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⑤④ **Silver halide light-sensitive photographic material.**

⑤⑦ A silver halide photographic material is disclosed which has high sensitivity and is improved in relation between light-sensitivity and fogginess, graininess and stability in development. The photographic material comprises a support having thereon a silver halide emulsion layer and a non-light-sensitive layer adjacently to the emulsion layer, and at least one of the silver halide emulsion layer and the non-light-sensitive layer contains substantially non-light-sensitive fine silver halide grains having a silver chloride content of not less than 20 mol% and the silver halide emulsion layer contains monodisperse light-sensitive silver halide grains substantially consisting of silver bromide or silver iodobromide.

EP 0 334 162 A1

SILVER HALIDE LIGHT-SENSITIVE PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

This invention relates to a silver halide light-sensitive photographic material which is high in both sensitivity and image-quality and excellent in processing stability and, more particularly, to a silver halide light-sensitive photographic material which is high in sensitivity, excellent in both relation of fogginess to sensitivity and graininess and stable in development processes.

BACKGROUND OF THE INVENTION

In recent years, there have been more serious demands for silver halide photographic emulsions and, particularly, higher-level demands for photographic characteristics such as a higher sensitivity, more excellent graininess, higher image sharpness and so forth.

As one of the answers to the above-mentioned demands, there are well known high sensitive emulsions, namely, silver iodobromide emulsions each containing an iodide in an proportion of from 0 to 10 mol% and there have also been well known methods for preparing those emulsions, namely, the methods for controlling pH and pAg conditions, such as an ammoniacal method, a neutral method, an acid method, and the precipitation methods such as a single-jet precipitation method, a double-jet precipitation method and so forth.

Based upon the above-given techniques and for the purposes of making sensitivity higher, improving graininess and achieving both high sharpness and low fogginess, various technical means have been researched to the extent of the minutest details and developed to put them to practical use. As for the silver iodobromide emulsions, much research and development has been made so as to control not only both of crystal habits and graininess distribution but also the iodide concentration distribution in individual silver halide grains.

The most orthodox method of achieving the photographic characteristics such as high sensitivity, excellent graininess, high sharpness, low fogginess and so forth is to improve the quantum efficiency of silver halides used. To achieve this purposes, the observations of solid-state physics have positively been adopted. For example, a study on theoretically calculating the above-mentioned quantum efficiency and observing the influence of grain size distribution, was disclosed at the 1980 Tokyo Symposium concerning the progress of Photography, titled 'The Interactions between Light and Materials', p. 91. According to this study, it is predicted that quantum efficiency could effectively be improved when a monodisperse type emulsion is prepared by narrowing the grain size distribution thereof. In addition to the above, it may be reasonable to consider that a monodisperse type emulsion could be advantageous for effectively achieving a high sensitivity, keeping low fogginess in the course of the so-called chemical sensitization process for sensitizing a silver halide emulsion, which will be detailed later.

As mentioned above, it may be considered that a monodisperse type emulsion is extremely effective for improving quantum efficiency during a light absorption and achieving low fogginess during a chemical sensitization. On the other hand, however, there are some defects which monodisperse type emulsions themselves intrinsically have. More concretely, with narrowly grain-distributed and uniformly chemical-sensitized emulsion grains, all the latent image nuclei formed on and/or in each grain are of the order of the same size and every grain, therefore, starts to develop at the same time when the emulsion is developed.

As a result, in the initial stage of a development, a number of bromide ions and iodine ions are produced, so that development is liable to be inhibited.

In the meantime, there has so far been a well-known technique in which color reproducibility and image quality may be improved or high sensitivity may be achieved by containing the fine grains of silver halides substantially not having light-sensitivity into a light-sensitive emulsion layer or a non-light-sensitive layer adjacent to the emulsion layer.

For example, Research Disclosure, Vol. 134, 1975, p. 47, No. 13452 describes a highly sensitizing method in which a finely grained reflective layer is provided to the lower layer adjacent to an emulsion layer and the emulsion of the upper layer may be highly sensitized by utilizing the light-scattering property of the reflective layer. In this method, however, some problems arise which make it causing this method to be difficult to put to practical use, because, the more an emulsion is sensitized, the more the emulsion

graininess and the fogginess are seriously deteriorated.

Japanese Patent Publication open to Public Inspection (hereinafter called Japanese Patent O.P.I. Publication) Nos. 53-99938/1978 and 59-170839/1984, and U.S. Patent Nos. 3,892,572 and 4,153,460 each describe methods in each of which a fine-grained and non-light-sensitive silver chloride emulsion is used in combination with a DIR compound. In those methods, however, not only may the desired sensitivity not be obtained, but also only the limited kinds of couplers may be contained in a light-sensitive emulsion layer subject to a high sensitization are limited.

Japanese Patent O.P.I. Publication No. 59-160135/1984 describes a layer arrangement where a relatively non-light-sensitive silver halide grain-containing layer is arranged adjacent to and between two light-sensitive emulsion layers having sensitivities different from each other. Also in this layer arrangement, the light-sensitive emulsion layers arranged adjacent to the non-light-sensitive silver halide grain-containing layer are limited to be of the same color-sensitivity and the fogginess cannot be inhibited from increasing satisfactorily.

Japanese Patent O.P.I. Publication Nos. 59-180555/1984 and 60-194450/1985 each disclose techniques in which high sensitization, excellent contrast or processing stability may be achieved by combining a specific inverted layer structure with fine-grained non-light-sensitive silver halide grains. Even in those techniques, the layer arrangements are limited to some peculiar arrangements and are not satisfactory for achieving a high sensitization.

Further, Japanese Patent O.P.I. Publication No. 61-246739/1986 describes a method in which a high sensitization may be achieved by combining core/shell type silver halide grains having a plurality of shells with non-light-sensitive silver halide fine grains, while keeping low fogginess. This method is still unsatisfactory from the viewpoint of making high sensitivity.

As mentioned above, in the conventional high sensitization techniques used so far for non-light-sensitive fine grains, it has been difficult to achieve a satisfactorily high sensitization, keeping both excellent graininess and the relation of fogginess to sensitivity.

OBJECTS OF THE INVENTION

It is an object of the invention to provide a silver halide photographic light-sensitive material capable of satisfactorily displaying the photographic characteristics of a monodisperse type emulsion having high sensitivity, excellent fog-sensitivity-to-fog property and an excellent graininess.

Another object of the invention is to provide a silver halide light-sensitive photographic material capable of displaying also a high processing stability in the course of development.

SUMMARY OF THE INVENTION

It was discovered that the objects of the invention can be achieved with a silver halide light-sensitive photographic material comprising a support having thereon a silver halide emulsion layer and a non-light-sensitive layer adjacently provided to said emulsion layer, wherein at least one of the silver halide emulsion layer and the non-light-sensitive layer contains substantially non-light-sensitive fine-grained silver halide having a silver chloride content of not less than 20 mol% and the silver halide emulsion layer contains monodisperse light-sensitive silver halide grains substantially consisting of silver bromide or silver iodobromide.

DETAILED DESCRIPTION OF THE INVENTION

The invention will now be described in more detail below.

Firstly, this invention is characterized by the following points.

1. Not only iodine ions but also bromine ions can be trapped very efficiently when these ions are released in the course of development, because non-light-sensitive silver halide fine grains having a substantially high silver chloride content are used. The invention is, therefore, very effective against development inhibition caused by halogen ions.

2. An increase in fog, one of the defects of the sensitizing techniques using silver halide fine grains, can be inhibited to the minimum, because the fogging level of a light-sensitive emulsion itself can be lowered by making use of a monodisperse type emulsion for a light-sensitive silver halide emulsion.

3. In the invention, sensitization can be achieved beyond expectations with low foginess and, at the same time, no graininess deterioration was found at all, because the following shortcomings can be cancelled out by each other, namely, one shortcoming is that monodisperse type emulsions seriously inhibit a development, because of the combination of a monodisperse type light-sensitive silver halide emulsion and non-light-sensitive silver halide fine grains each having a substantially high silver chloride content and, the other shortcoming is that fog is increased particularly when using the non-light-sensitive fine grains each having a substantially high silver chloride content.

4. In the invention, bromide and iodide ion concentration variation can be stabilized to a substantially low level in a layer being developed, because the halide ions are positively trapped by the non-light-sensitive silver halide fine grains each having a substantially high silver chloride content, in the course of development. It is therefore possible to provide a light-sensitive material less variable in photographic characteristics and excellent in processing stability without the variations of the bromide and iodide ion concentration in a developer.

5. In the invention, it is possible to provide a light-sensitive material excellent further in the fog-to-sensitivity relation when a compound represented by Formula A, which will be given later, is contained in at least one layer out of the light-sensitive emulsion layers and the non-light-sensitive layers adjacent to the emulsion layers.

The light-sensitive emulsions relating to the invention, which are used in light-sensitive emulsion layers, substantially comprise silver bromide and/or silver iodobromide. The expression, '--- substantially comprise ---' mentioned herein, means that they are allowed to contain any silver halides other than silver bromide or silver iodobromide, such as silver chloride, provided that the other silver halide does not hinder the effects of the invention. More precisely, in the case of silver chloride, it is contained desirably in a proportion of not more than 1 mol%.

The light-sensitive silver halide emulsions relating to the invention which are contained in light-sensitive emulsion layers, are of the monodisperse type. The term, 'monodispersive', means that the grain size distribution of the silver halide grains constituting an emulsion is not more than 20% in terms of the grain size variation coefficient. The variation coefficient should preferably be not more than 15%. Herein, such a variation coefficient is defined by the following equation:

$$\text{Variation coefficient (\%)} = \frac{\text{Standard deviation of grain size}}{\text{Average grain size}} \times 100$$

Such a variation coefficient is a scale for indicating the degrees of monodispersiveness.

Light-sensitive silver halide grains to be contained in the light-sensitive emulsion layers are allowed to take any form, such as a regular crystal form, a twinned crystal form, a tabular-grain form, an octahedral form, a cubic form, a dodecahedral form, a rhombic dodecahedral form, a tetracosahedral form, the mixed crystal forms thereof and so forth, and those forms may be so selected as to meet an application. The halogen composition of the above-mentioned light-sensitive silver halide grains may be either uniform inside the grains or of the so-called core/shell type structure including the multilayered core/shell type structure having two or more shells. These grains may be prepared in well known methods. They may be of the so-called conversion type, such as those described in, for example, British Patent No. 635,841 and U.S. Patent No. 3,622,318.

