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(54) Silver halide photographic emulsion.

(57) There is disclosed a silver halide photographic emulsion improved in sensitivity comprising silver halide grains having a chemical sensitization center comprising silver sulfide, gold sulfide or a mixture thereof, which is formed in the presence of a nucleus capable of accelerating the chemical sensitization center forming reaction on the surface of the silver halide grains and also in the presence of a compound adsorbent to the silver halide grains.

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FIELD OF THE INVENTION

The present invention relates to a silver halide photographic emulsion, and more particularly to a high-sensitivity silver halide photographic emulsion.

BACKGROUND OF THE INVENTION

There have lately been growing demands for still better photographic characteristics of silver halide emulsions, such as higher sensitivity, more excellent graininess, higher resolution, lower fog density and more sufficiently high optical density than those of conventional ones. Any of these demands, although seemingly different, can be mostly solved by technology for manufacturing low-fog and high-sensitivity silver halide emulsions, and it is no exaggeration to say that the most important problem for those skilled in the art is to develop a low-fog, high-sensitivity silver halide emulsion.

The most proper method for achieving the raising of the sensitivity of an emulsion is to reduce the inefficiency and increase the quantum efficiency of silver halide crystals in the course of exposure to light. Conventional means to increase the quantum efficiency is carried out by forming on the surface of or inside a silver halide crystal a chemical sensitization center composed of silver sulfide or gold sulfide or a mixture thereof, which functions as a sensitivity center that traps photoelectrons. The above means is generally known as sulfur sensitization or gold-sulfur sensitisation.

However, if an attempt is made to form a chemical sensitization center having a good electron trapping efficiency in accordance with a conventional chemical sensitization method, it results in the formation of a number of chemical sensitization centers which compete with one another for trapping photoelectrons in the process of exposure to light. thus causing the latent image forming efficiency to lower, i.e., bringing about lowering of the sensitivity.

As means to improve the above disadvantage of the conventional method there have been proposed techniques to control the chemical sensitization center formation in the presence of a chemical sensitization control agent or a chemical sensitization reforming agent in the chemical sensitisation process as described in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP O.P.I.) Nos. 126526/1983 and 201651/1989, U.S. Patent Nos. 2,131,038, 3,411,914 and 3,554,757, and Duffin, G.F., Photographic Emulsion Chemistry, Focal Press, London (1966), pp.138-143.

As other improving measures, JP O.P.I. No. 93447/1986 discloses various methods for selectively growing the chemical sensitization center at a specific point on a silver halide crystal.

However, as a result of our investigation, it has been found that the above improving measures are not sufficient to meet the recent high-level demand for raising the sensitivity.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a high-sensitivity silver halide photographic emulsion produced by an improved chemical sensitisation center forming process.

It is another object of the invention to provide a method for producing a high-sensitivity silver halide photographic emulsion.

The above objects of the present invention are accomplished by a silver halide photographic emulsion containing silver halide grains having a chemical sensitization center comprised of silver sulfide or gold sulfide or a mixture thereof formed in the presence of a nucleus capable of catalytically acting upon and accelerating the silver sulfide forming reaction (catalytic nucleus) on the surface of the silver halide crystal and also in the presence of a compound adsorbent to the silver halide crystal.

The emulsion of the present invention is prepared by forming the catalytic nucleus on the surface of the silver halide grain and then performing chemical sensitization in the presence of a compound adsorbent to the silver halide crystal.

DETAILED DESCRIPTION OF THE INVENTION

The nucleus capable of catalytically acting upon and accelerating the silver sulfide forming reaction (catalytic nucleus) is different from the foregoing specific site on a silver halide crystal defined in the previously mentioned JP O.P.I. No. 93447/1986. The catalytic nucleus in the invention is a specific point comprised of an element or a combination of elements other than halogen elements constituting silver halide; i.e., a specific point comprised of a noble metal element such as Ag, Au, Pt, Ir, Pd, etc. and/or a simple element such as S, Se, Te, etc. or a compound thereof such as silver sulfide, gold sulfide, silver selenide, gold selenide, or the like, but are not limited to the mentioned single substances and compounds.

Judgement of whether the specific point functions as a catalytic nucleus to accelerate the silver sulfide forming reaction can be made by measuring the rate of the silver sulfide forming reaction by a sulfur sensitizer. The silver sulfide forming reaction in the invention proceeds at a rate of at least 1.5 times as fast as the reaction in which silver halide is formed in the absence of the nucleus. The silver sulfide forming reaction rate can be measured in accordance with various methods known to those skilled in the art, such as a method for tracing the reaction by using a sulfur sensitizer that is labelled with a radioactive element; a method for spectroscopically measuring the amount of a produced silver sulfide; a method for measuring the changes in the proton ion concentration released by the reaction of a sulfur sensitizer; and the like. Reference can be made for these methods to H. Takiguchi, J. Imaging Sci., vol.32, p.20 (1988); E. Moisar, Ber. d. Bun- senges. Phys. Chem., vol.72, p.467 (1968); and D. J. Cash, J. Photogr. Sci., vol.20, p.107 (1972).

The catalytic nucleus forming process is preferably put prior to the process for forming silver sulfide sensitization center by a sulfur sensitizer. As the elemental substance or compound for use in the formation of the catalytic nucleus there may be utilized an elemental sulfur element or sulfur sensitizers, gold sensitizers and selenium sensitizers as described later. The proper amount (number of atoms or molecules) thereof depends on the conditions of factors such as silver halide crystals, the chemical sensitization process, etc.

The sulfur sensitizer for producing silver sulfide in the invention may be selected from among water-soluble sulfides, thiosulfates, thioureas, mercapto compounds and rhodanines, which are exemplified in U.S. Patent Nos. 1,574,944, 2,410,689, 2,278,947, 3,501,313 and 3,656,955, West German Patent No. 1,422,869, and Japanese Patent Examined Publication Nos. 20533/1974 and 28568/1983.

Preferred among these compounds are thiosulfates, thioureas and rhodanines, and the most preferred are thiosulfates.

The using amount of a sulfur sensitizer varies according to the type of a silver halide used, the kind of a compound used and ripening conditions, but is preferably from 1x10^{-4} to 1x10^{-7} mole per mole and more preferably 1x10^{-5} to 1x10^{-7} mole per mole of silver halide. It is preferable that the sulfur sensitizer be slowly added to have its reaction take place slowly, so that the reaction temperature is preferably as low as 40 to 60 ° C. The silver ion concentration of the reaction system (silver halide emulsion) is preferably as low as possible; pAg (absolute value of logarithm of reciprocal of silver ion concentration) is preferably 8.0 to 11.0.

