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(54) Silver halide photographic element for forming direct positive images and a method for forming said images.

(57) This invention relates to a silver halide photographic element capable of quickly forming direct positive images when using a processing solution having a high stability, and to an image forming process using the photographic element. More specifically, the invention relates to a silver halide photographic element for compute output (light-sensitive film for COM) and also to an image forming process using the photographic element.

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SILVER HALIDE PHOTOGRAPHIC ELEMENT FOR FORMING DIRECT POSITIVE IMAGES AND A METHOD FOR FORMING SAID IMAGES

FIELD OF THE INVENTION

This invention relates to a silver halide photographic element capable of quickly forming direct positive images when using a processing solution having a high stability, and to an image forming process using the photographic element. More specifically, the invention relates to a silver halide photographic element for computer output (light-sensitive film for COM) and also to an image forming process using the photographic element.

BACKGROUND OF THE INVENTION

The rapid progress of computers has resulted in the development of information industries. Various methods for printing out a large amount of recorded information have been vigorously investigated. As a recording element in this field, silver halide photographic elements having reversal processing aptitude are used. In the processing step of the reversal development process, the imagewise exposed silver halide photographic element is subjected to a first development to form negative images and, without being fixed, is bleached to remove reduced silver in the images. Then, the photographic element containing undeveloped remaining silver halide is light-exposed and subjected to a second development to form positive images. In the aforesaid process, the finishing speed of the film is slow since the processing step is complicated and also the maximum density (Dmax) and the minimum density (Dmin) are liable to deviate. Furthermore, in the aforesaid process, it is necessary to use a strong oxidizing agent such as potassium bichromate, etc., for bleaching, which causes a problem of environmental pollution.

As a process capable of solving the above problems, a photographic process of obtaining direct positive images without the need of a reversal processing step or a negative film is well known.

A process of forming positive images using a direct positive silver halide photographic element can be mainly classified into the following two types from the viewpoint of practical usefulness.

In one type, previously fogged silver halide emulsions are used and after development, direct positive images are obtained by destroying fogged nuclei (latent images) at exposed portions by utilizing a solarization or Herschel effect.

In another type, unfogged internal latent image type silver halide emulsions are used and direct positive images are obtained by applying a surface development after or while applying fogging treatment after image exposure.

The aforesaid internal latent image type silver halide photographic emulsion is a silver halide photographic emulsion of a type having the sensitive specks mainly in the inside of the silver halide grain and forming latent images mainly in the inside of the silver halide grain by light exposure.

The process of the latter type has generally a high sensitivity as compared with the process of the former type and is suitable for the uses of requiring high sensitivity. The present invention relates to the latter type process.

Various techniques are known in the field of the art and are mainly described, e.g., in U.S. Patents 2,592,250, 2,466,957, 2,497,875, 2,588,982, 3,317,322, 3,761,266, 3,761,276, and 3,796,577, British Patents 1,151,363, 1,150,553, and 1,011,062. Using these known processes, direct positive type photographic light-sensitive elements having a relatively high sensitivity can be prepared.

Also, details of the mechanism of direct positive image formation are described in T.H. James, The Theory of the Photographic Process, 4th Edition, Chapter 7, pages 182-193 and U.S. Patent 3,761,276.

It is believed that fogged nuclei are selectively formed at the surfaces only of silver halide grains in the unexposed portions by the so-called surface desensitizing action based on the internal latent images formed in the inside of the silver halide grains by an initial imagewise exposure and then a so-called ordinary surface development is applied to form photographic images (direct positive images) at the unexposed portions.

As described above, as a means for selectively forming fogged nuclei, a so-called "light fogging method" of applying a second light exposure on the entire surface of the light-sensitive element (e.g., British Patent 1,151,363) and a so-called "chemical fogging method" using a nucleating agent are known.

The latter method is described, e.g., in Research Disclosure, Vol. 151, No. 15162, pages 72-87, (November, 1976).

In these methods, the conventional chemical fogging method has the following disadvantages. That is, the nucleating agent used shows acts as a nucleating agent at a high pH of at least 12. At such a high pH condition, the developing agent is liable to deteriorate by air oxidation, which results in greatly reducing the development activity. Also, a long time is required for processing due to the slow development rate and if a developer of low pH is used, the processing time is further prolonged. Furthermore, even when pH of the developer is higher than 12, it takes a long time for finishing the development.

On the other hand, the light fogging method does not require a high pH condition and is relatively advantageous for practical use. However, when using such in the wide field of photography, there are various technical problems with this method. That is, since the light fogging method is based on the formation of fogged nuclei by the photodecomposition of silver halide, the proper exposure illuminance and the proper exposure amount in the method differ according to the kind and the characteristics of the silver halide being used. Thus, it is difficult to obtain a constant performance with this method. Furthermore, there is a disadvantage in that the development apparatus is complicated and expensive. Still further, there is a disadvantage of requiring a long time for the development.

As described above, it is difficult to stably obtain good direct positive images by the aforesaid conventional fogging methods. For solving these problems, compounds showing a nucleating action even below pH 12 are proposed in JP-A-52-69613 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), and U.S. Patents 3,615,615 and 3,850,638. However, these nucleating agents have a disadvantage in that the nucleating agents act with silver halide or decompose during the storage of the photographic light-sensitive elements containing them before processing, which results in reducing the maximum image density after processing.

U.S. Patent 3,227,552 describes that the development rate for an intermediate density is increased by using a hydroquinone derivative. However, even in the case of the hydroquinone derivative, the development rate is not sufficiently high and in particular, when the pH of the developer is below 12, the development rate is insufficient.

Also, JP-A-60-170843 describes that the maximum image density is increased by adding a mercapto compound having a carboxylic acid group or a sulfonic acid group. However, the effect obtained by the addition of the compound is less.

JP-A-55-134848 describes that the minimum image density is reduced by processing using a processing solution (pH 12.0) containing a tetraazaindene series compound in the presence of a nucleating agent to prevent the formation of re-reversed negative images. However, in the method, the maximum image density is not increased and also the development rate is not increased.

Furthermore, JP-B-45-12709 (the term "JP-B" as used herein means an "examined published Japanese patent application") describes that a triazoline-thione series compound or a tetrazoline-thione series compound is added to a light-sensitive element for forming direct positive images by a light fogging method. However, even by the method, it is difficult to obtain high maximum image density and a high development rate.

As described above, a technique of obtaining direct positive images having a high maximum image density and a low minimum image density in a short period of time has not been known.

Also, there is generally a problem that as the sensitivity of a direct positive silver halide emulsion is higher, the formation of re-reversed negative images in a high illuminance exposure is greater and in particular, in a light-sensitive film for COM, a high sensitivity in a short light exposure time is required and the prevention of the formation of the re-reversed negative images under a high illuminance exposure is important.

Also, Japanese Patent Application No. 61-136949 and JP-A-63-8740 describe techniques of solving the aforesaid problems but these methods are not sufficient from the point of the prevention of the re-reversed negative images.

SUMMARY OF THE INVENTION

A 1st object of this invention is to provide a process of quickly and stably forming direct positive images having a high Dmax and low Dmin by processing a previously unfogged internal latent image type silver halide photographic element in the presence of a nucleating agent.

A 2nd object of this invention is to provide a direct positive silver halide photographic element for a

COM film utilizing an internal latent image type silver halide emulsion and reversibility due to a nucleating agent.

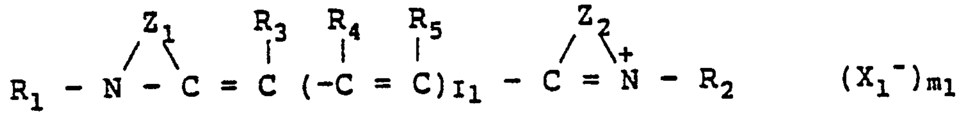
A 3rd object of this invention is to provide a direct positive silver halide photographic element having a low occurrence of re-reversed negative images in a high illuminance exposure.

A 4th object of this invention is to provide a process of forming direct positive images with a low deviation of Dmax and Dmin even when the pH of a developer is changed.

A 5th object of this invention is to provide a direct positive silver halide photographic element having a low deviation of Dmax and Dmin even when the photographic element is stored for a long period of time.

It has now been discovered that the aforesaid objects can be attained by the invention as described hereinafter.

That is, the invention is a process of forming a direct positive images comprising; (A) imagewise exposing a silver halide photographic element comprising a support having thereon at least one photographic emulsion layer containing previously unfogged internal latent image type silver halide grains, and, (B) developing the resulting photographic element, wherein said photographic emulsion layer or another hydrophilic colloid layer contains a nucleating agent and said photographic emulsion layer contains a sensitizing dye represented by formula (I) and wherein development is performed in the presence of a nucleating accelerator;



$$R_1 - \overset{\overset{Z_1}{\frown}}{N - C} = \overset{R_3}{\overset{|}{C}}\ (-\overset{R_4}{\overset{|}{C}} = \overset{R_5}{\overset{|}{C}})_{l_1} - \overset{\overset{Z_2}{\frown}}{C = \overset{+}{N}} - R_2 \qquad (X_1^-)_{m_1}$$

(I)

wherein Z_1 and Z_2, which may be the same or diffrent, each represents an atomic group forming a 5- or 6-membered nitrogen-containing heterocyclic nucleus; l_1 represents 0 or 1; R_1 and R_2, which may be the same or different, each represents a substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms or a substituted or unsubstituted alkenyl group having from 1 to 10 carbon atoms; R_3 and R_5 represents a hydrogen atom, said R_3 and R_1 and said R_5 and R_2 may combine with each other to form a 5- or 6-membered ring; R_4 represents a hydrogen atom or a substituted or unsubstituted lower alkyl group (e.g., methyl, ethyl, propyl, methoxy group, and phenethyl, and more preferably an alkyl group having from 1 to 5 carbon atoms); X_1 represents an acid anion group; m_1 represents 0 or 1, and when the dye shown by formula (I) is an intramolecular salt, m_1 is 0.

DETAILED DESCRIPTION OF THE INVENTION

In this invention, the term "nucleating agent" means a compound which acts on a previously unfogged internal latent image type silver halide emulsion, in the case of surface development of the emulsion, to form direct positive images.

As the nucleating agent which can be used in this invention, all of the compounds which have hitherto been developed for nucleating internal latent image type silver halides can be used. The nucleating agents can be used singly or as a mixture thereof. In more detail, the nucleating agent are described, e.g., in Research Disclosure, No. 22534, pages 50-54 (January, 1983) and these compounds are generally classified into hydrazine series compounds, quaternary heterocyclic compounds, and other compounds.

The hydrazine series nucleating agents are described, e.g., in Research Disclosure, No. 15162, pages 76-77 (November, 1976) and ibid., No. 23510, pages 346-352 (November, 1983) and practical examples are as follows.

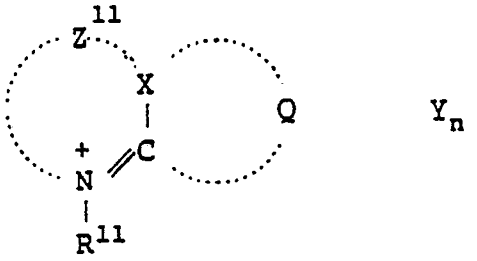
That is, examples of hydrazine series nucleating agent having an adsorptive group to silver halide are described in U.S. Patents, 4,030,925, 4,080,207, 4,031,127, 3,718,470, 4,269,929, 4,276,364, 4,278,748, 4,385,108, and 4,459,347, British Patent 2,011,391B, and JP-A-54-74729, JP-A-55-163533, JP-A-55-74536, and JP-A-60-179734.

Other hydrazine series nucleating agents are described, e.g., in JP-A-57-86829 and U.S. Patents 4,560,638, 2,563,785, and 2,588,982.

Examples of the quaternary heterocyclic series nucleating agent are described in Research Disclosure, No. 22534, ibid., No. 23213, pages 267-270 (August, 1983), JP-B-49-38164, JP-B-52-19452, and JP-B-52-

47326, JP-A 52-69613, JP-A-52-3426, JP-A-55-138742, and JP-B-60-11837, and U.S. Patent 4,306,016.

The useful nucleating agents for use in this invention are preferably the compounds shown by following formulae (N-I) and (N-II);



(N-I)

wherein Z^{11} represents a non-metallic atomic group necessary for forming a 5- or 6-membered heterocyclic ring, to which an aromatic ring or a heterocyclic ring may be further condensed, R^{11} represents an aliphatic group, X represents

$=\underset{|}{C}-$ or $-\underset{|}{N}-$,

Q represents a non-metallic atomic group necessary for forming a 4- to 12-membered non-aromatic hydrocarbon ring or a non-aromatic heterocyclic ring, at least one of the substituent for R^{11}, the substituent for Z^{11}, and the substituent for Q, however, contains an alkinyl group and further at least one of R^{11}, Z^{11}, and Q may have an adsorption accelerating group to silver halide, Y represents a pair ion for balancing electrostatic charges, and n represents a number necessary for balancing electrostatic charges

The nucleating agent shown by formula (N-I) described above is explained in more detail.

Examples of the heterocyclic ring completed by the non-metallic atomic group shown by Z^{11} are quinolinium, benzimidazolium, pyridinium, thiazolium, selenazolium, imidazolium, tetrazolium, indolenium, pyrrolidium, phenanthridinium, isoquinolium, and naphthopyridinium.

The heterocyclic ring formed by Z^{11} may be substituted and examples of the substituents are an alkyl group, an alkenyl group, an aralkyl group, an aryl group, an alkinyl group, a hydroxy group, an alkoxy group, an aryloxy group, a halogen atom, an amino group, an alkylthio group, an arylthio group, an acyloxy group, an acylamino group, a sulfonyl group, a sulfonyloxy group, a sulfonylamino group, a carboxy group, an acyl group, a carbamoyl group, a sulfamoyl group, a sulfo group, a cyano group, a ureido group, a urethane group, a carbonic acid ester group, a hydrazine group, a hydrazone group, and an imino group. When two or more substituents exist, they may be the same or different. Also, the aforesaid substituent may be substituted by the aforesaid substituent.

Furthermore Z^{11} may have a heterocyclic quaternary ammonium group which is completed through a proper linkage group L^1 (wherein L^1 is a divalent linkage group) as a substituent. In this case, the compound takes a so-called dimer structure.

The heterocyclic skeleton completed by Z^{11} is preferably quinolinium, benzimidazolium, pyridinium, acrydinium, phenanthridinium, naphthopyridinium, or isoquinolinium, more preferably quinolinium, naphthopyridinium, or benzimidazolium, and most preferably quinolinium.

The aliphatic group shown by R^{11} is preferably an unsubstituted alkyl group having from 1 to 18 carbon atoms or a substituted alkyl group the alkyl moiety of which has from 1 to 18 carbon atoms. As the substituent for the substituted alkyl group, there are the substituents described above for Z^{11}.

R^{11} preferably an alkinyl group and particularly preferably a propargyl group.

Q is an atomic group necessary for forming a 4-to 12-membered non-aromatic hydrocarbon ring or a non-aromatic heterocyclic ring and these rings may be substituted by the substituents described above for Z^{11}.

Examples of the non-aromatic hydrocarbon ring, which is the case when X is a carbon atom, are cyclopentane, cyclohexane, cyclohexene, cycloheptane, indane, and tetralin.

The non-aromatic heterocyclic ring has nitrogen, oxygen, sulfur, selenium, etc., as the hetero atom. When X is a carbon atom, examples of the non-aromatic heterocyclic ring are tetrahydrofuran, tetrahydropyran, butyrolactone, pyrrolidone, and tetrahydrothiophene. Also, when X is a nitrogen atom, examples thereof are pyrrolidine, piperidine, pyridone, piperazine, perhydrothiazine, tetrahydroquinoline, and indoline.

Preferred examples of the rings formed by Q are those wherein X is a carbon atom, such as cyclopentane, cyclohexane, cycloheptane, cyclohexene, indane, tetrahydropyran, and tetrahydrothiophene.

As described above, at least one of R^{11}, and the substituent for Z^{11} and the substituent for Q is an alkinyl group. The alkinyl group was already partially described above but is further explained in detail. The alkinyl group has preferably from 2 to 18 carbon atoms and specific examples thereof are ethynyl, propargyl, 2-butynyl, 1-methylpropargyl, 1,1-dimethylpropargyl, 3-butynyl, and 4-pentinyl. Furthermore, these groups may be further substituted by the substituents described as above for Z^{11}. The alkinyl is preferably propargyl and the case that R^{11} is propargyl is most preferred.

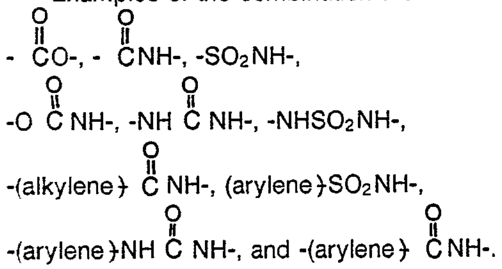
The substituents for R^{11}, Q, and Z^{11} may have an adsorption accelerating group to silver halide and a preferred adsorption accelerating group is shown by $X^{11}\{L^1\}_m$ (wherein X^{11} is an adsorption accelerating group to silver halide, L^1 is a divalent linkage group, and m is 0 or 1). Preferred examples of the adsorption accelerating group to silver halide shown by X^{11} are a thioamido group, a mercapto group, and a 5- or 6-membered nitrogen-containing heterocyclic group. These groups may be substituted by the substituents described above as the substituents for Z^{11}. As a thioamido group, an acyclic thioamido group (e.g., thiourethane and thioureido) is preferred.

As the mercapto group shown by X^{11}, a heterocyclic mercapto group (e.g., 5-mercaptotetrazole, 3-mercapto-1,2,4-triazole, 2-mercapto-1,3,4-thiadiazole, and 2-mercapto-1,3,4-oxadiazole) is preferred.

The 5- or 6-membered nitrogen-containing heterocyclic ring shown by X^{11} is composed of a combination of nitrogen, oxygen, sulfur, and carbon and the heterocyclic ring forming imino silver is preferred. Examples thereof are benzotriazole and aminothiazole.

The divalent linkage group shown by L^1 is an atom or an atomic group containing at least one of C, N, S, and 0. Practical examples thereof are an alkylene group, an alkenylene group, an alkinylene group, an arylene group, -O-, -S-, -NH-, -N=, -CO-, and $-SO_2-$(they may have a substituent). They may be used singly or as a combination thereof.

Examples of the combination are



$$-\overset{\overset{O}{\|}}{C}O-,\ -\overset{\overset{O}{\|}}{C}NH-,\ -SO_2NH-,$$

$$-O\overset{\overset{O}{\|}}{C}NH-,\ -NH\overset{\overset{O}{\|}}{C}NH-,\ -NHSO_2NH-,$$

$$-(\text{alkylene}\}\overset{\overset{O}{\|}}{C}NH-,\ (\text{arylene}\}SO_2NH-,$$

$$-(\text{arylene}\}NH\overset{\overset{O}{\|}}{C}NH-,\ \text{and}\ -(\text{arylene}\}\overset{\overset{O}{\|}}{C}NH-.$$

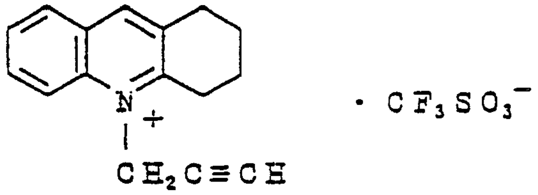
As a pair ion Y for balancing charges, there are, for example, bromide ion, chloride ion, iodide ion, p-toluenesulfonate ion, ethylsulfonate ion, perchlorate ion, trifluoromethanesulfonate ion, thiocyanate ion, BF_4^-, and PF_6^-.

The compound shown by formula (N-I) described above preferably has an adsorption accelerator to silver halide and, particularly preferably has a thioamide group, an azole group, or a heterocyclic mercapto group as the adsorption accelerating group X^{11}.

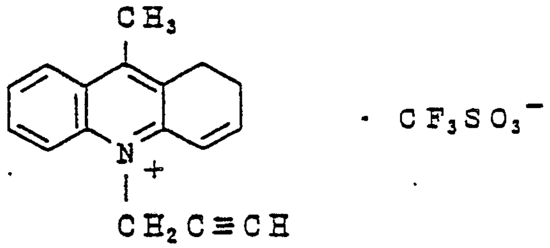
These compounds and the synthetic methods for preparing these compounds are described in Japanese Patent Application No. 62-17984 and the patents and literatures cited therein.

Specific examples of the compound shown by formula (N-I) are illustrated below but the invention is not limited to these compounds.