As for the light-sensitive emulsion contained in the above-mentioned light-sensitive emulsion layer, a single kind of monodisperse type emulsion only may be used and the mixture of two or more kinds of monodisperse type emulsions may also be used.

In the invention, it is allowed to use non-light-sensitive silver halide fine grains having a chloride content of not less than 20 mol%, preferably, not less than 50 mol% and, more preferably, not less than 70 mol%. The non-light-sensitive silver halide fine-grains are allowed to have any halogen composition such as silver chloride, silver chlorobromide, silver chloriodobromide and so forth and, among these compositions, silver chloride and silver chlorobromide are more preferably used.

The substantially non-light-sensitive silver halide fine grains, hereinafter called simply non-light-sensitive silver halide fine grains, relating to the invention are allowed to have monodispersiveness or polydispers-

siveness. In order to achieve the objects of the invention more effectively, monodisperse type grains are preferably used. The average grains sizes of the non-light-sensitive silver halide fine grains may freely be selected to meet the requirements for an application. However, a preferable average grain size is within the range of from 0.03 μ m to 0.5 μ m.

5 The non-light-sensitive silver halide fine grains may be used in any amount. When using these grains in the above-mentioned light-sensitive emulsion layers, these grains are used in a proportion of, preferably, from 5 to 30% by weight and, more preferably, from 5 to 25% by weight in terms of silver to the light-sensitive silver halide grains contained in the emulsion used. When using the fine grains in the above-mentioned non-light-sensitive layers, the grains are used in a proportion of, preferably, from 0.5mg to 10 mg/dm² and, more preferably, from 1mg to 10mg/dm² in terms of the silver content of the non-light-sensitive silver halide layer.

10 The non-light-sensitive silver halide fine grains relating to the invention may be used in a single kind or in the mixture of two or more kinds thereof. It is also allowed to use the different kinds of the non-light-sensitive silver halide fine grains in different layers. In addition, it is further allowed to jointly use the other non-light-sensitive silver halide fine grains than those of the invention, such as silver bromide or silver iodobromide. These non-light-sensitive silver halide fine grains may be prepared in any of the well known methods.

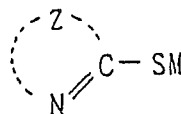
15 The expression, '--- substantially non-light-sensitive ---' mentioned herein, means that the grains are not substantially developed in a developer. However, the grains are allowed to have a low light-sensitivity to the extent that an image is not substantially affected by development.

20 As described above, the objects of the invention can more effectively be achieved by containing at least one of the compounds represented by the following Formula A into at least one layer of the above-mentioned light-sensitive silver halide emulsion layer and the above-mentioned non-light-sensitive silver halide layer adjacently provided to the silver halide emulsion layer.

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Formula A

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35 wherein Z represents a group consisting of atoms necessary to complete a 5- or 6-membered heterocyclic ring, provided that the atoms are selected from the group consisting of a carbon atom, a nitrogen atom, an oxygen atom, a sulfur atom and a selenium atom, and that the heterocyclic ring is allowed to have a condensed carbon ring.

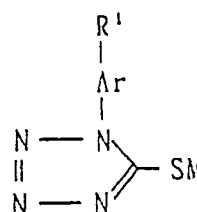
40 The heterocyclic rings include, for example, those of pyridine, pyrimidine, imidazole, benzoimidazole, naphthoimidazole, oxazole, benzoxazole, naphthoxazole, thiazoline, thiazole, benzothiazole, naphthothiazole, selenazole, benzoselenazole, naphthoselenazole, triazole, oxadiazole, thiadiazole, triazine, tetrazole, purine, azaindene or the like. Those heterocyclic rings may also be substituted with, for example, an aromatic group, an aliphatic group, a hydroxy group, an alkoxy group, an aryloxy group, an amino group, a nitro group, a halogen atom, carboxyl group or the salts thereof, a sulfo group or the salts thereof, a mercapto group, an alkylmercapto group, an acylamino group, a sulfamoyl group, a sulfoamino group, a carbamoyl group or the like groups.

45 Among the compounds represented by Formula A, the compounds represented by the following Formulas B through D are particularly preferable.

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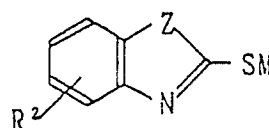
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Formula B



wherein Ar represents a phenyl group, a naphthyl group or a cyclohexyl group; R^1 represents a group capable of being a substituent of the group represented by Ar or a hydrogen atom; and M is synonymous with that denoted in Formula A.

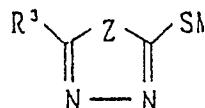
Formula C



wherein Z' represents a sulfur atom, an oxygen atom, a selenium atom or

$\begin{array}{c} H \\ | \\ -N- \end{array}$; R^2 represents a group capable of being a substituent of a benzene ring or a hydrogen atom; and M is synonymous with that denoted in Formula A.

Formula D



wherein Z'' represents a sulfur atom, an oxygen atom, a selenium atom or

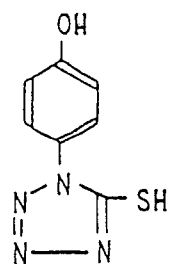


in which R^4 represents a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aralkyl group, $-COR^5$, $-SO_2-R^5$, $-NHCOR^6$ or $-NHSO_2-R^6$; R^5 represents an alkyl group, an aryl group, a cycloalkyl group, an aralkyl group or $-NH_2$; R^6 represents an alkyl group, an aryl group, a cycloalkyl group or an aralkyl group; R^3 represents a hydrogen atom, an alkyl group, an aryl group, a cycloalkyl group, an aralkyl group, an alkenyl group, an amino group or a heterocyclic group; and M is synonymous with that denoted in Formula A.

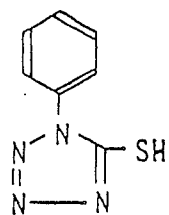
Some examples of the compounds will be given below.

Examples of the compounds represented by Formula B:

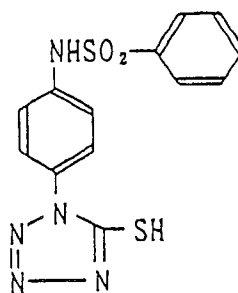
B-1



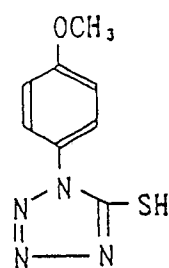
B-2



B-3



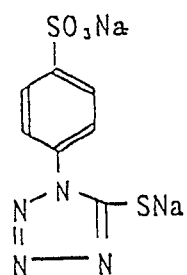
B-4



B-5

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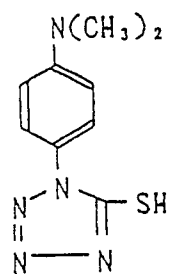
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B-6

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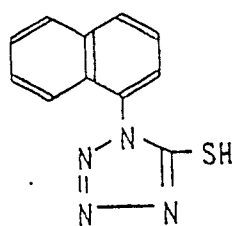
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B-7

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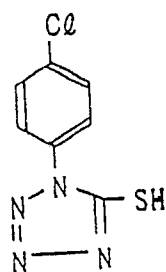
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B-8

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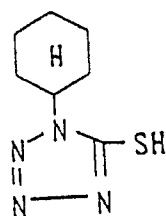
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B-9

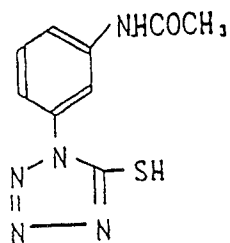
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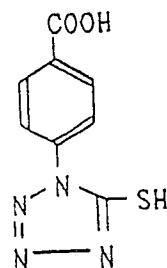


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B-10

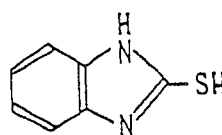


B-11



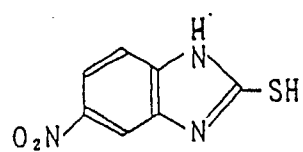
The above-given compounds have been well known and they may readily be prepared in the methods described in, for example, Japanese Patent O.P.I. Publication Nos. 56-111846/1981 and 58-95728/1983; U.S. Patent Nos. 2,403,927 and 3,295,976; and so forth or in any other methods correspondingly equivalent to the above-given methods.

C-1



C-2

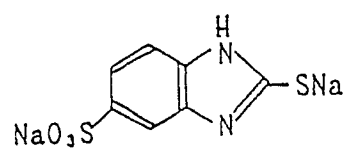
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C-3

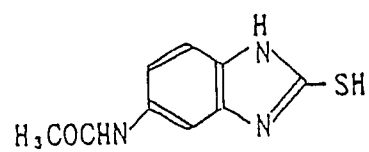
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C-4

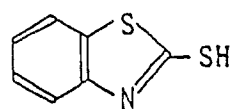
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C-5

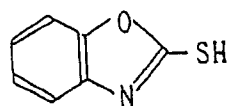
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C-6

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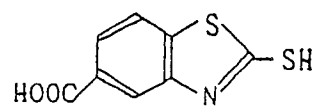


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C-7

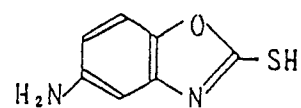
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C-8

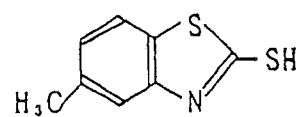
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C-9

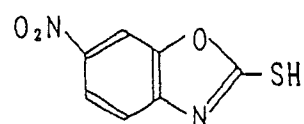
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C-10

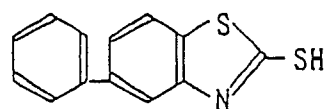
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C-11

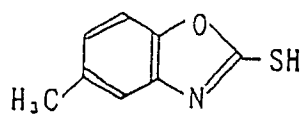
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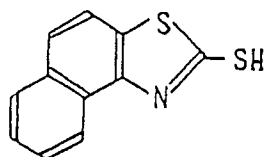
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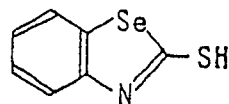
C-12



C-13



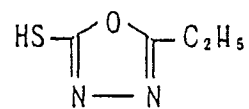
C-14



The above-given compounds may be prepared in the methods described in, for example, Japanese Patent Examined Publication No. 40-28496/1965; Japanese Patent O.P.I. Publication No. 50-89034/1975; U.S. Patent No. 2,824,001; Journal of Organic Chemistry, 1965, 39, 2469; Journal of Chemical Society, 1952, 4237; or in any other methods correspondingly equivalent to the above-given methods. Examples of the compounds represented by Formula D