The compound adsorbent to the silver halide crystals used in the invention is a stabilizer, antifoggant or spectrally sensitizing dye.

Examples of the stabilizer or antifoggant include azaindenes; azoles such as benzothiazolium salts, nitroindazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptobenzimidazoles, aminotirazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles such as 1-phenyl-5-mercaptotetrazole; mercaptopyrimidines, mercaptotriazines, thioketo compounds such as oxazolinethione compounds, benzenethiosulfinic acids, benzenesulfinic acids, benzenesulfonic acid amides, hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives and ascorbic acid derivatives. Preferred among these compounds are azaindenes.

The following are typical examples of the azaindenes, but are not limited thereto.

A-1	2,4-Dihydroxy-6-methyl-1,3a,7-triazaindene
A-2	2,5-Dimethyl-7-hydroxy-1,4,7a-triazaindene
A-3	5-Amino-7-Hydroxy-2-methyl-1,4,7a-triazaindene
A-4	4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene
A-5	4-Hydroxy-1,3,3a,7-tetrazaindene
A-6	4-Hydroxy-6-phenyl-1,3,3a,7-tetrazaindene
A-7	4-Methyl-6-hydroxy-1,3,3a,7-tetrazaindene
A-8	2,6-Dimethyl-4-hydroxy-1,3,3a,7-tetrazaindene
A-9	4-Hydroxy-5-ethyl-6-methyl-1,3,3a,7-tetrazaindene
A-10	2,6-Dimethyl-4-hydroxy-5-ethyl-1,3,3a,7-tetrazaindene
A-11	4-Hydroxy-5,6-dimethyl-1,3,3a,7-tetrazaindene
A-12	2,5,6-Trimethyl-4-hydroxy-1,3,3a,7-tetrazaindene
A-13	2-Methyl-4-hydroxy-6-phenyl-1,3,3a,7-tetrazaindene
A-14	4-Hydroxy-6-methyl-1,2,3a,7-tetrazaindene
A-15	4-Hydroxy-6-ethyl-1,2,3a,7-tetrazaindene
A-16	4-Hydroxy-6-phenyl-1,2,3a,7-tetrazaindene
A-17	4-Hydroxy-1,2,3a,7-tetrazaindene
A-18	4-Methyl-6-hydroxy-1,2,3a,7-tetrazaindene

A-19	7-Hydroxy-5-methyl-1,2,3,4,6-pentazaindene
A-20	5-Hydroxy-7-methyl-1,2,3,4,6-pentazaindene
A-21	5,7-Dihydroxy-1,2,3,4,6-pentazaindene
A-22	7-Hydroxy-5-methyl-2-phenyl-1,2,3,4,6-pentazaindene
A-23	5-Dimethylamino-7-hydroxy-2-phenyl-1,2,3,4,6-pentazaindene

The sensitizing dyes preferably used for the invention include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonole dyes. The most useful dyes are cyanine dyes, merocyanine dyes and complex merocyanine dyes.

These dyes may be ones having a basic heterocyclic nucleus, any of those nucleus usually utilized for cyanine dyes, such as a pyrroline nucleus, oxazoline nucleus, thiazoline nucleus, pyrrole nucleus, oxazole nucleus, thiazole nucleus, selenazole nucleus, imidazole nucleus, tetrazole nucleus and pyridine nucleus; nuclei formed with a alicyclic hydrocarbon ring fused to the above nuclei, such as an indolenine nucleus, benzindolenine nucleus, indole nucleus, benzoxazole nucleus, naphthooxazole nucleus, benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, benzimidazole nucleus and quinoline nucleus. These nuclei may be substituted on a carbon atom.

The aforementioned merocyanine dyes or complex merocyanine dyes each may have a ketomethylene-structural nucleus such as a 5- or 6-member heterocyclic nucleus including pyrazoline-5-one nucleus, thiohydantoin nucleus, 2-thioxazoline-2,4-dione nucleus, thiazolidine-2,4-dione nucleus, rhodanine nucleus and thiobarbituric acid nucleus.

Useful sensitizing dyes are described in West German Patent No. 929,080, U.S. Patent Nos. 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,655,394, 3,656,959, 3,672,897 and 3,694,217, British Patent No. 1,242,588, JP O.P.I. No. 54547/1991 and Japanese Patent Examined Publication No. 14030/1969.

These sensitizing dyes may be used alone or in combination. Combination of such sensitizing dyes are often used particularly for the purpose of supersensitization, typical examples of which are described in U.S. Patent Nos. 268,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,679,428, 3,703,377, 3,769,301, 3,814,609 and 3,837,862, British Patent No. 1,344,281 and Japanese Patent Examined Publication No. 4936/1968.

The following are typical examples of the sensitizing dye usable in the invention, but the invention is not limited by the examples.

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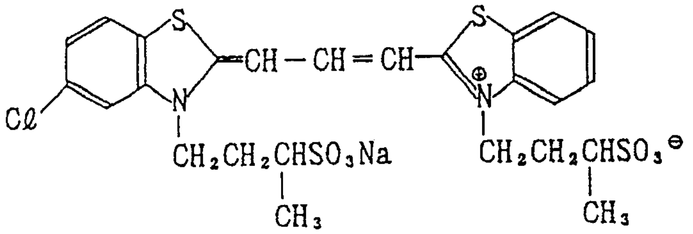

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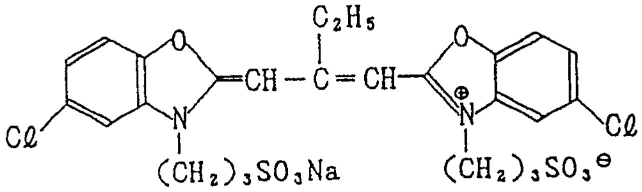

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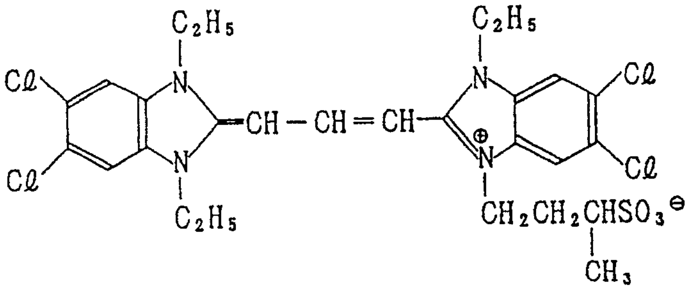