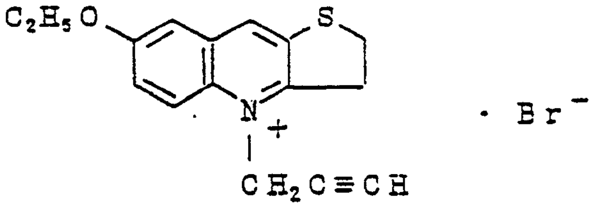
(N-I-1)



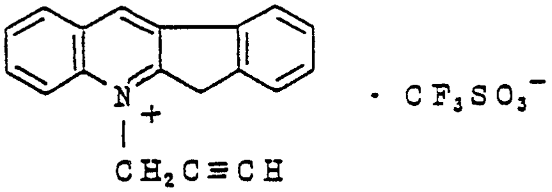
(N-I-2)



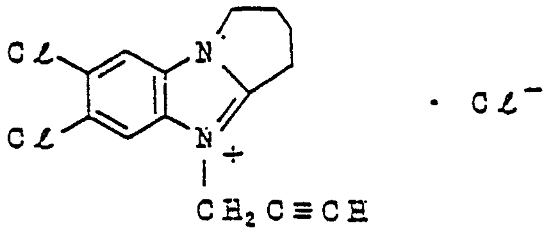
(N-I-3)



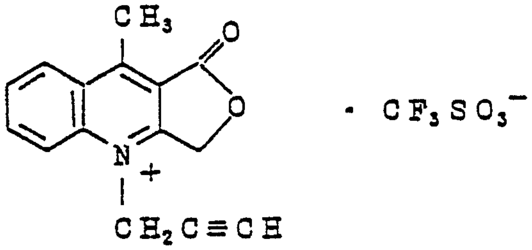
(N-I-4)



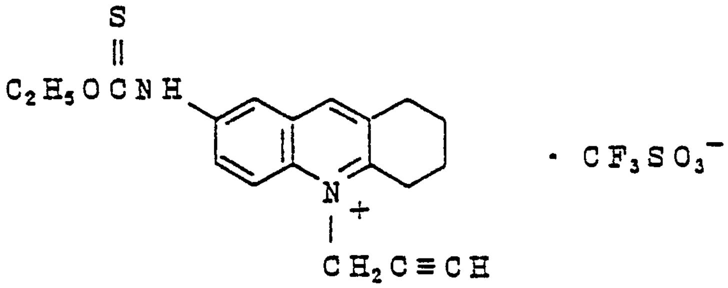
(N-I-5)



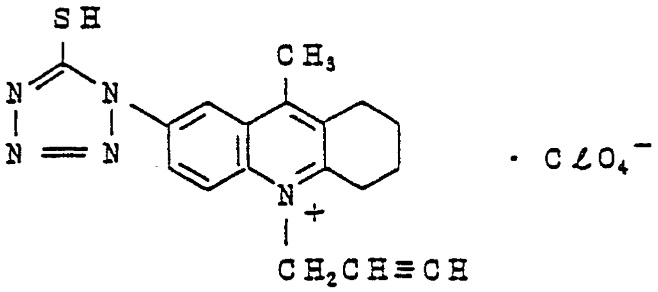
(N-I-6)



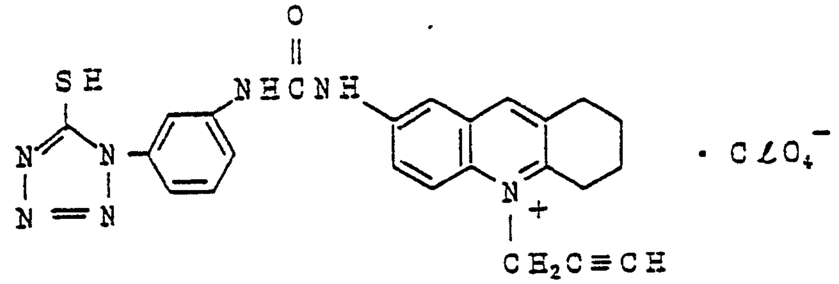
(N-I-7)



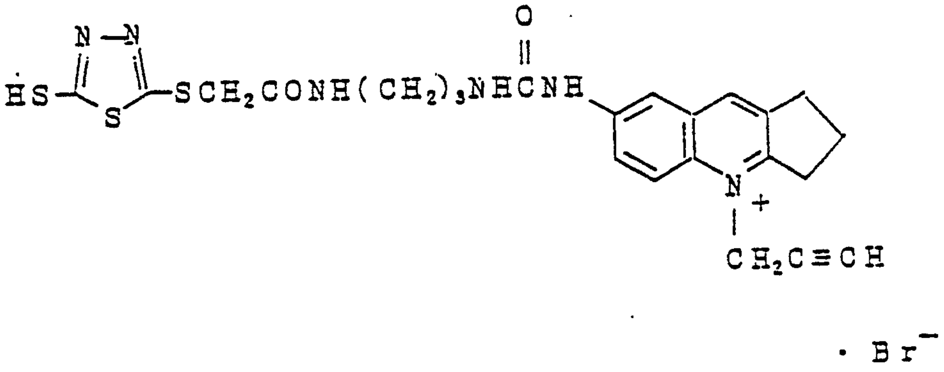
(N-I-8)



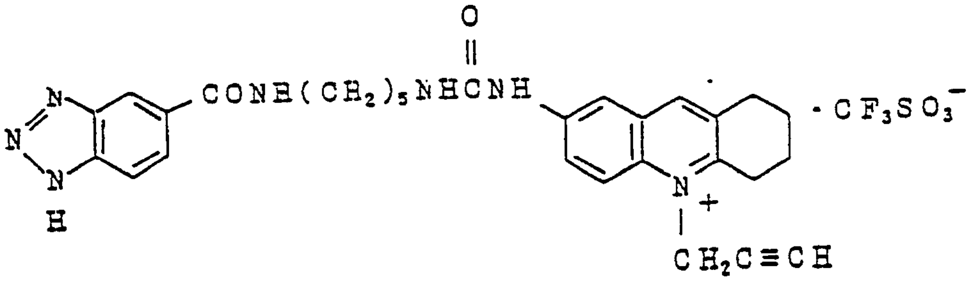
(N-I-9)



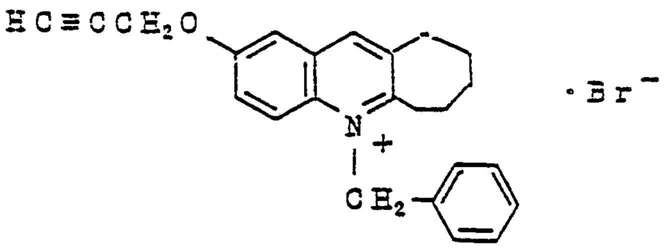
(N-I-10)



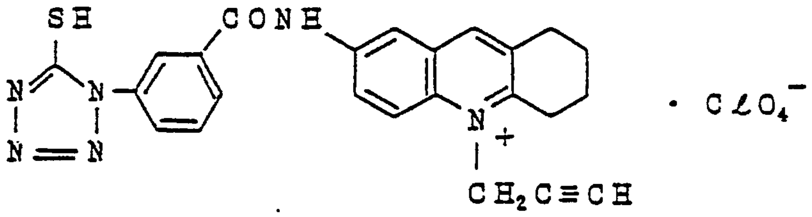
(N-I-11)



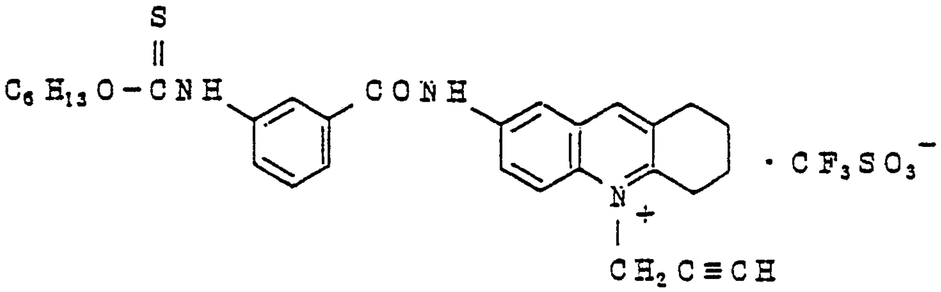
(N-I-12)



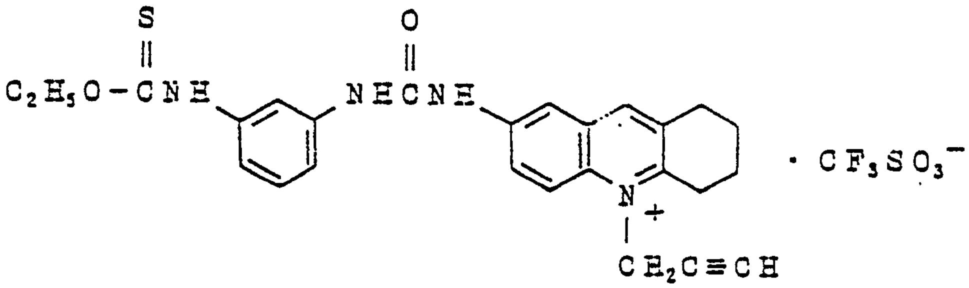
(N-I-13)



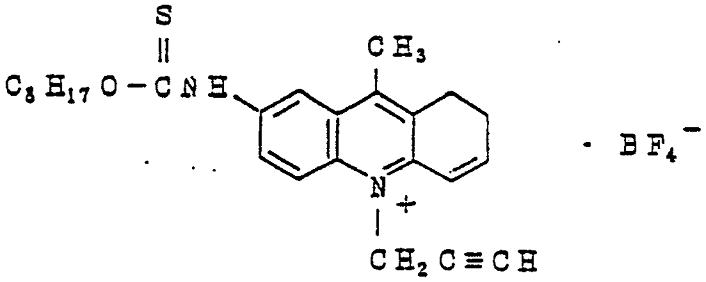
(N-I-14)



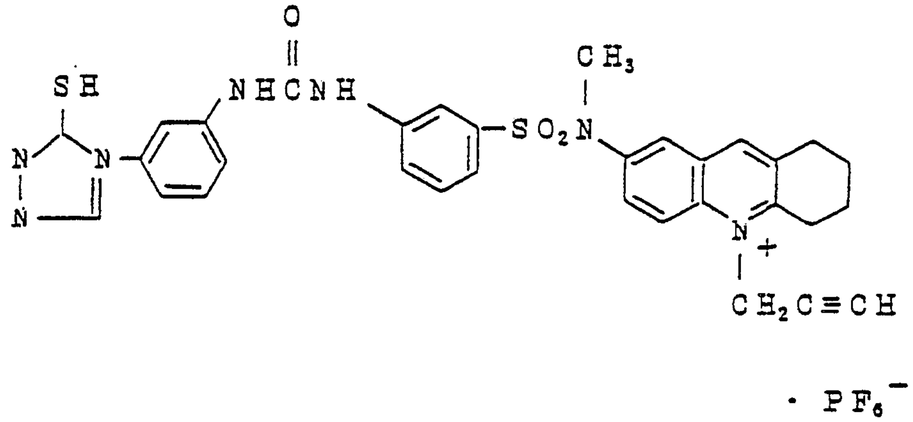
(N-I-15)



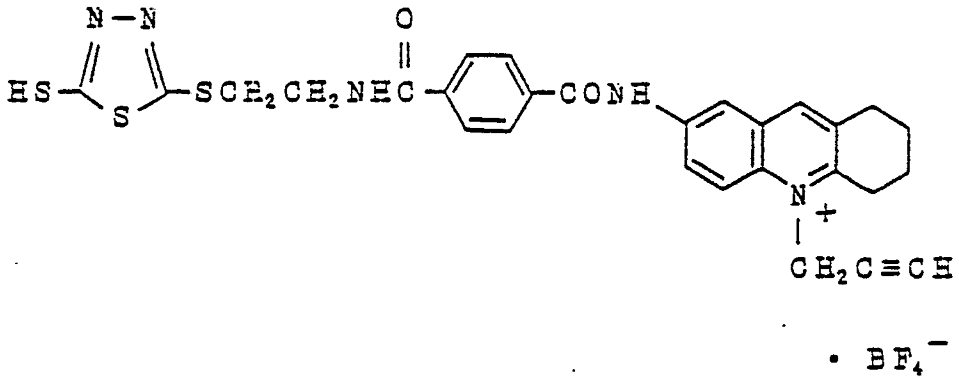
(N-I-16)



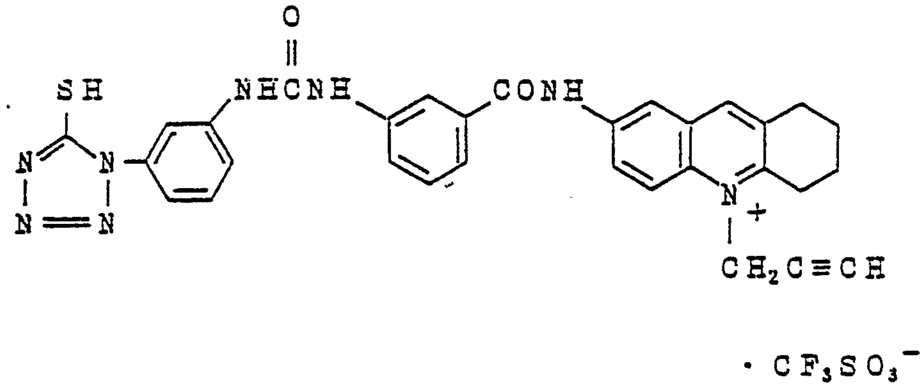
(N-I-17)



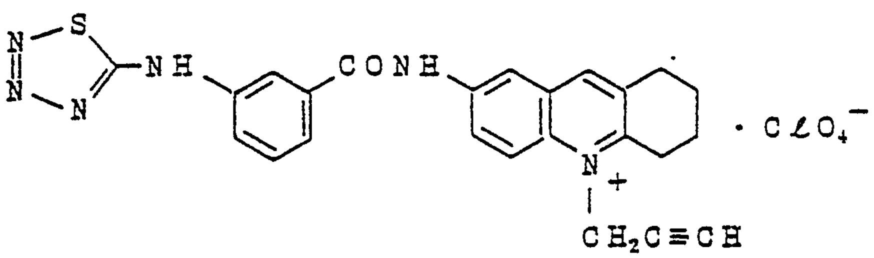
(N-I-18)



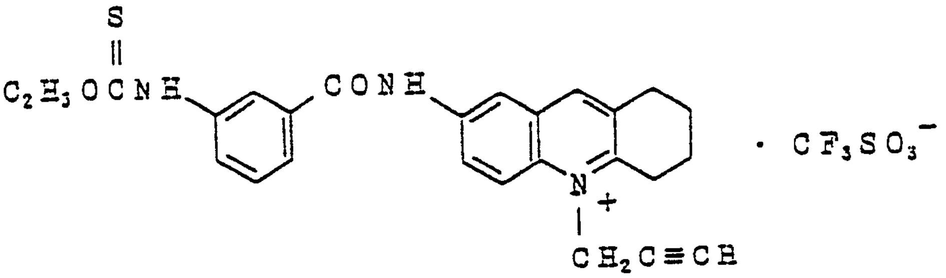
(N-I-19)



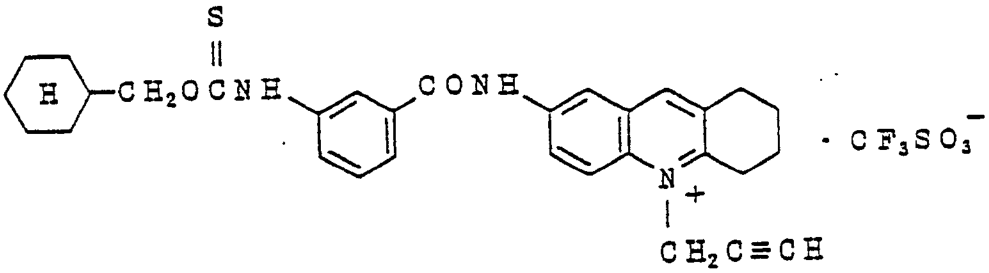
(N-I-20)



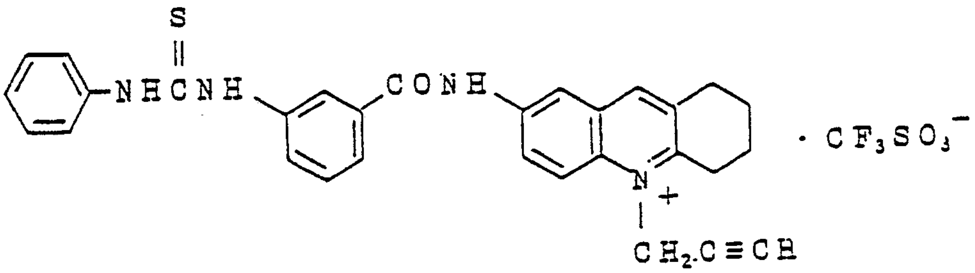
(N-I-21)



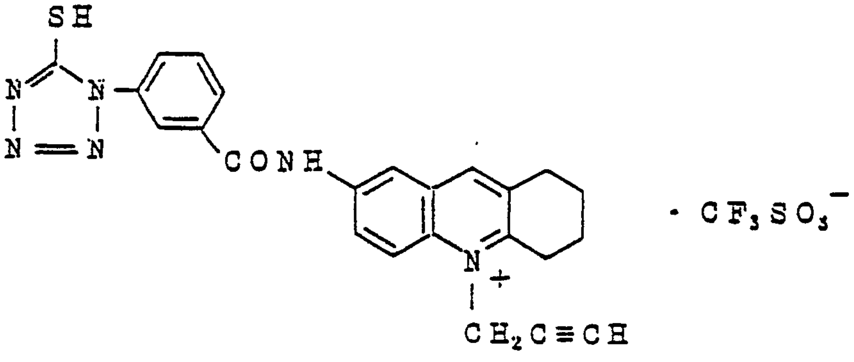
(N-I-22)



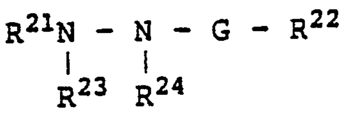
(N-I-23)



(N-I-24)



The aforesaid compounds can be synthesized by the methods described in the patents cited in Research Disclosure, No. 22534, pages 50-54 (January, 1983) and U.S. Patent 4,471,044 or similar methods to them.


$$R^{21}\underset{\displaystyle R^{23}}{N} - \underset{\displaystyle R^{24}}{N} - G - R^{22} \qquad \text{(N-II)}$$

wherein R^{21} represents an aliphatic group, an aromatic group, or a heterocyclic group; R^{22} represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, an aryloxy group, or an amino group; G represents a carbonyl group, a sulfonyl group, a sulfoxy group, a phosphoryl group, or an iminomethylene group (HN=C<); and R^{23} and R^{24} both represent a hydrogen atom or one of them represents a hydrogen atom and the other represents an alkylsulfonyl group, an arylsulfonyl group, or an acyl group, G, R^{23} and R^{24} may form a hydrazone structure (>N-N=C<) in the form including the hydrazine nitrogen. Also, if possible, the aforesaid group may be substituted by a substituent.

The aliphatic group shown by R^{21} in formula (N-II) is a straight chain, branched, or cyclic alkyl group, alkenyl group, or alkinyl group.

The aromatic group shown by R^{21} is a monocyclic or dicyclic aryl group such as, for example, a phenyl group and a naphthyl group.

The heterocyclic group shown by R^{21} is a 3- to 10-membered saturated or unsaturated heterocyclic ring containing at least one of nitrogen, oxygen, and sulfur and the ring may be a monocyclic ring or may form a condensed ring with an aromatic ring or a heterocyclic ring. The heterocyclic ring is preferably a 5- or 6-membered aromatic heterocyclic group such as, e.g., a pyridyl group, a quinolinyl group, an imidazolyl group, and a benzimidazolyl group.

R_{21} may be substituted by a substituent such as an alkyl group, an aralkyl group, an alkoxy group, an alkyl- or aryl-substituted amino group, an acylamino group, a sulfonylamino group, a ureido group, a urethane group, an aryloxy group, a sulfamoyl group, a carbamoyl group, an aryl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfinyl group, a hydroxy group, a halogen atom, a cyano group, a sulfo group and a carboxyl group. These groups may be further substituted.

Also, these groups may, if possible, combine with each other to form a ring.

R_{21} is preferably an aromatic group, an aromatic heterocyclic ring or an aryl-substituted methyl group, and more preferably an aryl group.

R_{22} is preferably as follows. That is, when G is a carbonyl group, R_{22} is preferably a hydrogen atom, an alkyl group (e.g., methyl, trifluoromethyl, 3-hydroxypropyl, and 3-methanesulfonamidopropyl,, an aralkyl group (e.g., o-hydroxybenzyl), or an aryl group (e.g., phenyl, 3,5-dichlorophenyl, o-methanesulfonamidophenyl, and 4-methanesulfonylphenyl), and is particularly preferably a hydrogen atom. Also, when G is a sulfonyl group, R_{22} is preferably an alkyl group (e.g., methyl), an aralkyl group (e.g., o-hydroxyphenyl methyl), an aryl group (e.g., a phenyl group), or a substituted amino group (e.g., dimethylamino).

As the substituent for the group shown by R_{22}, there are the substituents as the substituents for R_{21} described above and other substituents such as an acyl group, an acyloxy group, an alkyloxycarbonyl, an aryloxycarbonyl, an alkenyl, an alkinyl, and a nitro group.

These groups may be further substituted by the same group(s). Also, if possible, these groups may combine with each other to form a ring.

It is preferred hat R_{21} or R_{22}, in particular R_{21} contains a so-called ballast group. The ballast group has at least 8 carbon atoms and is composed of at least one of an alkyl group, a phenyl group, an ether group, an amido group, a ureido group, a urethane group, a sulfonamido group, and a thioether group.

Also, R_{21} or R_{22} may have a group shown by $\{X^{21}L^{2}\}_{m2}$ [wherein X^{21} has the same significance as X^{11} of formula (N-I) and is preferably a thioamido group (except thiosemicarbazide and the substituents thereof), a mercapto group or a 5- or 6-membered nitrogen-containing heterocyclic group, L^2 represents a divalent linkage group having the same significance as L^1 of formula (N-I), and m^2 represents 0 or 1], which accelerates the adsorption of the compound of formula (IV-II) to the surface of silver halide grains.

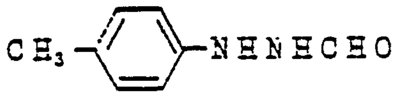
More preferably, X^{21} is a cyclic thioamido group (e.g., a mercapto-substituted nitrogen-containing heterocyclic ring such as 2-mercaptothiadiazole, 3-mercaptol,2,4-triazole, 5-mercaptotetrazole, 2-mercapto-1,3,4-oxadiazole, 2-mercaptobenzoxazole, etc.) or a nitrogen-containing heterocyclic group (e.g., benzotriazole, benzimidazole, and indazole).

R_{23} and R_{24} are most preferably a hydrogen atom, and G is most preferably a carbonyl group.

