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(54) Silver halide photographic light-sensitive material.

(57) A silver halide photographic light-sensitive material comprising a support having on at least one side thereof a silver halide emulsion layer comprising a silver halide emulsion containing silver halide grains, which is prepared by a process comprising forming the silver halide emulsion by mixing a silver salt and a halide salt in a dispersing medium and subjecting the emulsion formed to chemical ripening, wherein said silver halide grains are selenium-sensitized by adding a selenium compound during a period of the course of forming the silver halide emulsion and chemical ripening thereof; said grains being spectrally sensitized with a spectral sensitizing dye represented by the following Formula (I) or Formula (II),

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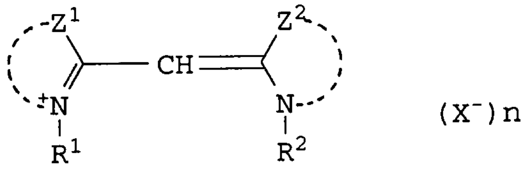
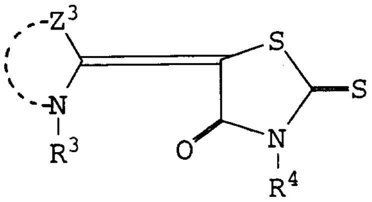
Formula (I)



Formula (II)



Field of the Invention

This invention relates to a silver halide photographic light-sensitive material and, particularly to a silver halide photographic light-sensitive material for regular-type X-ray photographic use, that is suitable for rapid development process.

Background of the Invention

In recent years, a high-temperature and rapid-processing has become feasible because of the introduction of an automatic processor, and a super-rapid processing for not longer than 45 seconds in a Dry-to-Dry system has been developed. In this type of systems, on the other hand, it has been customary to make a hardening reaction in the course of the processing steps, for providing a rapid processing aptitude.

Conventionally, glutaraldehyde has been used as a hardener, because of a high reactivity and a rapid hardening in a developer. However, it has not been admittable that glutaraldehyde is high in safety, because it has an irritating odor, or if it adheres to a human body. Further, with raising the issue of environmental protection, a rapid processing procedure has been so developed as to eliminate a hardening development in which glutaraldehyde is used.

For performing a rapid photographic processing without relying on such a hardening development as mentioned above, a silver halide photographic light-sensitive material is required to be satisfactorily hardened in advance. However, in the case of a silver halide photographic light-sensitive material for medical use that is required to have a high sensitivity and a high density (Dmax) and if the light-sensitive material is satisfactorily hardened in advance, a large amount of silver coated is required to provide desired photographic characteristics. An increase in silver coverage brings about, not only increased costs is increased, but also such a serious trouble as a lowering of rapid processability, an increase of fog and the deterioration of pressure resistance.

In recent years, in a silver halide photographic light-sensitive material for medical use, there have increased the transfer from a regular system to an ortho system combined with a rare-earth screen. In the latter system, a tabular silver halide emulsion has been used, because a large amount of ortho-sensitizing dyes can be adsorbed thereto; a high density can be obtained by a relatively small amount of silver coverage; a density-down is relatively small even when sufficiently hardened in advance; and desired photographic characteristics can be obtained even without further hardening. The facts mentioned above are also disclosed in, for example, Research Disclosure No. 22534, Jan., 1983, and so forth.

It has, however, been known that a tabular silver halide emulsion is not good in pressure resistance, such as an abrasion blackening trouble and a roller-mark produced through an automatic processor in a rapid processing, and that a pressure resistance and a processing stability are further deteriorated by increasing the hardening degrees of an emulsion layer.

As compared to a cubic, octahedral, spherical-formed silver halide grain, it has been known that a tabular grain having an equivalent volume is lowered in an inherent sensitivity (in a blue region) because of being thinner in thickness. As one of the improving means thereof, an increasing of an iodide content of a grain has been known to be effective. However, it has been very difficult to apply a tabular grain to a regular-type (or a blue-sensitive-type) light-sensitive material, because a rapid processability is deteriorated.

On the other hand, there has been known a technique for sensitizing an inherent sensitivity by making use of a blue-sensitizing dye. However, some kind of sensitizing dyes has a property to reduce the inherent absorption of silver halide, therefore, the technique has been so disadvantageous that the technique is difficult to be properly performed.

Japanese Patent Publication Open to Public Inspection (hereinafter referred to JP OPI Publication) No. 59-55426/1984 discloses a technique in which the processing stability of a tabular grain having an aspect ratio of not lower than 3 is improved by making use of a blue-sensitizing dye. However, this technique is to carry out rapid processing at a high temperature in which an aldehyde type hardener (or glutaraldehyde) is contained in a developer, that is not any technique relating to a rapid processing without having a development hardening step, nor any technique for enhancing a spectral sensitization.

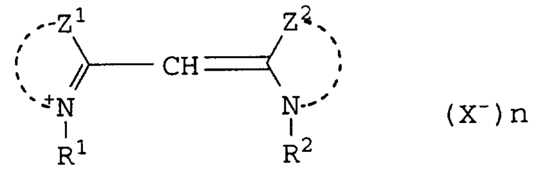
JP OPI Publication No. 4-291338/1992 discloses a sensitising technique in which zeromethine dye is used. However, this technique has had such a problem that not only the absolute value of a sensitivity is substantially low, but also a pressure resistance is not improved, and particularly that the characteristics are seriously deteriorated when sufficient hardening in advance for carrying out a non-hardening development. Therefore, a further improved technique has been demanded.

Summary of the Invention

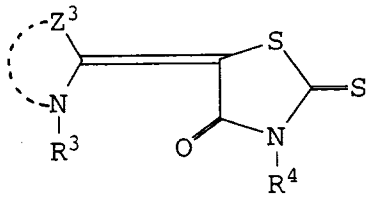
It is, accordingly, an object of the invention to provide a tabular silver halide photographic light-sensitive material having a high sensitivity and an improved pressure resistance, each capable of performing a non-hardening rapid processing, and having a satisfactory Dmax.

The above-mentioned problems were solved in the invention detailed below. To be concrete, the problems were solved by a silver halide photographic light-sensitive material comprising a support coated on at least one side of the support with at least one of tabular silver halide grain emulsion layers; wherein the emulsion grains are selenium-sensitized and spectrally sensitized by at least one of the dyes represented by the following Formulas (I) or (II).

Formula (I)



Formula (II)



wherein Z^1, Z^2 and Z^3 represent each a group consisting of non-metal atoms necessary for forming oxazole, benzoxazole, naphthoxazole, thiazole, benzothiazole or naphthothiazole; R^1, R^2 and R^3 represent each an alkyl or substituted alkyl group; R^4 represents an alkyl, substituted alkyl, aryl or substituted aryl group; X represents an acid anion; and n is an integer of 0 or 1.

In the above-given Formula (I), the heterocyclic nuclei completed by Z^1 or Z^2 may be exemplified as follows: An oxazole (such as oxazole, 4-methyl oxazole or 4,5-dimethyl oxazole), a benzoxazole (benzoxazole, 5-chlorobenzoxazole, 5-methyl benzoxazole, 5-methoxybenzoxazole, 5-phenyl benzoxazole or 5,6-dimethyl benzoxazole), a naphthoxazole (such as naphtho[1,2-d]oxazole, naphtho[2,1-d]oxazole or naphtho[2,3-d]oxazole), a thiazole, a benzothiazole and a naphthothiazole.

In Formula (I), for example, the alkyl groups represented by R^1 and R^2 include each group of methyl, ethyl, n-propyl and n-butyl; and the substituted alkyl groups represented thereby include the following groups, namely, a hydroxyalkyl group (such as a β-hydroxyalkyl group and, to be concrete, 2-hydroxyethyl, 3-hydroxypropyl or 4-hydroxybutyl), an acetoxyalkyl group (such as β-acetoxyethyl or γ-acetoxypropyl), an alkoxycarbonyl alkyl group (such as β-methoxycarbonyl ethyl, γ-methoxycarbonyl propyl or δ-ethoxycarbonyl butyl), a carboxyalkyl group (such as carboxymethyl, β-carboxyethyl, γ-carboxypropyl or δ-carboxybutyl), a sulfoalkyl group (such as β-sulfoethyl, γ-sulfopropyl, γ-sulfobutyl, δ-sulfobutyl, 2(3-sulfopropoxy)-ethyl or 2-[2-(3-sulfopropoxy)ethoxy]ethyl), an allyl group (such as a vinyl methyl group), a cyanoalkyl group (such as β-cyanoethyl group), a carbamoyl alkyl group (such as β-carbamoyl ethyl group), and an aralkyl group (such as benzyl, 2-phenylethyl or 2-(4-sulfophenyl) ethyl). The alkyl groups are each preferable to have 1 to 8 carbon atoms, and the substituted alkyl groups are each preferable to have 1 to 10 carbon atoms.

The heterocyclic nuclei completed by Z^3 denoted in the above-given formula (II) include, for example, the same as those represented by Z^1 and Z^2 denoted in the formula (I).

The groups represented by R^3 include the same groups represented by R^1 and R^2 each denoted in formula (I).

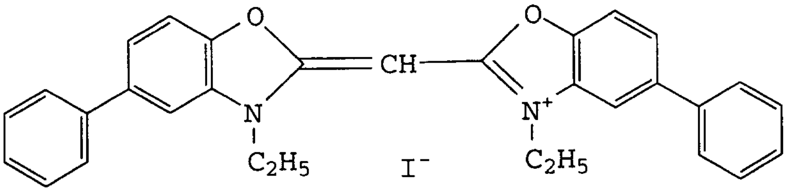
The alkyl groups represented by R^4 denoted in Formula (II) include, for example, each group of methyl, ethyl, n-propyl and n-butyl. The substituted alkyl groups represented thereby include, for example, a sulfoalkyl group (such as 2-sulfoethyl, 3-sulfopropyl, 3-sulfobutyl or 4-sulfobutyl), a carboxyalkyl group (such as 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl or carboxymethyl), a hydroxyalkyl group (such as 2-hydroxyethyl, 3-hydroxypropyl or 4-hydroxybutyl), an alkoxyalkyl group (such as 2-methoxyethyl or 3 methoxypropyl), an acyloxyalkyl group (such as 2-acetoxyethyl group), an alkoxycarbonylalkyl group (such as methoxycarbonylmethyl, 2-methoxycarbonylethyl or 4-ethoxycarbonylbutyl), a substituted alkoxyalkyl group (such as hydroxymethoxymethyl, 2-hydroxyethoxymethyl, 2-(2-hydroxyethoxy)ethyl, 2-(2-acetoxyethoxy)ethyl or acetoxymethoxymethyl), a dialkylaminoalkyl group (such as 2-dimethylaminoethyl, 2-diethylaminoethyl, 2-piperidinoethyl or 2-morpholinoethyl), an N-(N,N-dialkylaminoalkyl)-carbamoylalkyl group (such as N-[3-(N,N-dimethylamino)propyl]carbamoylmethyl, N-[2-(N,N-diethylamino) ethyl]-carbamoylmethyl, N-[3-(morpholino)propyl] carbamoylmethyl and N-[3-(piperidino)propyl]carbamoylmethyl, an N-(N,N,N-trialkyl ammonium alkyl)carbamoylalkyl group (such as each group of N-[3-(N,N,N-trimethyl ammonium)propyl] carbamoylmethyl, N-[3-(N,N,N-triethyl ammonium)propyl] carbamoylmethyl and N-[3-(N-methyl piperidino)propyl] carbamoylmethyl), an N,N,N-trialkyl ammonioalkyl group (such as N,N-diethyl-N-methyl ammonioethyl or N,N,N-triethyl ammonioethyl), a cyanoalkyl group (such as 2-cyanoethyl or 3-cyanopropyl), a carbamoylalkyl group (such as 2-carbamoylethyl or 3-carbamoylpropyl), a heterocyclic substituted alkyl group (such as tetrahydrofurfuryl or furfuryl), an allyl group (such as a vinylmethyl group), an aralkyl group (such as benzyl or 2-phenylethyl), an aryl group (such as phenyl, p-chlorophenyl, p-tolyl, p-methoxyphenyl, p-carboxyphenyl, p-methoxycarbonylphenyl, m-acetylaminophenyl, p-acetylaminophenyl, m-dialkylaminophenyl (e.g., an m-dimethylaminophenyl group), p-dialkylaminophenyl group (e.g., p-dimethylaminophenyl group). The alkyl groups are preferable to have 1 to 8 carbon atoms, and the substituted alkyl groups are preferable to have 1 to 10 carbon atoms. The following substituted alkyl groups are preferred; namely, each group of hydroxyalkyl, acetoxyalkyl, alkoxyalkyl, alkoxycarbonylalkyl, carboxyalkyl, sulfoalkyl, allyl, carbamoylalkyl, aralkyl and heterocyclic substituted alkyl.