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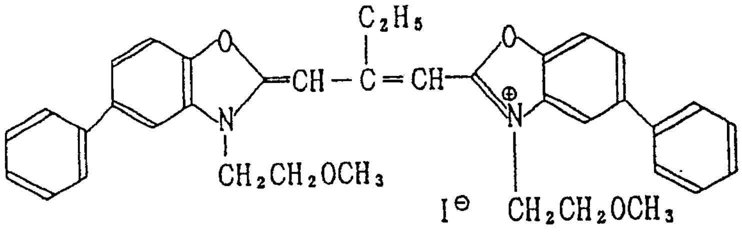

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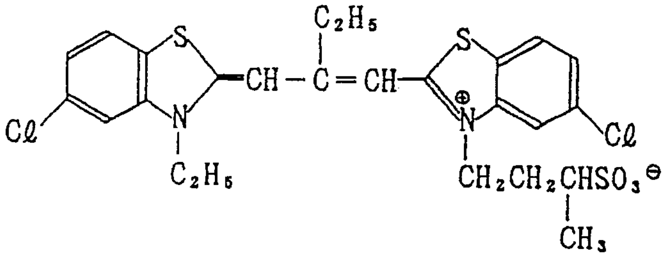
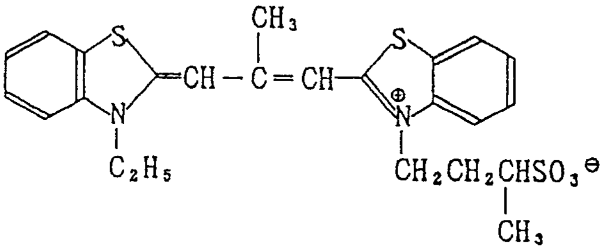


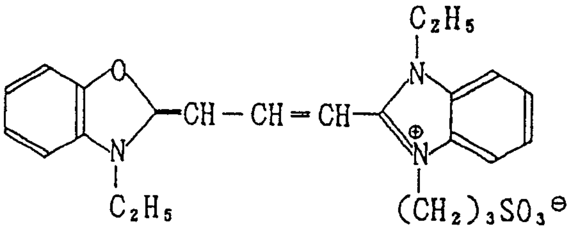
S
C₂H₅
CH − C = CH
S
⊕N
Cℓ
N
Cℓ
C₂H₅
CH₂CH₂CHSO₃⊖
CH₃

B − 6



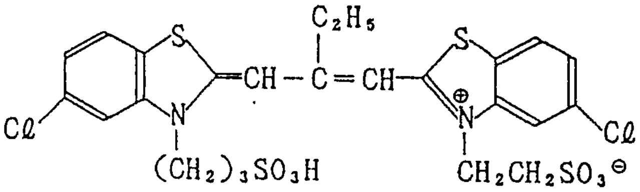
CH₃
S
CH − C = CH
S
N
⊕N
C₂H₅
CH₂CH₂CHSO₃⊖
CH₃

B − 7



C₂H₅
N
O
CH − CH = CH
N
⊕N
C₂H₅
(CH₂)₃SO₃⊖

B − 8



C₂H₅
S
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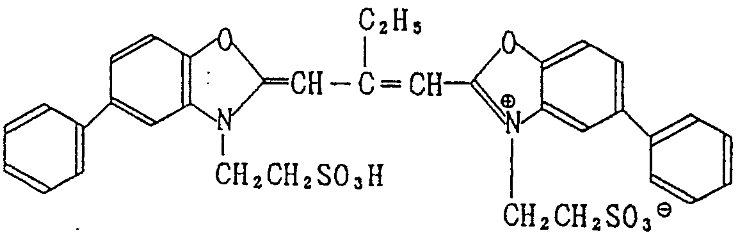
Cℓ
N
⊕N
Cℓ
(CH₂)₃SO₃H
CH₂CH₂SO₃⊖

B − 9



C₂H₅
O
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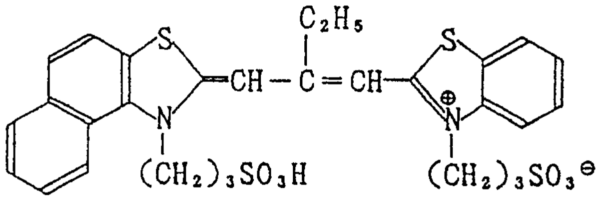
O
N
⊕N
CH₂CH₂SO₃H
CH₂CH₂SO₃⊖

B - 10



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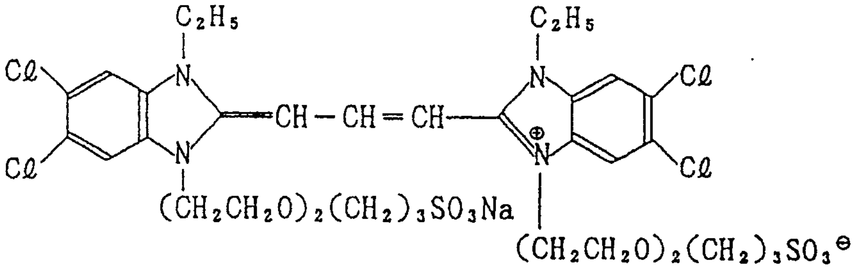

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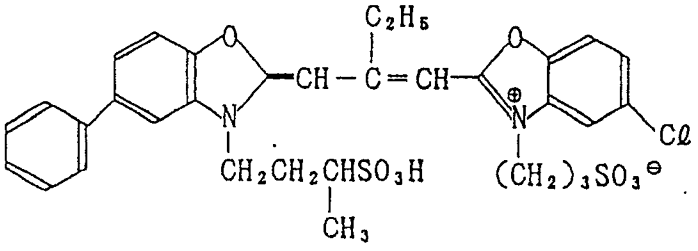

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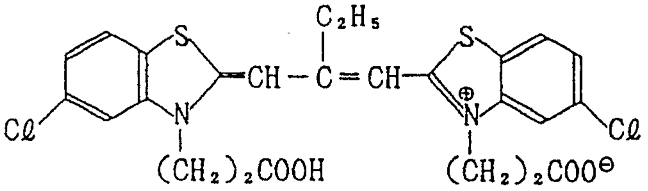

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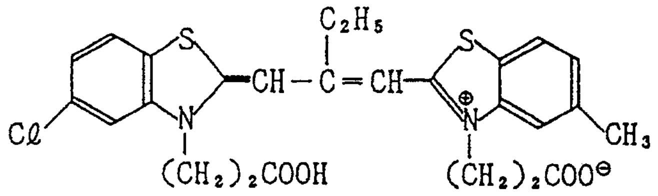