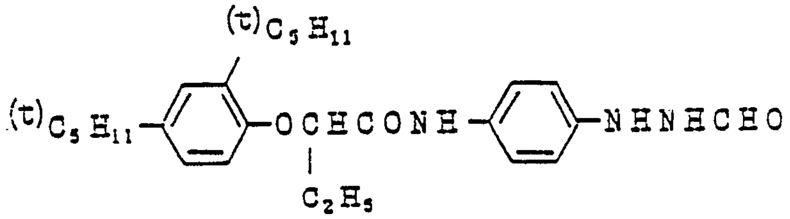
Also, it is more preferred that the nucleating agent shown by formula (N-II) has an adsorptive group to silver halide. The particularly preferred absorptive group to silver halide is a mercapto group, a cyclic thioamido group and a nitrogen-containing heterocyclic group as described for formula (N-I).

Specific examples of the compound shown by formula (N-II) described above are illustrated below but the invention is not limited to these compounds.

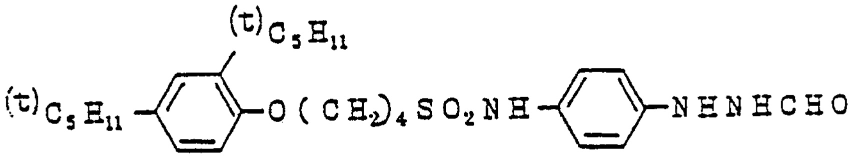
(N-II-1)



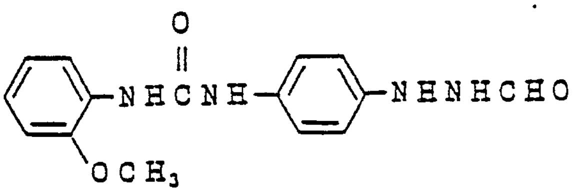
(N-II-2)



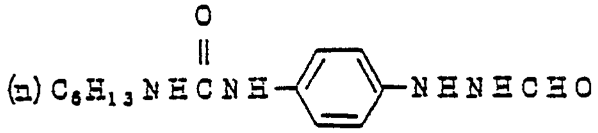
(N-II-3)



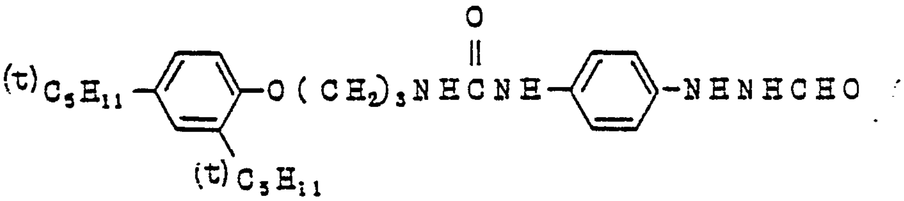
(N-II-4)



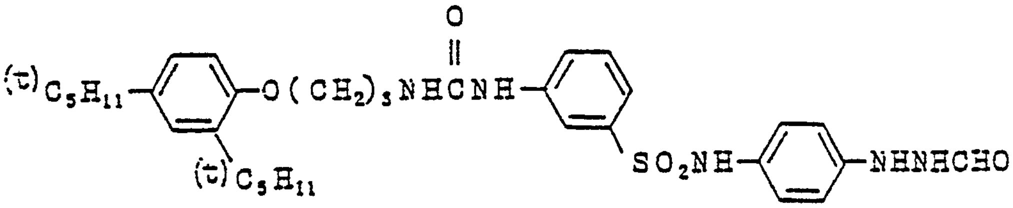
(N-II-5)



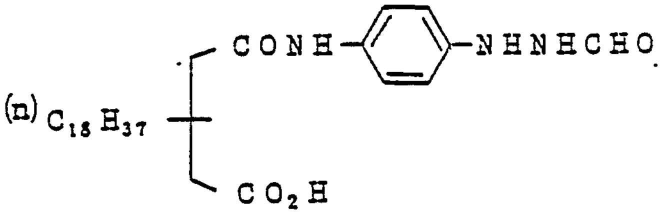
(N-II-6)



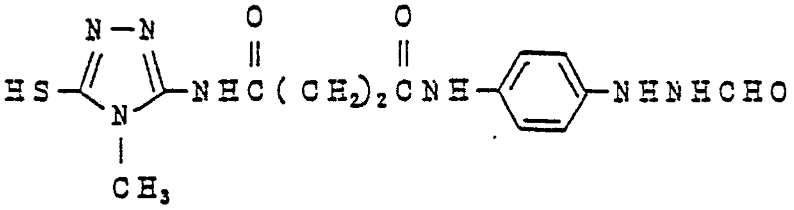
(N-II-7)



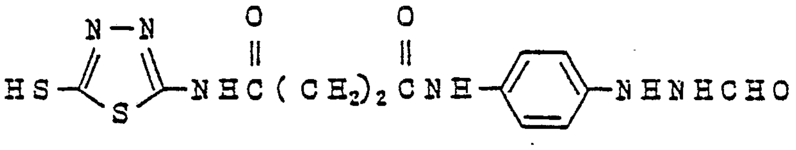
(N-II-8)



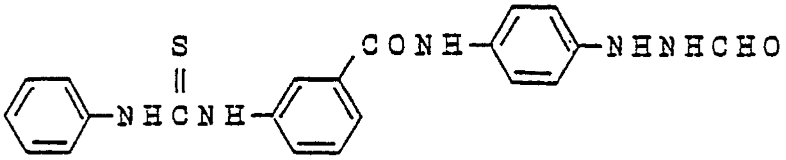
(N－Ⅱ－9)



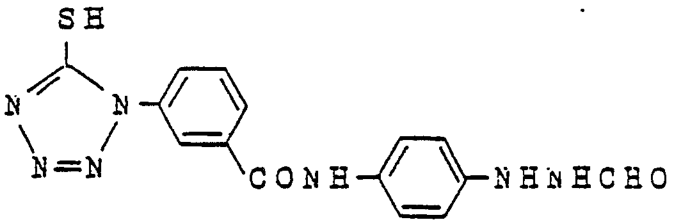
(N－Ⅱ－10)



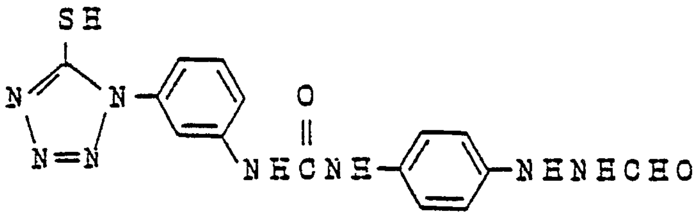
(N－Ⅱ－11)



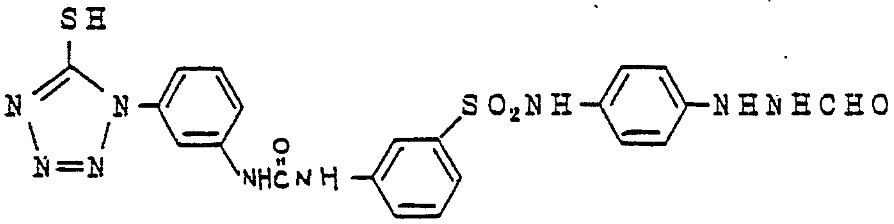
(N－Ⅱ－12)



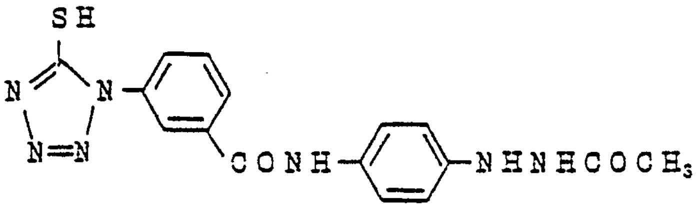
(N−II−13)



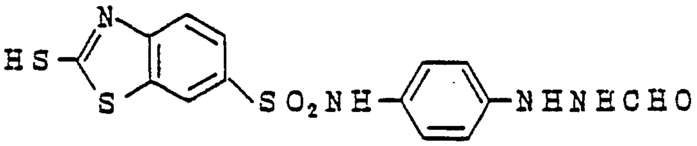
(N−II−14)



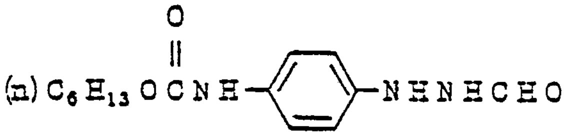
(N−II−15)



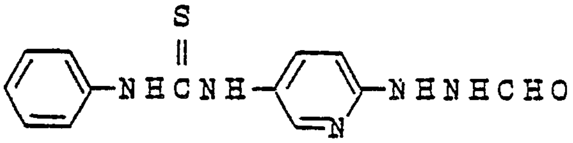
(N−II−16)



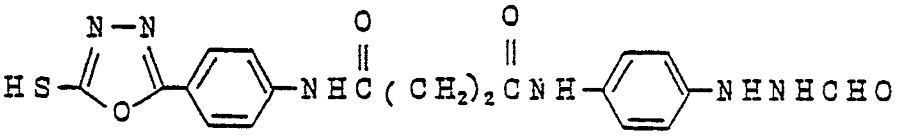
(N-Ⅱ-17)



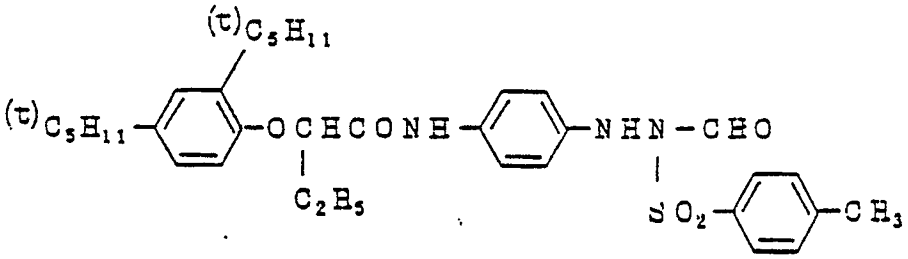
(N-Ⅱ-18)



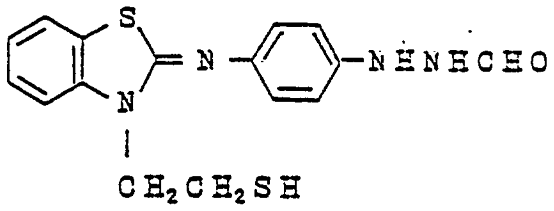
(N-Ⅱ-19)



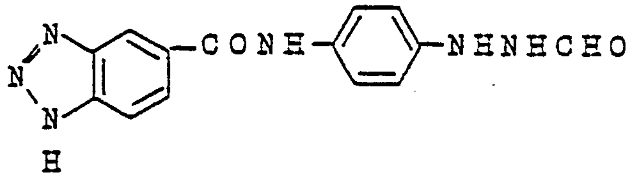
(N-Ⅱ-20)



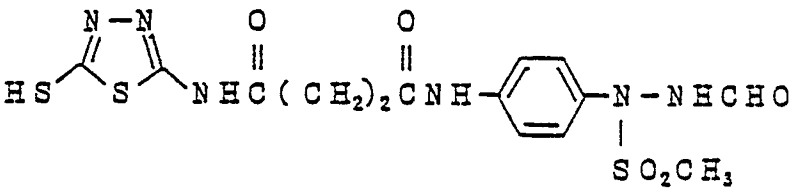
(N-II-21)



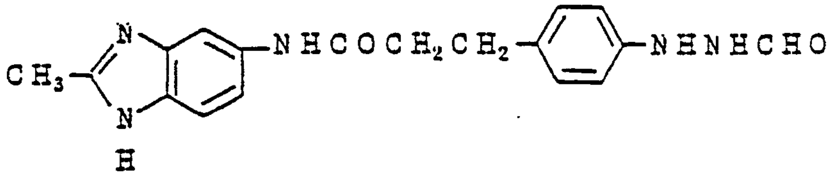
(N-II-22)



(N-II-23)



(N-II-24)



The compounds shown by formula (N-II) for use in this invention can be synthesized according to the methods described, e.g., in the patents cited in Research Disclosure, No. 15162, pages 76-77 (November, 1976), ibid., No. 22534, pages 50-54 (January, 1983), and ibid., No. 23510, pages 346-352 (November, 1983) and U.S. Patents 4,080,207, 4,269,924 and 4,276,364.

The compound shown by formula (N-I) or (N-II) in this invention may exit in any layer(s) of the photographic light-sensitive material being processed in this invention but preferably exist in the silver halide emulsion layer thereof. There is no particular restriction on the amount of the compound but the amount is usually in the range of from about 1×10^{-8} mol to about 1×10^{-2} mol, and preferably from 1×10^{-7} mol to 1×10^{-3} mol per mol of silver in the silver halide emulsion layer.

For further increasing the effect of the nucleating agent in this invention, it is preferred that the nucleating agent is used in combination with the following compounds.

That is, hydroquinones described in U.S. Patents 3,227,552 and 4,279,987, the chromans described in U.S. Patent 4,268,621, JP-A-54-103031, and Research Disclosure, No. 18264 (1979), the quinones described in Research Disclosure, No. 21206 (1981), the amines described in U.S. Patent 4,150,993, and JP-A-58-174757, the oxidizing agents described in JP-A-60-260039, and Research Disclosure, No. 16936 (1978), the catechols described in JP-A-55-21013, and JP-A-55-65944, the compound releasing a nucleating agent at development described in JP-A-60-107029, the thioureas described in JP-A-60-95533, and the spirobisindanes described in JP-A-55-65944.

In addition, in this invention, the use of the nucleating agent shown by formula (N-I) described above is preferred and in this case, it is preferred to employ the following embodiments (1) to (8) in order and embodiment (8) is most preferred.

(1) The case that the nucleating agent has an adsorption accelerating group to silver halide shown by X^{11} as a substituent.

(2) The aforesaid case (1), wherein the absorption accelerating group to silver halide shown by X^{11} is composed of a thioamido group, a heterocyclic mercapto group, or a nitrogen-containing heterocyclic ring forming imino silver.

(3) The aforesaid case (2), wherein the heterocyclic being completed by Z^{11} is quinolinium, isoquinolinium, naphthopyridinium or benzithiazolium.

(4) The aforesaid case (2), wherein the heterocyclic ring being completed by Z^{11} is quinolinium.

(5) The aforesaid case (2), Wherein R^{11}, or Z^{11} has an alkinyl group as a substituent.

(6) The aforesaid case (5), Wherein R^{11} is a propargyl group.

(7) The aforesaid case (2), wherein X^{11} is a thiourethane group as a thioamido group or X^{11} is a mercaptotetrazole as a heterocyclic mercapto group.

(8) The aforesaid case (6), wherein R^{11} combines with the heterocyclic ring formed by Z^{11} to form a ring.

Also, in the case of using the nucleating agent shown by aforesaid formula (N-II), it is preferred to employ the following embodiments (1) to (6) in order and embodiment (7) is particularly preferred.

(1) The case that the nucleating agent has an adsorption accelerating group to silver halide shown by X^{21} as a substituent.

(2) The aforesaid case (1), wherein the adsorption accelerating group to silver halide shown by X^{21} is a heterocyclic mercapto ring or a nitrogen-containing heterocyclic ring forming imino silver.

(3) The aforesaid case (3), wherein the group shown by G-R^{22} is a formyl group.

(4) The aforesaid case (3), wherein R^{23} and R^{24} are a hydrogen atom.

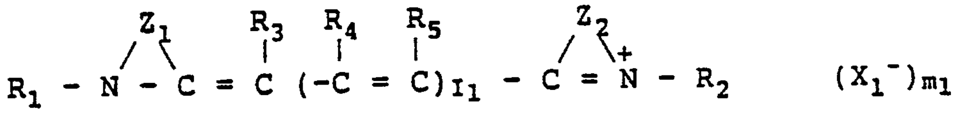
(5) The aforesaid case (3), wherein R^{21} is an aromatic group.

(6) The aforesaid case (2), wherein the heterocyclic mercapto group shown by X^2 is 5-mercaptotetrazole or 5-mercapto-1,2,4-triazole.

In this invention, the nucleating agent shown by formula (N-I) and the nucleating agent shown by formula (N-II) can be used together.

Next, the compound shown by formula (I) for use in this invention is explained.

The compound is a cyanine having the longest wavelength adsorption maximum on silver halide of not longer than 590 nm shown by formula (I)



$$R_1-\overset{Z_1}{\overbrace{N-C}}=\overset{R_3}{C}(-\overset{R_4}{C}=\overset{R_5}{C})_{l_1}-\overset{Z_2}{\overbrace{C=N^+}}-R_2 \qquad (X_1^-)_{m_1}$$

(I)

wherein Z_1 and Z_2, which may be the same or different, each represents an atomic group forming a 5- or 6-membered nitrogen-containing heterocyclic nucleus and l_1 represents 0 or 1. More preferred heterocyclic nuclei are as follows.

When l_1 is 0, Z_1 and Z_2, which may be the same or different, each represents thiazole, benzothiazole, naphthothiazole, dihydronaphthothiazole, selenazole, benzoselenazole, naphthoselenazole, dihydronaphthoselenazole, oxazole, benzoxazole, naphthoxazole, benzimidazole, naphthimidazole, pyridine, quinoline, imidazo[4,5-b]quinoquizaline, or 3,3-dialkylindolenine.

When l_1 is 1, Z_1 represents thiazoline, thiazole, benzothiazole, selenazoline, selenazole, benzoselenazole, oxazole, benzoxazole, naphthoxazole, imidazole, benzimidazole, naphthimidazole, or pyrroline and Z_2 represents oxazoline, oxazole, benzoxazole, naphthoxazole, thiazoline, selenazoline, pyrroline, benzimidazole, or naphthimidazole.

The nitrogen-containing heterocyclic nucleus shown by Z_1 or Z_2 may have one or more substituents. Examples of the preferred substituent are a lower alkyl group (which may be branched or may further have a substituent (e.g., a hydroxy group, a halogen atom, an aryl group, an aryloxy group, an arylthio group, a carboxy group, an alkoxy group, an alkylthio group, and an alkoxycarbonyl group) and is more preferably an alkyl group having from 1 to 10 carbon atoms (e.g., methyl, ethyl, butyl, chloroethyl, 2,2,3,3-tetrafluoropropyl, hydroxy, benzyl, tolylethyl, phenoxyethyl, phenylthio ethyl, carboxypropyl, methoxyethyl, ethylthioethyl, and ethoxycarbonylethyl)), a lower alkoxy group which may be a substituent as the substituent for the aforesaid alkyl group described above and is more preferably an alkoxy group having from 1 to 8 carbon atoms (e.g., methoxy, ethoxy, pentyloxy, ethoxymethoxy, methylthioethoxy, phenoxyethoxy, hydroxyethoxy, and chloropropoxy), a hydroxy group, a halogen atom, a cyano group, an aryl group (e.g., phenyl, tolyl, anisyl, chlorophenyl, and carboxyphenyl), an aryloxy group (e.g., tolyloxy, anisyloxy, phenoxy, and chlorophenoxy), an arylthio group (e.g., tolylthio, chlorophenylthio, and phenylthio), a lower alkylthio group which may be substituted by a substituent such as the substituent for the aforesaid lower alkyl group described above and is more preferably an alkylthio group having from 1 to 8 carbon atoms (e.g., methylthio, ethylthio, hydroxyethylthio, carboxyethylthio, chloroethylthio, and benzylthio), an acylamino group (more preferably an acylamino group having not more than 8 total carbon atoms, such as, for example, acetylamino, benzoylamino, methanesulfonylamino, and benzenesulfonylamino), a carboxy group, a lower alkoxycarbonyl group (more preferably an alkoxycarbonyl group having not more than 6 carbon atoms, such as, for example, ethoxycarbonyl and butoxycarbonyl), a perfluoroalkyl group (more preferably a perfluoroalkyl group having from 1 to 5 total carbon atoms, such as, for example, trifluoromethyl and difluoromethyl), and an acyl group (more preferably an acyl group having not more than 8 total carbon atoms, such as acetyl, propionyl, benzoyl, and benzenesulfonyl).

Specific examples of the nitrogen-containing heterocyclic nucleus shown by Z_1 and Z_2 are thiazoline, 4-methylthiazoline, thiazole, 4-methylthiazole, 4,5-dimethylthiazole, 4-phenylthiazole, benzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-ethylbenzothiazole, 5,6-dimethylbenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-butoxybenzothiazole, 5,6-dimethoxybenzothiazole, 5-methoxy-6-methylbenzothiazole, 5-chlorobenzothiazole, 5-chloro-6-methylbenzothiazole, 5-phenylbenzothiazole, 5-acetylaminobenzothiazole, 6-propionylaminobenzothiazole, 5-hydroxybenzothiazole, 5-hydroxy-6-methylbenzothiazole, 5-ethoxycarbonylbenzothiazole, 5-carboxybenzothiazole, naphtho[1,2-d]thiazole, naphtho[2,1-d]-thiazole, 5-methylnaphtho[1,2-d]thiazole, 8-methoxynaphtho[1,2-d]thiazole, 8,9-dihydronaphthothiazole, 3,3-diethylindolenine, 3,3-dipropylindolenine, 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, selenazoline, selenazole, benzoselenazole, 5-methylbenzoselenazole, 6-methylbenzoselenazole, 5-methoxybenzoselenazole, 6-methoxybenzoselenazole, 5-chlorobenzoselenazole, 5,6-dimethylbenzoselenazole, 5-hydroxybenzoselenazole, 5-hydroxy-6-methylbenzoselenazole, 5,6-dimethoxybenzoselenazole, 5-ethoxycarbonylbenzoselenazole, naphtho[1,2-d]selenazole, naphtho[2,1-d]selenazole, oxazole, 4-methyloxazole, 4,5-dimethyloxazole, 4-phenyloxazole, benzoxazole, 5-hydroxybenzoxazole, 5-methoxybenzoxazole, 5-phenylbenzoxazole, 5-phenethylbenzoxazole, 5-phenoxybenzoxazole, 5-chlorobenzoxazole, 5-chloro-6-methylbenzoxazole, 5-phenylthiobenzoxazole, 6-ethoxy-5-hydroxybenzoxazole, 6-methoxybenzoxazole, naphth[1,2-d]-oxazole, naphth[2,1-d]oxazole, naphth[2,3-d]oxazole, 1-ethyl-5-cyanobenzimidazole, 1-ethyl-5-chlorobenzimidazole, 1-ethyl-5,6-dichlorobenzimidazole, 1-ethyl-6-chloro-5-cyanobenzimidazole, 1-ethyl-6-chloro-5-trifluoromethylbenzimidazole, 1-propyl-5-butoxycarbonylbenzimidazole, 1-benzyl-5-methylsulfonylbenzimidazole, 1-allyl-5-chloro-6-acetylbenzimidazole, 1-ethylnaphth[1,2-d]imidazole, 1-ethyl-6-chloronaphth-[2,3-d]imidazole, 2-quinoline, 4-quinoline, 8-fluoro-4-quinoline, 6-methyl-2-quinoline, 6-hydroxy-2-quinoline, and 6-methoxy-2-quinoline.