D-1

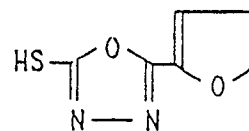
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D-2

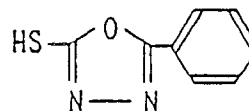
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D-3

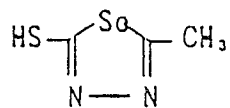
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D-4

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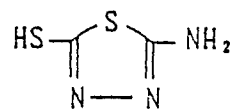
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D-5

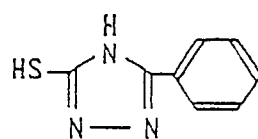
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D-6

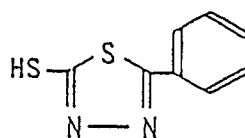
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D-7

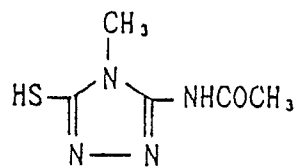
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D-8

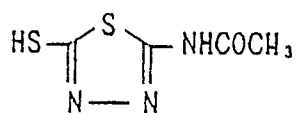
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D-9

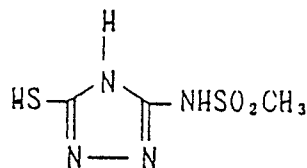
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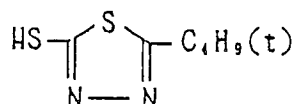
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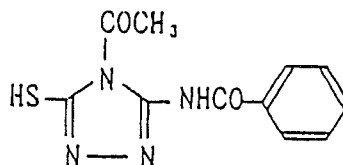
D-10



D-11



D-12



The above-given compounds may readily be prepared in the methods described in, for example, U.S. Patent Nos. 3,017,270 and 2,843,491; and Japanese Patent O.P.I. Publication Nos. 51-102639/1976 and 55-59463/1980; or in any other methods correspondingly equivalent to the above-given methods.

When the compounds represented by the foregoing formula A are used in the foregoing light-sensitive silver halide emulsion layers, the compound is used in an amount of preferably from 1×10^{-6} mol to 3×10^{-3} mol per mol of the light-sensitive silver halide emulsion used and, more preferably from 1×10^{-5} mol to 2×10^{-3} mol. When the compounds are used in the non-light-sensitive layers, the compound is used in an amount of preferably from 1×10^{-8} mol to 1×10^{-4} mol/dm² per layer and more preferably from 1×10^{-7} mol to 1×10^{-5} mol/dm².

It is also allowed to contain two or more kinds of the compounds represented by the foregoing Formula A in one single layer. When those compounds are contained in plural layers, the compounds to be contained in each layer may be the same as or different from each other.

The silver halide grains applicable to the invention may be prepared in the methods respectively described in, for example, P. Giakides, *Chimie et Physique Photographique*, Paul Montel, 1967; G.F. Daffin, *Photographic Emulsion Chemistry*, The Focal Press, 1966; V.L. Zelikman et al, *Making and Coating Photographic Emulsion*, The Focal Press, 1964; and so forth. Those methods include, for example, an acid-method, a neutral- method, an ammoniacal method. As the methods of reacting a soluble silver salt with a soluble halide salt, it is also allowed to use any of a single-jet precipitation method, a double-jet precipitation method and the combination thereof.

It is allowed to use a further method in which grains are produced in the presence of excessive silver ions, that is so-called the reverse precipitation method.

It is further allowed to use one of the double-jet precipitation methods, that is so-called a controlled double-jet precipitation method, in which a pAg value is kept constant in a liquid phase where silver halides are produced. In this method, a silver halide emulsion regular in crystal form and nearly uniform in grain size may be prepared.

It is also allowed to use the mixture of two or more kinds of silver halide emulsions each prepared separately. It is, however, preferable to use the above-mentioned double-jet precipitation method or the above-mentioned controlled double-jet precipitation.

In the case that a light-sensitive emulsion applicable to the invention has the so-called core/shell type structure or the multilayered core/shell type structure, the shells thereof may be provided in such a manner

that an ordinary halogen-conversion method or a method of newly coating silver halide is applied to the internal nuclei prepared in the foregoing method of preparing silver halide grains, after carrying out a desalting treatment, if required. Such halogen-conversion methods include, for example, those described in U.S. Patent Nos. 2,592,250 and 4,075,020; Japanese Patent O.P.I. Publication No. 55-127549/1980; and so forth. The methods of newly coating silver halides may be carried out in accordance with those described in, for example, Japanese Patent O.P.I. Publication Nos. 53-22408/1978 and 58-14829/1983; Japanese Patent Examined Publication No. 43-13162/1968; Journal of Photographic Science, 24, 198, 1976; and so forth. In order to provide each of the multilayered core-shell type emulsion grains with a shell of a layer from the 2nd layer on, it is allowed to similarly use the above-mentioned method of providing each of the internal nuclei of the emulsion grains with a shell.

In order to make grain sizes uniform, it is preferable to grow grains as quickly as possible in such a method as that described in, for example, British Patent No. 1,535,016 and Japanese Patent Examined Publication Nos. 48-36890/1973 and 52-16364/1977, in which the rate of adding an aqueous solution of silver nitrate or an alkali halide is varied according to the grain growth rate, or that described in, for example, U.S. Patent No. 4,242,445 and Japanese Patent O.P.I. Publication No. 55-158124/1980, in which the concentration of an aqueous solution is varied; each provided that the concentration of silver halide in the reacting solution should not exceed the critical saturation limit.

Any halide compounds produced when preparing the silver halide grains applicable to the invention, or any by-produced or unnecessary nitrates, ammonia salts or the like and compounds; they may be removed from the dispersion media of the grains.

In order to remove them, it is allowed to selectively use a method popularly applied to ordinary type emulsions such as a noodle-washing method; a dialyzing method; a sedimentation method utilizing an inorganic salt, an anionic surface active agent, anionic polymers such as polystyrenesulfonic acid, or gelatin derivatives such as acylated gelatin, carbamoylated gelatin and so forth; a flocculation-precipitation method; or the like methods.

The light-sensitive silver halide emulsions applicable to the invention can be optically sensitized to a desired wavelength region. There is no special limitation to the optical sensitization methods. Such an optical sensitization can be made by using, independently or in combination, optical sensitizers including, for example, cyanine dyes such as zeromethine dye, monomethine dye, dimethine dye, trimethine dye and so forth, merocyanine dyes, or the like. The combinations of the sensitizing dyes are often used especially with the purpose of making a supersensitization.

An emulsion is also allowed to contain, together with the sensitizing dyes, a dye not having any spectral sensitizing function in itself or a substance substantially not capable of absorbing visible rays of light, but capable of providing a supersensitization. The techniques of the above are described in, for example, U.S. Patent Nos. 2,688,545, 2,912,329, 3,397,060, 3,615,635 and 3,628,964; British Patent Nos. 1,195,302, 1,242,588 and 1,293,862; West German Patent (OLS) Nos. 2,030,326 and 2,121,780; Japanese Patent Examined Publication Nos. 43-4936/1968 and 44-14030/1969; Research Disclosure, Vol. 176, No. 17643, Dec., 1978 Issue, p. 23, Paragraph IV-J; and so forth. The selection of the above-mentioned dyes and substances may be so made freely as to meet the purposes and applications of light-sensitive materials, such as the wavelengths to which the light-sensitive materials are made sensitive, the sensitivity thereof and so forth.

The light-sensitive silver halide emulsions applicable to the invention may be treated in any of a variety of chemical sensitization methods which may also be applied to ordinary type emulsions.

In order to perform the chemical sensitization, it is allowed to follow such methods as those described in, for example, H. Frieser, Die Grundlagen der Photographische Prozesse mit Silberhalogeniden, Akademische Verlagsgesellschaft, 1968, pp. 675-734.

To be more concrete, it is allowed to use, independently or in combination, a sulfur sensitization method utilizing a compound containing sulfur capable of reacting with silver ions or an active gelatin, a selenium sensitization method, a reduction-sensitization method utilizing a reducing substance, a noble-metal sensitization method utilizing gold or other noble-metal compounds, and so forth.

The above-mentioned sulfur sensitizers applicable to the invention include those publicly known, such as thiosulfate, allylthiocarbamidothiourea, allylthioisocyanate, cystine, p-toluenethiosulfonate, rhodanine and so forth. Besides the above, it is also allowed to use the sulfur sensitizers described in, for example, U.S. Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313 and 3,656,955; German Patent No. 1,422,869; Japanese Patent Examined Publication No. 56-24937/1981; Japanese Patent O.P.I. Publication No. 55-45016/1980; and so forth. The sulfur sensitizer as given above may be added in such an amount as is enough to effectively make the sensitivity of an emulsion higher. The amounts thereof to be added are varied to a considerably wide extent according to various conditions such as the variations of pH values,

concentrations, silver halide grain sizes and so forth. As for the rough standard, it is preferable to add them in an amount of the order of from about 10^{-7} mol to about 10^{-1} mol per mol of silver halides used therein.

In the invention, a selenium sensitization may be made either in place of or in combination with the sulfur sensitization. The selenium sensitizers include, for example, aliphatic isoselenocyanates such as allylisoselenocyanate; selenoureas; selenoketones; selenoamides; selenocarboxylic acids and the esters thereof; seleno phosphates; selenides such as diethyl selenide and diethyl diselenide; and so forth. The concrete examples thereof are given in U.S. Patent Nos. 1,574,944, 1,602,592 and 1,623,499.

The amounts thereof to be added are varied to the considerably wide extent similar to the case of the above-mentioned sulfur sensitizers. As for the rough standard, they are preferably added in an amount in the order of from about 10^{-7} mol to 10^{-3} mol per mol of silver halides used.

As for the gold sensitizers applicable to the invention, a variety of gold compounds including those each having either a +1 valent gold-oxidation number or a +3 valent gold-oxidation number. The typical examples thereof include chlorauric acid, potassium chloraurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, pyridyl trichlorogold, and so forth.

The amounts of the gold sensitizers to be added are varied to meet various conditions. However, they are preferably added, as a rough standard, in an amount within the range of from about 10^{-9} mol to 10^{-1} mol per mol of silver halides used.

In the invention, the sensitization methods for light-sensitive silver halides emulsions may be combined with other sensitization methods utilizing such a metal compound as a compound of platinum, palladium, iridium or rhodium.