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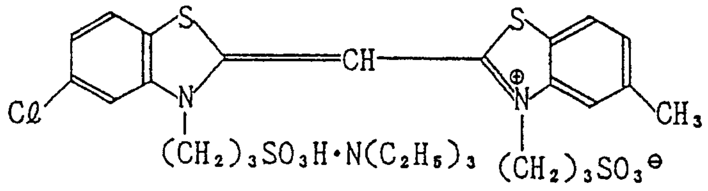

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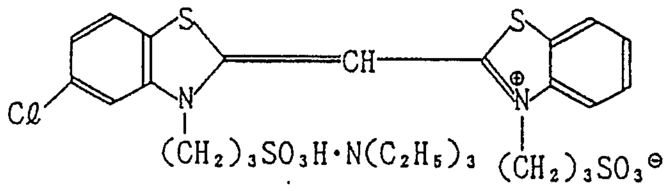

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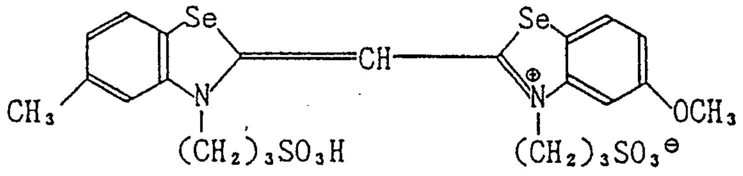

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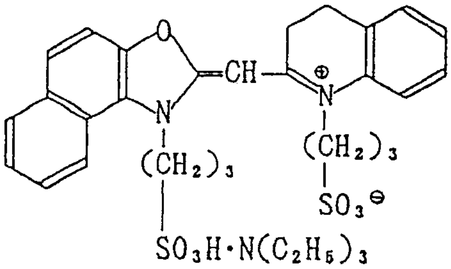

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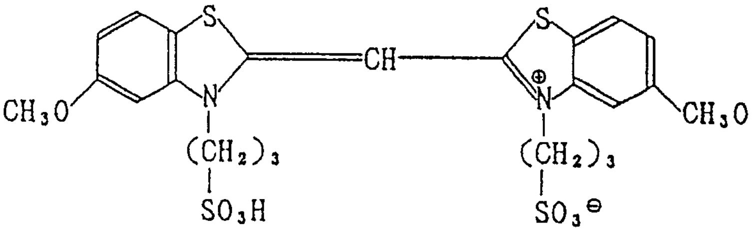

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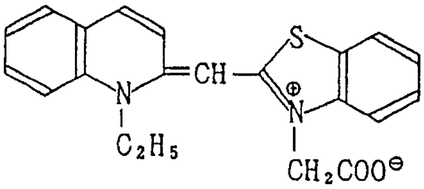

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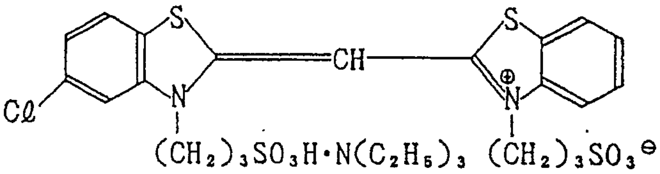

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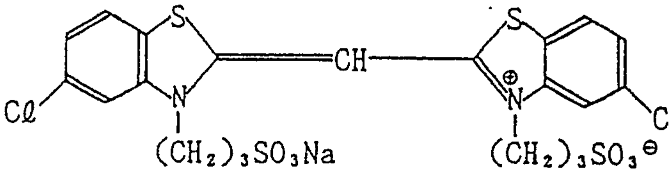

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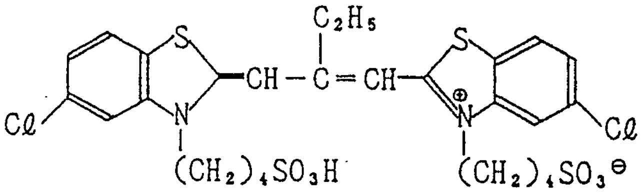

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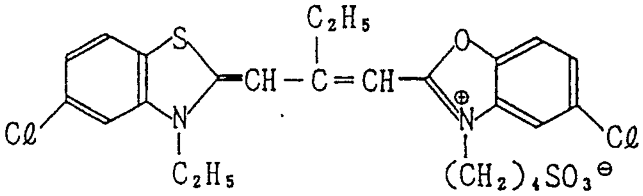

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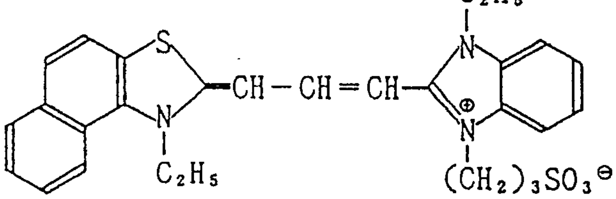

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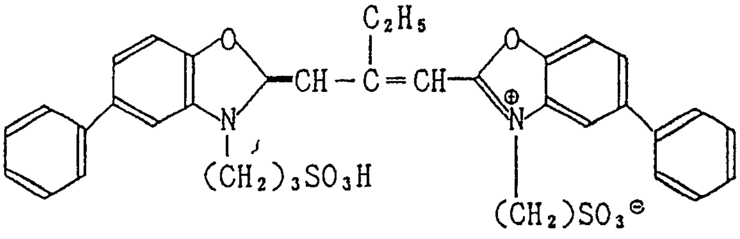

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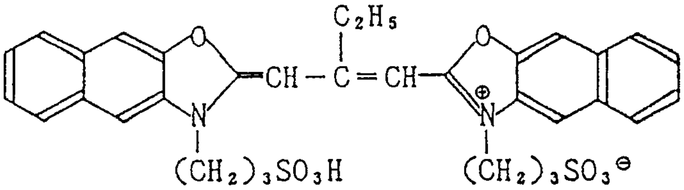


An emulsion, in addition to the aforementioned dyes, may also contain a dye which in itself has no spectral sensitization effect or a substance which does substantially not absorb any visible rays but shows supersensitization effect. For example, the emulsion may contain the nitrogen-containing heterocyclic group-substituted aminostilben compound described in U.S. Patent Nos. 2,933,390 and 3,635,721; the aromatic organic acid-formaldehyde condensate described in U.S. Patent No. 3,743,510; cadmium salts, azaindene compounds, or the like. The combined use of those as described in U.S. Patent Nos. 3,615,613, 3,615,641 and 3,635,721 are particularly useful.