In formula (I), R_1 and R_2, which may be the same or different, each represents an alkyl group or an alkenyl group each having not more than 10 carbon atoms and may have a substituent. As the preferred substituent for the alkyl group or the alkenyl group, there are, for example, a sulfo group, a carboxy group, a halogen atom, a hydroxy group, an alkoxy group having not more than 6 carbon atoms, an aryl group having not more than 8 carbon atoms, which may be substituted (e.g., phenyl, tolyl, sulfophenyl, and carboxyphenyl), a heterocyclic group (e.g., furyl and thienyl), an aryloxy group having not more than 8 carbon atoms, which may be substituted (e.g., chlorophenoxy, phenoxy, sulfophenoxy, and hydroxyphenoxy), an acyl group having not more than 8 carbon atoms (e.g., benzenesulfonyl, methanesulfonyl, acetyl, and propionyl), an alkoxycarbonyl group having not more than 6 carbon atoms (e.g., ethoxycarbonyl and butoxy carbonyl), a cyano group, an alkylthio group having not more than 6 carbon atoms (e.g., methylthio and ethylthio), an arylthio group having not more than 8 carbon atoms, which may be substituted (e.g., phenylthio and tolylthio), a carbamoyl group having not more than 8 carbon atoms, which may be substituted (e.g., carbamoyl and N-ethylcarbamoyl), and an acylamino group having not more than 8 carbon atoms (e.g., acetylamino and methanesulfonylamino).

The alkyl group or the alkenyl group may have one or more substituents.

Specific examples of the alkyl group or alkenyl group shown by R_1 and R_2 are methyl, ethyl, propyl, allyl pentyl, hexyl, methoxyethyl, ethoxyethyl, phenethyl, tolylethyl, sulfophenethyl, 2,2,2-trifluoroethyl, 2,2,3,3-tetrafluoropropyl, carbamoylethyl, hydroxyethyl, 2-(2 hydroxyethoxy)ethyl, carboxymethyl, carboxyethyl, ethoxycarbonylmethyl, sulfoethyl, 2-chloro-3-sulfopropyl, 3-sulfopropyl, 2-hydroxy-3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, 2-(2,3-dihydroxypropyloxy)ethyl, and 2-[2-(3-sulfopropyloxy)ethoxy]ethyl.

R_3 and R_5 represent a hydrogen atom. Also, R_3 and R_1 or R_5 and R_2 may combine with each other to form a 5- or 6-membered ring.

R_4 represents a hydrogen atom or a lower alkyl group which may be substituted (e.g., methyl, ethyl, propyl, methoxyethyl, phenethyl, and more preferably an alkyl group having not more than 5 carbon atoms).

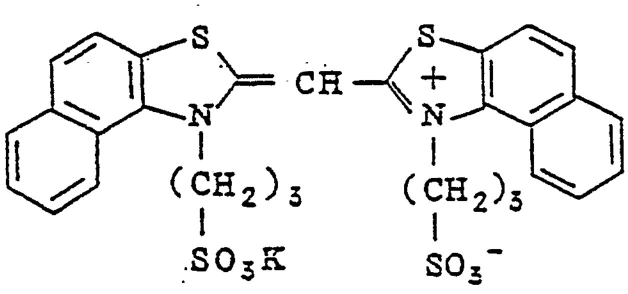
Also, in formula (I), X_1 represents an acid anion residue and m_1 represents 0 or 1 and when the dye shown by the formula forms an intramolecular salt, m_1 is 0.

In the preferred sensitizing dye shown by aforesaid formula (I), l_1 is 1, Z_1 is an atomic group necessary for forming a heterocyclic nucleus such as oxazole, benzoxazole, naphthoxazole, etc., Z_2 is an atomic group necessary for forming a heterocyclic nucleus such as benzimidazole or naphthimidazole (the heterocyclic nucleus shown by Z_1 and Z_2 may have at least one substituent as described above but when Z_2 represents a benzimidazole nucleus or a naphthimidazole nucleus, the substituent is preferably an electron attractive substituent), at least one of said R_1 and R_2 is a group having a sulfo group or a carboxy group, or a hydroxy group, and R_4 is a hydrogen atom.

In the particularly preferred sensitizing dyes shown by formula (I), Z_1 is an atomic group forming a benzoxazole nucleus, Z_2 is an atomic group forming a benzimidazole nucleus, at least one of R_1 and R_2 is a group having a sulfo group or a carboxy group, R_4 is a hydrogen atom, and l_1 is 1. The heterocyclic nucleus shown by Z_1 and Z_2 may have at least one substituent as described above. When Z_1 or Z_2 is a benzimidazole nucleus, the particularly preferred substituent is chlorine, fluorine, a cyano group, an alkoxycarbonyl group having not more than 5 total carbon atoms, an acyl group having not more than 7 total carbon atoms, or a perfluoroalkyl group having not more than 4 carbon atoms, such as trifluoromethyl group, etc., and when Z_1 and Z_2 represents other heterocyclic nucleus, the particularly preferred substituent is a phenyl group having not more than 8 carbon atoms, which may be substituted, an alkyl group having not more than 5 carbon atoms, an alkoxy group having not more than 5 carbon atoms, an acylamino group having not more than 5 total carbon atoms, a carboxy group, an alkoxycarbonyl group having not more than 5 total carbon atoms, a benzyl group, a phenethyl group, or chlorine.

Specific non-limiting examples of the sensitizing dyes shown by aforesaid formula (I) are illustrated below.

I - 1



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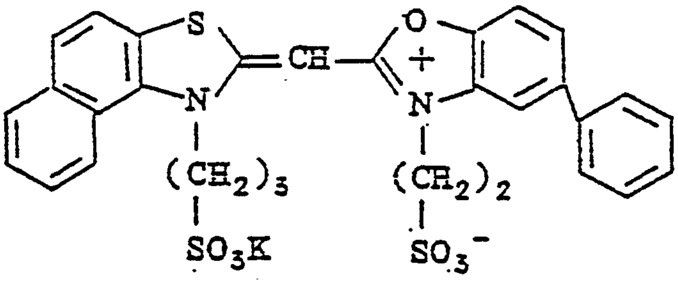
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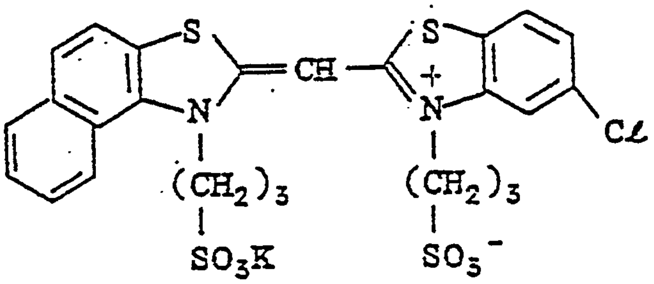
+
N
N
(CH2)3
(CH2)2
SO3K
SO3-

I - 3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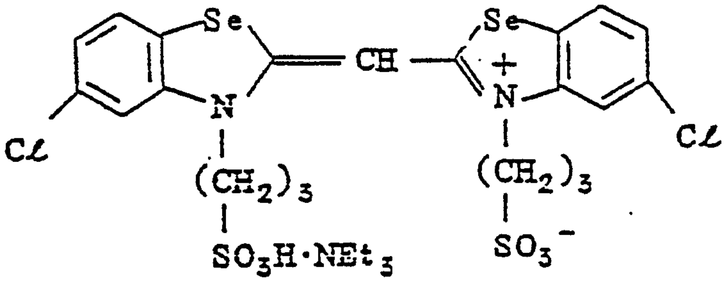
S
+
N
N
Cℓ
(CH2)3
(CH2)3
SO3K
SO3-

I - 4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CH
Se
+
N
N
Cℓ
Cℓ
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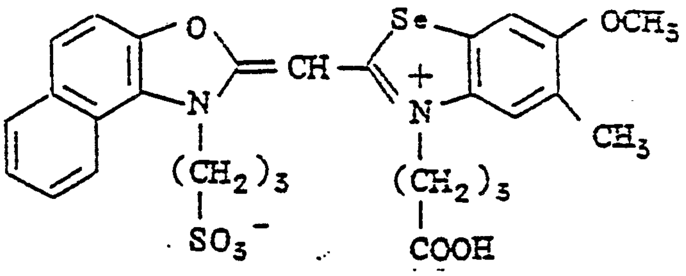
(CH2)3
SO3H·NEt3
SO3-

I - 5



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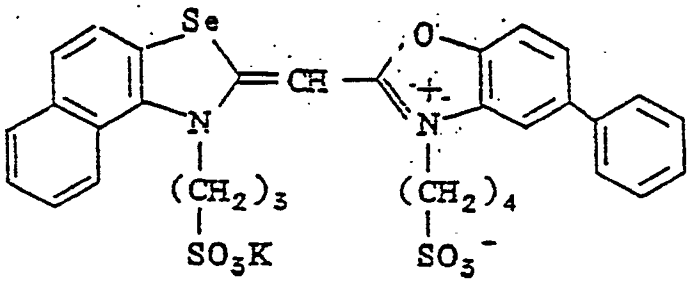

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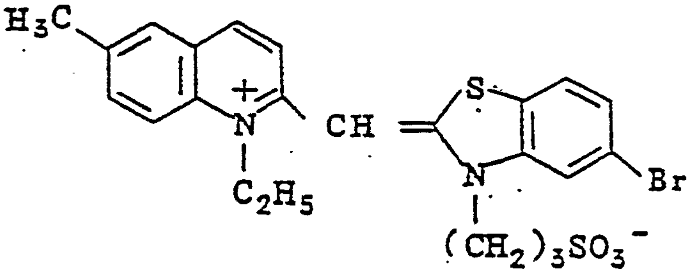

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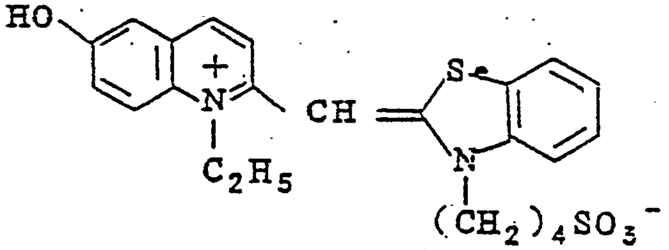

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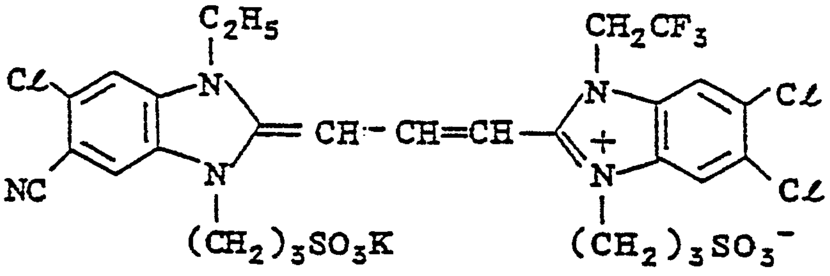

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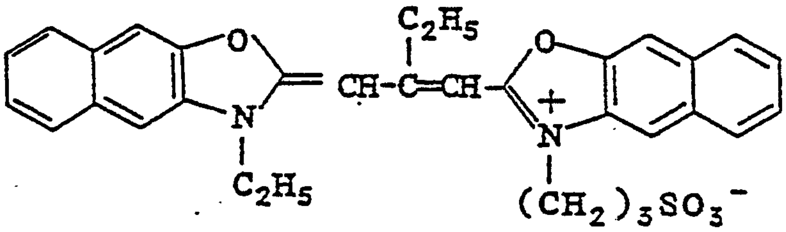

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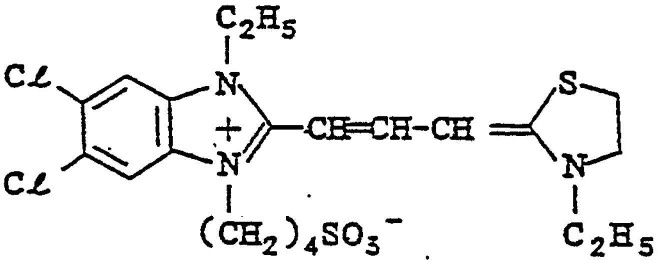

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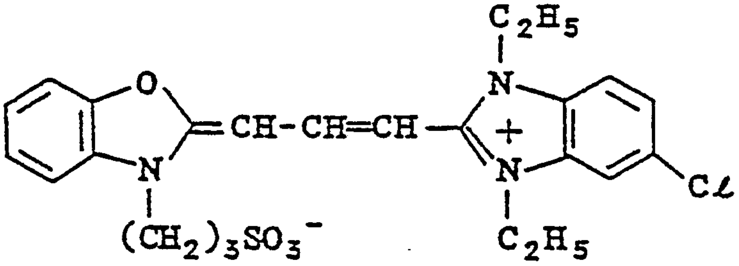

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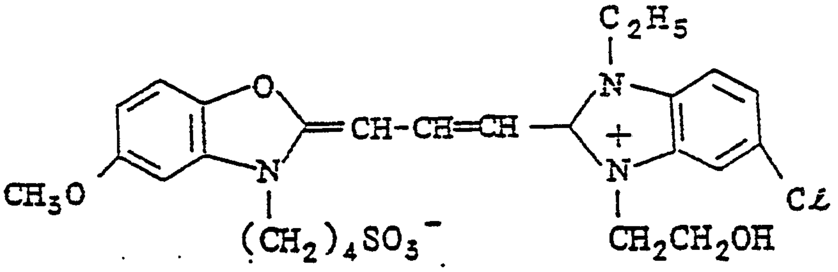

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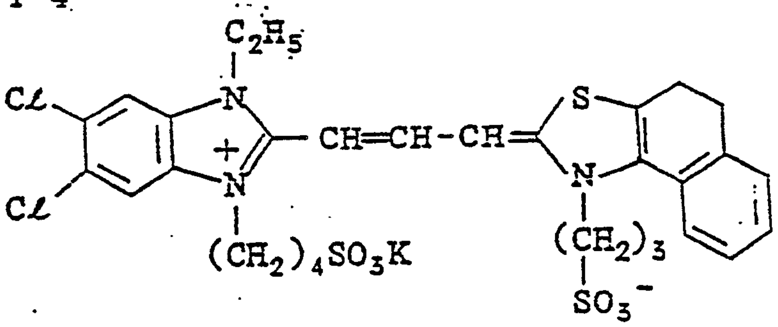

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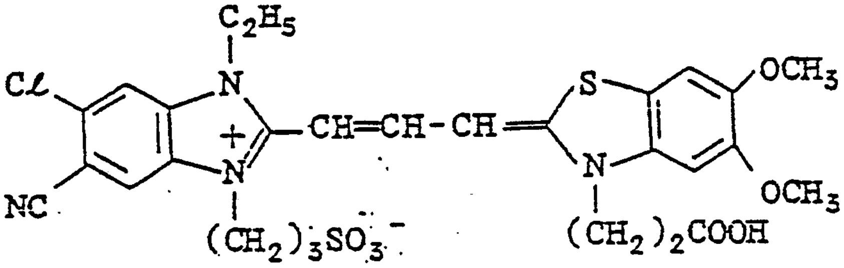

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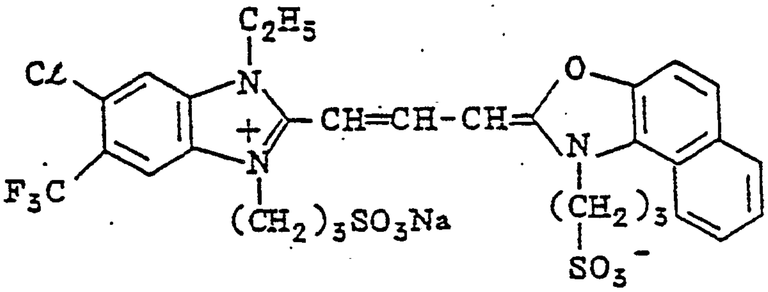

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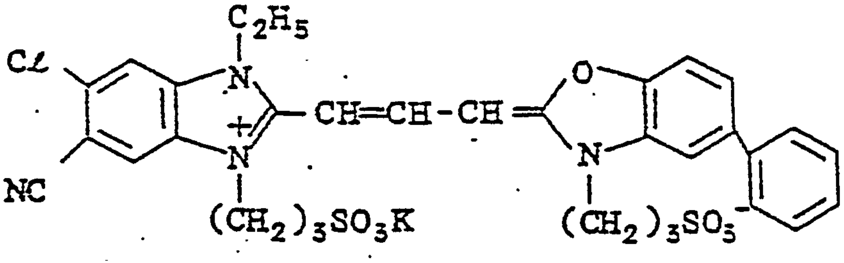

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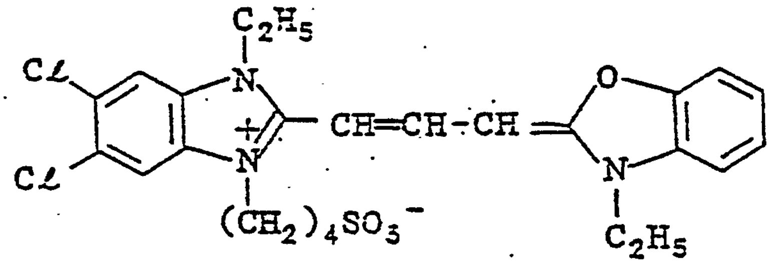

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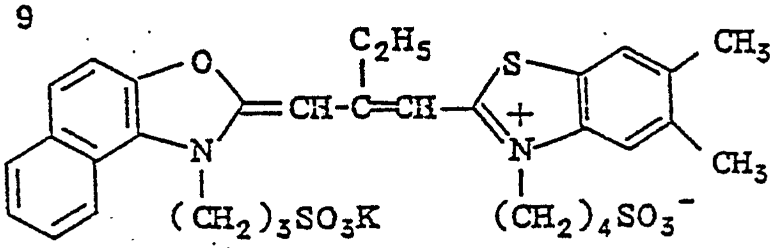

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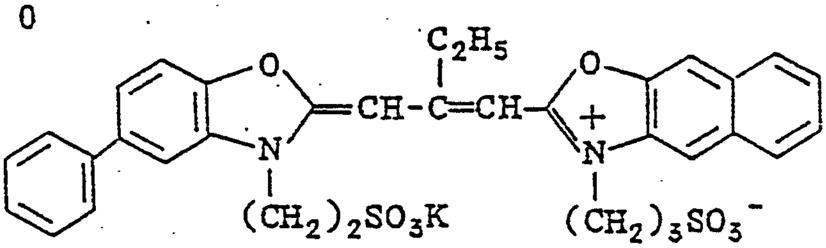

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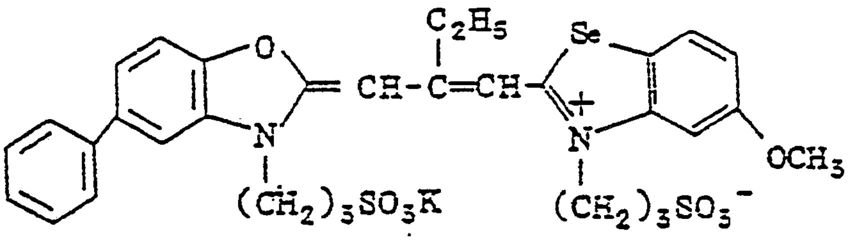

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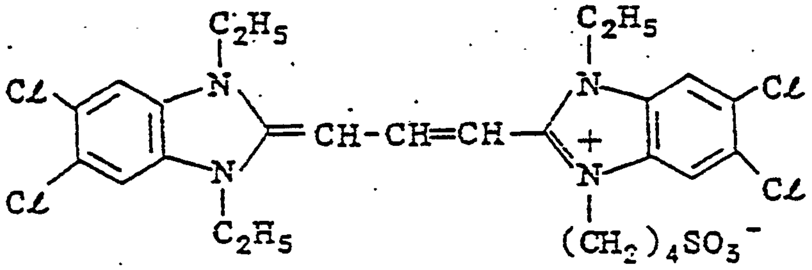

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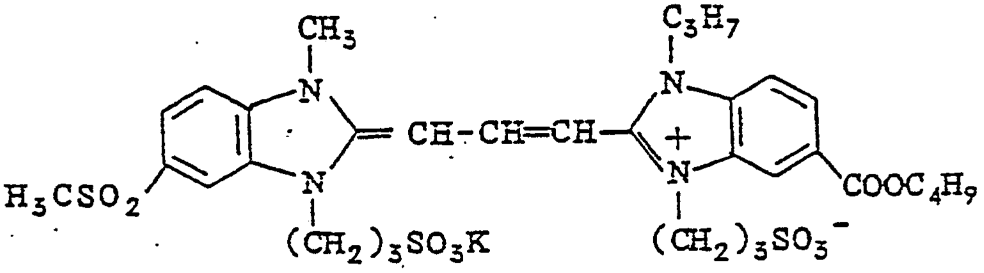