In the invention, it is also allowed to use a reduction-sensitization method in combination. The reduction-sensitizers applicable thereto shall not specially be limitative, but they include, for example, stannous chloride, thiourea dioxide, hydrazine derivatives and silane compounds.

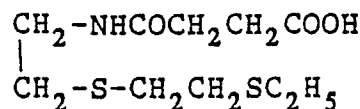
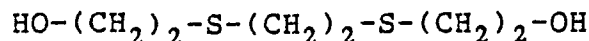
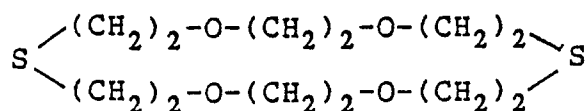
Such reduction-sensitization is preferably carried out in the course of growing light-sensitive silver halide grains or after completing a sulfur sensitization and/or a gold sensitization.

In the invention, a remarkably high sensitization can be achieved with a light-sensitive silver halide emulsion, when a chemical sensitization is applied to the emulsion in the presence of a silver halide solvent.

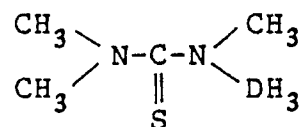
The silver halide solvents applicable to the invention include, for example, (a) organic thioethers such as those described in U.S. Patent Nos. 3,271,157, 3,531,289 and 3,574,628, Japanese Patent O.P.I. Publication Nos. 54-1019/1979 and 54-158917/1979, and so forth; (b) thiourea derivatives such as those described in Japanese Patent O.P.I. Publication Nos. 53-82408/1978, 55-77737/1980 and 55-2982/1980, and so forth; (c) silver halide solvents each having a thiocarbonyl group sandwiched between an oxygen or sulfur atom and a nitrogen atom, such as those described in Japanese Patent O.P.I. Publication No. 53-144319/1978; (d) imidazoles such as those described in Japanese Patent O.P.I. Publication No. 54-100717/1979; (e) sulfites; (f) thiocyanates; and so forth. The amounts thereof to be added are varied according to the kinds thereof. However, in the case of a thiocyanate, for example, it is preferably added in an amount within the range of from 5 mg to 1 g per mol of silver halides used.

Some typical examples thereof will be given below.

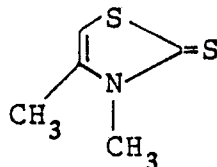
(a)



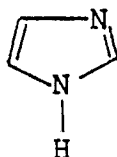
(b)



(c)



(d)



(e)



(f)



The light-sensitive silver halide emulsions applicable to the invention may be doped with a variety of dopants when the grains thereof are formed. Among the dopants, the internal dopants include, for example, silver, sulfur, iridium, gold, platinum, osmium, rhodium, tellurium, selenium, cadmium, zinc, lead, thallium, iron, antimony, bismuth, arsenic and so forth.

In order to dope the above-given dopants, the water-soluble salts thereof or the complex salts thereof may be made coexistingly when each shell is formed.

The binders applicable to the silver halide emulsions used in the invention or the dispersion media applicable to the preparation of the emulsions include, for example, hydrophilic colloids applicable to ordinary type silver halide emulsions. Such hydrophilic colloids include, for example, not only gelatin, lime-treated or acid-treated, but also those exemplified as follows.

Gelatin derivatives such as described in U.S. Patent No. 2,614,928, those prepared through the reaction of gelatin with aromatic sulfonyl chloride, acid chloride, acid anhydride, isocyanate or 1,4-diketones;

Gelatin derivatives such as described in U.S. Patent No. 3,118,766, those prepared through the reaction of gelatin with trimellitic acid anhydride;

Gelatin derivatives such as described in Japanese Patent Examined Publication No. 39-5514/1964, those prepared through the reaction of gelatin with an organic acid having an active halogen;

Gelatin derivatives such as described in Japanese Patent Examined Publication No. 42-26845/1967, those prepared through the reaction of gelatin with an aromatic glycidyl ether;

Gelatin derivatives such as described in U.S. Patent No. 3,186,846, those prepared through the reaction of gelatin with maleimide, maleamic acid, unsaturated aliphatic diamide or the like;
 Sulfoalkylated gelatins such as described in British Patent No. 1,033,189;
 Polyoxyalkylene derivatives of gelatin such as described in U.S. Patent No. 3,312,553;

5 and so forth:

Macromolecular graft-gelatin compounds including, for example,

Acrylic acid and methacrylic acid, and their esters or amides or monovalent or polyvalent alcohol, and the compounds prepared by grafting together gelatin and acryl or methacryl nitrile, styrene or other vinyl monomers independently or in combination;

10 Synthetic hydrophilic macromolecular substances including,

Homopolymers comprising monomers as the component thereof, such as vinyl alcohol, N-vinyl pyrrolidone, hydroxyalkyl (metha)acrylate, (metha)acryl amide, N-substituted (metha)acryl amide or the like, or the copolymers of the above-given monomers;

Copolymers of the above-given monomers and (metha)acrylate, vinyl acetate, styrene or the like;

15 Copolymers of either one of the above-given monomers and maleic anhydride, maleamic acid or the like; and so forth: and

Natural hydrophilic macromolecular substances other than gelatin, including casein, agar, arginic acid polysaccharide and so forth.

The above-given hydrophilic colloids may be used independently or in the a thereof.

20 The light-sensitive silver halide emulsions applicable to the invention are allowed to contain a variety of popular stabilizers and antifoggants to meet the purposes of using the emulsions. Those stabilizers and antifoggants include, for example,

Azoles or imidazoles such as benzothiazolium salts, nitroindazoles, nitrobenzimidazoles, chloroben-
 zimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzthiazoles, mercaptobenzimidazoles
 25 and mercaptothiadiazoles;

Triazoles such as aminotriazoles, benzotriazoles and nitrobenzotriazoles;

Tetrazoles such as mercaptotetrazoles including particularly 1-phenyl-5-mercaptotetrazole, and so forth;
 Mercaptopyrimidines;

Mercaptotriazines including thioketo compounds such as oxazolinthione;

30 Azaindenes such as triazaindenes, tetraazaindenes including particularly 4-hydroxy substituted (1,3,3a,7)-
 tetraazaindenes, pentaazaindenes and so forth; and

Benzenethiosulfonic acid, benzenesulfinic acid, benzenesulfonic amide, imidazolium salts, tetrazolium salts,
 polyhydroxy compounds, and so forth.

It is preferable to add these additives either when a chemical sensitization is completed or before an
 35 emulsion is coated.

In the silver halide photographic light-sensitive materials of the invention, the photographic emulsion
 layers and other hydrophilic colloidal layers thereof are allowed to contain organic or inorganic hardeners
 including, for example, chromium salts such as chrome alum, chromium acetate and so forth, aldehydes
 such as formaldehyde, glyoxal, glutar aldehyde and so forth; N-methylol compounds such as dimethylol
 40 urea, methyloldimethyl hydantoin and so forth; dioxane derivatives such as 2,3-dihydroxydioxane and so
 forth; active vinyl compounds such as 1,3,5-triacryloyl-hexahydro-S-triazine, 1,3-vinylsulfonyl-2-propanol and
 so forth; active halogen compounds such as 2,4-dichloro-6-hydroxy-S-triazine and so forth; and
 mucohalogen acids such as mucochloric acid, mucophenoxychloric acid and so forth. The above-given
 hardeners may be used independently or in combination.

45 In the silver halide photographic light-sensitive materials of the invention, the photographic emulsion
 layers and other hydrophilic colloidal layers thereof are also allowed to contain water-insoluble or slightly-
 water-soluble synthetic polymer dispersions, with the purposes of improving the dimensional stability of the
 light-sensitive materials and so forth. Such synthetic polymers include, for example, those each comprising
 a monomer component which is a single or a combination of alkyl (metha)acrylate, alkoxyalkyl (metha)-
 50 acrylate, glycidyl (metha)acrylate, (metha)acrylamide, vinyl esters including vinyl acetate and so forth,
 acrylonitrile, olefin, styrene, and so forth, or a monomer component which is a further combination of the
 above-given monomer and acrylic acid, methacrylic acid, α,β -unsaturated dicarboxylic acid, hydroxyalkyl
 (metha)acrylate, sulfoalkyl (metha)acrylate, styrenesulfonic acid and so forth.

If required, the silver halide light-sensitive photographic material relating to the invention is also allowed
 55 to contain a development accelerator such as benzyl alcohol, polyoxyethylene type compounds and so
 forth; an image stabilizer such as those of the chroman, coumaran, bisphenol or phosphite type; a lubricant
 such as wax, glyceride of higher fatty acid, higher alcohol ester of higher fatty acid and so forth; a
 development controller; a developing agent; a plasticizer; and a bleaching agent. A variety of surfactants

such as those of anionic, cationic, nonionic or amphoteric type may also be used in the photographic material to serve as a coating aid, permeation improver to a processing solution or the like, defoaming agent or a raw material for controlling the various physical properties of a light-sensitive material. The effective antistatic agents include, for example, diacetyl cellulose, styrene-parfluoroalkyl sodium maleate
 5 copolymer, the alkali salts of the reacted products of styrene-maleic anhydride copolymer with p-aminobenzene sulfinic acid, and so forth. Matting agents include, for example, polymethacrylic acid methyl, polystyrene, alkali-soluble polymers and so forth, and, further, colloidal silica oxide may also be used. The latexes which are to be added for improving the physical properties of layers include, for example, a copolymer of a monomer such as an acryl ester or a vinyl ester or the like and another monomer having an
 10 ethylene group. The gelatin plasticizers include, for example, glycerol and glycol type compounds. Thickeners include, for example, a sodium styrene-maleate copolymer, an alkylvinylether-maleic acid copolymer, and so forth.

The silver halide light-sensitive photographic materials of the invention can be provided with an ample latitude when they contain a mixture of at least 2 kinds of the emulsions different from each other in grain
 15 sizes and sensitivities or they are coated with such emulsions onto a plurality of the layers thereof.

The silver halide light-sensitive photographic materials of the invention can effectively be utilized for a variety of applications such as those of black-and-white photography, X-ray photography, color photog-
 20 raphy, infra-red photography, microphotography, silver-dye bleaching process, reversal photography, diffusion-transfer process, high-contrast photography, photothermography, heat-developable light-sensitive materials and so forth.