The compounds preferably applicable to the invention include, for example, those containing an oxazole, benzoxazole or naphthoxazole each represented by Z^1 denoted in Formula (I) and a thiazole, benzothiazole or naphthothiazole each represented by Z^2; and the compounds represented by Formula (II).

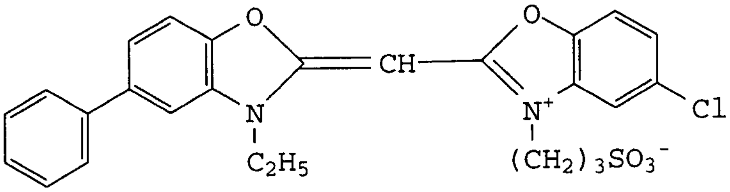
Now, the typical examples of the compounds represented by Formulas (I) and (II) will be given below. However, the compounds represented thereby shall not be limited thereto.

Examples of the compounds

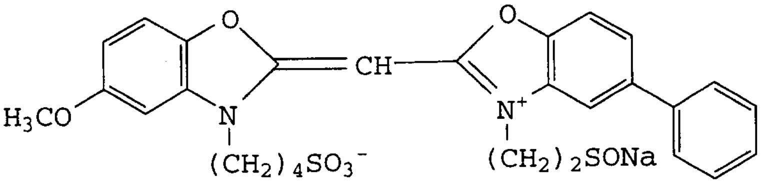
I-1


O
CH
O
N
C_2H_5
I^-
N^+
C_2H_5

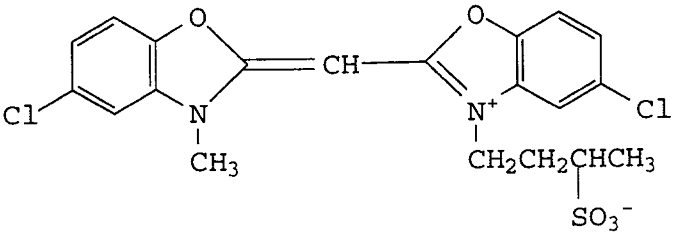
I-2


O
CH
O
N
C_2H_5
N^+
$(CH_2)_3SO_3^-$
Cl

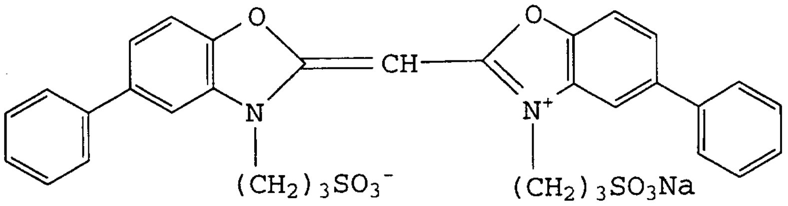
I-3


O
CH
O
H_3CO
N
$(CH_2)_4SO_3^-$
N^+
$(CH_2)_2SONa$

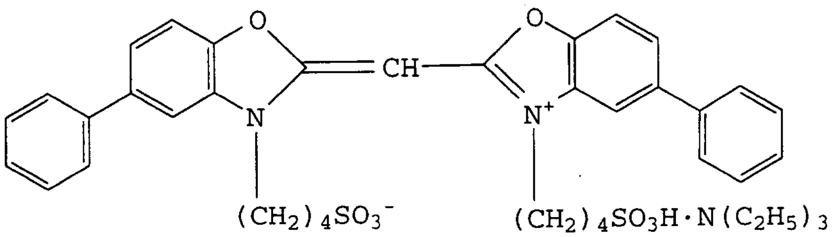
I-4


O
CH
O
Cl
N
CH_3
N^+
Cl
$CH_2CH_2CHCH_3$
SO_3^-

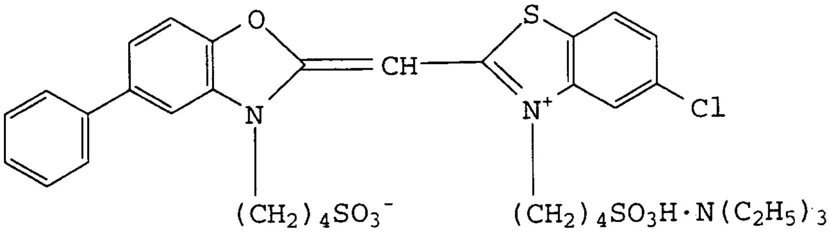
I-5


O
CH
O
N
N+
(CH2)3SO3-
(CH2)3SO3Na

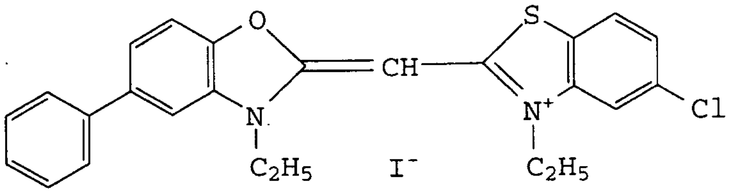
I-6


O
CH
O
N
N+
(CH2)4SO3-
(CH2)4SO3H·N(C2H5)3

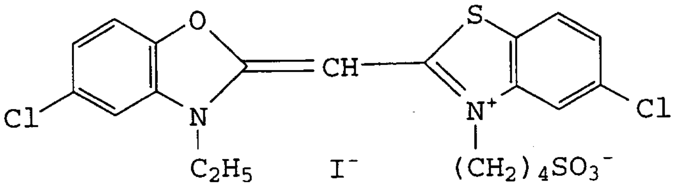
I-7


O
CH
S
N
N+
Cl
(CH2)4SO3-
(CH2)4SO3H·N(C2H5)3

I-8


O
CH
S
N
N+
Cl
C2H5
I-
C2H5

I-9



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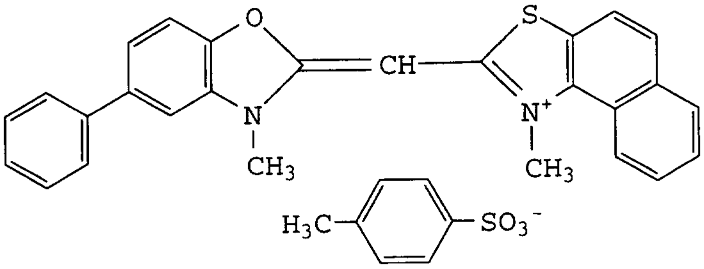

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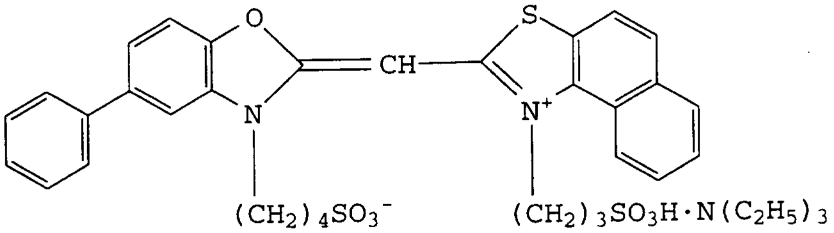

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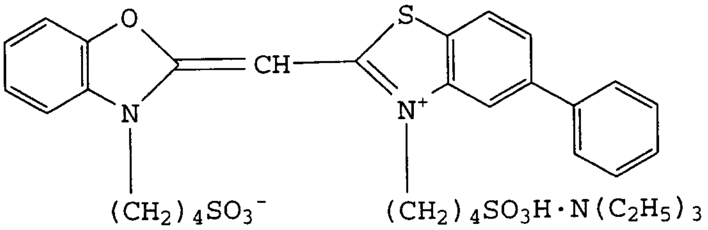

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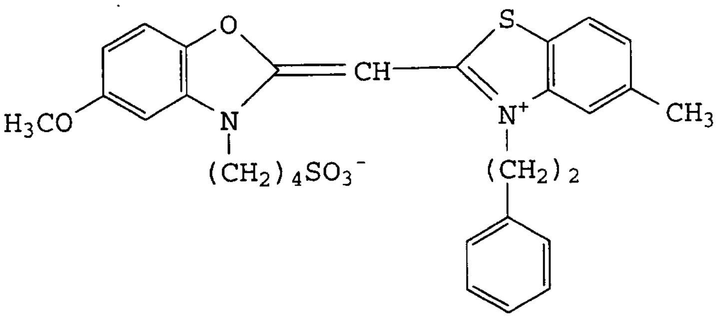
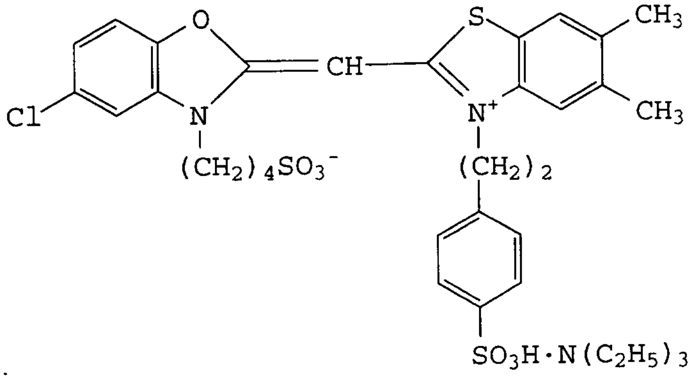
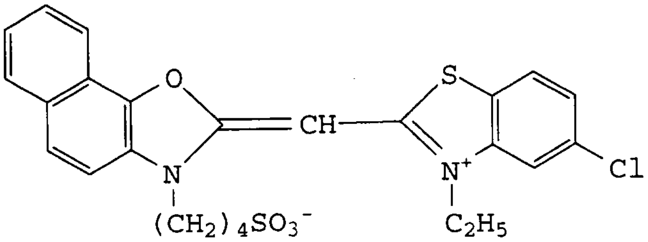

O
CH
S
H3CO
N
N+
CH3
(CH2)4SO3-
(CH2)2

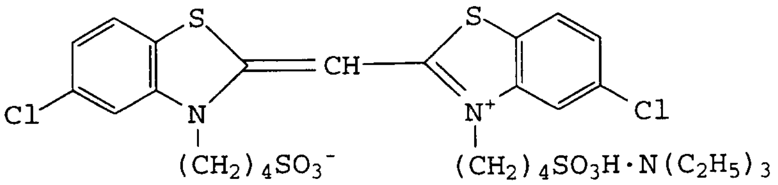
I-14


O
CH
S
CH3
Cl
N
N+
CH3
(CH2)4SO3-
(CH2)2
SO3H·N(C2H5)3

I-15


O
CH
S
N
N+
Cl
(CH2)4SO3-
C2H5

I-16



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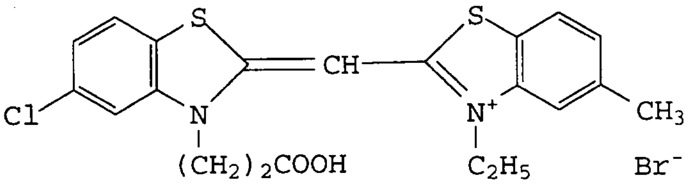