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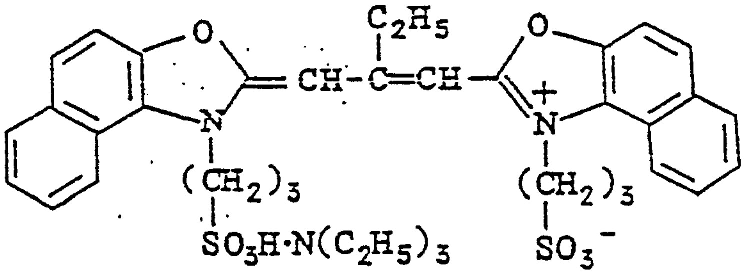

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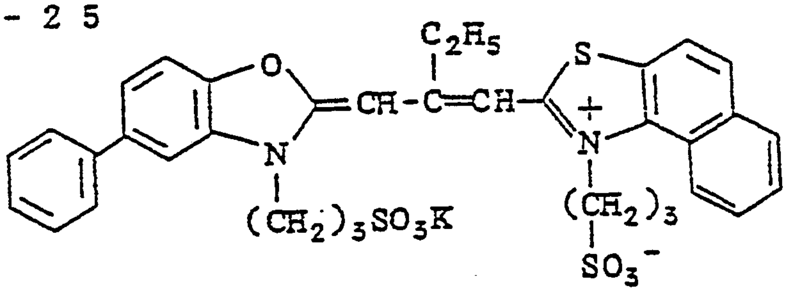

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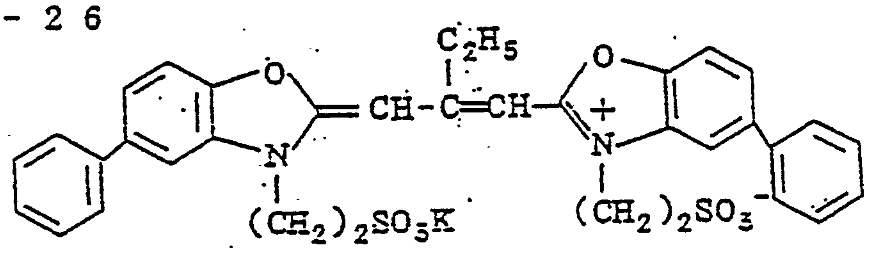

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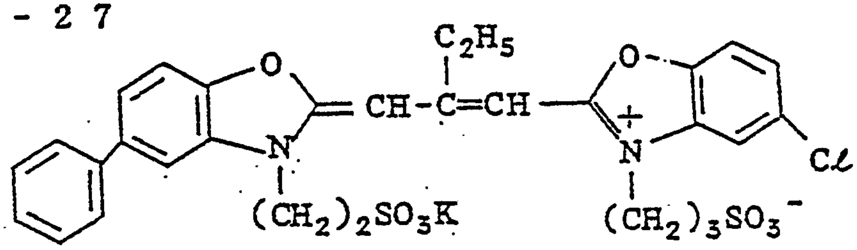
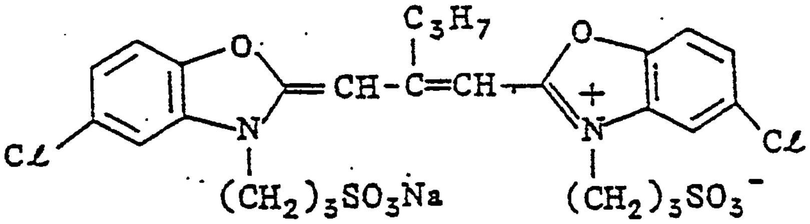


I - 28



The compounds shown by formula (I) described above are known compounds and can be synthesized according to the methods described in JP-A-52-104917, JP-B-48-25652 and JP-B-57-22368, F.M. Hamer, The Chemistry of Heterocyclic Compounds, Vol. 18, A. Weissberger ed., The Cyanine Dyes and Related Compounds, published by Interscience, New York, 1964, D.M. Sturmer, The Chemistry of Heterocyclic Compounds, Vol. 30, page 441, edited by A. Weissberger and E.C. Taylor, published by John Willey and Sons, New York.

The compound shown by formula (I) in this invention is incorporated in the internal latent image type silver halide emulsion layer preferably in an amount of from 10^{-6} to 10^{-2} mol, more preferably from 10^{-5} to 10^{-3} mol, per mol of silver halide.

The term "nucleation accelerator" in this invention means a compound which has substantially no function as the nucleating agent described hereinbefore but functions to accelerates the action of a nucleating agent to increase the maximum density of direct positive images and/or to shorten the development time necessary for obtaining a constant direct positive image density.

The nucleation accelerators which are advantageously used in this invention are shown by following formula (II):

$A[\{Y_1\}_{n1}R]_{m1}$ (II)

wherein A represents a group adsorbing to silver halide.

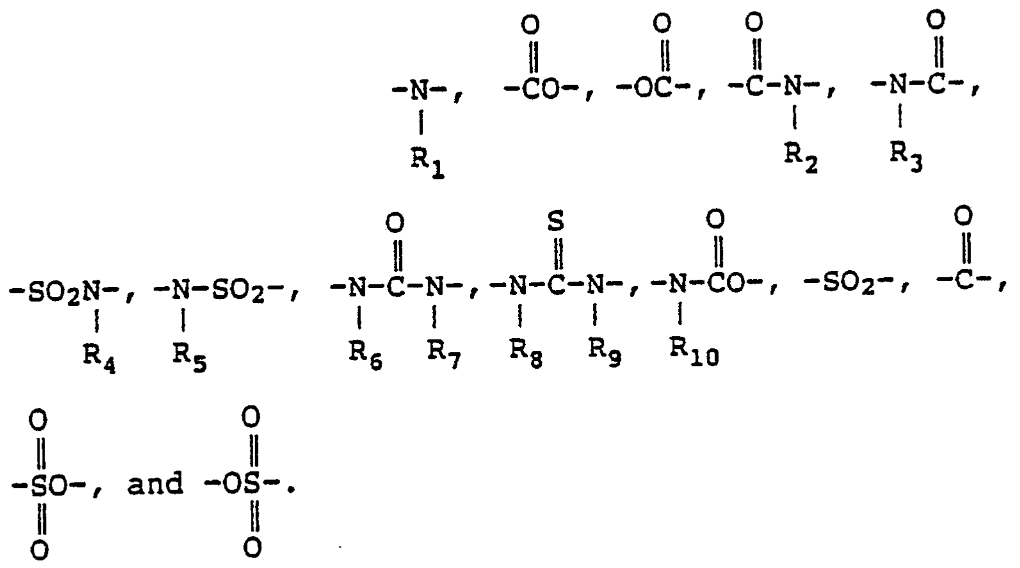
As the group adsorbing to silver halide, there are a compound having a mercapto group bonding to a heterocyclic ring, a heterocyclic compound capable of forming imino group, and a hydrocarbon compound having a mercapto group.

Examples of the mercapto compound bonding to a heterocyclic ring are substituted or unsubstituted mercaptoazoles (e.g., 5 mercaptotetrazoles, 3-mercapto-1,2,4-triazoles, 2-mercaptoimidazoles, 2-mercapto-1,3,4-thiadiazoles, 5-mercapto 1,2,4-thiadiazoles, 2-mercapto-1,3,4-oxadiazoles, 2-mercapto-1,3,4-selenadiazoles, 2-mercaptoxazoles, 2-mercaptothiazoles, 2-mercaptobenzoxazoles, 2-mercaptobenzimidazoles, and 2-mercaptobenzimidazoles) and substituted or unsubstituted mercaptopyrimidines (e.g., 2-mercaptopyrimidines).

Examples of the heterocyclic compound capable of forming imino silver are indazoles, benzimidazoles, benztriazoles, benzoxazoles, benzthiazoles, imidazoles, thiazoles, oxazoles, triazoles, tetrazoles, azaindenes, pyrazoles, and indoles each may be substituted.

As hydrocarbon compounds having a mercapto group, there are, for example, alkylmercaptans, arylmercaptans, alkenylmercaptans, and aralkylmercaptans.

In formula (II), Y_1 represents a divalent linkage group composed of an atom or an atomic group selected from hydrogen atom, carbon atom, nitrogen atom, oxygen atom, and sulfur atom. Examples of the divalent linkage group are -S-, -O-,



$$-\underset{\underset{R_1}{|}}{N}-,\ -\overset{\overset{O}{\|}}{C}O-,\ -O\overset{\overset{O}{\|}}{C}-,\ -\overset{\overset{O}{\|}}{C}-\underset{\underset{R_2}{|}}{N}-,\ -\underset{\underset{R_3}{|}}{N}-\overset{\overset{O}{\|}}{C}-,$$

$$-SO_2\underset{\underset{R_4}{|}}{N}-,\ -\underset{\underset{R_5}{|}}{N}-SO_2-,\ -\underset{\underset{R_6}{|}}{N}-\overset{\overset{O}{\|}}{C}-\underset{\underset{R_7}{|}}{N}-,\ -\underset{\underset{R_8}{|}}{N}-\overset{\overset{S}{\|}}{C}-\underset{\underset{R_9}{|}}{N}-,\ -\underset{\underset{R_{10}}{|}}{N}-\overset{\overset{O}{\|}}{C}O-,\ -SO_2-,\ -\overset{\overset{O}{\|}}{C}-,$$

$$-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}O-,\ \text{and}\ -O\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-.$$

Each of these linkage groups may be bonded to A or a heterocyclic ring as described below through a straight chain or branched alkylene group (e.g., methylene, ethylene, propylene, butylene, hexylene, and 1-methylethylene) or a substituted or unsubstituted arylene group (e.g., phenylene and naphthylene).

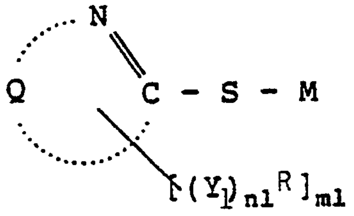
In the aforesaid formulae, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9 and R_{10} each represents a hydrogen atom, a substituted or unsubstituted alkyl group (e.g., methyl, ethyl, propyl, and n-butyl), a substituted or unsubstituted aryl group (e.g., phenyl and 2-methylphenyl), a substituted or unsubstituted alkenyl group (e.g., propenyl and 1-methylvinyl), or a substituted or unsubstituted aralkyl group (e.g., benzyl and phenethyl).

In formula (II), R represents an organic group containing at least one of a thioether group, an amino group (including a form of salt), an ammonium group, an ether group, and a heterocyclic group (including a form of salt). As such an organic group, there are the groups each formed by the combination of the aforesaid group and a group selected from a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group and a substituted or unsubstituted aryl group.

Specific examples of the organic group are hydrochlorides of dimethylaminoethyl, aminoethyl, diethylaminoethyl, dibutylaminoethyl, or dimethylaminopropyl; as well as dimethylaminoethylthioethyl, 4-dimethylaminophenyl, 4-dimethylaminobenzyl, methylthioethyl, ethylthiopropyl, 4-methiothio-3-cyanophenyl, methylthiomethyl, trimethylammonioethyl, methoxyethyl, methoxyethoxyethoxyethyl, methoxyethylthioethyl, 3,4- dimethoxyphenyl, 3-chloro-4-methoxyphenyl, morpholinoethyl, 1-imidazolylethyl, morpholinoethylthioethyl, pyrrolidinoethyl, piperidinopropyl, 2-pyridylmethyl, 2-(1-imidazolyl)ethylthioethyl, pyrazolylethyl, triazolylethyl, and methoxyethoxyethoxyethoxycarbonylaminoethyl.

In formula (II), n_1 represents 0 or 1 and m_1 represents 1 or 2.

In the compounds shown by formula (II) described above, the compounds shown by following formulae (III) to (VIII) are preferred.



(III)

wherein Q represents an atomic group necessary for forming a 5- or 6-membered heterocyclic ring formed by preferably at least one kind of atoms of carbon atom, nitrogen atom, oxygen atom, sulfur atom, and selenium atom.

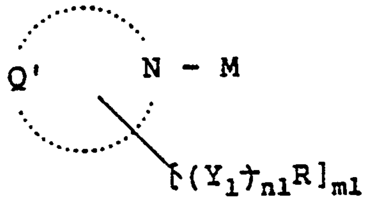
Examples of the heterocyclic ring are tetrazoles, triazoles, imidazoles, thiadiazoles, oxadi azoles, selenadiazoles, oxazoles, thiazoles, benzoxazoles, benzthiazoles, benzimidazoles, and pyrimidines.

In formula (III), M represents a hydrogen atom, an alkali metal atom (e.g., sodium and potassium), an ammonium group (e.g., trimethylammonium and dimethylbenzylammonium), or a group capable of forming hydrogen atom or an alkali metal atom under an alkaline condition (e.g., acetyl, cyanoethyl, and methanesulfonyl).

Each of the aforesaid heterocyclic rings may be substituted by a nitro group, a halogen atom (e.g., chlorine and bromine), a mercapto group, a cyano group, a substituted or unsubstituted alkyl group (e.g., methyl, ethyl, propyl, t-butyl, and cyanoethyl), a substituted or unsubstituted aryl group (e.g., phenyl, 4-methanesulfonamidophenyl, 4-methylphenyl, 3,4-dichlorophenyl, and naphthyl), a substituted or unsubstituted alkenyl group (e.g., allyl), a substituted or unsubstituted aralkyl group (e.g., benzyl, 4-methylbenzyl, and phenethyl), a substituted or unsubstituted sulfonyl group (e.g., methanesulfonyl, ethanesulfonyl, and p-toluenesulfonyl), a substituted or unsubstituted carbamoyl group (e.g., carbamoyl, methylcarbamoyl, and phenylcarbamoyl), a substituted or unsubstituted sulfamoyl group (e.g., sulfamoyl, methylsulfamoyl, and phenylsulfamoyl), a substituted or unsubstituted carbonamido group (e.g., acetamido, benzamido), a substituted or unsubstituted sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido, and p-toluenesulfonamido), a substituted or unsubstituted acyloxy group (e.g., acetyloxy and benzoyloxy), a substituted or unsubstituted sulfonyloxy group (e.g., methanesulfonyloxy group), a substituted or unsubstituted ureido group (e.g., ureido, methylureido, ethylureido, and phenylureido), a substituted or unsubstituted thioureido group (e.g., thioureido and methylthioureido), a substituted or unsubstituted acyl group (e.g., acetyl and benzyl), a substituted or unsubstituted oxycarbonyl group (e.g., methoxycarbonyl and phenoxycarbonyl), a substituted or unsubstituted oxycarbonylamino group (e.g., methoxycarbonylamino, phenoxycarbonylamino, and 2-ethylhexyloxycarbonylamino), carboxylic acid or the salt thereof, sulfonic acid or the salt thereof, or a hydroxy group. In this case, however, it is preferred from the point of the nucleation accelerating effect that the heterocyclic ring is not substituted by the aforesaid carboxylic acid or the salt thereof, sulfonic acid or the salt thereof, or the hydroxy group.

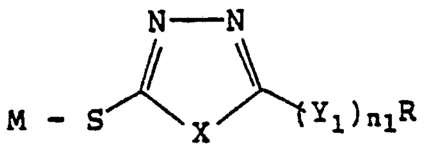
The heterocyclic ring shown by Q of formula (III) is preferably tetrazoles, triazoles, imidazoles, thiadiazoles, and oxadiazoles.

In formula (III) described above, Y_1, R, m_1, and n_1 have the same significance as those in formula (II).



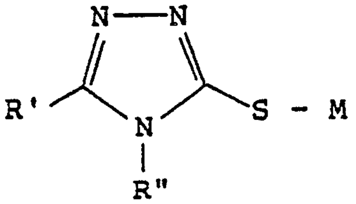
(IV)

wherein Y_1, R, m_1, n_1 and M have the same significance as those in formula (II) and Q' represents an atomic group necessary for forming a 5- or 6-membered heterocyclic ring capable of being formed with imino silver, and represents preferably an atomic group necessary for forming a 5- or 6-membered heterocyclic ring composed of atoms selected from carbon, nitrogen, oxygen, sulfur, and selenium. Also, the heterocyclic ring may be condensed to a carbon aromatic ring or a heterocyclic aromatic ring. Examples of the heterocyclic ring formed by Q′ are indazoles, benzimidazoles, benzotriazoles, benzoxazoles, benzthiazoles, imidazoles, thiazoles, oxazoles, triazoles, tetrazoles, tetraazaindenes, triazaindenes, diazaindenes, pyrazoles, and indoles.



(V)

wherein M, R, Y_1, and n_1 have the same significance as those in formula (III) and X represents an oxygen atom, a sulfur atom, or a selenium atom, and is preferably a sulfur atom.

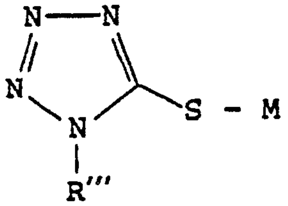


(VI)

wherein R′ represents a hydrogen atom, a halogen atom (e.g., chlorine and bromine), a nitro group, a mercapto group, an unsubstituted amino group, a substituted or unsubstituted alkyl group (e.g., methyl and ethyl), a substituted or unsubstituted alkenyl group (e.g., propenyl and 1-methylvinyl), a substituted or unsubstituted aralkyl group (e.g., benzyl and phenethyl), a substituted or unsubstituted aryl group (e.g., phenyl and 2-methylphenyl), or $(Y_1)_{n1}R$.

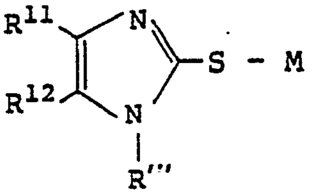
R″ represents a hydrogen atom, an unsubstituted amino group or $(Y_1)_{n1}R$ and when R′ and R″ represent $(Y_1)_{n1}R$, they may be the same or different. At least one of said R′ and R″, however, represents $(Y_1)_{n1}R$.

M, R, Y_1, and n_1 have the same significance as in formula (III).



(VII)

wherein R‴ represents $(Y_1)_{n1}R$ and M, R, Y_1, and n_1 have the same significance as those in formula (III).



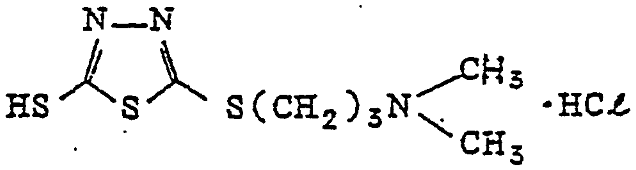
(VIII)

wherein R^{11} and R^{12} each represents a hydrogen atom, a halogen atom (e.g., chlorine and bromine), a substituted or unsubstituted amino group (e.g., amino and methylamino), a nitro group, a substituted or unsubstituted alkyl group (e.g., methyl and ethyl), a substituted or unsubstituted alkenyl group (e.g., propenyl and 1-methylvinyl), a substituted or unsubstituted aralkyl group (e.g., benzyl and phenethyl), or a substituted or unsubstituted aryl group (e.g., phenyl and 2-methylphenyl).

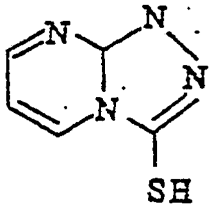
M and R‴, have the same significance as those in aforesaid formula (VII).

Specific examples of the compounds shown by formulae (II) to (VIII) being used in this invention are illustrated below but the invention is not limited to them.