The compound adsorbent to silver halide to be made present as a control agent in the chemical sensitization center forming process of the invention may be used alone or in combination of a plurality of kinds thereof. When a silver halide emulsion needs to be spectrally sensitized, it is preferable that a spectral sensitization dye be used in combination as a control agent for the chemical sensitization process. In this instance, good results can often be obtained when a compound such as the foregoing stabilizer or antifoggant is used in combination to raise the covering rate on the surface of silver halide crystals.

The covering rate on the surface of silver halide crystals by the adsorbent compound is preferably not less than 50%, and more preferably not less than 70%.

As the gold sensitizer usable in combination in the invention there may be used various gold compounds having a gold oxidation number of either +1 or +3. Typical examples of the gold sensitizer include chloroaurates, potassium chloroaurate, auric chloride, potassium-auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, pyridyltrichlorogold and gold complexes with organic sulfur compounds.

The adding amount of the gold sensitizer differs according to various conditions, but is preferably about 10^{-7} to 10^{-1} mole per mole of silver halide. The gold sensitizer for forming a chemical sensitization center is preferably added after completion of the silver sulfide forming process.

In the invention, other chemical sensitizers additionally usable in combination include selenium sensitizers such as aliphatic isoselenocyanates such as allyl isoselenocyanate, selenoureas, selenoketones, selenoamides, selenocarboxylic acids and esters thereof, selenophosphates, diethyl selenide and diethyl diselenide. Particular examples of the above sensitizers are described in U.S. Patent Nos. 1,574,944, 1,602,592 and 1,623,499, and also include the amines and reductive substances such as stannous salts described in U.S. Patent Nos. 2,487,850, 2,518,698, 2,521,925, 2,521,926, 2,419,973, 2,694,637 and 2,983,619, and the salts of noble metals such as platinum, palladium, iridium and rhodium described in U.S. Patent Nos. 2,448,060, 2,566,245 and 2,566,263.

The chemical ripening with the compound of the invention may be performed satisfactorily in the presence of a solvent for silver halide, such as a thiocyanate, thioether, tetra-substituted thiourea or the like.

The silver halide emulsion of the invention may be of an arbitrary silver halide composition such as silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide or silver chloride, which can be prepared in accordance with an appropriate one of the methods described in P. Glafkides, Chimie et Physique Photographique (Paul Montel, 1967); G. F. Duffin, Photographic Emulsion Chemistry (The Focal Press, 1966); and V. L. Zelikman, Making and Coating Photographic Emulsion (The Focal Press, 1964); i.e., can be prepared in accordance with any one of the acidic, neutral and ammoniacal methods. The mixing of an aqueous silver salt solution and an aqueous halide solution for the reaction thereof may be made in any of the single-jet precipitation process, double-jet process and combination of both processes, and further may also be made in the process of forming silver halide grains in the presence of excessive silver ions, the so-called reverse precipitation process. As one form of the double-jet process there may be used a process for maintaining pAg constant in the liquid phase in which silver halide is produced, the so-called controlled double-jet process.

The silver halide grain size distribution of the silver halide emulsion of the invention may be either wider or narrower.

The silver halide grains contained in the silver halide emulsion of the invention may be regular-form grains such as octahedral or tetradecahedral grains, irregular-form grains such as spherical grains, twin planes-having grains or grains in the complex form of these grains. The silver halide grain may be of a substantially uniform composition-having structure, a core/shell type double structure or a multiphase structure. In the case of a core/shell type silver halide grain, it is preferably of a heterogeneous halide composition of core and shell phases.

The invention may apply to the sensitization of a tabular silver halide grain emulsion. The tabular silver halide grain is one having a diameter/thickness ratio of not less than 3, wherein the 'diameter' means the diameter of a circle equivalent in the area to the projection area of a grain, and the 'thickness' is expressed in terms of the distance between the two parallel surfaces constituting a tabular silver halide grain.

The composition and structure of the tabular silver halide grain are the same as those of the previously mentioned silver halide grain.

The silver halide crystal grain contained in the silver halide emulsion of the invention may be joined with a different composition-having silver halide by epitaxial junction to the host silver halide crystal, and may also be joined with a non-silver halide compound such as silver thiocyanate or lead oxide. In the silver halide grain forming or ripening process, a chalcogen compound such as of sulfur, selenium and tellurium, a cadmium salt, a zinc salt, a lead salt, thalium, an iridium salt or complex salt, a rhodium salt or complex salt, or an iron salt or complex salt may be present together.

Also, the core phase of the silver halide grain may be subjected to reduction sensitization as described in Japanese Patent Examined Publication No. 1410/1983 and Moisar et al, Journal of Photographic Science, vol.25 (1977), pp.19-27.

The silver halide emulsion of the invention may, for the purpose of raising the sensitivity and contrast or of development acceleration, contain, e.g., polyalkylene oxide or the ether, ester or amine derivative thereof, a thioether compound, a thiomorpholine, a quaternary ammonium salt, a urethane derivative, a urea derivative, an imidazole derivative or a 3-pyrazolidone derivative; for example, the emulsion may contain those described in U.S. Patent Nos. 2,400,532, 2,423,549, 2,716,062, 3,617,280, 3,772,021 and 3,808,003.

The silver halide emulsion of the invention may contain an antifoggant and a stabilizer even after completion of the chemical sensitization process. Compounds usable as the antifoggant or stabilizer are described in the section entitled 'Antifoggrants and Stabilizer' at page 107 of Product Licensing Index, vol.92.

The silver halide emulsion of the invention may also contain known photographic additives.

The known photographic additives include the compounds disclosed in Research Disclosure RD-17643 (Dec. 1978) and RD-18716 (Nov. 1979), which are listed in the following table.

Additives	RD-17643		RD-18716
	Page	Section	Page and column
Chemical sensitizers	23	III	648 to upper right
Sensitizing dyes	23	IV	648 right to upper right
Development accelerators	29	XXI	648 to upper right
Antifoggants	24	VI	649 to down right
Stabilizers	' '	' '	' '
Antistain agents	25	VII	650 left to right
Image stabilizers	' '	' '	
UV absorbing agents	25 - 26	VII	649 right to 650 left
Filter dyes	' '	' '	' '
Brightening agents	24	V	
Hardeners	26	X	651 right
Coating aids	26 - 27	XI	650 right
Surfactants	' '	' '	650 right
Plasticizers	27	XII	' '
Sliding agents	' '	' '	
Antistatic agents	' '	' '	' '
Matting agents	28	XVI	650 right
Binders	26	IX	651 right

The emulsion of the light-sensitive material of the invention may contain a dye forming coupler capable of forming a dye as a result of its coupling reaction with the oxidation product of an aromatic primary amine developing agent such as a p-phenylenediamine derivative or an aminophenol derivative.