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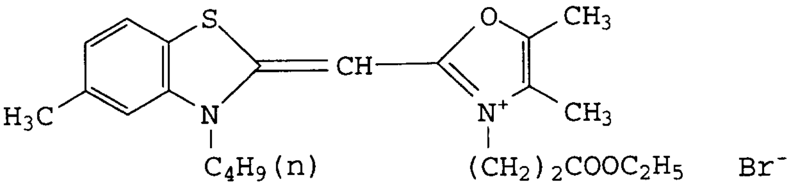

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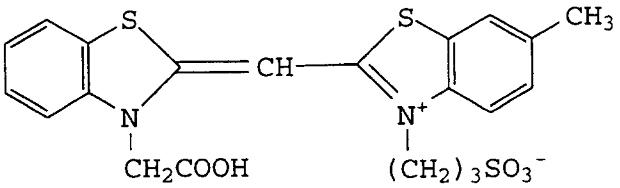

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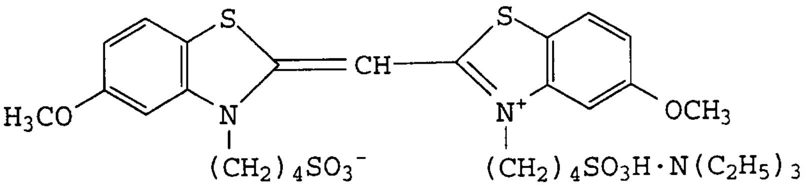

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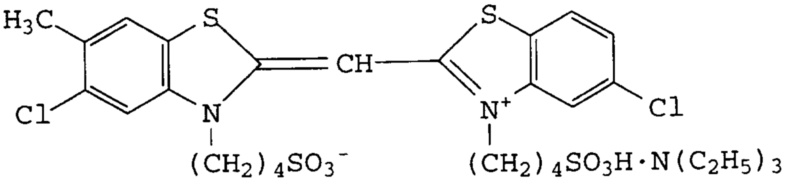

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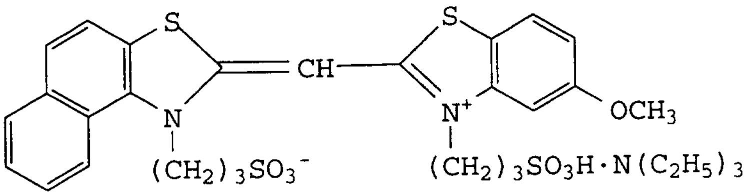

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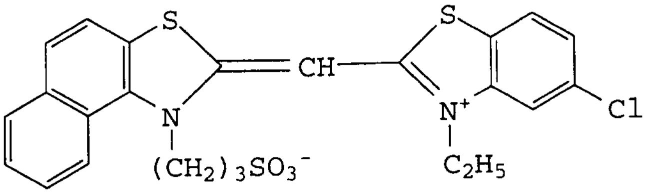

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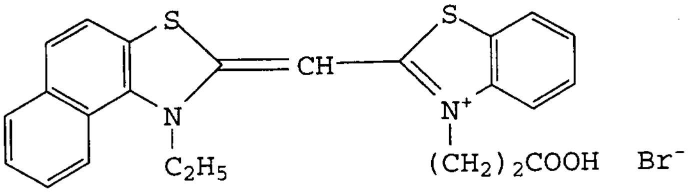

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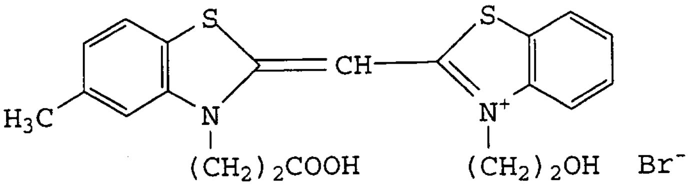

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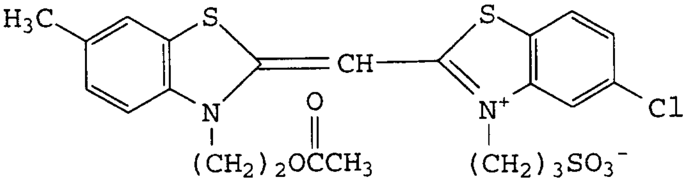

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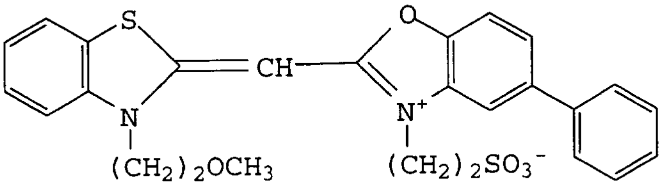

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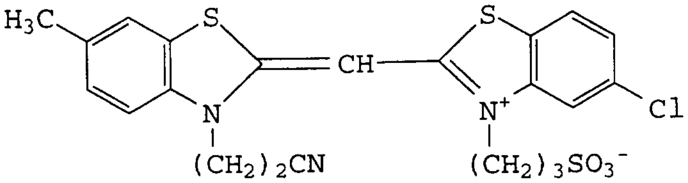

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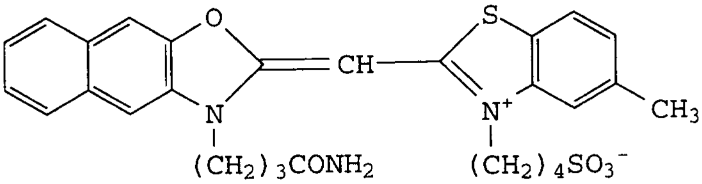

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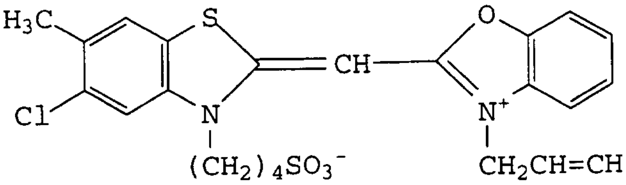
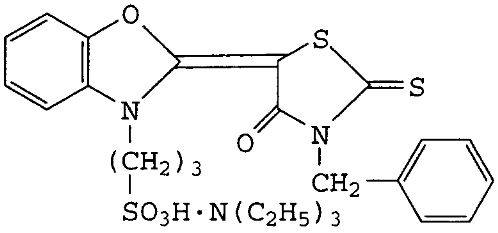


II-1



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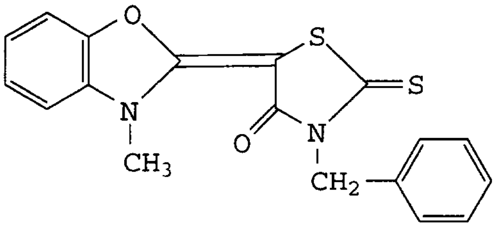

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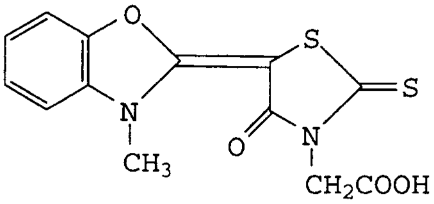

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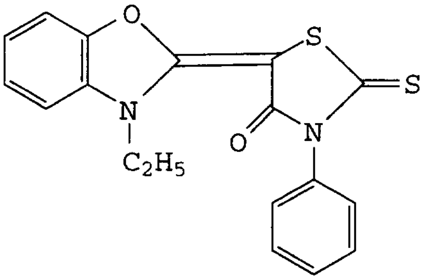

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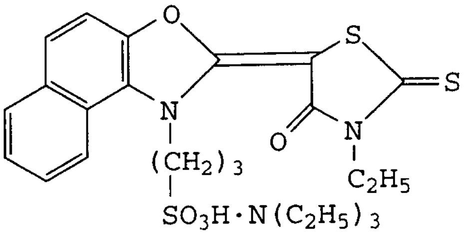

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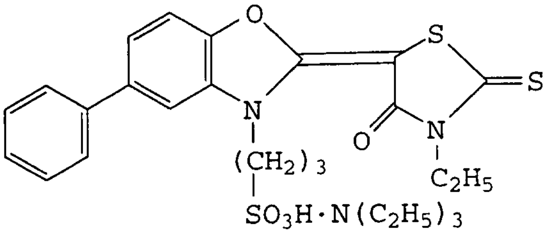

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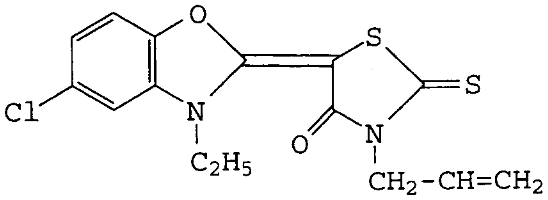

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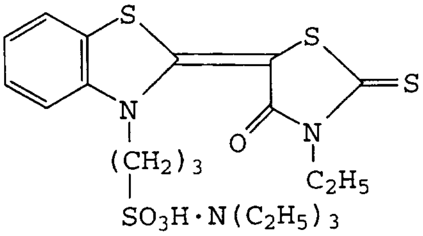

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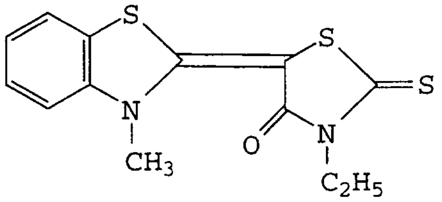

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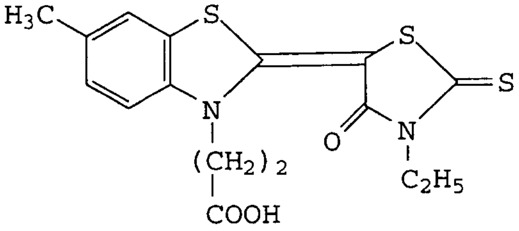

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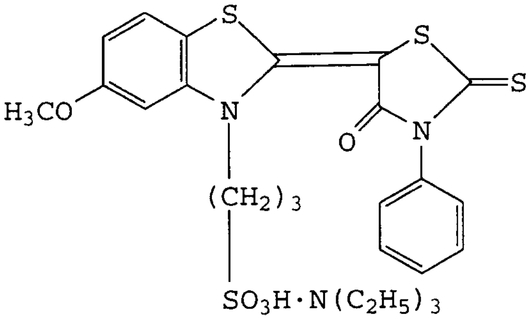

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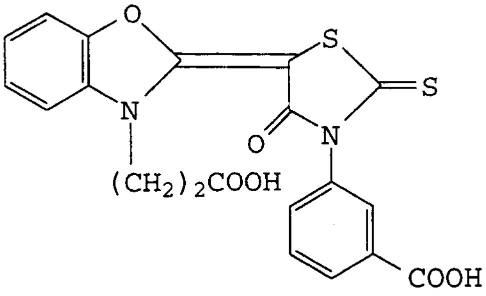

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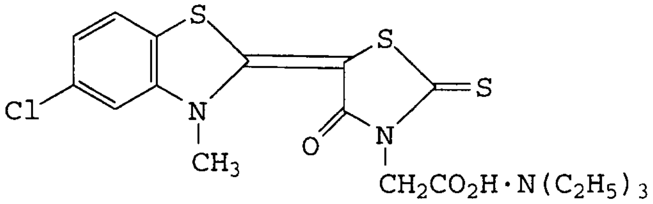

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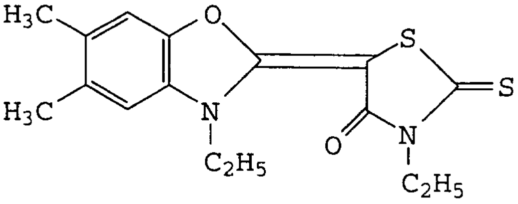