The invention may be applied to a color photographic light-sensitive material by applying the method and materials usually applied to ordinary type color light-sensitive materials. To be more concrete, cyan, magenta and yellow couplers are contained coordinately into the light-sensitive emulsions so prepared as to be sensitive to red, green and blue rays of light, respectively. For example, the magenta couplers include
 25 those of 5-pyrazolone, pyrazolobenzimidazole, pyrazolotriazole, cyanoacetylcumarone, open-chained acylacetoneitrile, and so forth. The yellow couplers include, those of acylacetoamide such as benzoylacetoanilides and pivaloylacetoanilides, and so forth. The cyan couplers include those of naphthol, phenol, ureido and so forth. It is usual that a red-sensitive emulsion layer contains a cyan-dye forming coupler, a green-sensitive emulsion layer contains a magenta-dye forming coupler and a blue-sensitive
 30 emulsion layer contains a yellow-dye forming coupler. If should the necessity arise, it is also allowed to have different combinations than the above. It is preferable that the above-mentioned couplers should be those of the non-diffusible type each having a hydrophobic group, that is the so-called ballast group, in the molecules of the couplers. Such couplers may be of either 4-equivalent type or 2-equivalent type with respect to silver, and they may also be either a colored coupler capable of displaying a color correction
 35 effect or a coupler capable of releasing a development inhibitor while a development is being carried out, that is the so-called DIR coupler. Besides the DIR couplers, it is allowed to contain a non-dye forming DIR coupling compound which is capable of rendering a colorless coupling reaction product from which a development inhibitor is discharged.

Besides the above, it is allowed to jointly use the publicly known antifading agents such as a
 40 hydroquinone derivative, a gallic acid derivative, a p-alkoxyphenol, a bisphenol and so forth.

The silver halide photographic light-sensitive materials of the invention are allowed to contain a UV absorbent in the hydrophilic colloidal layers thereof. Such UV absorbents applicable thereto include, for example, a benzotriazole compound substituted with an aryl group, a 4-thiazolidone compound, a benzophenone compound, a cinnamate compound, a butadiene compound, a benzoxazole compound, a UV-
 45 absorbable polymer, and so forth. The above-given UV absorbents may also be fixed to the inside of the above-mentioned hydrophilic colloidal layers.

The light-sensitive emulsion layers of the color light-sensitive photographic material may be constituted either in the so-called normal layer arrangement or in the so-called inverted layer arrangement.

The silver halide light-sensitive photographic materials of the invention are also allowed to contain a
 50 water-soluble dyestuff in the hydrophilic colloidal layers thereof, so as to serve as a filter dye or with the various purposes of, for example, preventing irradiation and so forth. Such dyestuffs include, for example, the dyes of oxonol, hemioxonol, styryl, merocyanine, cyanine, and azo. Among those dyestuffs, the oxonol, hemioxonol and merocyanine dyes are useful.

The silver halide light-sensitive photographic materials of the invention are also allowed to contain
 55 anticolor-foggants including, for example, a hydroquinone derivative, an aminophenol derivative, a gallic acid derivative, an ascorbic acid derivative and so forth.

In the silver halide light-sensitive photographic materials of the invention, the photographic emulsion layers and other hydrophilic colloidal layers thereof may be coated over a support or other layers in any

publicly known method. Such coating methods include, for example, a dip-coating method, a roller-coating method, a curtain-coating method, an extrusion-coating method and so forth. Among those methods, the methods described in, for example, U.S. Patent Nos. 2,681,294, 2,761,791 and 3,526,528 are advantageous.

The supports for the light-sensitive photographic materials include, for example, baryta paper sheet, polyethylene-coated paper sheet, polypropylene synthetic paper sheet, glass plate, cellulose acetate film, cellulose nitrate film, polyvinyl acetal film, polypropylene film, polyester films such as polyethyleneterephthalate film, polystyrene film and so forth, each of which are usually used. The above-given supports may be selectively used to meet the various applications.

Upon exposing a silver halide light-sensitive photographic material of the invention to light, it may be developed in any publicly known process which is used, commonly.

A black-and-white developer is an alkaline solution containing such a developing agent as a hydroxybenzene, an aminophenol, an aminobenzene or the like. Besides the above, such developers may also contain the sulfites, carbonates, bisulfites, bromides, iodides or the like of an alkali-metal. When such light-sensitive photographic material is for color photographic use, it may be color-developed in any color-developing process which is usually used. In a reversal process, a color-development is carried out in such a manner that, after a light-sensitive material is developed with a black-and-white negative developer first, it is exposed to white light or treated in a bath containing a fogging agent and is then color-developed with an alkaline developer containing a color developing agent. The processing methods shall not be limitative, but may be freely selected. Among those processing methods, the typical methods include, for example, a method in which, after color-development is completed, a bleach-fixation is carried out and, if required, a washing and stabilizing step is further carried out, or another method in which, after a color-development is completed, a bleaching step and a fixing step are carried out separately and, if required, a washing and stabilizing step is further carried out. Such color-developer is generally comprised of an aqueous alkaline solution containing a color developing agent. As for such color developing agents, it is allowed to use publicly known primary aromatic amine type developing agents including, for example, phenylenediamines such as 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N- β -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- β -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- β -methanesulfonamidoethylaniline, 4-amino-3-methyl-N-ethyl-N- β -methoxyethylaniline, and so forth.

Besides the above, the color developer is also allowed to contain the color developing agents described in, for example, L.F.A. Mason, Photographic Processing Chemistry, Focal Press, 1966, pp. 226-229; U.S. Patent Nos. 2,193,015 and 2,592,364; Japanese Patent O.P.I. Publication No. 48-64933/1973; and so forth.

Further, besides the above, such color developers are also allowed to contain a pH buffer, a development inhibitor, an antifoggant and so forth and, if required, a hard-water softener, a preservative, an organic solvent, a development accelerator, a dye-forming coupler, a competing coupler, a foggant, an auxiliary developing agent, a thickener, a polycarboxylic chelating agent, an antioxidant and so forth.

A photographic emulsion layer is usually bleached after it is color-developed. Such a bleaching step may be carried out either at the same time a fixing step is carried out or separately. The bleaching agents applicable thereto include, for example, polyvalent metal compounds such as iron (III), cobalt (IV), chromium (VI), copper (II) and so forth, a peroxy acid, a quinone, a nitroso compound and so forth.

Such bleaching agents or bleach-fixers are allowed to contain a variety of additives, as well as the bleaching accelerators such as those described in, for example, U.S. Patent Nos. 3,042,520 and 3,241,966, Japanese Patent Examined Publication Nos. 45-8506/1970 and 45-8836/1970, and so forth; and the thiol compounds described in, Japanese Patent O.P.I. Publication No. 53-657332/1978.

EXAMPLES

The invention will be further detailed with reference to the following examples. It is, however, to be understood that the embodiments of the invention shall not be limited thereto.

Example 1

With respect to the grain sizes distribution of light-sensitive materials and the halogen compositions of non-light-sensitive silver halide fine grains, the influences thereof upon sensitivity-to-fog characteristics were examined.

Preparation of Sample

Sample I was prepared by coating the following light-sensitive emulsion layers and non-light-sensitive layers in order over a subbed cellulose triacetate film base.

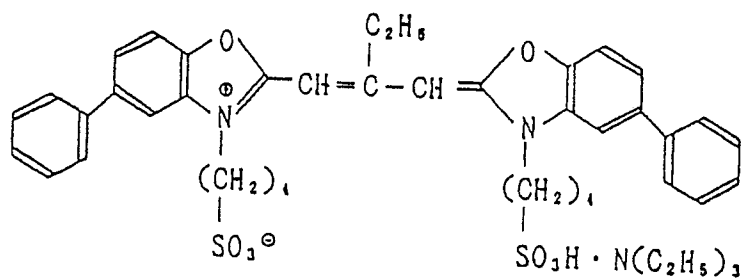
In all the examples hereinafter described, the amounts of the materials added into each light-sensitive material will be expressed in a an amount per sq. meter of the light sensitive material prepared, and the amounts of silver halides and colloidal silver will be expressed in terms of the silver contents, respectively.

Layer 1 : A non-light-sensitive layer containing 0.8 g of gelatin

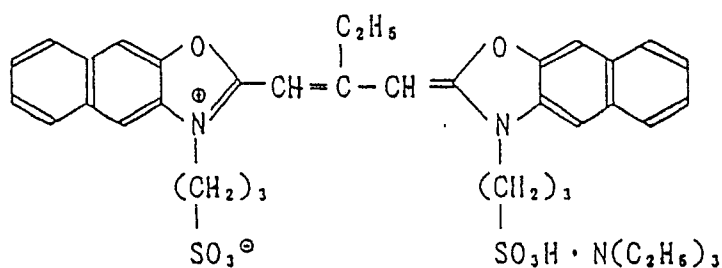
Layer 2 : A green-light-sensitive emulsion layer, which was prepared in the following manner.

A 1.0 μ m average grain sized polydisperse type silver iodobromide emulsion A having a grain size variation coefficient of 24% and an average iodide content of 4 mol% was chemically sensitized, in an ordinary method, with both sodium thiosulfate and potassium chloroaurate and was then color-sensitized to be green-sensitive by adding the following green-sensitive sensitizing dye (a) in an amount of 12.0 $\times 10^{-5}$ mol per mol of silver halides used and a similar dye (b) in an amount of 11.0 $\times 10^{-5}$ mol per the same, respectively. Further, the resulting emulsion was added with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene in an amount of 7 $\times 10^{-3}$ mol per mol of silver halides used for the purposes of stabilizing the emulsion and preventing fog production.