The dye forming coupler is usually so selected as to form an appropriate dye that absorbs a specific spectral light to which a relevant emulsion layer is sensitive; that is, a yellow dye forming coupler is used for a blue-sensitive emulsion layer, a magenta dye forming coupler for a green-sensitive emulsion layer and a cyan dye forming coupler for a red-sensitive emulsion layer.

However, the silver halide color photographic light-sensitive material may be prepared to have coupler-emulsion combinations different from the above according to purposes.

Each dye forming coupler preferably comprises a group having not less than 8 carbon atoms, the so-called ballasting group, which makes the coupler non-diffusible. The dye forming coupler may be either a four-equivalent coupler that requires reduction of 4 silver ions for forming one molecule of a dye or a two-equivalent coupler that requires reduction of 2 silver ions for forming one molecule of a dye. The dye forming coupler includes colored couplers having color correction effect and compounds capable of releasing photographically useful fragments as a result of its coupling reaction with the oxidation product of a developing agent, said photographically useful fragments including development inhibitors, development accelerators, bleaching accelerators, developing agents, silver halide solvents, toning agents, hardeners, fogging agents, antifoggants, chemical sensitizers, spectral sensitizers and desensitizers. Of these couplers, the coupler that releases a development inhibitor, while developing is in progress, to improve the sharpness and graininess of a developed image is called a DIR coupler.

The DIR coupler may be replaced by a DIR compound that produces a colorless compound and at the same time releases a development inhibitor as a result of its coupling reaction with the oxidation product of a developing agent.

The DIR coupler and DIR compound used include those in which an inhibitor is linked directly to the coupling position thereof and those in which an inhibitor is so linked through a divalent group to the coupling position thereof as to be released by the intramolecular nucleophilic reaction or intramolecular electron-transfer reaction inside the group split off as a result of their coupling reaction (called timing DIR coupler and timing DIR compound). The inhibitor includes one that becomes diffusible after being released and one that is not so much diffusible; either one of these may be used alone or both may be used in combination. A colorless coupler (also called competing coupler) that effects coupling reaction with the oxidation product of an aromatic primary amine developing agent but forms no dye may be used in combination with a dye forming coupler.

As the yellow dye forming coupler there may be suitably used known acetanilide couplers. Of these couplers, benzoylacetanilie and pivaloylacetanide compounds are advantageous.

Usable examples of the yellow dye forming coupler are disclosed in U.S. Patent Nos. 2,875,057, 3,265,506, 3,408,194, 3,551,155, 3,582,322, 3,725,072 and 3,891,445, West German Patent No. 1,547,868, West German OLS Patent Nos. 2,219,917, 2,261,361 and 2,414,006, British Patent No. 1,425,020, Japanese Patent Examined Publication No. 10783/1976, JP O.P.I. Nos. 26133/1972, 73147/1973, 6341/1975, 87650/1975, 123342/1975, 130442/1975, 21827/1976, 102636/1976, 82424/1977, 115219/1977 and 95346/1983.

As the magenta dye forming coupler there may be used known 5-pyrazolone couplers, pyrazolobenzimidazole couplers, pyrazolotriazole couplers, open-chain acylacetonitrile couplers and indazolone couplers.

Useful examples of the magenta dye fourming coupler are disclosed in U.S. Patent Nos. 2,600,788, 2,983,608, 3,062,653, 3,127,269, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,834,908 and 3,891,445, West German Patent No. 1,810,464, West German OLS Patent Nos. 2,408,665, 2,417,945, 2,418,959 and 2,424,467, Japanese Patent Examined Publication No. 6031/1965, JP O.P.I. Nos. 74027/1974, 74028/1974, 129538/1974, 60233/1975, 159336/1975, 20826/1976, 26541/1976, 42121/1977, 58922/1977 and 55122/1978, and Japanese Patent Application No. 110943/1980.

As the cyan dye forming coupler there may be used known phenol or naphthol couplers which include alkyl group-, acylamino group- or ureido group-substituted phenol couplers, naphthol couplers formed from 5-aminonaphthol, and two-equivalent-type naphthol couplers into which an oxygen atom as a split-off group is introduced.

Useful examples of the cyan dye forming coupler are disclosed in U.S. Patent Nos. 3,779,763, 2,895,826 and 3,488,193, JP O.P.I. Nos. 98731/1983, 37557/1985, 225155/1985, 222853/1985, 185335/1984, 2377448/1985, 52423/1978, 48237/1979, 27147/1981, 3142/1986, 96523/1986, 39045/1986, 50136/1986, 99141/1986 and 105545/1986, and Japanese Patent Examined Publication Nos. 11572/1974.

The photographic light-sensitive material containing the silver halide emulsion of the invention is produced by coating the emulsion layers and other necessary layers thereof on a support which retains a good flatness and excellent dimensional stability during its manufacture or processing. Materials usable as the support include nitrocellulose film, cellulose ester film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film, polycarbonate film, glass, paper, metals, polyolefin, and paper laminated with, e.g., polyethylene or polypropylene. The support may, in order to improve its adhesiveness to the photographic emulsion layers, be subjected to hydrophilic surface treatment such as saponification treatment, corona discharge treatment, subbing treatment and setting treatment.

The light-sensitive material containing the silver halide emulsion of the invention may be processed according to the known photographic processing method with use of the processing solutions described in Research Disclosure RD-17643, pp. 20-30 (Dec. 1978).

The photographic processing method may be either for black-and-white processing to provide a silver image or for color photographic processing to obtain a color image. The processing is carried out usually at a temperature of 18 ° C to 50 ° C, but it is possible to process the light-sensitive material at a temperature of lower than 18 ° C or higher than 50 ° C.

The photographic light-sensitive material containing the silver halide emulsion of the invention may be used as various light-sensitive materials for color and black-and-white photographic use, such as color negative film for camera use, color reversal film for camera use, color photographic paper, color positive film, color reversal paper; direct positive, heat-developable and silver dye bleach color light-sensitive materials; and black-and-white photographic light-sensitive materials used as X-ray film, lithographic film, microphotographic film, camera film for general use, and black-and-white photographic paper.