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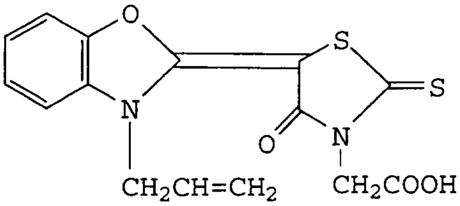

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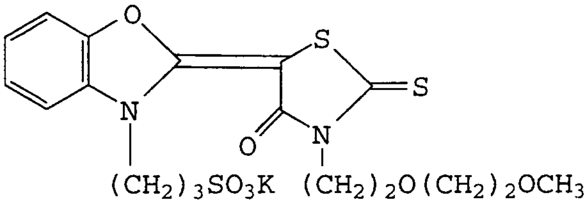

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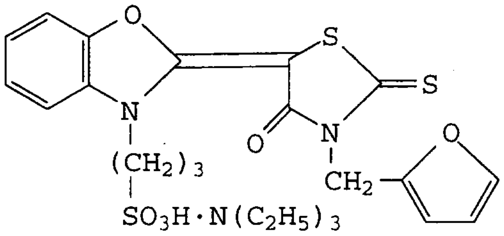

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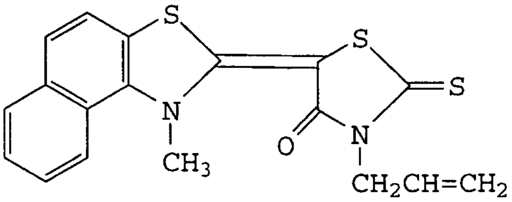

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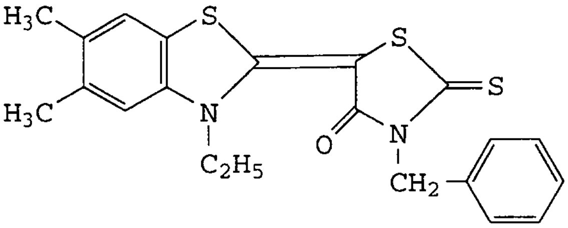

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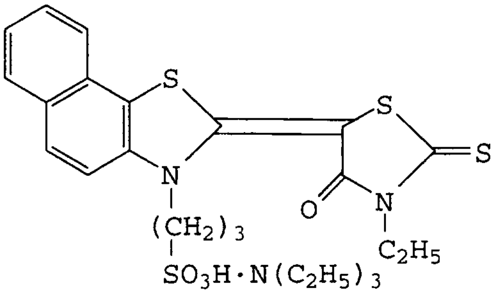

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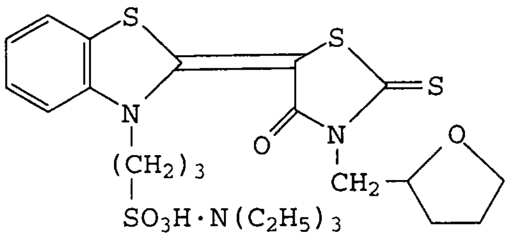

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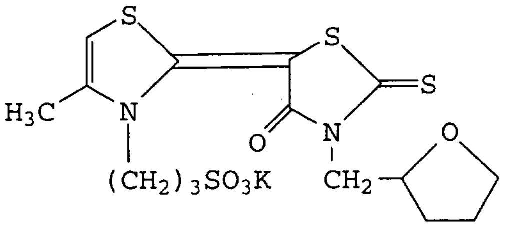

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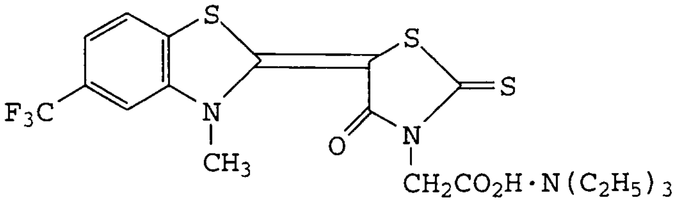

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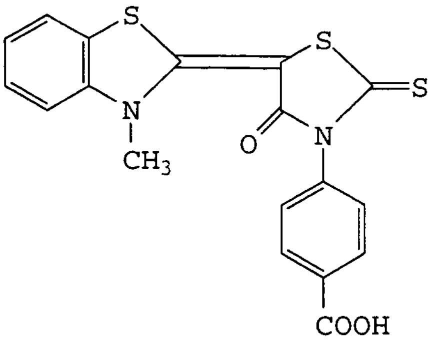

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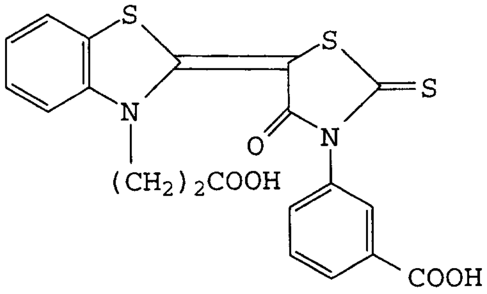

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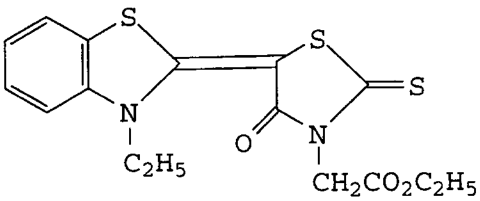

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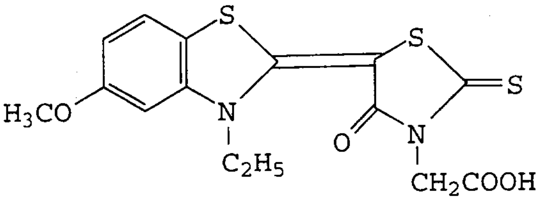

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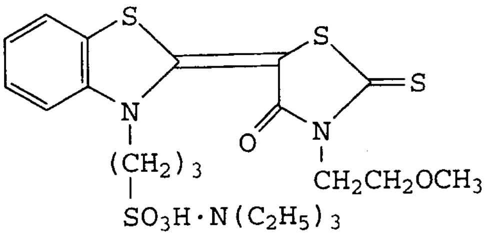


The sensitizing dyes represented by Formulas (I) and (II) have been well-known and they can readily be available. They can also readily be synthesized according to the descriptions of the following literature.

F.M. Hamer, "The chemistry of heterocyclic compounds; The cyanine dyes and related compounds", 1964, John Wiley & Sons, (New York & London), p. 58 & p. 536.

The sensitizing dyes relating to the invention, which are represented by Formula (I) or (II), may be used independently or in combination.

The dye represented by Formula (I) or (II) may be added in an amount preferably within the range of 5×10^{-6} to 5×10^{-3} mols per mol of a silver halide content of a silver halide emulsion layer comprising tabular grains.

The dye represented by Formula (I) or (II) may be added in any stage in the course of preparing a silver halide photographic light-sensitive material. It is, however, preferable to add them at any point of time between after the completion of a grain formation and before the completion of a chemical sensitization, and it is more preferable to add them at any point of time between the point of time when completing the grain formation and the point of time before starting the chemical sensitization.

The sensitizing dyes relating to the invention, which are represented by Formulas (I) or (II), are preferably added in the form of a solution in which the dyes are dissolved in a suitable organic solvent such as methanol, phenoxyethanol and phenylethanol, or in a mixed solvent of these organic solvent and water or an amine.

The above-mentioned tabular silver halide grains are to have an average grain-diameter within the range of, preferably, 0.3 to 3.0μm and, particularly, 0.5 to 1.5μm.

The tabular silver halide grains relating to the invention are to have a mean ratio of grain-diameter/grain-thickness (hereinafter referred to as an average aspect ratio) of not lower than 1.2, and within the range of, preferably 1.5 to 20.0 and, particularly 2.0 to 10.0.

The tabular silver halide grains relating to the invention are to have an average thickness of, preferably not thicker than 1.0μm, particularly not thicker than 0.5μm and, further preferably not thicker than 0.3μm.

The advantages of these tabular silver halide grains are disclosed as that a spectral sensitization efficiency can be improved and that the graininess and image-sharpness of an image can be made higher, in the patent publications including, for example, British Patent No. 2,112,157 and U.S. Patent Nos. 4,439,520, 4,433,048, 4,414,310 and 4,434,226. The emulsion thereof can be prepared in the processes detailed therein.

In the invention, the grain-diameter of the tabular silver halide grain is defined as the diameter of a circle having the area equivalent to the projected area of the subject grain, that is determined by observing an electron-microscopic photograph of the grain.

In the invention, the thickness of a tabular silver halide grain is defined as the distances between two parallel principal plane face constituting the tabular silver halide grain.

The thickness of a tabular silver halide grain can be obtained from an electron-microscopic photograph of a subject silver halide grain with the shade thereof, or from an electron-microscopic photograph of a section of a subject sample coated with a silver halide emulsion on a support and then dried up.

For determining an average aspect ratio, a series of 100 samples at minimum are to be measured.

In a silver halide emulsion of the invention, the proportion of the tabular silver halide grains to the whole silver halide grain is not less than 50% by projected area, preferably not less than 60% and, particularly not less than 70%.

A tabular silver halide grain relating to the invention is preferable to be of the monodisperse type. The term, 'monodisperse type', herein means that the variation coefficient of a grain-size, i.e., (a standard deviation of a grain-size / an average grain-size x 100), is not more than 25%, preferably not more than 20% and, particularly not more than 15%.

A silver halide emulsion relating to the invention may have any halide compositions such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide, and silver chloroiodobromide. However, from the viewpoint of a high sensitivity, silver iodobromide is preferred. An average silver iodide content thereof is to be within the range of 0.1 to 4.0 mol% and, preferably 0.5 to 3.0 mol%. Further from the viewpoint of a rapid processability, silver chloroiodobromide may also be used.

When making use of silver chloroiodobromide, silver chloride may be contained therein at any positions within the grains. It is particularly preferable to localize silver chloride on the surface of a grain or the neighborhood thereof.

A tabular silver halide emulsion relating to the invention may have a uniform halogen composition in the grains thereof, or may also contain localized silver iodide therein. However, those containing silver iodide localized around each center of the grains thereof may preferably be used. A tabular silver halide emulsion may also be prepared with reference to such a process as described in, for example, JP OPI Publication Nos. 58-113926/1983, 58-113927/1983, 58-113934/1983 and 62-1855/1987 and European Patent Nos. 219,849 and 219,850. The processes for preparing a monodisperse type tabular silver halide emulsion may be referred to that detailed in JP OPI Publication No. 61-6643/1986.

A tabular silver iodobromide emulsion having a high aspect ratio can be prepared in such a manner that an aqueous silver nitrate solution is added to an aqueous gelatin solution having a pBr being kept to be not higher than 3.0 so as to produce twinned seed crystals, or both of an aqueous silver nitrate solution and an aqueous halide solution are added at the same time so as to produce twinned seed crystals, and the seed crystals are then grown up in a double-jet method. The sizes of a tabular silver halide grains may be controlled by a temperature at the time of forming the grains, an adding speed a silver salt and an aqueous halide solution, and so forth.

In a silver halide emulsion relating to the invention, an average silver iodide content or an average silver chloride content thereof may be controlled by changing the composition of an aqueous halide solution to be added, that is a ratio of a bromide, iodide or chloride content thereof. When preparing a silver halide emulsion of the invention, a silver halide solvent such as ammonia, thioether thiocyanate and thiourea may further be used, if required.

For removing a soluble salt from an emulsion (or for carrying out a desalting step), the emulsion may be subjected to such a washing process as a noodle-washing process and a flocculation-precipitation process. Among the preferable washing/desalting processes, the particularly preferable desalting processes include, for example, a process in which an aromatic hydrocarbon type aldehyde resin containing a sulfo group is used, such as described in JP Examined Publication No. 35-16086/1960 and another process in which a macromolecular type flocculant is used, such as the exemplified compounds G3 and G8 given in JP OPI Publication No. 63-158644/1988.