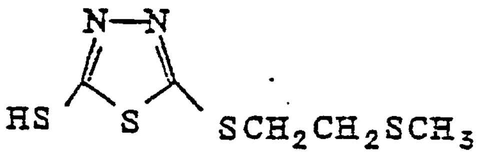
II - 1



II - 2



II - 3



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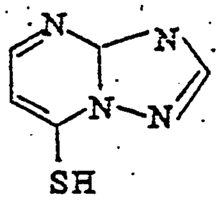

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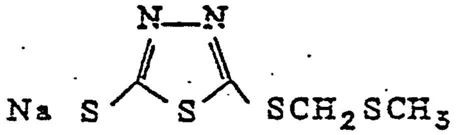

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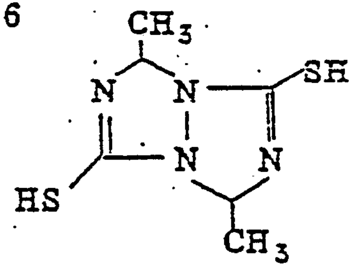

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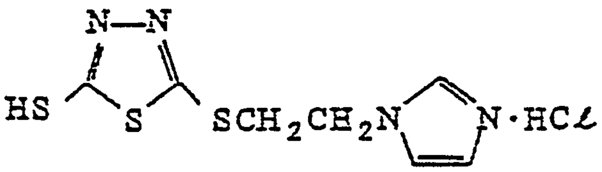

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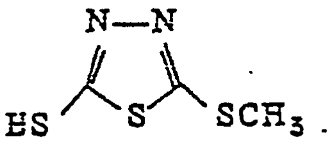

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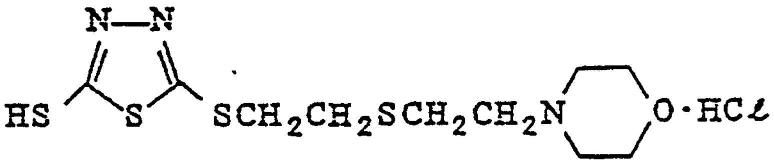

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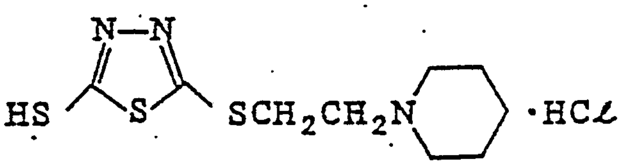

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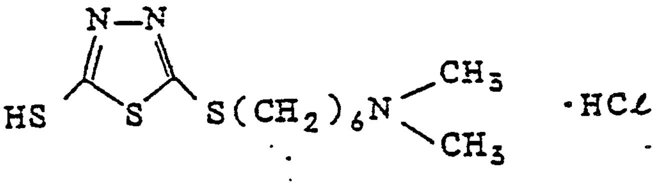

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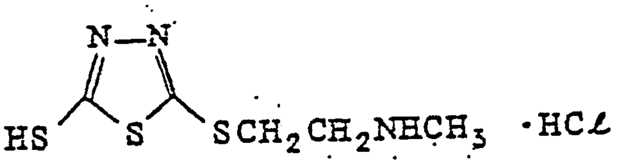

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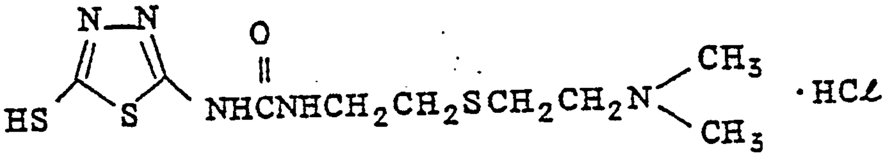

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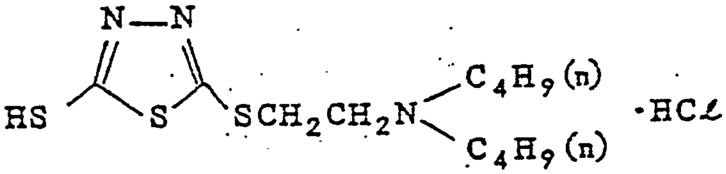

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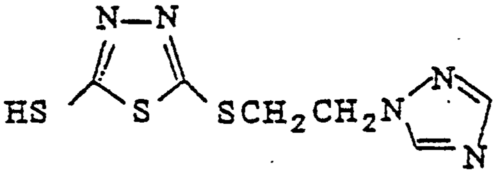

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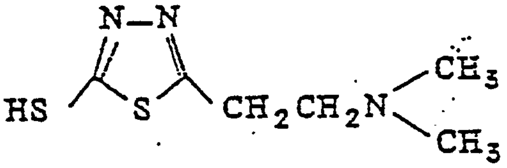

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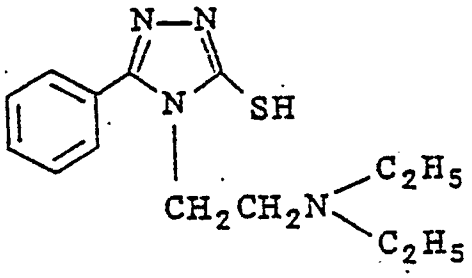
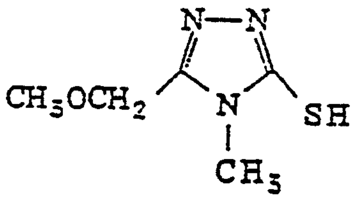


II - 18

II - 1 9



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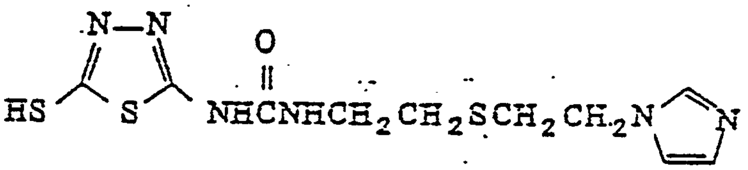
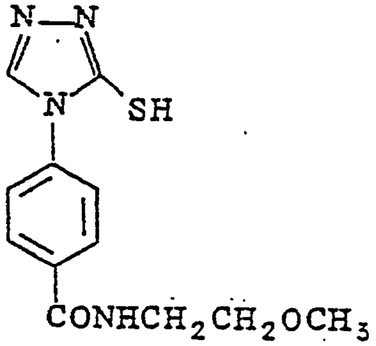


II - 2 1



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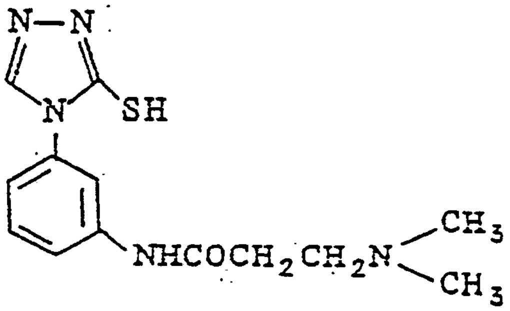

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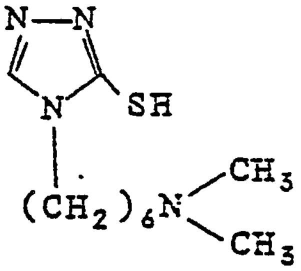

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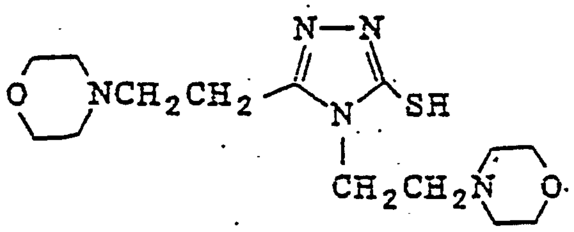

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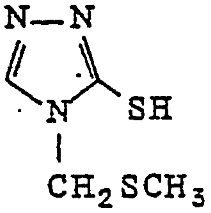

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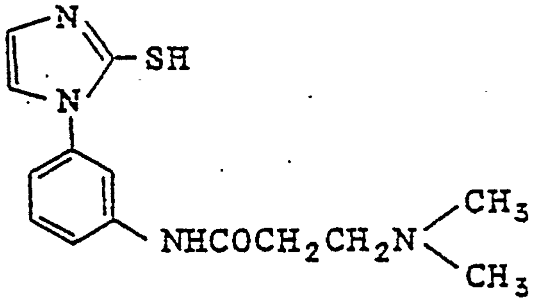

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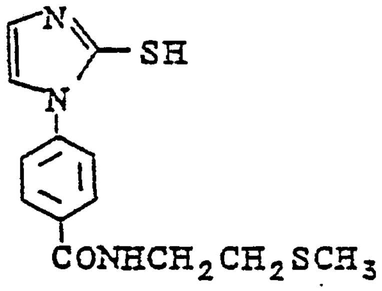

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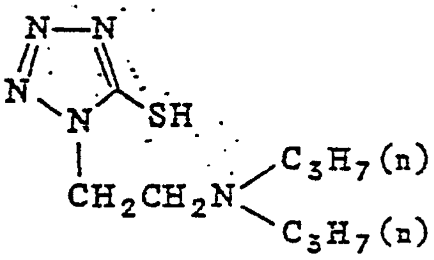

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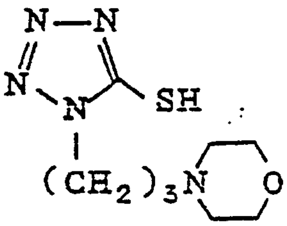

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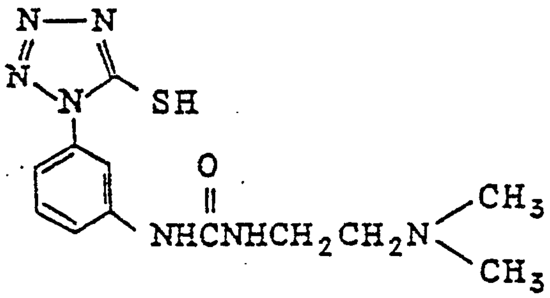

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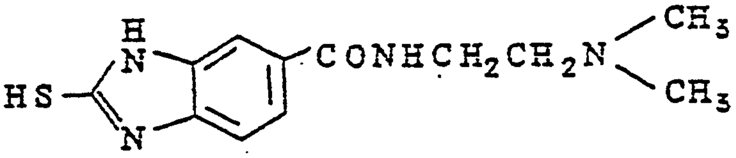

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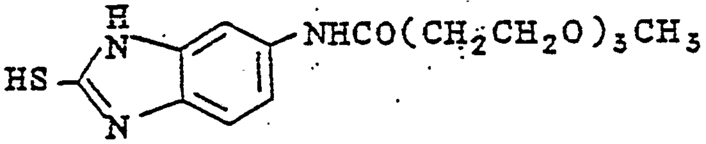

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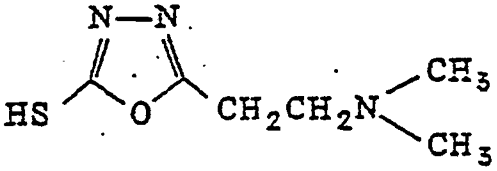

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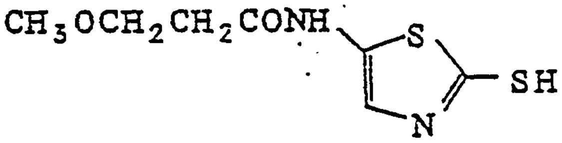

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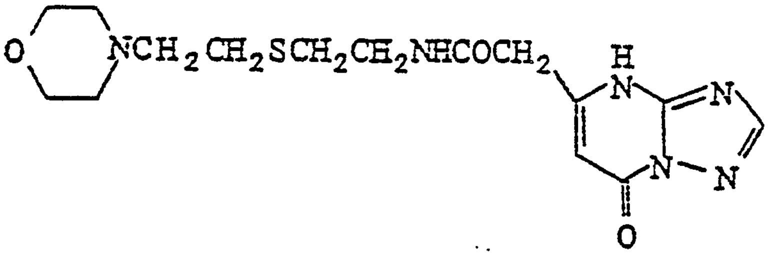

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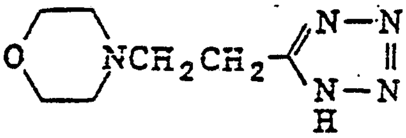

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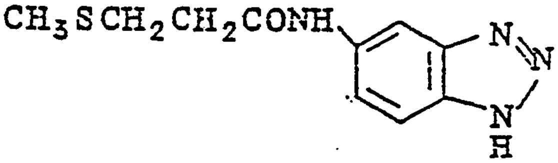

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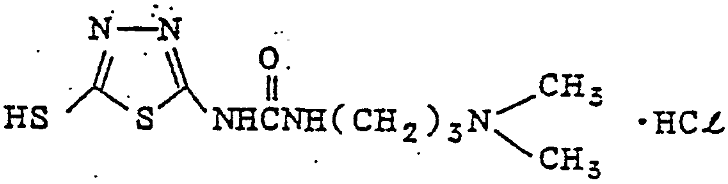

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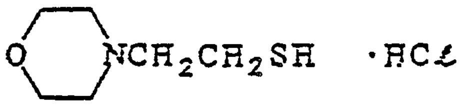

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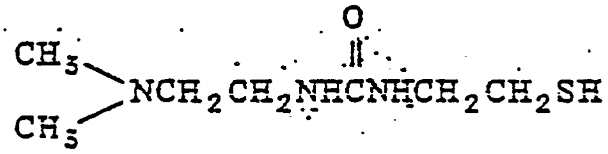
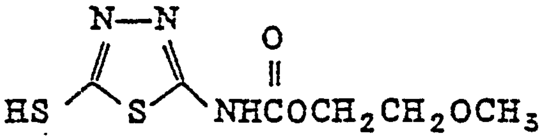


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>NCH_2CH_2NH\overset{O}{\overset{\|}{C}}NHCH_2CH_2SH$$

II - 41



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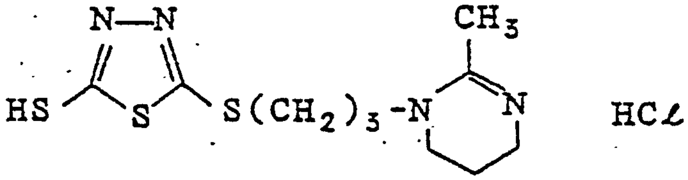

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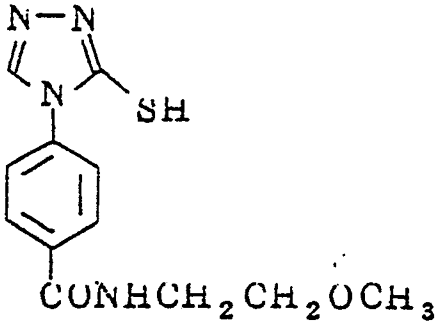

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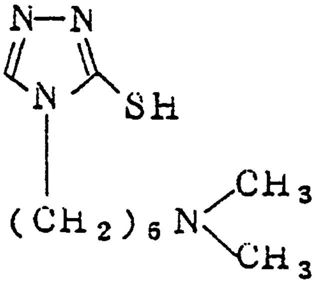

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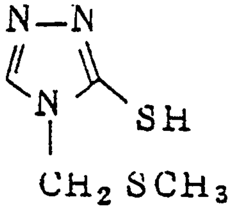

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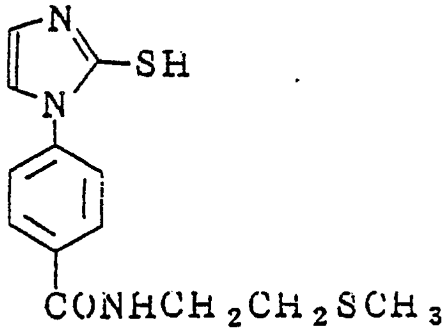

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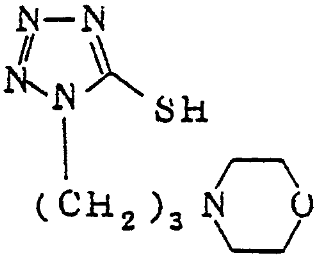

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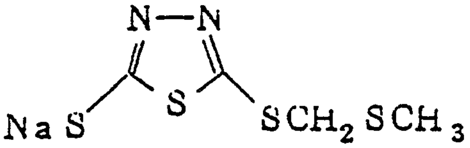

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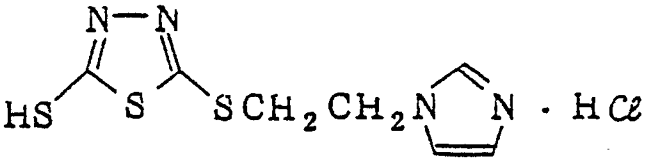

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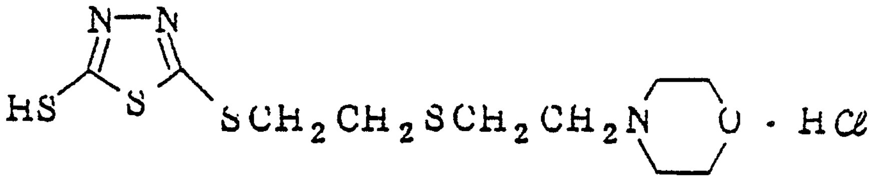

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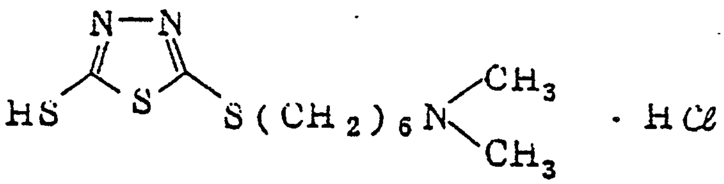

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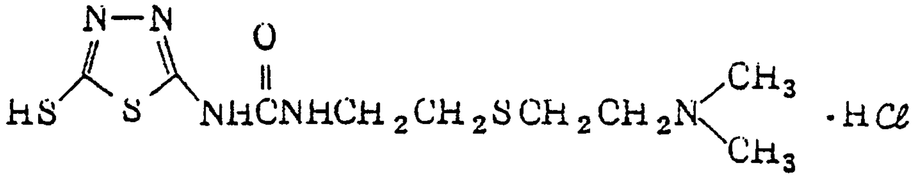

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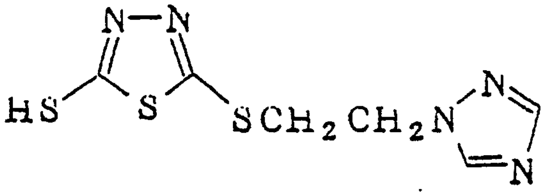

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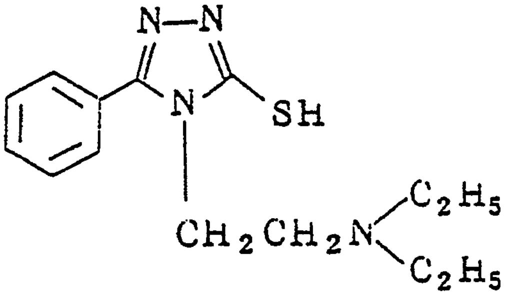

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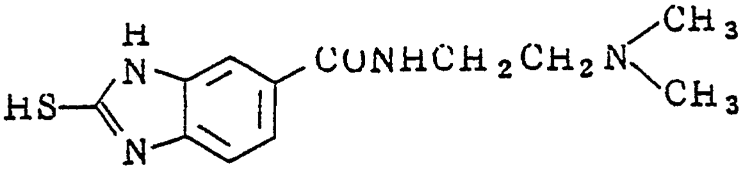
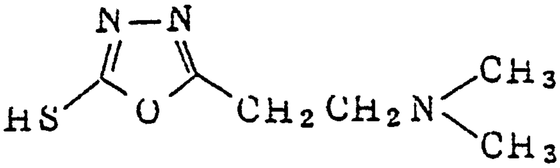


II-56



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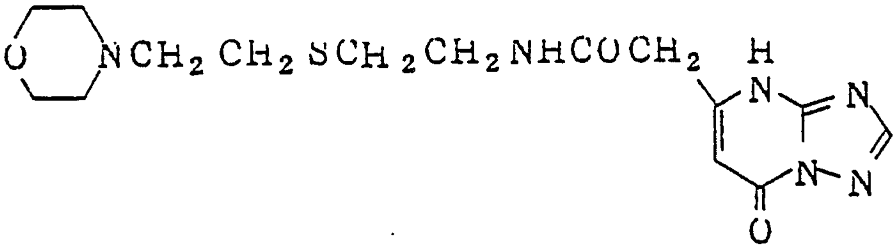
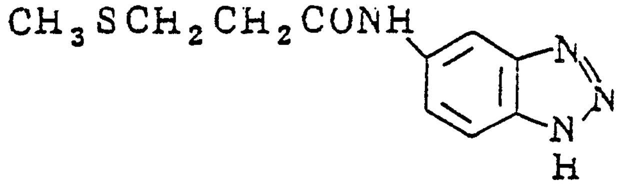
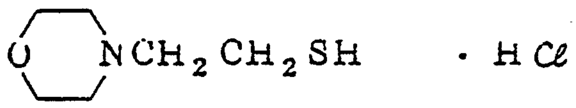


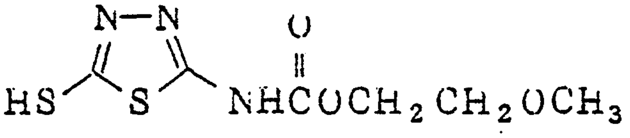
II-58



II-59



II-60



The nucleation accelerators for use in this invention can be synthesized by the methods described in Berichte der Deutschen Chemischen Gesellschaft, 28, 77 (1895), JP-A-50-37436 and JP-A-51-3231, U.S. Patents 3,295,976 and 3,376,310, Berichte der Deutschen Gesellschaft, 22, 568 (1889), ibid., 29, 2483 (1896), Journal of Chemical Society, 1932, 1806, Journal of the American Chemical Society, 71, 4000 (1949), U.S. Patents 2,585,388 and 2,541,924, Advance in Heterocyclic Chemistry, 9, 165 (1968), Organic Synthesis, IV, 569 (1963), Journal of the American Chemical Society, 45, 2390 (1923), Chemische Berichte, 9, 465 (1876), JP-B-40-28496 and JP-B-43-4135, JP-A-50-89034, U.S. Patents 3,106,467, 3,420,670, 2,271,229, 3,137,578, 3,148,066, 3,511,663, 3,060,028, 3,271,154, 3,251,691, 3,598,599, 3,148,066, 3,615,616, 3,420,664, 3,071,465, 2,444,605, 2,444,606, 2,444,607, and 2,935,404, and JP-A-63-106656.

The nucleating accelerator can be incorporated in the photographic light-sensitive material or a processing solution but is preferably incorporated in the internal latent image type silver halide emulsion or other hydrophilic colloid layers (e.g., interlayer and protective layer) of the photographic light-sensitive material. It is particularly preferred that the nucleating accelerator exists in the silver halide emulsion layer or a layer adjacent thereto.

The addition amount of the nucleation accelerator is preferably from 10^{-6} to 10^{-2} mol, and more preferably from 10^{-5} to 10^{-2} mol per mol of silver halide.

Also, when the nucleation accelerator is added to a processing solution, i.e., to a developer or the pre-bath thereof, the amount thereof is preferably from 10^{-8} to 10^{-3} mol, and more preferably from 10^{-7} to 10^{-4} mol per liter of the solution.

The previously unfogged internal latent image type silver halide emulsion for use in this invention is a silver halide emulsion containing silver halide grains having previously unfogged surfaces and forming latent images mainly in the inside thereof. More practically, the maximum density of the silver halide emulsion in the case of coating a definite amount of the emulsion on a transparent support, light-exposing the emulsion layer for a definite time of from 0.01 second to 10 seconds, developing it by developer A shown below (internal type developer) for 6 minutes at 20 °C, and measuring the density by an ordinary photographic density measuring method is preferably at least 5 times, and more preferably at least 10 times higher than the maximum density thereof obtained by coating and light-exposing the emulsion by the same manners as above and developing the emulsion layer by developer B shown below (surface developer) for 5 minutes at 18 °C.