The invention is suitable particularly for high-sensitivity color light-sensitive materials. In multilayer color light-sensitive materials, it is preferable to apply thereto a technique to change the order of the layer arrangement for making both high sensitivity and high-quality image consistent with each other, a technique to have an arbitrary color-sensitive emulsion layer composed of three identical color-sensitive sub-layers for more improving the graininess, and a technique to provide a reflective layer consisting of fine-grained silver halide underneath a high-sensitivity layer, particularly a high-speed blue-sensitive layer, for further increasing the sensitivity. Of these techniques, the technique to change the layer arrangement is described in U.S. Patent Nos. 4,184,876, 4,129,446, 4,186,016, 4,186,011, 4,267,264, 4,173,479, 4,157,917 and 4,165,236, British Patent No. 1,560,965, 2,138,962 and 2,137,372, and JP O.P.I. Nos. 177552/1984, 180556/1984 and 204038/1984. And the technique for the reflective layer is described in JP O.P.I. No. 160135/1984.

EXAMPLES

The invention is illustrated further in detail below by the following examples, but the invention is not limited thereto.

EXAMPLE 1

A monodispersed core/shell-type silver iodobromide emulsion (containing octahedral regular crystals having a cubic equivalent grain diameter of 1.3μm, a grain diameter variation coefficient of 18%, an average silver iodide content of 7.6 mol%: inside high iodide-containing type) was prepared by a double-jet process with use of a device disclosed in JP O.P.I. No. 160128/1987.

The above emulsion was divided into four equal parts, to three parts of them were added the sulfur compounds or a gold compound as shown in Table-1, and each part was kept at 60° C for one hour to form a catalytic nucleus. After that, 90 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene were added to each divided emulsion. The remaining part of the above emulsion was used for comparison, and prepared adding thereto an equal amount of the above azaindene compound without giving rise to the catalytic nucleus.

Next, after cooling the emulsion to 50° C, to the emulsion was added 3.0×10^{-6} mol per mol of silver halide of sodium thiosulfate partially labelled with a radioactive element ^{35}S as a reagent for producing silver sulfide, and the reaction rate thereof was measured in accordance with a method for tracing the radioactive element.

Measurement of the reaction rate was made in accordance with the method described in the previously mentioned publication J. Imaging Sci., vol.32, p.20 (1988).

Table-1

Emulsion No.	Added compound	Added amount (mol/mol AgX)
Em - 1	--	--
Em - 2	S - I	4.0×10^{-6}
Em - 3	S - II	5.0×10^{-7}
Em - 4	Au - I	3.0×10^{-6}

S - I: 1-Ethyl-3-(2-thiazolyl)thiourea
S - II: Sulfur element
Au - I: Chloroauric acid

The results of measurement of the rate of the silver sulfide producing reaction by sodium thiosulfate are shown in Table-2.

Table-2

Emulsion No.	Relative reaction rate	Remarks
Em - 1	1.0	Comparison
Em - 2	2.1	Invention
Em - 3	1.8	,,
Em - 4	1.5	,,

As is apparent from Table-2, the silver sulfide producing reaction rates of the emulsions in which a catalytic nucleus is given before adding sodium thiosulfate are faster than the rate of the comparative emulsion.

EXAMPLE 2

To each of the same emulsions (Em-1 to Em-4) as in Example 1 was added spending one hour the same amount of non-radioactive sodium thiosulfate instead of the radioactive sodium thiosulfate in Example 1 to thereby effect the chemical ripening of the emulsions.

After completion of the chemical ripening, to each emulsion were added further appropriate amounts of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene as a stabilizer, saponin as a coating aid, and 2,4-dichloro-6-hydroxy-s-triazine as a hardener.

Each of the obtained emulsions was coated on a subbed polyester support and then dried, whereby Samples 1 to 4 were prepared.

Each sample was exposed for 1/50 sec through a usual sensitometry wedge, and developed for 30 seconds in the following developer solution at 35°C, then fixed, washed and dried. After that, the photographic characteristics (sensitivity and fog) of each processed sample were measured.

The obtained results are shown in Table-3.

The photographic sensitivity is expressed in terms of the reciprocal of the logarithm of an exposure amount necessary to obtain an optical density of a fog value plus 0.1, but in Table-3, the sensitivity of each sample is shown with a relative value to the sensitivity of Sample 1 set at 100.

<u>Developer</u> (for black-and-white light-sensitive material)

1-Phenyl-3-pyrazolidone	1.5 g
Hydroquinone	30 g
5-Nitroindazole	0.25g
Potassium bromide	5 g
Anhydrous sodium sulfite	55 g
Potassium hydroxide	30 g
Nitric acid	10 g
Glutaraldehyde (25%)	5 g

Water to make 1 liter

Table-3

Sample No.	Fog	Sensitivity	Remarks
1	0.01	100	Comparison
2	0.01	150	Invention
3	0.01	165	' '
4	0.02	840	' '

As is apparent from Table-3, Samples 2, 3 and 4, in which the emulsions of the invention are used, have higher sensitivities than Sample 1.

EXAMPLE 3

An emulsion containing tabular grains was prepared by a similar double-jet process as in Example 1. The emulsion grains had an average iodide content of 9.8 mol% (inside high iodide-containing type), a cubic equivalent grain diameter of 1.2μm, a grain diameter variattion coefficient of 20%, and diameter/thickness ratio of 4.3.

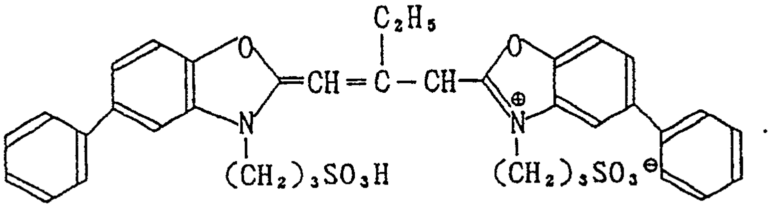
Next, the above emulsion was divided into two equal parts. One part was named Em-5 to be used as a comparative emulsion, and to the other was added 2.5×10^{-6} mol per mol of silver halide of 5,5-dimethylrhodanine gold complex salt to thereby endow a catalytic nucleus comprised of gold in a similar manner as in Example 1, and this was named Em-6.

To Em-5 were added per mol of silver halide 170mg (total amount) of spectral sensitizing dyes D-1, D-2 and D-3, 4×10^{-4} mol of ammonium thiocyanate, 3.7×10^{-6} mol of sodium thiosulfate and 1.0×10^{-6} mol of chloroauric acid, and thus the emulsion was subjected to optimum sulfur-gold sensitization at 50° C.