A silver halide emulsion relating to the invention is selenium-sensitized. The expression, " be selenium-sensitized", means that a tabular silver halide grain relating to the invention has a selenium-sensitization nucleus in any position of the grain. Thus, in the present invention, selenium-sensitization is carried out at a time during a period from before completing grain growth to before completing chemical sensitization. The preferable position thereof is the surface of the grain and/or the neighborhood of the surface.

In the invention, the expression, "the neighborhood of the surface", means an internal in a depth of a position not more than 600nm, preferably not more than 200nm and, more preferably not more than 70nm, from the surface of the grain.

As for a process for selenium-sensitizing an objective position in the neighborhood of a grain of the invention, it is preferable to carry out such a process that a grain-growing step is temporarily suspended in operation and a selenium sensitizer is added thereto so that the shell-layer surface may be selenium-sensitized, and that the grain growing step is then resumed to continue the operation.

During the period of silver halide grain growth, a selenium-sensitizer may be added either by splitting it into several parts or continuously for a certain period of time.

In a selenium-sensitizing nucleus closest to the surface of a grain to be finally formed, the depth of the nucleus may be varied by applying a selenium-sensitizing process while carrying out a grain-growing step and then by controlling an amount of silver to be added to a grain-regrowing step to be carried out thereafter.

In the present invention, selenium sensitization may be performed at a time during a period from a time at which 70% or more, preferably 80% or more, more preferably 90% or more, of the whole silver salt has been added to the completion of chemical sensitization process.

A selenium-sensitization relating to the invention can be performed in any conventionally known process. To be concrete, such a selenium-sensitization may usually be carried out by adding an labile type selenium compound and/or a non-labile type selenium compound and then by stirring an objective emulsion at a high temperature preferably at not lower than 40°C for a specific period. It is preferable to use a selenium-sensitization in which an labile type selenium sensitizer is used, such as detailed in JP Examined Publication No. 44-15748/1969. The typical unstable type selenium-sensitizers include, for example, an aliphatic isoselenocyanate such as allylisoselenocyanate; a selenourea; a selenoketone; a selenoamide; a selenocarboxylic acid and the esters thereof; and a selenophosphate. Among them, some of the preferable labile type selenium compounds will be given below.

(1) A colloidal elemental selenium;

(2) An organic selenium compound (that is, a compound having a selenium atom made double-bonded to a carbon atom of an organic compound, by a covalent bond);

a) An isoselenocyanate

including, for example, an aliphatic isoselenocyanate such as allylisoselenocyanate;

b) A selenourea (including those in an enol form)

including, for example, a selenourea; an aliphatic selenourea such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, dioctyl, tetramethyl, N-(β-carboxyethyl)-N,N'-diethyl, N,N-dimethyl, diethyl and dimethyl; an aromatic selenourea having one or more aromatic groups, such as phenyl and tolyl; and a heterocyclic selenourea having a heterocyclic group, such as pyridyl and benzothiazolyl;

Among those selenoureas, N,N'-tetra-substituted selenourea is particularly preferable. The preferable substituents include, for example, R, RCO- and ArCO-, in which R represents an alkyl group or a perfluoroalkyl group (preferably having C of 1 to 7); and Ar represents a halogen or a phenyl group substitutable with a lower alkoxy group.

c. A selenoketone including, for example, selenoacetone, selenoacetophenone, selenoketone having an alkyl group made bonded to $=C=Se$, and selenobenzophenone;

d. A selenoamide including selenoamide; and

e. Selenocarboxylic acid and the esters thereof including, for example, 2-selenopropionic acid, 3-selenobutyric acid, and methyl-3-selenobutyrate;

(3) Others:

a. A selenide including, for example, diethyl selenide, diethyl diselenide and triphenylphosphine selenide; and

b. A selenophosphate including, for example, tri-p-triselenophosphate and tri-n-butylselenophosphate.

A preferable series of the labile selenium compounds are given above. However, these compounds shall not be limited thereto. Speaking of an labile selenium compound for serving as a sensitizer for a photographic emulsion, the structure thereof may not be particularly essential for the skilled ones in the art, as far as a selenium is unstable, but it has generally been recognized that the structure thereof has not any role, except that an organic portion of a selenium-sensitizer molecule carries the selenium and make it present in the unstable form in an emulsion. In the invention, an labile selenium compound having such a broad concept as mentioned above can advantageously be used.

It is also allowed to use a selenium-sensitization using a non-labile selenium sensitizer therein, such as those detailed in JP Examined Publication Nos. 46-4553/1971, 52-34492/1977 and 52-34491/1977. The non-labile selenium compounds include, for example, selenious acid, potassium selenocyanide, a selenazole, a quaternary ammonium salt of a selenazole, diaryl selenide, diaryl diselenide, 2-thioselenazolidine dione, 2-selenoxazolidine dione, and the derivatives thereof.

A non-labile selenium sensitizer and a thioselenazolidine dione compound each detailed in JP Examined Publication No. 52-38408/1977 are also effective.

Such a selenium sensitizer as mentioned above may be dissolved in water, an organic solvent such as methanol and ethanol independently or a mixed solvent thereof, and the mixture thereof is then added in the course of carrying out a chemical sensitization. Such a selenium sensitizer as mentioned above shall not be limited to a single kind thereof, but tow or more kinds thereof may also be used in combination. It is also preferable to make use of an labile selenium compound and a non-labile selenium compound in combination.

An amount of a selenium sensitizer applicable to the invention to be added may be so varied as to meet the activities thereof, the kinds and sizes of silver halides and the temperatures and times for ripening the emulsion. However, it is added in an amount of, preferably, not less than 1×10^{-8} mols per mol of silver halide used and, more preferably, within the range of not less than 1×10^{-7} mols to not more than 5×10^{-5} mols.

A selenium sensitization can become more effective when it is carried out in the presence of a silver halide solvent.

The silver halide solvents applicable to the invention include, for example, (1) such an organic thioether as mentioned in U.S. Patent Nos. 3,271,157, 3,531,289 and 3,574,628 and JP OPI Publication Nos. 54-1019/1979 and 54-158917/1979; (2) such a thiourea derivative as mentioned in JP OPI Publication Nos. 53-82408/1978, 55-77737/1980 and 55-2982/1980; (3) such a silver halide solvent having a thiocarbonyl group sandwiched between an oxygen or sulfur atom and a nitrogen atom as mentioned in JP OPI Publication No. 53-144319/1978; (4) such an imidazole as mentioned in JP OPI Publication No. 54-100717/1979; (5) a sulfite; and (6) a thiocyanate.

The particularly preferable solvents include, for example, a thiocyanate and a tetramethyl thiourea. An amount of a solvent applicable thereto may be so varied as to meet the kinds thereof. However, in the case of a thiocyanate, an preferable amount thereof to be applied is to be within the range of 1×10^{-4} mols to 1×10^{-2} mols per mol of silver halide used.

A reduction-sensitization may also be applied to the interior of the grains of a silver halide emulsion of the invention. Such a reduction-sensitization may be applied to a silver halide emulsion in a process in which a reducing compound is added; another process that is so-called a silver ripening process for passing the emulsion grains through a state of excessive silver ions having a pAg of 1 to 7; a further process that is so-called a high-pH ripening process for passing the emulsion grains through the state of a high-pH having a pH of 8 to 11; or the like. The above-mentioned processes may also be applied in combination.

The a reducing compound-adding process is preferable from such a viewpoint that the reduction-sensitization degrees can delicately be controlled.

As for the foregoing reducing compounds, either of an inorganic or organic compound may be used. They include, for example, thiourea dioxide, a stannous salt, an amine or polyamine, a hydrazine derivative, a formamidine sulfonic acid, a silane compound, a borane compound, ascorbic acid and the derivatives thereof, and a sulfite. Among them, thiourea dioxide, stannous chloride and dimethylamine borane are particularly preferable. The amounts of those reducing compound to be added are varied according to the reductivity thereof, the kinds of silver halides and the emulsion preparation conditions such as dissolving conditions. However, they may be suitably added in an amount within the range of $1x10^{-8}$ to $1x10^{-2}$ mols per mol of silver halide used. It is preferable to dissolve the above-mentioned reducing compounds in water or an organic solvent such as an alcohol and then to add while growing silver halide grains.

After completing the step of a desalting process, it is preferable that a silver halide emulsion of the invention is chemically ripened in a selenium sensitization process and in the other chemical sensitization than the selenium sensitization. Thus, a silver halide grain emulsion of the invention is a surface-sensitive emulsion, i.e., emulsion that forms latent images primarily on the surfaces of the silver halide grains. Therefore, an internal latent image-forming silver halide grain emulsion that forms latent images predominantly in the interior of the silver halide grains is outside the scope of the present invention.

The temperatures for carrying out a chemical ripening process may freely be selected. It is, however, within the range of 20 ° C to 80 ° C, preferably 30 ° C to 70 ° C and, particularly 35 ° C to 65 ° C.

The chemical sensitization processes other than the above-mentioned selenium sensitization process include, for example, a chalcogen sensitization process and such a noble metal sensitization process as a gold sensitization process. It is preferable to carry out a sulfur sensitization process and a gold sensitization process in combination.

For carrying out a sulfur sensitization process, such a sensitizer as a thiosulfate, thiourea allylthiocarbamide, cystine, p-toluene thiosulfate and rhodanine may be used. Besides the above, it is also allowed to use a sulfur sensitizer such as those described in, for example, U.S. Patent Nos. 1,574,944 and 3,656,955; German Patent No. 1,422,869; JP Examined Publication No. 56-24937/1981; and JP OPI Publication No. 55-45016/1980. Such a sulfur sensitizer as given above may be added in an amount sufficient to enhance an emulsion sensitivity effectively. The amount thereof to be added can widely be varied under various conditions such as those of pH values, temperatures and silver halide grain sizes. However, a rough standard thereof is preferably within the range of $5x10^{-8}$ to $5x10^{-5}$ mols per mol of silver contained in a silver halide emulsion relating to the invention.

For carrying out a gold sensitization process, the following gold sensitizers may be used. Namely, a chloroaurate, an gold•thiourea complex salt, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric amide, ammonium aurothiocyanate and pyridyl trichlorogold. The amounts of those gold sensitizers to be added are widely varied under various conditions. It may be added in an amount within the range of, preferably, $5x10^{-7}$ to $5x10^{-3}$ mols and, more preferably, $2x10^{-6}$ to $4x10^{-4}$ mols, each per mol of a silver halide emulsion of the invention.

To a silver halide emulsion of the invention, it is preferable to add a finely grained silver halide emulsion, after completing the grain formation.

The above-mentioned fine grains of silver halides include, for example, silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodochloride, silver iodobromide and silver chloroiodobromide. Among them, silver bromide and silver iodide are preferred. The grain size (diameter) of each of those silver halide fine grains is not larger than 0.12μm, preferably within the range of 0.001 to 0.10μm and, more preferably 0.006 to 0.06μm.

In the case of applying silver iodide fine grains to the invention, γ type AgI in a cubic crystal form and β type AgI in a hexagonal crystal form have generally been known as silver iodide. However, they may have either one of the crystal structures and they may also be of the mixture thereof.

In the invention, when making use of the fine grains of silver bromide, silver chloride or a silver chlorobromide, those fine grains are each preferable to be of a non-twinned crystal substantially having no twinned plane, that is so-called a normal crystal or a single twinned crystal having one twinned plane.

Silver halide fine grains applicable to the invention are preferable to be excellent in monodispersibility and to be prepared in a double-jet precipitation process while controlling the temperature, pH and pAg thereof.

When the average grain size of silver halide grains relating to the invention is regarded as d (μm), silver halide fine grains may be added in an amount of preferably not more than 1/100d mols, and within the range of, more preferably 1/20000d to 1/300d mols and, most preferably 1/5000d to 1/500d mols, each per mol of a silver content of an emulsion used in the invention.