Sensitizing dye (a)

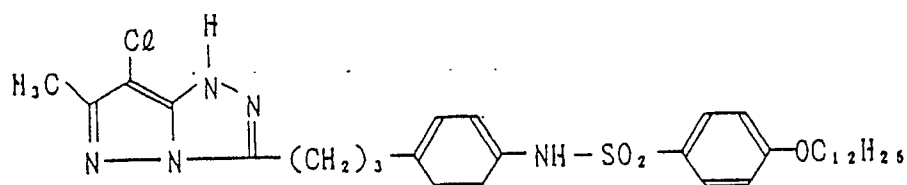


Sensitizing dye (b)

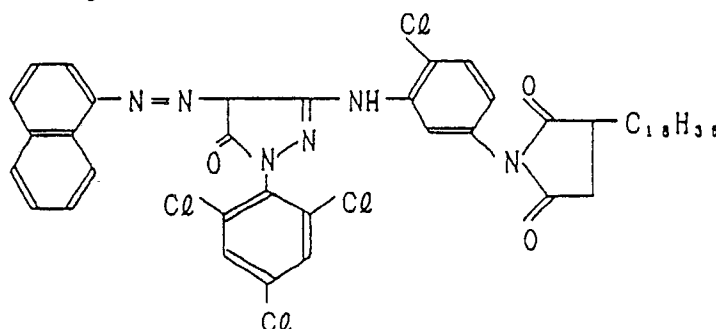


The above-mentioned color-sensitized and chemically sensitized polydisperse type silver iodobromide emulsion in an amount of 1.8g was added with a solution consisting of 0.5g of di-tertiary nonylphenol DNP dispersion in which 0.20g of magenta coupler M-1 and 0.05g of colored magenta coupler CM-1 were dissolved, and 1.9g of gelatin. The resulting coating solution was coated over Layer 1, so that the green light-sensitive emulsion layer was formed.

Magenta coupler, M-1



Colored magenta coupler, CM-1



Layer 3 : A non-light-sensitive layer containing 0.04g of n-dibutyl phthalate DBP dispersion in which 0.07g of 2,5-diethyl hydroquinone were dissolved, and 0.8g of gelatin.

Into the above-mentioned three layers, a gelatin hardener and a surfactant were also added, besides the above-described compositions.

Sample 2 was prepared in the same manner as in Sample 1, except that the polydisperse type silver iodobromide emulsion A of Sample 1 was replaced by a 1.0 μ m grain-sized monodisperse type silver iodobromide emulsion B having a grain-size variation coefficient of 11% and an average iodide content of 4 mol%.

Samples 3 through 11 shown in Table-2 were then prepared in the same manner as in Samples 1 and 2, except that substantially non-light-sensitive silver halide fine grains shown in Table-1 were added to Layer 1 in both Samples 1 and 2.

Table-1

Emulsion No.	Sensitivity	Composition	Content mol%	Average grain-size μ m	Dispersion status	Grain-size variation coefficient
A	Yes	AgBrI	I 4	1.0	Poly	24
B	Yes	AgBrI	I 4	1.0	Mono	11
C	Yes	AgBrI	I 6	0.38	Mono	17
D	Yes	AgBrI	I 5.6	1.6	Mono	11
a	None	AgBrI	I 2	0.27	Mono	19
b	None	AgClBr	Cl 30	0.40	Mono	14
c	None	AgCl	Cl 100	0.49	Mono	13
d	None	AgBr	Br 100	0.38	Mono	17
e	None	AgClBr	Cl 5	0.40	Mono	13
f	None	AgClBr	Cl 70	0.40	Mono	14
g	None	AgCl	Cl 100	0.12	Mono	17

The above-described non-light-sensitive silver halide fine grains, a to g, may be prepared in an ordinary method and those for a monodisperse type emulsion having a grain-size variation coefficient of not more than 20% as shown in Table-1.

Evaluation

Samples 1 through 11 each prepared by the above-mentioned sample preparation method were coated and dried. Then, they were cut into an appropriate sample size and were treated through a series of the steps of exposure -processing - measurement. Thus, the resulting samples were subjected to the sensitometric evaluation.

Exposure

The samples were exposed to green light through a wedge in an ordinary method.

Processing

Each sample already exposed to light was processed in the following processing steps.

Processing step	Processing time
Color developing	3min. 15sec.
Bleaching	6min. 30sec.
Washing	3min. 15sec.
Fixing	6min. 30sec.
Washing	3min. 15sec.
Stabilizing	1min. 30sec.
Drying	

The compositions of the processing solutions used in the above-given processing steps were as follows.

[Color developer]

	4-amino-3-methyl-N-(β -hydroxyethyl)- aniline sulfate	4.57g
5	Sodium sulfite, anhydrous	4.25g
	Hydroxylamine sulfate	2.0g
	Potassium carbonate, anhydrous	37.5g
10	Sodium bromide	1.3g
	Trisodium nitrilotriacetate, monohydrate	2.5g
15	Potassium hydroxide	1.0g
	Add water to make	1 liter
	[Bleaching solution]	
20	Ferric-ammonium ethylenediamine- tetraacetate	100.0g
	Diammonium ethylenediaminetetraacetate	10.0g
25	Ammonium bromide	150.0g
	Glacial acetic acid	10.0 ml
30	Add water to make	1 liter
	Adjust pH with aqueous ammonia to be	pH 6.0
	[Fixer]	
35	Ammonium thiosulfate	175.0g
	Ammonium sulfite, anhydrous	8.6g
40	Sodium metasilfite	2.3g
	Add water to make	1 liter
	Adjust pH with acetic acid to be	pH 6.0
45	[Stabilizer]	
	Formalin, in a 37% aqueous solution	1.5ml
50	Konidux, manufactured by Konica Corporation	7.5ml
55	Add water to make	1 liter

The results of the sensitometric measurements are shown in Table-2.

The sensitivity of each sample is expressed by a reciprocal number of an exposure capable of giving a

total optical density of a minimum optical density that is a fog level on the characteristic curve obtained through the sensitometric measurement of the subject sample and +0.1 of the fog level, and each sensitivity is also expressed in terms of a relative value to the sensitivity of Sample-1 that is regarded as a value of 100.

Table-2

	Layer 2, Light-sensitive layer	Layer 1, Non-light-sensitive layer	Evaluation	
			Fog	Sensitivity
1	A	-	0.12	100
2	B	-	0.09	114
3	A	a	0.14	112
4	A	b	0.16	114
5	A	c	0.19	110
6	B	a	0.10	126
7	B	d	0.11	129
8	B	e	0.11	130
9	B	b	0.10	139
10	B	f	0.12	156
11	B	c	0.13	172

From the results shown in the above Table-2, the following facts were found.

1. By comparing Samples 1, 3, 4 and 5 with each other, it is found that they cannot be put to practical use when combining a polydisperse type emulsion and non-light-sensitive silver halide fine grains, because they have little effect on increasing sensitization and, in particular, the more the chloride content of the non-light-sensitive silver halide fine grains is increased, the more the fog increase becomes remarkable.

2. Meanwhile, when comparing Samples 2 and 6 through 11 with each other, it is found that, when the light-sensitive emulsion has a monodispersibility, a fog increase was also observed as the chloride content of the non-light-sensitive silver halide fine grains is increased. However, the fog increase was inhibited to a very low level as compared with the case of using polydisperse type emulsion. It is also found that the sensitization effects of the Samples 9 through 11 which correspond to the invention are much greater than in the cases of Samples 6 and 7 which are other than the samples of the invention and the non-light-sensitive silver halide fine grains thereof do not contain any chloride. It is further found that Sample 8, having a low chloride content, displays little sensitization effects.

Example 2

The effects of the invention were examined when the compounds represented by the foregoing Formula A of the invention were added. In order to prove that a sensitizing effect is not derived from the scattering effect of non-light-sensitive silver halide fine grains, a sample containing small grain-sized light-sensitive emulsion was prepared.

Preparation of the sample

Sample 12 was prepared by coating the following light-sensitive emulsion layers and the non-light-sensitive layers in order over a subbed cellulose triacetate film base.

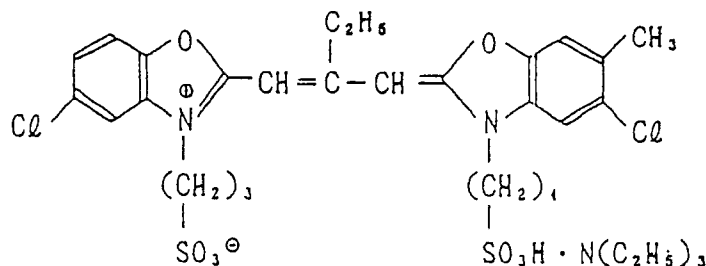
Layer 1 : A non-light-sensitive layer containing 0.8g of gelatin.

Layer 2 : A green light-sensitive emulsion layer, which was prepared in the following manner.

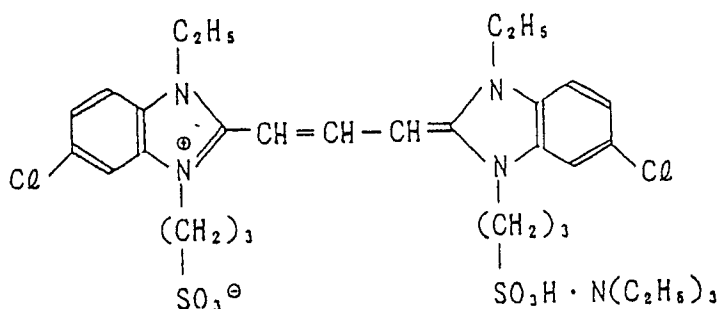
A 0.38 μ m grain-sized monodisperse type silver iodobromide emulsion C having a grain-size variation coefficient of 17% and an average iodide content of 6 mol% was chemically sensitized, in an ordinary

method, with both sodium thiosulfate and potassium chloroaurate and was then color-sensitized to be green-sensitive by adding the following green-sensitive sensitizing dye (c) in an amount of 2.5×10^{-5} mol per mol of silver halides used and a similar dye (d) in an amount of 1.2×10^{-5} mol per the same, respectively. Further, the resulting emulsion was added with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene in an amount of 7×10^{-3} mol per mol of silver halides used for the purposes of stabilizing the emulsion and preventing fog production.

Sensitizing dye (c)

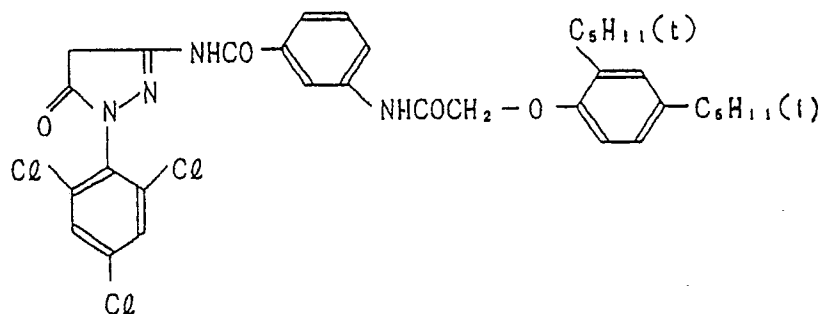


Sensitizing dye (d)



The above-mentioned color-sensitized and chemically sensitized monodisperse type silver iodobromide emulsion in an amount of 1.5g was added with a solution consisting of 0.9g of tricresyl phosphate TCP dispersion in which 1.1g of magenta coupler M-2 and 0.3g of colored magenta coupler CM-1 were dissolved, and 1.2g of gelatin. The resulting coating solution was coated over Layer 1, so that the green light-sensitive emulsion layer was formed.