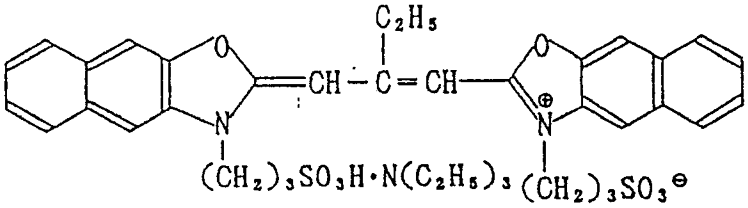
To Em-6 were added the same spectral sensiting dyes D-1 to D-3 and ammonium thiocyanate in the same amounts as in above and then added 20mg of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene. Next, 3.7×10^{-6} mol of sodium thiosulfate was added in one hour to thereby subject the emulsion to optimum sulfur-gold sensitization at 50° C.

After that, 850mg of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene were further added as a stabilizer to the emulsion. Spectral sensitizing dyes

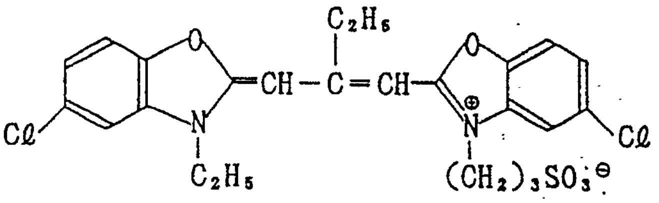
D-1



D-2



D-3



Subsequently, to each of the above emulsions was added a coupler solution prepared by dissolving per mol of silver halide 80g of a magenta coupler 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amylphenoxyacetamido)benzamido]-5-pyrazolone and 2.5g of a colored magenta coupler 1-(2,4,6-trichlorophenyl)-4-(1-naphthylazo)-3-(2-chloro-5-octadecenylsuccinimidoanilino)-pyrazolone by heating in a mixture of 120g of tricresyl phosphate and 240mg of ethyl acetate and then dispersing the solution into 550ml aqueous 7.5% gelatin solution containing 5g of sodium triisopropylnaphthalenesulfonate.

Next, an appropriate amount of sodium 2-hydroxy-4,6-dichlorotriazine as a hardener was added to each of the emulsions prepared above, and then the emulsion was so coated on a subbed triacetate support as to have a coating weight of silver of 2.0g/m^2 and then dried to thereby provide Samples 5 and 6.

Each of Samples 5 and 6 was exposed through an optical wedge in the usual manner, processed in accordance with the following color processing steps, and then the photographic characteristics of the processed samples were evaluated. The results are given in Table 4.

The sensitivity shown in the table is a value relative to the sensitivity of Comparative sample 5 set at 100.

Processing step (at 38°C)	Processing time
Color developing	3 min. 15 sec.
Bleaching	6 min. 30 sec.
Washing	3 min. 15 sec.
Fixing	6 min. 30 sec.
Washing	3 min. 15 sec.
Stabilizing	1 min. 30 secon.
Drying	

The compositions of the processing solutions used in the above precedure are as follows:

Color developer

4-Amino-3-methyl-N-ethyl-N-β-hydroxyethyl-aniline sulfate	4.75g
Anhydrous sodium sulfite	4.25g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydroux potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate monohydrate	2.5 g
Potassium hydroxide	1.0 g

Water to make 1 liter.

Adjust pH to 10.6 with sodium hydroxide.

Bleaching bath

Ferric-ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g

Glacial acetic acid	10.0 g

Water to make 1 liter.

Adjust pH to 6.0 with ammonia water.

Fixing bath

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

Water to make 1 liter.

Adjust pH to 6.0 with acetic acid.

Stabilizing bath

Formalin (37% aqueous solution)	1.5ml
Koniducks (product of KONICA Corp.)	7.5ml

Water to make 1 liter.

Table-4

Sample No.	Fog	Sensitivity	Remarks
5	0.15	100	Comparison
6	0.14	135	Invention

As is apparent from Table-4, the sensitivity of Sample 6, in which the emulsion of the invention is used, is higher than that of Comparative sample 5.

Claims

1. A silver halide photographic emulsion containing silver halide grains having a chemical sensitization center comprising silver sulfide or gold sulfide or a mixture thereof, wherein the sensitization center is formed in the presence of a nucleus capable of accelerating the chemical sensitization center forming reaction to produce the chemical sensitisation center on the surface of the silver halide grains and also in the presence of a compound adsorbent to the silver halide grains.

2. A silver halide emulsion of claim 1, wherein the nucleus comprises an element or a combination of elements selected from a group of Ag, Au, Pt, Ir, Pd, S, Se and Te.

3. A silver halide emulsion of claim 1, wherein the chemical sensitization center forming reaction proceeds at a rate of at least 1.5 times the reaction in which the chemical sensitization center is formed in the absence of the nucleus.

4. A method for preparing a silver halide emulsion containing silver halide grains which comprises:
   (1) forming a nucleus on the surface of the silver halide grain which is capable of accelerating a

chemical sensitization center forming reaction by adding a sulfur-containing compound, a selenium-containing compound, a noble metal-containing compound or a combination thereof, and then
(2) performing chemical sensitization further by adding a sulfur sensitizer in the presence of a compound adsorbent to the the silver halide grains.

5. A method of claim 4, wherein the nucleus is formed by adding at least one of elemental sulfurs, thiosulfates, thioureas, rhodanines, selenoureas and gold compounds.

6. A method of claim 4, wherein in (2), a gold sensitizer is further added.

7. A method of claim 1, wherein the chemical sensitization is performed in the presence of a compound selected from azaindene or azole antifoggants and cyanine or merocyanine dyes.

8. A method of claim 7, wherein the chemical sensitization is performed in the presence of a compound selected from triazaindenes, tetraazaindenes, pentaazaindenes and cyanine dyes.

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 6541

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.5)
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 35 (P-994)(3978) 23 January 1990, & JP-A-01 271743 (FUJI PHOTO FILM COMPANY LTD.) 30 October 1989, * the whole document * – – –	1-8	G 03 C 1/09
D,A	JOURNAL OF IMAGING SCIENCE. vol. 32, no. 1, February 1988, SPRINGFIELD US pages 20 - 27; H.Takiguchi: "EFFECTS OF TETRAAZAINDENE ON REACTION AND AGGREGATION PROCESSES IN SULFURSENSITIZATION WITH THIOSULFATE" * the whole document * – – – – –	1-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	14 August 91	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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