Silver halide fine grains may be added at any point of time in the course from the point of time when carrying out a chemical ripening step to the point of time immediately before starting a coating step, and they may preferably be added in the course of carrying out the chemical ripening step. The term, 'a chemical ripening step', herein means a period of time between the point of time when completing the formation of the grains of an emulsion relating to the invention and when completing a desalting treatment, and the point of time when completing chemical ripening. The methods for completing a chemical ripening step include, for example, a temperature lowering method, a pH lowering method and a method of making use of a chemical ripening stopper, each of which have been known. Taking an emulsion stability into consideration, the method of making use of a chemical ripening stopper is preferable. Those chemical ripening stoppers include, for example, a halide (such as potassium bromide and sodium chloride) and an organic compound having been known as an antifoggant or a stabilizer (such as 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene). They may be used independently or in combination.

Silver halide fine grains may be added in several parts with some time intervals, or a further chemical ripened emulsion may also be added after adding the silver halide fine grains.

When adding silver halide fine grains, the temperature of an emulsion solution relating to the invention is to be within the range of, preferably 30 to 80 ° C and, particularly 40 to 65 ° C.

The invention is preferably embodied preferably under the conditions where a part of or the whole of silver halide fine grains are vanished in the course between the time after adding the grains and the time immediately before carrying out a coating operation and, more preferably, under the conditions where not less than 20% of the silver halide fine grains added therein are to be vanished immediately before carrying out a coating operation.

The quantitative determination of a vanished amount thereof can be accomplished in the following manner; an emulsion or a coating solution, to which silver halide fine grains were added, is centrifuged under suitable conditions and then the absorption spectra of a supernatant are measured. Thereafter, the resulting absorption spectra are compared to the absorption spectra of silver halide grains having an already known density so that the quantitative determination can be obtained.

Silver halide grains of the invention can contain a metal belonging to VIII group of the periodic table.

A metal belonging to VIII group of the periodic table may be added so as to be contained inside of silver halide grains usually in such a manner that the metal is made present as the metal compound thereof when forming the grains, and it may also be added continuously or in several parts.

It is also preferable to carry out a process in which the above-mentioned metal is added in advance to an aqueous silver salt solution and/or an aqueous halide solution and silver halide grains are precipitated by making use of the aqueous solution(s).

A compound of a metal belonging to the VIII group of the periodic table herein means a metal compound of iron, iridium, platinum, palladium, nickel, rhodium, osmium, ruthenium and cobalt. It is the matter of course that not only the above-mentioned metal compounds, but also the metal ions and metal atoms thereof may also be contained in silver halide grains relating to the invention.

A silver halide emulsion layer and non-light-sensitive hydrophilic colloidal layer each relating to the invention are hardened so that the dissolving time thereof (that is the melting time thereof) can be within the range of 5 to 150 minutes, preferably 7 to 90 minutes and, particularly 10 to 60 minutes.

The above-mentioned dissolving time can be confirmed in the following manner, for example; a sample cut into a 5mm x 20mm sized piece is dipped in an aqueous 1.5 wt% sodium hydroxide solution being kept at 50 ° C so as to be in a non-stirring state and then a period of time until a hydrophilic colloidal layer is eluted out is measured.

A desired dissolving time (or a desired melting time) can be obtained in such a means that the control is made with a layer hardener. For this purpose, any one of the conventionally known layer hardeners may be used independently or in combination.

For example, the following compounds may be used; namely, a chromium salt (such as chromium alum and chromium acetate), an aldehyde (such as formaldehyde, glyoxal and glutar aldehyde), an N-methylol compound (such as diethylol urea and methylol dimethyl hydantoin), a dioxane derivative (such as 2,3-dihydroxy dioxane), an active vinyl compound (such as 1,3,5-triacryloyl-hexahydro-2-triazine and 1,3-vinylsulfonyl-2-propanol), an active halogen compound (such as 2,4-dichloro-6-hydroxy-3-triazine), a mucohalogeno acid (such as mucochromic acid and mucophenoxychromic acid), an isoxazole, dialdehyde starch, 2-chloro-6-hydroxy triazino gelatin, and a carbamoyl pyridinium compound.

It is preferable that a layer can be hardened by making use of such a hardener as mentioned above so that a swelling rate in water can be not higher than 200%, preferably not higher than 160% and, particularly not higher than 120%.

In an emulsion relating to the invention, a variety of photographic additives can be used in the steps before or after carrying out a physical or chemical ripening step. The well-known additives include, for example, the compounds given in Research Disclosure (RD) No. 71643 (Dec., 1978), ibid., No. 18716 (Nov., 1979) and, ibid., No. 308119 (Dec., 1989). The kinds of the compounds and the pages of the RDs where the compounds, each given in the above-mentioned three issues thereof, will be indicated below.

Additive	RD-17643		RD-18716		RD-308119	
	Page	Class	Page	Class	Page	Class
Chemical sensitizer	23	III	648 Upper R.996		996	III
Sensitizing dye	23	IV	648-649		996-8	IV
Desensitizing dye	23	IV			998	IVB
Dye	25-26	VIII	649-650		1003	VIII
Development accelerator	29	XXI	648 Upper R.			
Antifoggant· stabilizer	24	IV	649 Upper R.		1006-7	VI
Whitening agent	24	V			998	VI
Hardener	26	X	651 L.		1004-5	X
Surfactant	26-7	XI	650 R		1005-6	XI
Antistatic agent	27	XII	650 R		1006-7	XIII
Plasticizer	27	XII	650 R		1006	XII
Lubricant	27	XII				
Matting agent	28	XVI	650 R		1008-9	XVI
Binder	26	XXII			1003-4	IX
Support	28	XVII			1009	XVII

The supports applicable to a light-sensitive material relating to the invention include, for example, those described in the foregoing RD-17643, p.28 and, ibid., RD-308119, p.1009.

A suitable support include those made of a plastic film. To such a support as mentioned above, an under-coat layer may also be provided and/or a corona-discharge or UV-irradiation may further be treated, so as to improve a coated layer to readily adhere to the surface of the support.

EXAMPLES

Now, the examples of the invention will be detailed below. However, the invention shall not be limited to the examples given below.

Example 1

Preparation of Tabular Silver Halide Emulsion

A seed emulsion comprising silver iodobromide was prepared by making use of the following solutions.

[A_1]	
Hydrogen peroxide-treated ossein gelatin	40g
Potassium bromide	75.1g
Add water to make	4000ml

[B_1]	
Silver nitrate	600g
Add water to make	803ml

[C_1]	
Hydrogen peroxide-treated ossein gelatin	16.1g
Potassium bromide	393.7g
Potassium iodide	35.1g
Add water to make	803ml

[D_1]	
Aqueous ammonia (in a 28% solution)	235ml

An apparatus disclosed in JP OPI Publication No. 62-160128/1987 was used, and six units each of nozzles for supplying Solutions B_1 and C_1 were provided to the lower part of each stirring propeller for mixing the solutions, respectively.

Solutions B_1 and C_1 were each added, at a flow rate of 62.8 ml/min in a controlled double-jet method, to Solution A_1 stirred at a high speed of 430 rpm and at 40°C. From 4 min. 46 sec. after starting the addition thereof, the flow rate was gradually increased so as to be the final flow rate of 105 ml/min. The whole adding time was 10 min. 45 sec. While adding Solutions B_1 and C_1, the pBr of the solution being prepared was kept at 1.3 with a (3.5N) potassium bromide solution.

After completing the addition, the temperature of the resulting mixed solution was lowered linearly to 20°C by taking 10 minutes, and Solution D_1 was added thereto with stirring at 460 rpm by taking 20 seconds. The resulting solution was subjected to an Ostwald ripening treatment for 5 minutes. In the course of the ripening treatment, the bromine concentration, ammonia concentration and pH of the resulting ripened solution were 0.025 mol/liter, 0.63 mols/liter and 11.7, respectively.

Immediately thereafter, acetic acid was added thereto and neutralized so that the mixture thereof could have a pH of 5.6, and the ripening treatment was then stopped in operation. For removing the excessive salts, a desalting treatment was carried out by making use of an aqueous solution of Demol N (manufactured by Kao-Atlas Corp.) and an aqueous solution of magnesium sulfate, so that seed emulsion Em-1 could be prepared.

When observing Em-1 through an electron microscope, it was proved to be comprised of globe-shaped grains having an average grain-size of 0.28μm and a grain-size variation coefficient of 21%.

Growth of Seed Grain Emulsion

Successively, there prepared a silver halide grain emulsion relating to the invention, which is mainly comprised of tabular twinned crystals, by making use of comparative seed emulsion Em-1 and the following three kinds of solutions.

Preparation of Emulsion

The resulting seed emulsion was taken in an amount equivalent to 0.027 mols per mol of silver halide of a final emulsion. It is then so dissolved as to be dispersed in an aqueous gelatin solution having a temperature of 62°C and containing a copolymer of polypropylene oxide (or PO) and polyethylene oxide (or EO), (having an EO/PO ratio of 0.33 and a molecular weight of 1400), that was served as a defoamer. In succession, an aqueous 3.5N silver nitrate solution and an aqueous 3.4N potassium bromide solution were each minutes added by a controlled double-jet method over a period of 97 at an accelerated adding rate, so that the adding rate at the time when completing the addition could be 2.3 times as fast as at the time when starting the addition. In the whole course of adding the solutions, the temperature, pH and pAg thereof were constantly kept at 62°C, 5.8 and 8.9, respectively. Further, the resulting mixture was desalted in the same manner as in the case of the seed emulsion preparation. The resulting emulsion was proved to be a tabular silver halide grain emulsion having an average grain-size of 1.30μm, an average thickness of 0.32μm and an average aspect ratio of 4.1. The resulting emulsion is hereinafter referred to as EM-1.

Preparation of Silver Iodide Fine Grains

To 5000ml of a 5.2 wt% gelatin solution containing 0.008 mols of potassium iodide, 1500ml of an aqueous solution containing 1.06 mols each of silver nitrate and potassium iodide was added at a constant adding rate by taking 35 minutes. The temperature in the course of preparing fine grains was kept at 40°C. When confirming the resulting silver iodide grains through a 60000X electron microscope, the grains were each proved to be a mixture of β-AgI and γ-AgI having an average grain-size of 0.05μm.

Chemical Sensitization of Emulsion

While keeping the resulting EM-1 stirred at 52°C, the foregoing sensitizing dyes relating to the invention, I-6, I-7, I-16, II-1, II-3 and II-13, were added respectively to separate methanol solutions as shown in Table 1, so that the amount of each sensitizing dye added could be 140mg per mol of a silver content of EM-1. 10 minutes thereafter, 60mg of ammonium thiosulfate, 1.45mg of chloroauric acid and 13.8mg of sodium thiosulfate, each per mole of silver, were added thereto as the chemical sensitizers. 30 minutes thereafter, the foregoing silver iodide finely grained emulsion was further added in an equivalent amount of 1.37×10^{-3} mols and, after passing a specific period of time, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 1-phenyl-5-mercaptotetrazole were each so added thereto as to be stabilized. Therefore, the resulting emulsions were chemically ripened at optimum, respectively. The resulting emulsions are hereinafter referred to as EM-2 through EM-7, respectively.

Besides the above, a selenium-sensitized emulsions EM-8 through EM-13 were each prepared in quite the same manner as in EM-2 through EM-7, except that N,N-dimethyl selenourea was further added in an amount of 8×10^{-7} together with chloroauric acid, as the chemical sensitizers.

