in an amount of 0.01 to 100 mg per mole of the silver halide.

12. The silver halide emulsion according to Claim 11, wherein said sulfur sensitizer is added in an amount of 0.1 to 10 mg per mole of the silver halide.

13. The silver halide emulsion according to Claim 1, wherein said silver halide grains are carried out a gold sensitization.

14. The silver halide emulsion according to Claim 13, wherein said gold sensitization is carried out in the presence of at least one gold sensitizer selected from the group consisting of chloroaurate, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate and pyridyltrichlorogold.

15. The silver halide emulsion according to Claim 1, wherein said selenium sensitization and sulfur sensitization is carried out in the presence of a solvent for silver halide.

16. The silver halide emulsion according to Claim 15, wherein said solvent for silver halide is a solvent selected from the group consisting of an organic thioether, a thiourea derivative, a solvent having a thiocarbonyl group sandwiched between an oxygen atom or a sulfur atom and a nitrogen atom, an imidazole, a sulfite and a thiocyanate.

17. The silver halide emulsion according to Claim 16, wherein said solvent for silver halide is a thiourea derivative or a thiocyanate.

0122125

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 84 30 2347

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	FR-A-1 450 841 (KODAK-PATHE) * Example 5; claims *	1-17	G 03 C 1/06 G 03 C 1/02
X	US-A-3 442 653 (J.S. DUNN et al.) * Example 1; claims *	1-17	
A	GB-A-2 055 221 (DU PONT DE NEMOURS) * Claims *	5,6	
A	US-A-3 420 670 (K.M. MILTON) * Example 1; claim 1 *	13	
A	EP-A-0 072 695 (KONISHIROKU PHOTO INDUSTRY) * Claims *	15	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

G 03 C 1/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-06-1984	PHILOSOPH L.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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