Surface Developer B:	
Metol	2.5 g
ℓ-Ascorbic Acid	10 g
$NaBO_2 \cdot 4H_2O$	35 g
KBr	1 g
Water to make	1 liter
Internal Developer A	
Metol	2 g
Sodium Sulfite (anhydrous)	90 g
Hydroquinone	8 g
Sodium Carbonate (mono-hydrate)	52.5 g
KBr	5 g
KI	0.5 g
Water to make	1 liter

Practical examples of the internal latent image type silver halide emulsions are conversion type silver halide emulsions described in British Patent 1,011,062 and U.S. Patents 2,592,250 and 2,456,943 and core/shell type silver halide emulsions described in JP-A-47-32813, JP-A-47-32814, JP-A-52-134721, JP-A-52-156614, JP-A-53- 60222, JP-A-53-66218, JP-A-53-66727, JP-A-55-127549, JP-A-57-136641, JP-A-58-70221, JP-A-59-208540, JP-A-59-216136, JP-A-60-107641, JP-A-60-247237, JP-A-61-2148, JP-A-61-3137, JP-A-62-194248, JP-B-56-18939, JP-B-58-1412, JP-B-58-1415, JP-B-58-6935, JP-B-58-108528, U.S. Patents 3,206,313, 3,317,322, 3,761,266, 3,761,276, 3,850,637, 3,923,513, 4,035,185, 4,395,478, 4,504,570, European Patent 17148,and Research Disclosure, No. 16345 (November, 1977).

The typical composition of the silver halide for the silver halide emulsion for use in this invention is silver chloride, silver bromide or a mixed silver halide such as silver chlorobromide, silver chloroiodobromide, and silver iodobromide. The silver halide emulsion which is preferably used in this invention is silver chloro(iodo)bromide, silver (iodo)chloride, or silver (iodo)bromide containing from 0 to 3 mol% silver iodide.

The mean grain size (shown by the diameter of the grains when the grain is spherical or similar to spherical, and shown, in the case of cubic grains, the long side length as the grain size) of the silver halide grains is preferably from 0.1 µm to 2 µm, and particularly preferably from 0.15 µm to 1 µm.

Also, the thickness of the shell is preferably from 0.01 µm to 1 µm, and more preferably from 0.05 µm to 0.5 µm.

The grain size distribution of the silver halide grains may be narrow or broad but for improving the graininess and sharpness of images formed, a so-called mono-dispersed emulsion wherein at least 90%, in particular at least 95% by grain number or weight of the entire silver halide grains are within ±40% (more preferably within ±30%, and most preferably within 20%) of the mean grain size is preferably used in this invention. Also, for satisfying the desired gradation for the photographic light-sensitive material, two or more kinds of mono-dispersed silver halide emulsions each having a different grain size can be used for emulsion layers having substantially the same color sensitivity or plural silver halide grains each having the same mean grain size but having different sensitivity may be used for one emulsion layer or separate layers. Furthermore, a combination of two or more poly-dispersed silver halide emulsions or a combination of a mono-dispersed emulsion and a poly-dispersed emulsion can be used as a mixture for one emulsion layer or for double or multi layers. The silver halide grains for use in this invention may have a regular crystal form such as cubic, octahedral dodecahedral, tetradecahedral, etc., an irregular crystal form such as spherical, etc., or a composite form of these crystal forms. Also, the silver halide grains may be tabular grains and in this case, a tabular grain silver halide emulsion wherein tabular grains having an aspect ratio (length/thickness) of at least 5, in particular at least 8, account for at least 50% of the total projected area of the silver halide grains can be used in this invention. An emulsion composed of silver halide emulsions having these different crystal forms can be used.

The silver halide emulsion for use in this invention can be prepared in the presence of a silver halide solvent. As the silver halide solvent, there are organic thio ethers described in U.S. Patents 3,271,157, 3,531,289, and 3,574,628, JP-A-54-1019 and JP-A-54-158917 and thiourea derivatives described in JP-A-53-82408, JP-A-55-77737, and JP-A-55-2982.

The silver halide emulsion for use in this invention can be chemically sensitized in the inside of the grains or at the surface of the grains by a sulfur sensitization, a selenium sensitization, a reduction sensitization, and a noble metal sensitization solely or as a combination thereof.

To the silver halide emulsion for use in this invention can be added sensitizing dyes (e.g., cyanine dyes and merocyanine dyes) described in JP-A-55-52050, pages 45 to 53 in addition to the sensitizing dyes specified in this invention for increasing the sensitivity. These sensitizing dyes may be used singly or as a combination thereof and a combination of sensitizing dyes is frequently used for super color sensitization.

The silver halide emulsion may further contain a dye which does not have a spectral sensitization action by itself or a material which does not substantially adsorb visible light but shows a super color sensitization effect together with the sensitizing dyes.

Useful sensitizing dyes, combinations of dyes showing super color sensitization, and materials showing super color sensitization are described in Research Disclosure, Vol. 176, No. 17643, IV, A-J (December, 1978).

These sensitizing dyes described above may be added in an amount of from 10^{-5} to 10^{-3} mol per mol of silver halide.

The sensitizing dye, etc., can be added in any step of producing a silver halide photographic emulsion or in any step from the production of the emulsion to coating. For example, the sensitizing dye, etc., may be added to a silver halide emulsion at the formation of silver halide grains, at physical ripening, or at chemical ripening.

The silver halide emulsion layer or another hydrophilic colloid layer in this invention may also contain water-soluble dyes as filter dyes, irradiation prevention, or other various purposes. As a filter dye, there are dyes for further reducing the photographic sensitivity and dyes having light absorption in the region of mainly from 350 nm to 600 nm for increasing the safety for safelight.

These dyes are incorporated in a silver halide emulsion layer or added together with a mordant to a light-insensitive hydrophilic colloid layer disposed on a silver halide emulsion layer followed by fixing.

The amount of the dye differs according to a mol extinction coefficient but is usually from 10^{-2} g/m^2 to 1 g/m^2, and preferably from 50 mg/m^2 to 500 mg/m^2.

Specific examples of the dye are described in JP-A-63-64039.

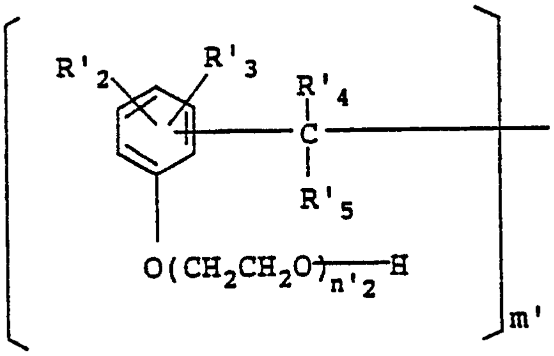
The photographic light-sensitive materials for use in this invention can further contain various compounds for preventing the formation of fog during the production, storage and/or photographic processing of the photographic materials or stabilizing the photographic performance thereof. That is, there are many compounds known as antifoggants or stabilizers. For example, there are azoles such as benzothiazolium salts, nitroindazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptothiadiazoles, aminotriazoles, benzothiazoles, nitrobenztriazoles, etc.; mercaptopyrimidines, mercaptotriazines; thioketo compounds such as oxazolinethione; azaindenes such as triazaindenes, tetraazaindenes (in particular, 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes), pentaazaindenes; benzenethiosulfonic acid, benzenesulfinic acid, benzenesulfonic acid amide, etc.

The photographic light-sensitive materials for use in this invention may contain in the photographic emulsion layers or another hydrophilic colloid layers a developing agent such as polyalkylene oxide or the derivatives thereof (such as the ethers, esters, amines, etc.), thioether compounds, thiomorpholines, quaternary ammonium salt compounds, urethane derivatives, urea derivatives, imidazole derivatives, dihydroxybenzenes, 3-pyrazolidines, etc., for increasing the sensitivity and contrast and for the purpose of development acceleration. In these compounds, dihydroxybenzenes (hydroquinone, 2-methylhydroquinone, catechol, etc.), 3- pyrazolidones (1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, etc.) and polyalkylene oxide compounds shown below are preferred. They are usually used in an amount of not more than 5 g/m^2. A dihydroxybenzene is more preferably used in an amount of from 0.01 to 1 g/m^2 and a 3-pyrazolidone is used more preferably in an amount of from 0.01 to 0.2 g/m^2.

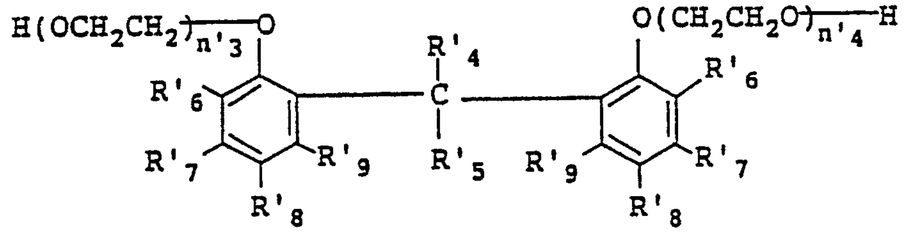
Next, polyalkylene oxide compounds for use in this invention are described.

The polyalkylene oxide compounds are used for greatly improving so-called discrimination by increasing the maximum image density without increasing the minimum image density. By using the polyalkylene oxide compound, the coating amount of silver can be reduced in the case of obtaining a definite density, which increases the development acceleration and reduces the cost for processing.

As the polyalkylene oxide compounds for use in this invention, there are those shown by following formulae ((XI-1), (XI-2), and (XI-3); $R'_1\text{-}A'\!\left(CH_2CH_2O\right)_{n'_1}\!\!-\!H$ (XI-1)



(XI-2)



(XI-3)

wherein R'_1 represents a substituted or unsubstituted alkyl group having from 1 to 30 carbon atoms, a substituted or unsubstituted alkenyl group, or a substituted or unsubstituted aryl group; A' represents -O-, -S-, -COO-,

$-\underset{|}{N}-R'_{10}$, $CO-\underset{|}{N}-R'_{10}$, or $-SO_2\underset{|}{N}-R'_{10}$

(wherein R'_{10} represents a hydrogen atom or a substituted or unsubstituted alkyl group);

R'_2, R'_3, R'_7, and R'_9 each represents a hydrogen atom, a substituted or unsubstituted alkyl group, an aryl group, an alkoxy group, a halogen atom, an acyl group, an amido group, a sulfonamido group, a carbamoyl group, or a sulfamoyl group.

Also, R'_6 and R'_8 in formula (XI-3) each represents a substituted or unsubstituted alkyl group, an aryl group, an alkoxy group, a halogen atom, an acyl group, an amido group, a sulfonamido group, a carbamoyl group, or a sulfamoyl group.

In the formula (XI-3), the substituents for the two phenyl groups may be bilaterally symmetric or asymmetric.

R'_4 and R'_5 each represents a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group.

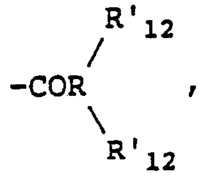
In the above formulae, said R'_4 and R'_5, said R'_6 and R'_7, and said R'_8 and R'_9 may combine with each other to form a substituted or unsubstituted ring.

In the aforesaid formulae, n'_1, n'_2, n'_3, and n'_4 each shows the average polymerization degree of ethylene oxide and is a number of from 2 to 50, and m' shows an average polymerization degree and is a number of from 2 to 50.

The preferred polyalkylene oxide compounds shown by the aforesaid formulae are as follows.

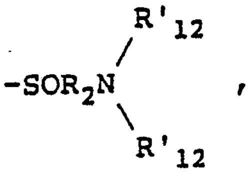
In formula (XI-1), R'_1 is preferably an alkyl group having from 4 to 24 carbon atoms, an alkenyl group, or an alkylaryl group, and is particularly preferably hexyl, dodecyl, isostearyl, oleyl, t-butylphenyl, 2,4-di-t-butylphenyl, 2,4-di-t-pentylphenyl, p-dodecylphenyl, m-pentadecaphenyl, t-octylphenyl, 2,4-dinonylphenyl, octylnaphthyl, etc.

In formulae (XI-2) and (XI-3), R'_2, R'_3, R'_6, R'_7, R'_8 and R'_9 each is a substituted or unsubstituted alkyl group having from 1 to 20 carbon atoms, such as methyl, ethyl, i-propyl, t-butyl, t-amyl, t-hexyl, t-octyl, nonyl, decyl, dodecyl, trichloromethyl, tribromomethyl, 1-phenylethyl, 2 phenyl-2-propyl, etc., a substituted or unsubstituted aryl group such as phenyl, p-chlorophenyl, etc., a substituted or unsubstituted alkoxy group shown by $-OR'_{11}$ (wherein R'_{11} represents a substituted or unsubstituted alkyl group having from 1 to 20 carbon atoms or an aryl group), a halogen atom such as chlorine, bromine, etc., an acyl group shown by $-COR'_{11}$ an amido group shown by $-NR'_{12}COR'_{11}$ (wherein R'_{12} represents a hydrogen atom or an alkyl group having from 1 to 20 carbon atoms, and so forth), a sulfonamido group shown by $-NR'_{12}SO_2R'_{11}$, a carbamoyl group shown by



$$-COR\begin{matrix} R'_{12} \\ R'_{12} \end{matrix},$$

or a sulfamoyl group shown by



$$-SOR_2N\begin{matrix} R'_{12} \\ R'_{12} \end{matrix},$$

also R'_2, R'_3, R'_7, and R'_9 may be a hydrogen atom. Furthermore, R'_6 and R'_8 are preferably an alkyl group or a halogen atom, and particularly preferably a tertiary alkyl group such as bulky t-butyl, t-amyl, t-octyl, etc. Also, R'_7 and R'_9 are particularly preferably a hydrogen atom. That is, the compound of formula (XI-3) synthesized from a 2,4-di-substituted phenol is particularly preferred.

R'_4 and R'_5 are preferably a hydrogen atom, a substituted or unsubstituted alkyl group (e.g., methyl, ethyl, n-propyl, i-propyl, n heptyl, l-ethylamyl, n-undecyl, trichloromethyl, and tribromomethyl), or a substituted or unsubstituted aryl group (e.g., α-furyl, phenyl, naphthyl, p-chlorophenyl, p-methoxyphenyl, and m-nitrophenyl).

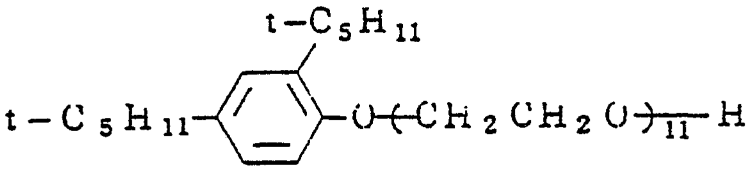
Also, said R'_4 and R'_5, said R'_6 and R'_7 and said R'_8 and R'_9 may combine with each other to form a substituted or unsubstituted ring such as, e.g, a cyclohexyl ring. In these cases, R'_4 and R'_5 are particularly preferably a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, a phenyl group, or a furyl group.

Also, n'_1, n'_2, n'_3, and n'_4 are particularly preferably a number of from 5 to 30 and n'_3 and n'_4 may be the same or different.

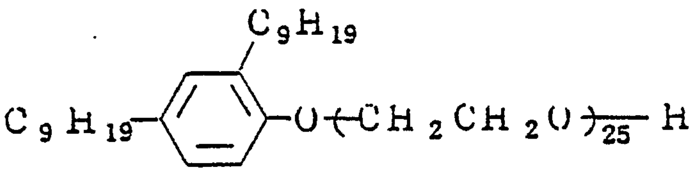
These polyalkylene oxide compounds are described in U.S. Patents 2,982,651, 3,428,456, 3,457,076, 3,454,625, 3,552,972, and 3,655,387, JP-B-51-9610, JP-A-53-29715, JP A-54-89626, JP-A-58-3435, JP-A-58-8743, and Hiroshi Horikawa, Shin Kaimen Kassei Zai (New Surface Active Agents), published by Sankyo Shuppan K.K., (1975).

Specific non-limiting examples of the polyalkylene oxide compounds which are preferably used in this invention are illustrated below. XI-1 $C_{15}H_{31}COO(CH_2CH_2O)_{15}$ H XI-2
$C_{18}H_{35}O(CH_2CH_2O)_{25}$ H XI-3 $C_{16}H_{33}O(CH_2CH_2O)_{12}$ H XL-4
$C_{16}H_{45}O(CH_2CH_2O)_{25}$ H

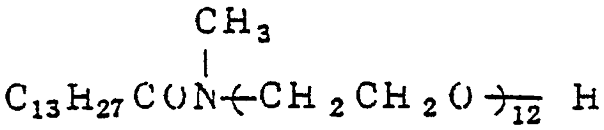
XI-5



XI-6

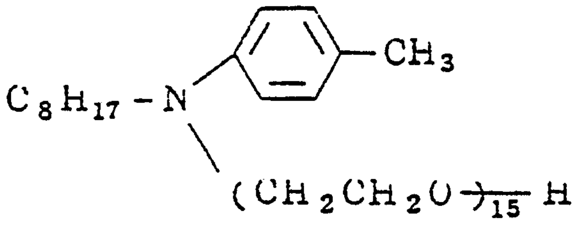


XI-7

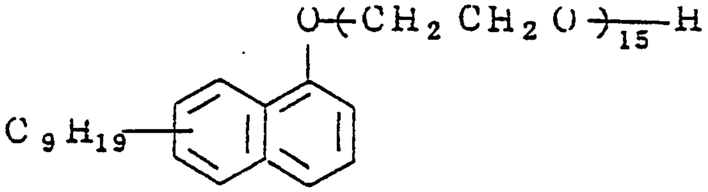


$$C_{13}H_{27}CO\overset{\overset{\displaystyle CH_3}{|}}{N}\!\left(CH_2CH_2O\right)_{12}H$$