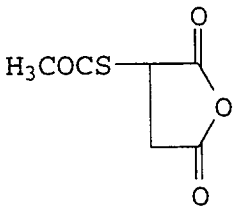
Preparation of Internally Selenium-Sensitized Emulsion

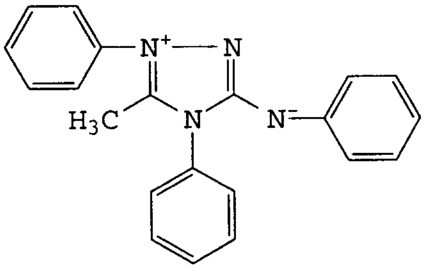
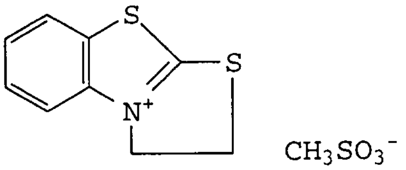
The addition of the aqueous silver nitrate solution and halide solution of Emulsion EM-1 were temporarily stopped at the time when 80% of silver nitrate solution was added, and ammonium thiocyanate and N,N-dimethyl thiourea were then added thereto so as to be in the amounts thereof of 7.8×10^{-6} mols and 1.1×10^{-6} mols each per mol of the silver used in the emulsion to be finally prepared, respectively. Four (4) minutes thereafter, the remaining aqueous silver nitrate solution and halide solution were further added. When observing the resulting emulsion through an electron microscope, the configuration of the resulting emulsion was proved to be approximately the same as that of EM-1. The resulting emulsion is hereinafter referred to as EM-14.

The sensitizing dyes relating to the invention same as those used in EM-2 through EM-7 were added respectively to each of EM-14, and the same gold-sulfur sensitizers as those used in EM-2 through EM-7 were further added thereto, respectively. The resulting emulsions are hereinafter referred to as EM-15 through EM-20, respectively.

Emulsion-layer coating solutions were prepared, by adding the following additives to the resulting chemically ripened emulsions EM-1 through EM-7, EM-8 through EM-13 and EM-15 through EM-20, respectively. At the time, the following protective-layer coating solution was also prepared. The amounts of the resulting coating solutions to be coated were determined so that the silver contents and gelatin contents of the solutions could be in the amounts of 2.5 g/m^2 and 1.85 g/m^2 each per one coated surface, respectively, and each support was simultaneously coated on both-side thereof at a coating speed of 80m per minute by making use of two units of slide-hopper type coating machine. Each of the resulting emulsion-layers was dried up for 2min.20sec., so that the coated samples No. 1 through No. 18 were prepared. As for the support, there used a 175µm-thick and 0.15 density blue-colored polyethylene terephthalate film base for X-ray film use, which was prepared in the following manner; a copolymeric aqueous dispersed solution for serving as a subbing solution was prepared by diluting it so as to have a concentration of a 10 wt% copolymer comprising three monomers, glycidyl methacrylate of 50 wt%, methyl acrylate of 10 wt% and butyl methacrylate of 40 wt%, and the resulting subbing solution was then subbed on the above-mentioned film base.

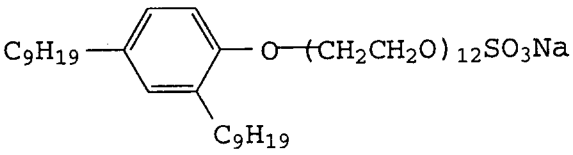
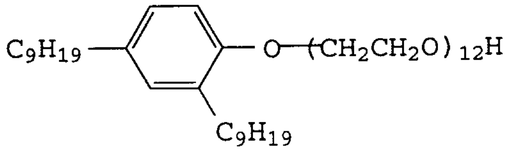
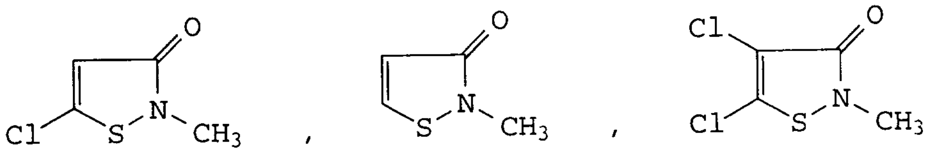
The following additives were used in the emulsion. The amounts thereof used are each indicated by an amount per mol of silver halide.

1,1-dimethylol-1-bromo-1-nitromethane	70mg
t-butyl-catechol	82mg
Polyvinyl pyrrolidone (having a molecular weight of 10,000)	1.0g
Styrene-maleic anhydride copolymer	25g
Nitrophenyl-triphenyl phosphonium chloride	50mg
Ammonium 1,3-dihydroxybenzene-4-sulfonate	2.0 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	1.5mg
	7.2 mg

	150 mg
	80 mg
$C_4H_9OCH_2CH(OH)CH_2N(CH_2COOH)_2$	1g
1-phenyl-5-mercaptotetrazole	15mg
Diethylene glycol	7g
Dextran (having an average molecular weight of 60,000)	600mg
Sodium polyacrylate (having an average molecular weight of 36,000)	2.5g

Next, the following solution was prepared for a protective layer coating solution. The amounts of the additives added thereto are each indicated by an amount per liter of the coating solution.

Lime-processed inert gelatin	68g
Acid-processed gelatin	2g
Sodium i-amyl-n-decyl sulfosuccinate	0.3g
Polymethyl methacrylate (i.e., a matting agent having an area average particle-size of 3.5μm)	1.1g
Silicon dioxide (a matting agent having an area average particle-size of 1.2μm)	0.5g

Rudox AM (colloidal silica manufactured by DuPont)	230g
$(CH_2=CHSO_2CH_2)_2O$, (a layer hardener)	200mg
An aqueous 40% glyoxal solution, (a layer hardener)	2.0ml
	1.0 g
	0.4 g
 (50:46:4)	0.1 g

Sensitometry (Evaluation of Photographic Characteristics)

Sensitometry was carried out in the following manner.

A subject sample was held between two sheets of intensifying screens (manufactured by Konica Corp.) and, thereto X-rays were irradiated with a tube-voltage of 80 kvp and a tube-current of 50mA, for 0.05 seconds through an aluminum-made wedge. Thereafter, a series of developing and fixing treatments thereof were carried out by making use of a roller-transport type automatic processor and the following developer and fixer. The details thereof are as follows.

Composition of Developer

Part A (for a 12-liter preparation)

Potassium hydroxide	450g
Potassium sulfite (in a 50% solution)	2280g
Diethylenetetramine pentacetate	120g
Sodium hydrogen bicarbonate	132g
5-methyl benzotriazole	1.2g
1-phenyl-5-mercaptotetrazole	0.2g
Hydroquinone	340g
Add water to make	5000ml

Part-B (for a 12-liter preparation)

Glacial acetic acid	170g
Triethylene glycol	185g
1-phenyl-3-pyrazolidone	22g
5-nitroindazole	0.4g
N-acetyl-DL-penicillamine	1.2g

Starter

Glacial acetic acid	120g
Potassium bromide	225g
Add water to make	1.0 liter

Composition of Fixer

Part-A (for 18-liter preparation)

Ammonium thiosulfate (in 70 wt/vol %)	6000g
Sodium sulfite	110g
Sodium acetate•trihydrate	450g
Sodium citrate	50g
Gluconic acid	70g
1-(N,N-dimethylamino)-ethyl -5-mercaptotetrazole	18g

Part-B

Aluminium sulfate	800g

In the preparation of a developer, Part-A and Part-B were added at the same time to approximately 5 liters of water and water was further added with stirring so as to make 12 liters in total. The pH thereof was controlled to be 10.40 with glacial acetic acid. The resulting solution was used as a developer.

The foregoing starter was added in an amount of 20 ml per liter of the developer, and the pH thereof was controlled to be 10.26, so that the resulting solution could be used.

In the preparation of a fixer, Part-A and Part-B were added at the same time to approximately 5 liters of water and water was further added with stirring so as to make 18 liters in total. The pH thereof was controlled to be 10.4.6 with sulfuric acid and NaOH. The resulting solution was used as a fixer.

The processing treatments were carried out for 90 seconds in a dry-to-dry system. The temperatures in the course of carrying out the processing were 32°C in the developing treatment, 33°C in the fixing treatment and 50°C in the drying treatment. The sensitivities each obtained therefrom were expressed in terms of the reciprocals of an exposure capable of giving a density of fog + 0.5, and indicated by a value relative to the sensitivity obtained from Sample No.1 that was regarded as the standard value of 100.

Evaluation on Roller-mark occurrence

A pressure mark (so-called a roller-mark) produced by a roller of an automatic processor was evaluated in the following manner. A processing treatment was carried out through an automatic processor under the unexposed conditions and in the same manner as in the above-mentioned sensitometric evaluation. The roller-marks produced therein were each visually evaluated upon classifying them into the following 5 grades.

Grade 5: No roller-mark produced;
Grade 4: Few roller-marks produced;
Grade 3: A few roller-marks produced (within a practical applicability);
Grade 2: Many roller-marks produced (Out of the practical applicability); and
Grade 1: Remarkably numerous roller-marks produced.

Samples No.1 through No. 18, each cut into a 5mm x 20mm size were each dipped in an aqueous 1.5 wt% sodium hydroxide solution being kept at 50 ° C. When the resulting meting time of each sample was measured, it was within the range of 15min. to 20min. Therefore, each sample after processed was satisfactory in dryness.

The results thereof will be shown in the following Table 1.

Table 1

Sample No.	Em No.	Sensitizing dye	Chemical sensitization	Position of selenium nuclei of grains	Photographic characteristics			Roller-mark
					Fog	Sensitivity	Dmax	
1(Comparison)	EM-2	I-6	Gold-Sulfur	-	0.04	100	2.69	2
2(Comparison)	EM-3	I-7	Gold-Sulfur	-	0.04	92	2.66	2
3(Comparison)	EM-4	I-16	Gold-Sulfur	-	0.05	97	2.72	2
4(Comparison)	EM-5	II-1	Gold-Sulfur	-	0.05	103	2.68	1
5(Comparison)	EM-6	II-3	Gold-Sulfur	-	0.04	97	2.66	1
6(Comparison)	EM-7	II-13	Gold-Sulfur	-	0.05	100	2.68	2
7(Invention)	EM-8	I-6	Gold-Sulfur-Selenium	Surface	0.04	120	3.10	4
8(Invention)	EM-9	I-7	Gold-Sulfur-Selenium	Surface	0.04	115	3.13	4
9(Invention)	EM-10	I-16	Gold-Sulfur-Selenium	Surface	0.04	117	3.15	4
10(Invention)	EM-11	II-1	Gold-Sulfur-Selenium	Surface	0.04	128	3.35	3
11(Invention)	EM-12	I-3	Gold-Sulfur-Selenium	Surface	0.04	125	3.28	3
12(Invention)	EM-13	II-13	Gold-Sulfur-Selenium	Surface	0.04	119	3.21	4
13(Invention)	EM-15	I-6	Gold-Sulfur-Selenium	Interior	0.03	143	3.35	5
14(Invention)	EM-16	I-7	Gold-Sulfur-Selenium	Interior	0.03	140	3.42	5
15(Invention)	EM-17	I-16	Gold-Sulfur-Selenium	Interior	0.03	152	3.40	5
16(Invention)	EM-18	II-1	Gold-Sulfur-Selenium	Interior	0.03	160	3.50	5
17(Invention)	EM-19	II-3	Gold-Sulfur-Selenium	Interior	0.03	157	3.38	5
18(Invention)	EM-20	II-13	Gold-Sulfur-Selenium	Interior	0.03	155	3.44	5

According to the invention, as is obvious from Table 1, it is shown that a light-sensitive material having the photographic characteristics high in sensitivity, low in fog and excellent in the maximum density. Resistance the roller-mark production can also be so excellent that almost no roller-mark production could be confirmed. Further, the photographic characteristics and roller-mark production resistance were proved to be more excellent when selenium nuclei are each positioned in the interior than on the grain surfaces.

Example 2

Preparation of Hexagonal Tabular Twinned-Crystal Seed Emulsion

A hexagonal tabular seed emulsion was prepared in the following manner.