Magenta coupler M-2



Layer 3 : A non-light-sensitive layer containing 0.3g of dioctyl phthalate DOP dispersion in which 0.1g of 2,5-di-t-octyl hydroquinone were dissolved, 0.08g of yellow colloidal silver and 0.6g of gelatin.

Into the above-mentioned three layers, a gelatin hardener and a surfactant were also added, besides the

above-described compositions.

Samples 13 through 19 were prepared in the same manner as in Sample 12, except that the substantially not light-sensitive silver halide fine grains shown in Table-1 were added into Layer 1 of Sample 12 as shown in Table-3 and the exemplified compound C-5 in an amount shown in Table-3 was added into

Exemplified compound C-5

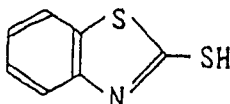


Table-3

	Layer 2, Light-sensitive layer *	Layer 1, Non-light- sensitive layer	Evaluation		
			Fog	Sensitivity	
12	-	-	0.04	100	Comparison
13	C-5	-	0.02	94	
14	-	a 0.3g	0.06	104	
15	C-5	a 0.3g	0.03	92	
16	-	f 0.3g	0.05	128	Invention
17	-	g 0.15g	0.05	124	
18	C-5	g 0.15g	0.03	132	
19	C-5	g 0.3g	0.04	151	

* In this column, Numbers of Exemplified compound added into Layer 2 are indicated.

All the emulsions used in Layer 2 were monodisperse type emulsion C.

The exemplified compounds were each added in an amount of 2.0×10^{-4} mol per mol of silver halides used.

Sample evaluations were made in the same manner as in Example-1. The results of the sensitometric evaluations are shown in Table-3 in which the sensitivity of each sample is expressed in terms of a relative value to that of Sample 12 which is regarded as a value of 100.

The following facts can be proved from the results shown in Table-3.

1. When comparing Sample Nos. 12, 14, 16 and 17, Sample No. 14 that is other than the samples of the invention is least sensitized in comparison with Sample No. 12 and, in contrast with the above, Sample No. 16 of the invention displays remarkable sensitizing effects. The results of the comparison are due to the

fact that, in Example-1, the non-light-sensitive layer containing AgBrI 0.27 μ m-grain-sized substantially non-light-sensitive emulsion 'a' displayed the effects of an optically scattering layer and, in Sample No. 14, the same non-light-sensitive layer did not play the same role. On the other hand, Sample No. 16 is sensitized, because the 0.40 μ m-grain-sized substantially non-light-sensitive silver chlorobromide emulsion 'f' can effectively play the role of a halogen-ion trap in the course of development. The effects of the invention can apparently be proved from the fact that Sample No. 17 can display a remarkable sensitization effect because the non-light-sensitive layer of Sample No. 17 contains 0.12 μ m-grain-sized substantially non-light-sensitive chloride emulsion 'g' which doesn't have an effective scattering function to green rays of light.

2. When comparing Sample Nos. 12, 13, 17, 18 and 19 it is found that the halogen-ion trapping sensitization effect of the invention can further be promoted when fog production is more effectively controlled by containing Exemplified Compound C-5 into the light-sensitive emulsion layers.

Example-3

A multilayer-coated sample was prepared. With respect to the sample, the effects of the invention were examined especially on sensitivity-to-fog characteristics, graininess and processing stability.

Preparation of the sample

Each of the following layers was coated in order over a subbed cellulose triacetate film base, thereby forming a color light-sensitive material, Sample No. 20, comprising 13 layers including blue, green and red light-sensitive layers, was prepared.

Layer 1 : An antihalation layer containing 0.4 g of black colloidal silver and 3.0 g of gelatin

Layer 2 : A low-speed red light-sensitive emulsion layer containing 1.4 g of a red light-sensitized low speed red-sensitive silver iodobromide emulsion having a silver iodide content of 7 mol%, 1.2 g of gelatin, and 0.65 g of tricresyl phosphate, TCP, dissolved therein 0.8 g of 1-hydroxy-4-(β -methoxyethylaminocarbonylmethoxy)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide (hereinafter called C-1), 0.075 g of disodium 1-hydroxy-4-[4-(1-hydroxy- δ -acetamido-3,6-disulfo-2-naphthylazo)phenoxy]-N-[δ -(2,4-di-t-amylphenoxy) butyl]-2-naphthamide (hereinafter called colored cyan coupler CC-1), 0.015 g of 1-hydroxy-2-[δ -(2,4-di-t-amylphenoxy)-n-butyl]naphthamide, and 0.07 g of 4-octadecylsuccinimido-2-(1-phenyl-5-tetrazolylthio)-1-indanone (hereinafter called DIR compound D-1)

Layer 3 : An interlayer containing 0.04 g of n-dibutyl phthalate, DBP, dissolved therein 0.07 g of 2,5-di-t-octyl hydroquinone (hereinafter called antistaining agent HQ-1), and 0.8 g of gelatin

Layer 4 : A low-speed green light-sensitive emulsion layer containing 0.80 g of a green-sensitized low-speed silver iodobromide emulsion having a silver iodide content of 6 mol%, 2.2 g of gelatin, and 0.95 g of TCP dissolved therein 0.8 g of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amyl-phenoxyacetamido)benzamido]-5-pyrazolone (hereinafter called magenta coupler M-1), 0.15 g of 1-(2,4,6-trichlorophenyl)-4-(1-naphthylazo)-3-(2-chloro-5-octadecenylsuccinimidoanilino)-5-pyrazolone (hereinafter called colored magenta coupler CM-1) and 0.016 g of DIR compound D-1

Layer 5 : The same layer as Layer 3

Layer 6 : A low-speed blue light-sensitive emulsion layer containing 0.2 g of a blue-sensitized low-speed silver iodobromide emulsion having a silver iodide content of 4 mol%, 1.9 g of gelatin, and 0.6 g of TCP dissolved therein 1.5 g of α -pivaloyl- α -(1-benzyl-2-phenyl-3,5-dioxoimidazolidine-4-yl)-2-chloro-5-(α -dodecyloxycarbonyl)-ethoxycarbonyl]acetanilide (hereinafter called Y-1)

Layer 7 : The same layer as Layer 3

Layer 8 : A high-speed red light-sensitive emulsion layer containing 1.3 g of a high-speed red light-sensitive silver iodobromide emulsion, 1.2 g of gelatin, and 0.23 g of TCP dissolved therein 0.21 g of cyan coupler C-1 and 0.02 g of colored cyan coupler CC-1

Layer 9 : The same layer as Layer 3

Layer 10 : A high-speed green light-sensitive emulsion layer containing 1.8 g of a green-sensitized high-speed green sensitive silver iodobromide emulsion, 1.9 g of gelatin, and 0.25 g of TCP dissolved therein 0.20 g of magenta coupler M-1 and 0.049 g of colored magenta coupler CM-1

In Layer 10, the above-described high-speed green-sensitive silver iodobromide emulsion was prepared in the following manner.

A monodisperse type silver iodobromide emulsion D having a grain-size of 1.6 μ m was prepared to be

of a multilayered core:shell type structure, by following the procedures described in Japanese Patent O.P.I. Publication No. 60-86659/1985, so as to have a grain-size variation coefficient of 11%, an average iodide content of 5.6%. Such a core/shell type structure was comprised of a nucleus and three shells, namely, the 1st shell to the 3rd shell from the inside of each grain, and the iodide contents and the volumetric occupancy of each shell were as follows; 15 mol% and 22% for the 1st shell, 5 mol% and 39% for the 2nd shell and 0.3 mol% and 27% for the 3rd shell, respectively. Thus prepared emulsion D was chemically sensitized in an ordinary method, with sodium thiosulfate and potassium aurochloride, and the foregoing sensitizing dyes (a) and (b) were added in the amounts of 7.5×10^{-5} and 7.0×10^{-5} mol each per mol of silver halide used, and the resulted emulsion was color-sensitized to green-light, respectively. Further for the purposes of stabilizing the emulsion and preventing it from fogging, 4-hydroxy-6-methyl-1,3,3a,7-tetrazindene was added in an amount of 7×10^{-3} mol per mol of the silver halide used.

Layer 11 : The same layer as the 3rd layer

Layer 12 : A high-speed blue-sensitive emulsion layer containing 1.0 g of a high-speed silver iodobromide emulsion color-sensitized to blue-light, 1.5 g of gelatin, and 0.65 g of TCP into which 1.30 g of yellow coupler Y-1 were dissolved

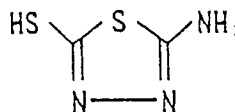
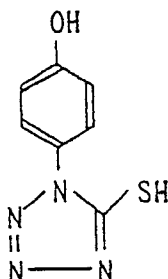
Layer 13 : A protective layer containing 2.3 g of gelatin.

Each of the above-mentioned layers were added with a gelatin hardener and a surfactant, besides the above-given compositions.

Sample No. 21 through Sample No. 36 each were prepared in the same manner as in Sample No. 20, except that Layer 9 through Layer 11 of Sample No. 20 were each added with the substantially non-light-sensitive silver halide fine grains shown in Table-4 and the following Exemplified compounds B-1 and D-5.

Exemplified compound B-1

Exemplified compound D-5



The amounts of the exemplified compounds B-1 and D-5 shown in Table-5 are indicated in each by the amount per mol of silver halide used.

Table-4

Sample No.	Layer 9, Non-light-sensitive layer	Layer 10, light-sensitive layer *	Layer 11, Non-light-sensitive layer
20	-	-	-
21	-	B-1	-
22	-	D-5	-
23	-	-	g 0.2 g
24	-	f 0.2 g	-
25	f 0.4 g	-	-
26	-	B-1, f 0.2 g	-
27	f 0.4 g	B-1	-
28	f 0.4 g	D-5	-
29	c 0.4 g	-	-
30	c 0.4 g	B-1	-
31	c 0.4 g	D-5	-
32	c 0.2 g	-	g 0.2 g
33	a 0.4 g	-	-
34	-	a 0.2 g	-
35	a 0.4 g	B-1	-
36	-	D-5, a 0.2 g	-

*. Every emulsion used was D.