A_2	
Ossein gelatin	24.2g
Distilled water	9657ml
$H\text{-}[CH_2CH_2O]_m\text{-}[CH(CH_3)\text{-}CH_2O]_{17}\text{-}[CH_2CH_2O]_n\text{-}OH$ (wherein $m + n = 5.6$; the molecular weight = 1700) (in a 10% methanol solution)	6.78ml
KBr	10.8g
A 10% nitric acid solution	114ml

B_2	
An aqueous 2.5N $AgNO_3$ solution	2825ml

C_2	
KBr	824g
KI	23.5g
Add distilled water to make	2825ml

D_2	
An aqueous 1.75N KBr solution	The following silver-potential controllable amount

At 35°C and by making use of a mixing-stirrer described in JP Examined Publication Nos. 58-58288/1983 and 58-58289/1983, 464.3ml each of Solutions B_2 and C_2 were added to Solution A_2 in a double-jet method by taking 2 minutes, so that a nucleus formation was carried out.

After stopping the addition of Solutions B_2 and C_2, the temperature of resulting mixture solution A_2 was raised to 60°C by taking 60 minutes and the pH thereof was set at 5.0 with a 3% KOH solution. Thereafter, Solutions B_2 and C_2 were each added again at a flow-rate of 55.4ml/min for 42 minutes by a double-jet method. The silver electrode potentials between the time when raising the temperature of Solution A_2 from 35°C to 60°C and the time when the double-jetting Solutions B_2 and C_2 again, such potentials were controlled with Solution D_3 so as to be +8mv and +16mv, respectively; (wherein a saturated silver-silver chloride electrode was used as a standard electrode, and the potential was measured with a silver-ion selection electrode.)

After completing the addition of the solutions, the pH was adjusted to be 6 with a 3% KOH solution. Immediately after that, a desalting and washing treatments were carried out. The resulting seed emulsion was proved through an electron microscope that the seed emulsion Em-2 was comprised of hexagonal tabular silver halide grains out of which not less than 90% of the whole projected area had the maximum ratio of the adjacent sides within the range of 1.0 to 2.0, and that the average thickness of the hexagonal tabular grains was 0.06μm and the average grain-size (converted into the diameter of a circle having the same area thereof) was 0.57μm.

Preparation of Emulsion

The resulting hexagonal tabular seed emulsion Em-2 was taken in an equivalent amount of 0.023 mols per mol of silver of the emulsion and was then so dissolved as to be dispersed in an aqueous gelatin solution being kept at 60°C and containing a copolymer of polypropylene oxide (PO) and polyethylene oxide (EO). An aqueous silver nitrate solution was prepared in advance so that an average silver iodide content of the finally formed growth grains was to be 1.05 mol%. Successively, the resulting aqueous silver nitrate solution and a halide solution comprising potassium bromide and potassium iodide were each added by a double-jet method over a period of 107 minutes, while keeping the pH = 5.8 and pAg = 9.0 at 60 ° C all along. Resultingly, a tabular silver iodobromide emulsion EM-21 having an average grain-size of 1.51μm, an average thickness of 0.25μm and an average aspect ratio of 6.04 could be prepared.

The resulting emulsion EM-21 was chemically sensitized while keeping a temperature of 50 ° C. Thereto, ammonium thiocyanate of 52mg, chloroauric acid of 1.4mg and sodium thiosulfate•pentahydrate of 15.0mg were each added. After 32 minutes passed therefrom, the silver iodide fine-grain type emulsion described in Example 1 was added in an equivalent amount of 1.80×10^{-3} mols. Thereafter, 2.34g of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added so that the emulsion could be stabilized and was then subjected to an optimum chemical sensitization.

Ten minutes before starting the chemical sensitization, sensitizing dyes relating to the invention I-6, I-7, I-16, II-3, II-13, II-23 and II-26 were each added in an amount of 160mg per mol of silver halide, so that seven kinds of emulsions were prepared, respectively.

The resulting chemically sensitized emulsions are hereinafter referred to as EM-22 through EM-28, respectively.

Preparation of Internally Selenium-Sensitized Emulsion

The addition of the aqueous silver nitrate solution and halide solution of Emulsion EM-21 were temporarily stopped at the time when 90% of the silver nitrate solution was added, and ammonium thiocyanate and N,N-dimethyl selenourea were then added thereto so as to be in the amounts thereof of 7×10^{-6} mols and 2×10^{-6} mols each per mol of the silver used in the growth emulsion to be finally prepared, respectively. Four (4) minutes thereafter, the remaining aqueous silver nitrate solution and halide solution were further added to form the shell portions of the grains. Immediately after forming the shells, a desalting and washing treatments were carried out, so that emulsion EM-29 could be prepared. The configuration of the resulting emulsion grains were each proved to be approximately the same as those of EM-28.

The sensitizing dyes relating to the invention same as those used in EM-22 through EM-28 were added respectively to each of EM-29, and the same chemical sensitizers were further added thereto, respectively. Thereafter, the surfaces of the resulting grains were gold•sulfur-sensitized. The resulting emulsions are hereinafter referred to as EM-30 through EM-36, respectively.

The resulting EM-22 through EM-28 and EM-30 through EM-36 were coated on the respective samples, so that Samples No. 19 through No. 32 could be prepared.

The resulting samples were each evaluated in quite the same manner as in Example 1. The results thereof will be shown in Table 2.

Table 2

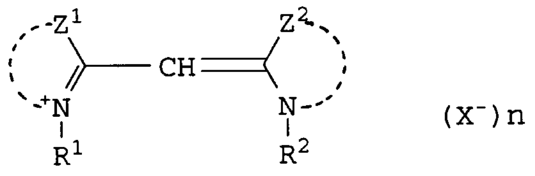
Sample No.	Em No.	Sensitizing dye	Chemical sensitization	Position selenium-sensitized	Photographic characteristics			Roller-mark
					Fog	Sensitivity	Dmax	
19 (Comparison)	EM-22	I-6	Gold-Sulfur	-	0.05	82	2.89	2
20 (Comparison)	EM-23	I-7	Gold-Sulfur	-	0.05	85	2.92	2
21 (Comparison)	EM-24	I-16	Gold-Sulfur	-	0.05	85	2.85	2
22 (Comparison)	EM-25	II-3	Gold-Sulfur	-	0.04	81	2.90	1
23 (Comparison)	EM-26	II-13	Gold-Sulfur	-	0.05	84	2.88	1
24 (Comparison)	EM-27	II-23	Gold-Sulfur	-	0.04	82	2.90	2
25 (Comparison)	EM-28	II-26	Gold-Sulfur	-	0.04	82	2.94	2
26 (Invention)	EM-30	I-6	Gold-Sulfur-Selenium	Interior	0.03	125	3.60	4
27 (Invention)	EM-31	I-7	Gold-Sulfur-Selenium	Interior	0.03	128	3.52	4
28 (Invention)	EM-32	I-16	Gold-Sulfur-Selenium	Interior	0.03	124	3.57	4
29 (Invention)	EM-33	II-3	Gold-Sulfur-Selenium	Interior	0.03	140	3.60	5
30 (Invention)	EM-34	II-13	Gold-Sulfur-Selenium	Interior	0.03	137	3.58	4
31 (Invention)	EM-35	II-23	Gold-Sulfur-Selenium	Interior	0.03	135	3.55	5
32 (Invention)	EM-36	II-26	Gold-Sulfur-Selenium	Interior	0.03	135	3.60	4

As is obvious from Table 2, it was proved that, according to the invention, a high sensitivity, a low fog, a high maximum density and an excellent roller mark production resistance can be achieved even in the case of a tabular silver iodobromide emulsion grown up from a hexagonal tabular twinned crystal seed emulsion.

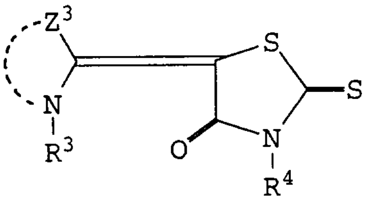
Claims

1. A silver halide photographic light-sensitive material comprising a support having on at least one side thereof a silver halide emulsion layer comprising a silver halide emulsion containing silver halide grains, which is prepared by a process comprising:
   (i) forming the silver halide emulsion by mixing a silver salt and a halide salt in a dispersing medium and
   (ii) subjecting the emulsion formed to chemical ripening, wherein said silver halide grains are selenium-sensitized by adding a selenium compound during a period of the course of forming the silver halide emulsion and chemical ripening thereof; said grains being spectrally sensitized with a spectral sensitizing dye represented by the following Formula (I) or Formula (II),

   Formula (I)

   Formula (II)

   wherein Z^1, Z^2 and Z^3 each represent a group of nonmetallic atoms necessary for forming oxazole, benzoxazole, naphthoxazole, thiazole, benzothiazole or naphthothiazole; R^{1}, R^2 or R^3 each represent a substituted or unsubstituted alkyl group; R^4 represents a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; X is an acid anion; and n is an integer of 0 or 1.

2. The photographic material of claim 1, wherein said silver halide grains are tabular grains having an average diameter of 0.3 to 3.0 µm and having an average aspect ratio of grain diameter to grain thickness of not less than 1.2.

3. The photographic material of claim 2, wherein said tabular grains account for at least 50% of projected area of total silver halide grains contained in the silver halide emulsion.

4. The photographic material of claim 1, wherein said selenium compound is selected from an elemental selenium, an isoselenocyanate, a selenourea, a selenoketone, a selenoamide, a selenocarboxylic acid and an ester thereof, a selenide, and a selenophosphate.

5. The photographic material of claim 5, wherein said selenium compound is added after at least 70% of the whole silver salt used for forming the emulsion has been added and before the completion of the addition of the silver salt.

6. The photographic material of claim 1, wherein said selenium compound is added after the start of chemical ripening and before the completion thereof.

7. The photographic material of claim 1, wherein selenium compound is added in the presence of a silver halide solvent selected from a thioether, a thiourea, an imidazole, a sulfite and a thiocyanate.

8. The photographic material of claim 1, wherein said sensitizing dye is added at a time during a period from the time after forming the silver halide grains to the time before completing chemical sensitization.

9. The photographic material of claim 1, wherein silver halide fine grains having a grain size of 0.12 μm or less are added at a at a time during the course of the chemical sensitization.

10. The photographic material of claim 1, wherein said silver halide grains are silver iodobromide having an iodide content of 0.1 to 4.0 mol%.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 6432

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)
P,X	EP-A-0 563 708 (FUJI PHOTO FILM CO., LTD) 6 October 1993 * page 1, line 1 - page 1, line 46 * * page 16, line 42 - page 17, line 44 * * page 18, line 12 - page 26, line 12 * * page 31, line 33 - page 31, line 55 * * example 2, emulsion c, dye ExS-7 * * page 57, line 53 - page 57, line 58 * ---	1-10	G03C1/09 G03C1/16
X	EP-A-0 514 675 (FUJI PHOTO FILM CO., LTD) 25 November 1992 * page 2, line 3 - page 2, line 8 * * page 3, line 40 - page 3, line 45 * * page 5, line 56 - page 6, line 34 * * page 8, line 16 - page 16, line 20 * * page 18, line 53 - page 19, line 41 * * example 1 * ---	1-10	
X	EP-A-0 512 496 (FUJI PHOTO FILM CO., LTD) 11 November 1992 * page 4, line 50 - page 5, line 52 * * page 19, line 12 - page 26, line 47 * * examples 2,3 * ---	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.5) G03C
A	EP-A-0 487 010 (E. I. DU PONT DE NEMOURS AND COMPANY) 27 May 1992 * claim 1 *	1	
D	& JP-A-4 291 338 (...) 15 October 1992 ---	1	
A	EP-A-0 443 453 (FUJI PHOTO FILM CO., LTD) 28 August 1991 * claim 1 * -----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	14 July 1994	Markowski, V

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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
....
& : member of the same patent family, corresponding document