. In the column, exemplified compound Nos. non-light-sensitive emulsions and the amount added are shown.

. Exemplified compounds were each added in an amount of 1.0×10^{-4} mol per mol of silver halide.

55 Evaluation

With respect to each of thus prepared Samples No. 20 through No. 36, the sensitometric evaluation was tried in the same manner as in Example-1, except that they were exposed to neutral light in place of green-

light.

Granularity, RMS, was measured through green-light, and the graininess of each sample was obtained by scanning the magenta dye-image of each sample already subjected to the sensitometric evaluations, by making use of a microdensitometer having a circular scanning aperture of 25 μ m, when the density was in a total of fog plus 0.8, so as to find the density variations. Then, the graininess of each sample was expressed in values obtained by multiplying the resulting standard deviation of the density variations by 1000 and made relative to the value of the control sample which was regarded as a value of 100. The greater these relative graininess values are, the more the graininess is undesirably coarse.

Processing stability was measured in the same manner as in ordinary sensitometry, except that the sodium bromide concentration was changed in the color developer used. In the case that a sodium bromide concentration of a color developer is changed, the less the sensitometry is changed, the better the processing stability.

The results of the evaluation are shown in Table-5.

Table-5

Sample No.	Sodium bromide 1.3g/liter of developer(control)			Sodium bromide 1.17g. liter of developer		Sodium bromide 1.43g/liter of developer	
	Fog	Speed	RMS	Fog	Speed	Fog	Speed
20	0.40	100	32	0.43	119	0.38	77
21	0.37	97	25	0.40	125	0.36	72
22	0.38	92	25	0.40	115	0.35	66
23	0.42	116	37	0.44	124	0.39	94
24	0.43	124	35	0.46	139	0.40	103
25	0.41	135	33	0.43	147	0.39	121
26	0.41	126	32	0.42	144	0.38	102
27	0.38	145	24	0.39	160	0.36	129
28	0.40	140	27	0.42	158	0.38	134
29	0.42	138	35	0.45	150	0.40	126
30	0.39	160	26	0.41	169	0.37	143
31	0.39	152	28	0.41	163	0.38	133
32	0.43	143	36	0.47	150	0.40	130
33	0.42	109	40	0.46	131	0.39	86
34	0.43	98	48	0.48	110	0.39	85
35	0.39	107	35	0.40	135	0.38	86
36	0.40	98	40	0.46	114	0.38	80

From the results shown in Table-5, the following facts are found.

1. When comparing Sample Nos. 20, 23, 24, 25, 29 and 32 with each other, when silver halide fine grains having a relatively high chloride content are contained in a light-sensitive emulsion layer or a non-light-sensitive layer anterior or posterior to the emulsion layer, the speed of a light-sensitive emulsion may be remarkably raised, but no serious graininess deterioration cannot be observed. On the other hand, when silver iodobromide fine grains not containing chloride are contained therein, as in the cases of Sample Nos. 33 through 36, not only is the a sensitization effect very little, but also the graininess is seriously deteriorated.

2. When the compound represented by Formula-A is contained in a light-sensitive emulsion, the fogginess and graininess can effectively be improved. (Refer to Sample Nos. 20, 21 and 22.)

On the other hand, in the case that a system contains silver halide fine grains having a high chloride content, when adding the compound represented by Formula-A into the system, not only the improvements in fogginess and graininess can be observed, but also the sensitization effects can be remarkably displayed by adding silver halide fine grains having a high chloride content. (Refer to Sample Nos. 26, 27, 28, 30 and 31.)

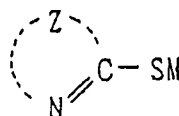
Further, even if the compound represented by Formula-A is added into a system containing conventional silver iodobromide fine grains, any sensitization effect of silver halide fine grains cannot be amplified, although some improved effects on fogginess and graininess may be observed. (Refer to Sample Nos. 35 and 36).

3. When observing the sensitometric behavior while changing the sodium bromide concentration of a color developer, the system of the invention containing silver halide fine grains having a high chloride content is proved to be able to provide a light-sensitive material having little sensitometric change and an excellent processing stability, as compared with a system not containing any silver halide fine grains or another system containing silver iodobromide fine grains which do not contain any chloride.

Claims

1. A silver halide light-sensitive photographic material comprising a support having thereon a silver halide emulsion layer and a non-light-sensitive layer adjacent to said emulsion layer, wherein at least one of said silver halide emulsion layer and said non-light-sensitive layer contains substantially non-light-sensitive fine silver halide grains having a silver chloride content of not less than 20 mol%, and said silver halide emulsion layer contains monodisperse light-sensitive silver halide grains substantially consisting of silver bromide or silver iodobromide.
2. The material of claim 1, wherein said substantially non-light-sensitive fine silver halide grains have a silver chloride content of not less than 50 mol%.
3. The material of claim 2, wherein said substantially non-light-sensitive fine silver halide grains have a silver chloride content of not less than 70 mol%.
4. The material of claim 1, wherein said substantially non-light-sensitive fine silver halide grains are monodisperse grains.
5. The material of claim 1, wherein said substantially non-light-sensitive fine silver halide grains have an average grain size of from 0.03 μm to 0.5 μm .
6. The material of claim 1, wherein said substantially non-light-sensitive fine silver halide grains are contained in said silver halide emulsion layer.
7. The material of claim 6, wherein said substantially non-light-sensitive fine silver halide grains contained in said silver halide emulsion layer in a portion of from 5% to 30% by weight to said light sensitive silver halide grains contained in said silver halide emulsion layer in terms of silver.
8. The material of claim 7, wherein said substantially non-light-sensitive fine silver halide grains contained in said silver halide emulsion layer in a portion of from 5% to 25% by weight to said light sensitive silver halide grains contained in said silver halide emulsion layer in terms of silver.
9. The material of claim 1, wherein said substantially non-light-sensitive fine silver halide grains are contained in said non-light-sensitive layer.
10. The material of claim 9, wherein said substantially non-light-sensitive fine silver halide grains are contained in said non-light-sensitive layer in an amount of from 0.5 mg/dm^2 to 20 mg/dm^2 in terms of silver.
11. The material of claim 10, wherein said substantially non-light-sensitive fine silver halide grains are contained in said non-light-sensitive layer in an amount of from 1 mg/dm^2 to 10 mg/dm^2 in terms of silver.
12. The material of claim 1, wherein said monodisperse light-sensitive silver halide grains have a grain size variation coefficient of not more than 20%.
13. The material of claim 12, wherein said monodisperse light-sensitive silver halide grains have a grain size variation coefficient of not more than 15%.
14. The material of claim 1, wherein at least one of said light-sensitive silver halide emulsion layer and said non-light-sensitive layer contains a compound represented by the following formula A;

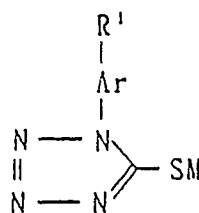
Formula A



wherein Z is a group of atoms necessary to complete a five- or six-member heterocyclic ring provided that said atoms are selected from the group consisting of a carbon atom, a nitrogen atom, an oxygen atom, a sulfur atom and a selenium atom, and said heterocyclic ring may have a condensed carbon ring; M is a hydrogen atom, an alkali metal atom or an ammonium group.

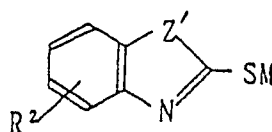
15. The material of claim 14, wherein said compound represented by Formula A is a compound represented by the following Formula B, C or D;

Formula B



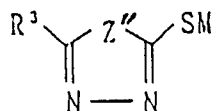
wherein Ar is a phenyl group, a naphthyl group or a cyclohexyl group; R¹ is a hydrogen atom or a group capable of being a substituent of the group represented by Ar; and M is synonymous with that denoted in Formula A,

Formula C



wherein Z' is a sulfur atom, an oxygen atom, a selenium atom or an -NH- group; R² is a hydrogen atom or a group capable of being a substituent of a benzene ring; and M is synonymous with that denoted in Formula A,

Formula D



wherein Z'' is a sulfur atom, an oxygen atom, a selenium atom or an -NR⁴- group in which R⁴ is a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aralkyl group, a -COR⁵ group, an -SO₂-R⁵ group, an -NHCOR⁶ group or an -NHSO₂-R⁶ group; R⁵ is an alkyl group, an aryl group, a cycloalkyl group, an aralkyl group or an -NH₂ group; R⁶ is an alkyl group, an aryl group, a cycloalkyl group or an aralkyl group; R³ is a hydrogen atom, an alkyl group, an aryl group, a cycloalkyl group, an aralkyl group, an alkenyl group, an amino group or a heterocyclic group; M is synonymous with that denoted in Formula A.



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.4)																
X,Y	EP-A-0 189 840 (FUJI) * Claims * ----	1-15	G 03 C 1/02 G 03 C 1/34 G 03 C 1/46																
Y	DE-A-3 635 388 (KONISHIROKU) * Claims; page 10, lines 53-60; formulas * ----	1,14,15																	
Y	EP-A-0 040 771 (AGFA-GEVAERT) * Claims; page 5, line 20 - page 19 * ----	1-15																	
Y	GB-A-1 000 001 (KODAK) * Claims * -----	1-13																	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)																
			G 03 C																
The present search report has been drawn up for all claims																			
Place of search THE HAGUE		Date of completion of the search 07-07-1989	Examiner BUSCHA A.J.																
<table border="0"><tr><td>CATEGORY OF CITED DOCUMENTS</td><td>T : theory or principle underlying the invention</td></tr><tr><td>X : particularly relevant if taken alone</td><td>E : earlier patent document, but published on, or</td></tr><tr><td>Y : particularly relevant if combined with another</td><td>after the filing date</td></tr><tr><td>document of the same category</td><td>D : document cited in the application</td></tr><tr><td>A : technological background</td><td>L : document cited for other reasons</td></tr><tr><td>O : non-written disclosure</td><td>.....</td></tr><tr><td>P : intermediate document</td><td>& : member of the same patent family, corresponding</td></tr><tr><td></td><td>document</td></tr></table>				CATEGORY OF CITED DOCUMENTS	T : theory or principle underlying the invention	X : particularly relevant if taken alone	E : earlier patent document, but published on, or	Y : particularly relevant if combined with another	after the filing date	document of the same category	D : document cited in the application	A : technological background	L : document cited for other reasons	O : non-written disclosure		P : intermediate document	& : member of the same patent family, corresponding		document
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