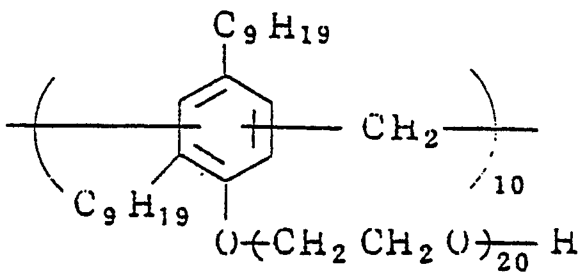
XI-8



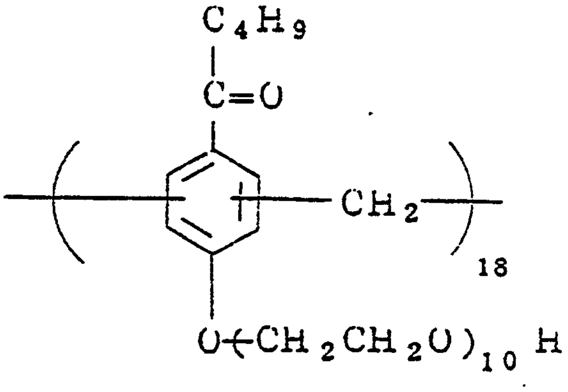
XI-9



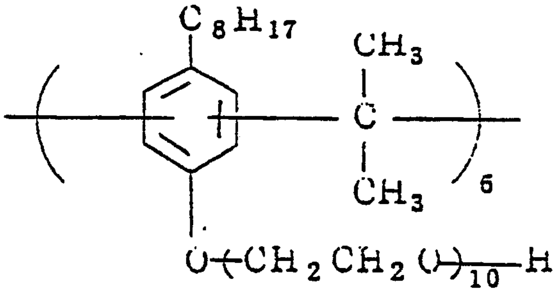
XI-10



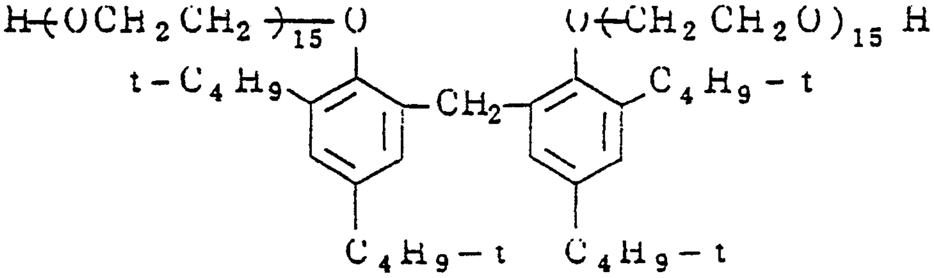
XI-11



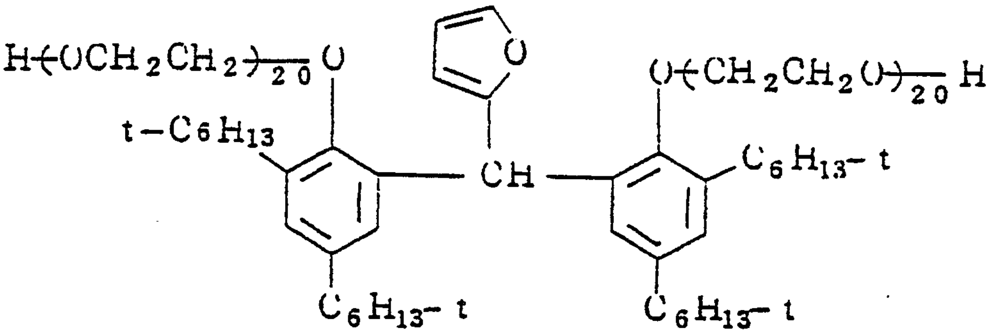
XI-12



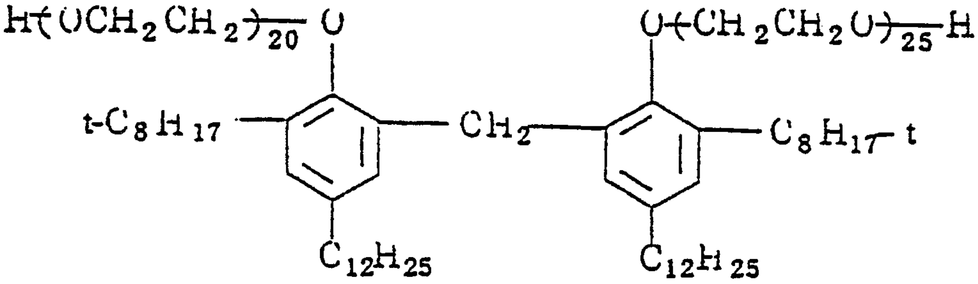
XI-13



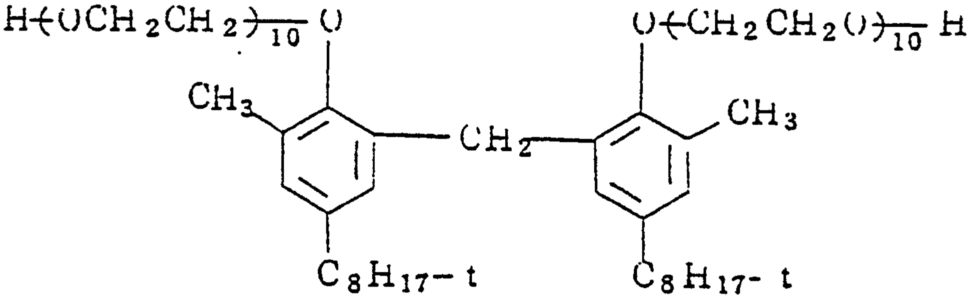
XI-14



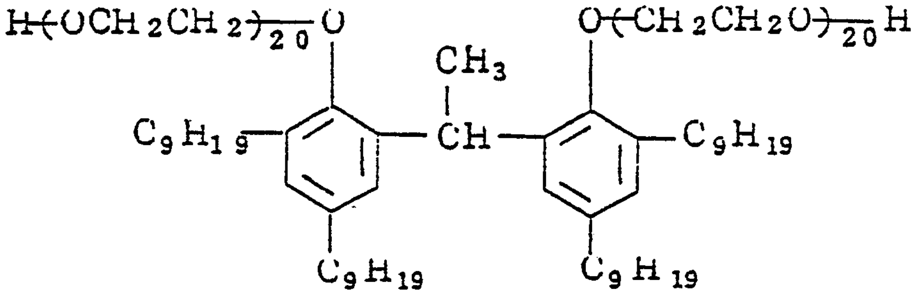
XI-15



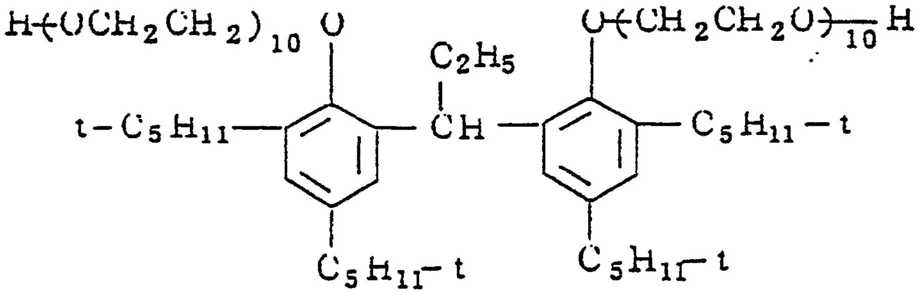
XI-16



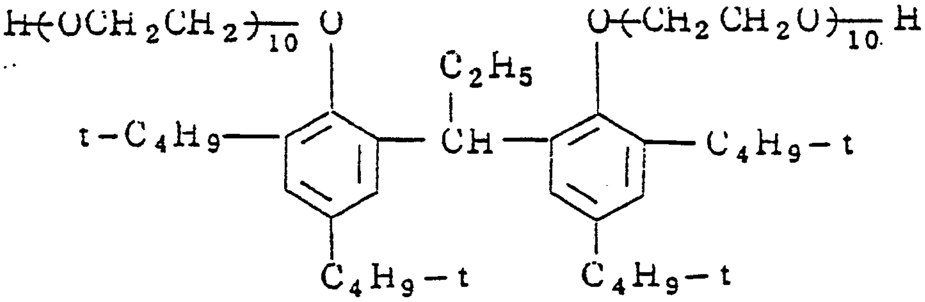
XI-17



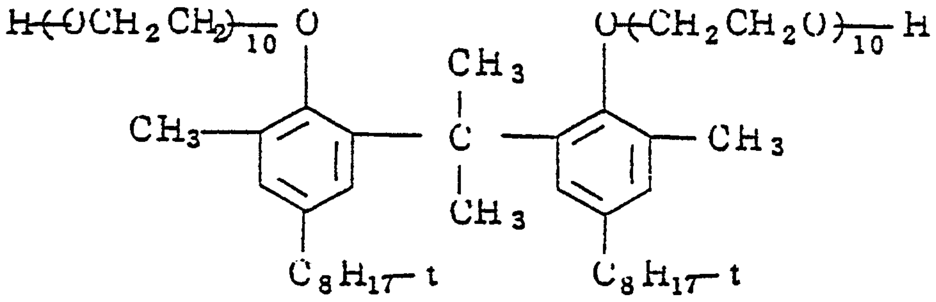
XI-18



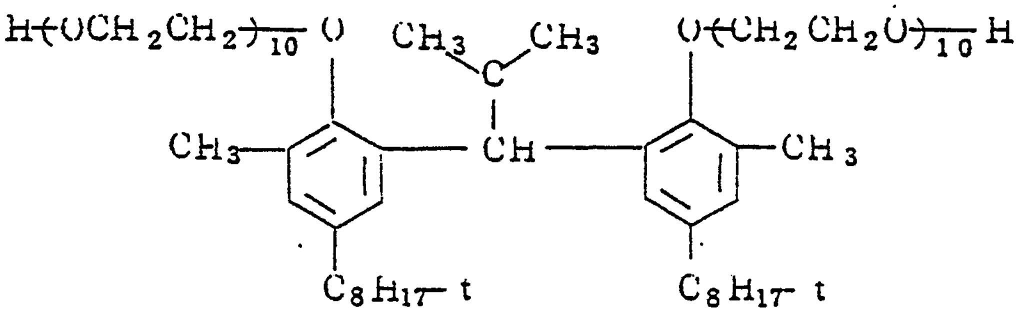
XI-19



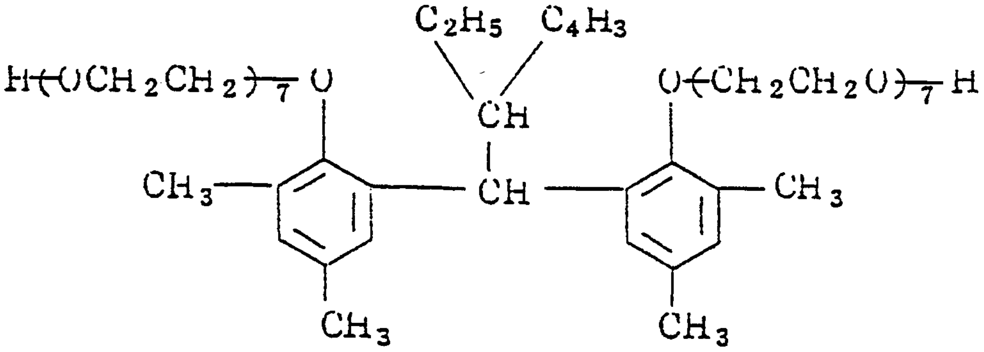
XI-20



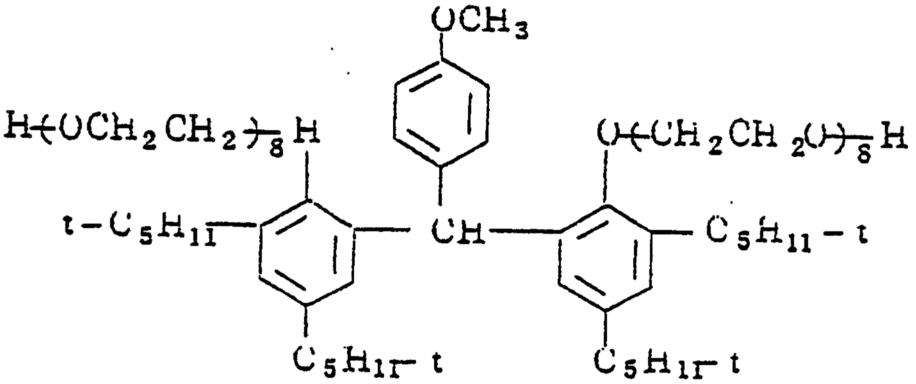
XI-21



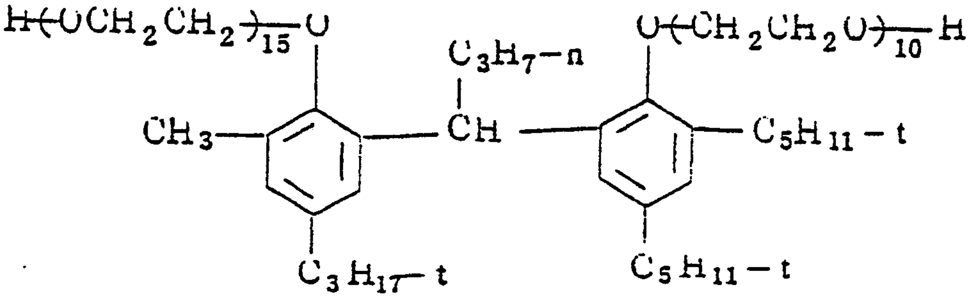
XI-22



XI-23



XI-24



The amount of the polyalkylene oxide compound shown by formula (XI-1), (XI-2) or (XI-3) for use in this invention is from 5 to 500 mg, and particularly preferably from 10 to 300 mg per square meter of the photographic light-sensitive element.

The photographic light-sensitive elements for use in this invention may contain an inorganic or organic hardening agent in the silver halide photographic emulsion layers and another hydrophilic colloid layers. Examples of the hardening agent are active vinyl compounds (e.g., 1,3,5-triacryloyl-hexahydro-s-triazine, bis(vinylsulfonyl)methyl, ether, and N,N′-methylenebis-[β-(vinylsulfonyl)propionamide], active halogen compounds (e.g., 2,4-dichloro-6-hydroxy-s-triazine), mucohalogenic acids (e.g., mucochloric acid), N-carbamoylpyridinium salts (e.g., (1-morpholinocarbonyl-3-pyridinio)methanesulfonate , and haloamidinium salts (e.g., 1-(1-chloro-1-pyridinomethylene)pyrrolidinium and 2-naphthalenesulfonate). They can be used singly or as a combination thereof. In these compounds, the active vinyl compounds described in JP-A-53-41220, JP-A-53-57257, JP-A-59-162546, and JP-A-60-80846, and the active halogen compounds described in U.S. Patent 3,325,287 are preferred.

The photographic light-sensitive element for use in this invention may further contain various kinds of surface active agents in the photographic emulsion layers or another hydrophilic colloid layers for the purposes of coating aid, static prevention, slidability improvement, sticking prevention, and the improvement of photographic characteristics (e.g., development acceleration, contrast increase and sensitization).

Examples of the surface active agents are nonionic surface active agents such as saponin (steroid series), alkylene oxide derivatives (e.g., polyethylene glycol, a polyethylene glycol/polypropylene glycol condensation product, polyethylene glycol alkyl ethers, polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines, polyalkylene glycol alkylamides, and polyethylene oxide addition products of silicone), glycidol derivatives (e.g., alkenylsuccinic acid polyglyceride and alkylphenol polyglyceride), fatty acid esters of polyhydric alcohol, alkyl esters of saccharides, etc.; anionic surface active agents having an acid group (e.g., a carboxy group, a sulfo group, a phospho group, a sulfuric acid ester group, and a phosphoric acid ester), such as alkylcarboxylates, alkylsulfonates, alkylbenzenesulfonates, alkylnaphtha lenesulfonates, alkylsulfuric acid esters, alkylphosphoric acid esters, N-acyl-N-alkyltaurines, sulfosuccinic acid esters, sulfoalkyl polyoxyethylene alkylphenyl ethers, polyoxyethylene alkylphosphoric acid esters, etc.; amphoteric surface active agents such as amino acids, aminoalkylsulfonic acids, aminoalkylsulfuric acid esters, aminoalkyl phosphoric acid esters, alkylbetaines, amine oxides, etc.; and cationic surface active agents such as alkylamine salts, aliphatic quaternary ammonium salts, aromatic quaternary ammonium salts, heterocyclic ammonium salts (e.g., pyridinium and imidazolium), phosphonium or sulfonium salts containing an aliphatic ring or heterocyclic ring, etc.

Also, for static prevention, the nitrogen-containing surface active agents described in JP-A-60-80849, etc., can be preferably used.

The photographic light-sensitive elements for use in this invention can further contain the photographic emulsion layers and/or another hydrophilic colloid layers a matting agent such as silica, magnesium oxide, barium strontium sulfate, polymethyl methacrylate particles, etc., for the purpose of sticking prevention.

Also, the photographic light-sensitive elements for use in this invention may contain a dispersion of a water-insoluble or water sparingly soluble synthetic polymer for improving the properties of the photographic layers. Examples of the polymer are the polymers or copolymers of alkyl (meth)acrylate, alkoxyacryl (meth)acrylate, glycidyl (meth)acrylate, etc., solely or as a combination thereof, or as a combination of the aforesaid monomer and acrylic acid, methacrylic acid, etc.

As the binder or protective colloid for the photographic emulsion layers and another layer of the photographic light-sensitive materials, gelatin is advantageously used but another hydrophilic colloid can be used. Examples of such hydrophilic colloid are proteins such as gelatin derivatives, graft polymers of gelatin and other polymers, albumin, casein, etc.; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfuric acid esters, etc.; saccharide derivatives such as sodium alginate, starch derivatives, etc.; and various synthetic polymers or copolymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole, polyvinylpyrazole, etc.

As gelatin, limed gelatin as well as acid-treated gelatin may be used. Furthermore, gelatin hydrolyzed products and gelatin enzyme decomposition products can be also used.

For the silver halide emulsion layer in this invention can be used a polymer latex such as a latex of alkyl acrylate.

As the support for the photographic light-sensitive element for use in this invention, films of cellulose triacetate, cellulose diacetate, nitro cellulose, polystyrene, polyethylene terephthalate, etc., can be used.

In particular, for COM films, it is important that the film has excellent antistatic property and a support having high electric conductivity is preferably used.

For developing the photographic light-sensitive elements in this invention, various developing agents can be used. For example, there are polyhydroxybenzenes such as hydroquinone, 2-chlorohydroquinone, 2-methylhydroquinone, catechol, pyrogallol, etc.; aminophenols such as p-aminophenol, N-methyl-p-aminophenol, 2,4-diaminophenol, etc.; 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hyrdoxymethyl 3-pyrazolidone, 5,5-dimethyl-1-phenyl-3-pyrazolidone, and ascorbic acids. They can be used singly or as a combination thereof.

Specific examples of the developers for use in this invention are described in JP-A-58-55928.

Also, for obtaining dye images in the presence of dye-forming couplers in this invention, an aromatic primary amine developing agent, preferably a p-phenylenediamine series developing agent can be used. Specific examples thereof are 4--amino-3-methyl-N,N-dimethylaniline hydrochloride, N,N-diethyl-p-phenylenediamine, 3-methyl-4-amino-N-ethyl-N-β-(methanesulfonamido)ethylaniline, 3-methyl-4-amino-N-ethyl-N-(β-sulfoethyl)aniline, 3-ethoxy-4-amino-N ethyl-N-(β-sulfoethyl)aniline, and 4-amino-N-ethyl-N-(β-hydroxyethyl)aniline.

The developing agent described above may exist in an alkaline processing composition (processing element) or in a layer of the photographic light-sensitive element.

When a DRR compound is used in this invention, a silver halide developing agent which can cross-oxidize the DRR compound can be used in this invention.

The developer may contain sodium sulfite, potassium sulfite, ascorbic acid, reductants (e.g., piperidinohexose reductant), etc., as a preservative.

In this invention, direct positive images can be obtained by developing the photographic light-sensitive element using a surface developer.

The development by a surface developer is induced by the latent image or fogging nucleus present at the surface of silver halide grains.

In this invention, it is preferred that the developer contains no silver halide solvent but the developer may contain a silver halide solvent (e.g., a sulfite) if the internal latent images do not substantially contribute to the development until the development by the surface development center of the silver halide grains is completed.

The developer may further contain sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium tertiary phosphate, sodium metaborate, etc., as an alkali agent or a buffer. The content of the agent is selected such that the pH of the developer became from 10.0 to 12.0, preferably not higher than 11.5, and more preferably not higher than 11.0.

The developer may further contain a color developer accelerator such as benzyl alcohol, etc. Furthermore, for reducing the minimum density of direct positive images formed, it is advantageous that the developer contains a compound which is usually used as an antifoggant, such as benzimidazoles (e.g., 5-nitro benzimidazole) and benzotriazoles (e.g., benzotriazole and 5-methylbenzotriazole).

The invention is described more practically by the following non-limiting examples.

EXAMPLE 1

A silver halide emulsion (Emulsion A) was prepared by the following method.

Emulsion A

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to a 3% aqueous gelatin solution in the presence of 13 mg per mol of silver nitrate of 1,8-dihydroxy-3,6-dithiaoctane solvent with vigorously stirring at 75°C over a period of 5 minutes to provide an octahedral silver bromide emulsion having a mean grain size of 0.15 µm. After adjusting the pAg of the emulsion to 8.20, 115 mg of sodium thiosulfate and 115 mg of chloroauric acid (tetra-hydrate) per mol of silver were added to the emulsion followed by heating to 75°C for 50 minutes to perform chemical sensitization.

By following the same procedure as above using the silver bromide grains thus obtained as the core under the sample precipitation condition as above while controlling the pAg of the system to 7.50, crystals were further grown to provide a cubic mono-dispersed core/shell silver bromide emulsion having a mean grain size of 0.25 µm.

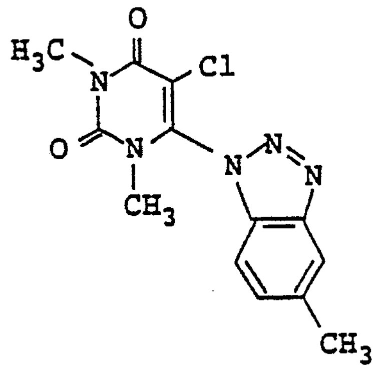
After washing with water and desalting the emulsion, 3.4 mg of sodium thiosulfate and 3.4 mg of chloroauric acid (tetra-hydrate) per mol of silver were added to the emulsion and the mixture was heated to 75°C for 60 minutes to perform chemical sensitization and to provide an internal latent image type silver halide emulsion (Emulsion A).

Emulsion A thus obtained was split into 10 portions and to each portion of the emulsion were added the sensitizing dye, the nucleating agent, and the nucleation accelerator defined in this invention as shown in Table 1 below. Furthermore, 5×10^{-4} mol/mol-Ag of 4-hydroxy-6-methyl-1,3,3,3a-tetraazaindene and 1×10^{-3} mol/mol-Ag of 5-methylbenzotriazole were added thereto as stabilizers and also 80 mg/m^2 of 1,3-divinylsulfonyl-2-propanol was added thereto as a hardening agent.

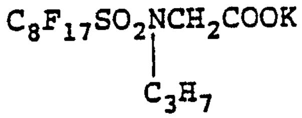
On the other hand, to 1000 mg/m^2 of an aqueous gelatin solution for a surface protective layer were added 30 mg/m^2 of barium strontium sulfate having a mean particle size of 1.0 µm as a matting agent, 50 mg/m^2 of hydroquinone, 20 mg/m^2 of a compound having the structure (1) shown below, and 25 mg/m^2 of sodium p-dodecylbenzenesulfonate and 5 mg/m^2 of a surface active agent having the structure (2) shown below as coating aids.

Then, the aforesaid silver halide emulsion and the aforesaid gelatin solution were simultaneously coated on a polyethylene terephthalate film at a silver coverage of 1.6 g/m^2. Thus, Samples 1 to 10 were prepared.

(1)



(2)



$$C_8F_{17}SO_2\underset{\displaystyle C_3H_7}{\underset{|}{N}}CH_2COOK$$

Each of the sample was exposed to a xenon flash light of 3.75×10^5 lux through a continuous wedge for 10^{-4} second. Then, each sample was developed using a Proster Plus developer (made by Eastman Kodak Company) for 30 seconds at 35°C and stopped, fixed, and washed in the conventional manner to provide positive images.

The results obtained are shown in Table 2 below.

In Table 2, Dmax means the maximum density of the reversal image, Dmin means the minimum density thereof, and Sp-df means an intermediate point sensitivity. The intermediate point sensitivity is defined by a logE value from a standard value of giving a density of

$$\frac{Dmax+Dmin}{2}.$$

. The standard value was selected such that the sensitivity was higher as the logE value was larger. Also, $\Delta\log E_{0.2}$ is defined as the difference between the reversal sensitivity giving a density of Dmin + 0.2 and the re-reversal negative sensitivity giving a density of Dmin + 0.2 shown by the difference in LogE value and is called the "sensitivity width". As is clear from the definition, a larger sensitivity width means that the re-reversal negative is more reluctantly formed.

Table 1

Sample No.		Nucleating Agent		Nucleating Accelerator		Sensitizing Dye	
		Kind	Amount*	Kind	Amount*	Kind	Amount*
1	Comparison Sample	-	0	-	0	-	0
2	"	N-1-7	3.4×10^{-6}	-	"	-	"
3	"	N-1-21	2.5×10^{-6}	-	"	-	"
4	"	N-1-15	2.5×10^{-6}	-	"	-	"
5	"	N-1-7	3.4×10^{-6}	II-1	8.8×10^{-4}	-	"
6	"	N-1-21	2.5×10^{-6}	"	"	-	"
7	"	N-1-15	2.5×10^{-6}	"	"	-	"
8	Invention	N-1-7	3.4×10^{-6}	"	"	I-12	1.2×10^{-3}
9	"	N-1-21	2.5×10^{-6}	"	"	"	"
10	"	N-1-15	2.5×10^{-6}	"	"	"	"

(*) Mol/Mol-Ag

Table 2

Sample No.		Dmin	Dmax	Sp-df	$\Delta\log E_{0.2}$
1	Comparison Sample	No Reversal Characteristics			
2	"	0.15	1.00	1.82	1.08
3	"	0.15	0.93	1.85	1.12
4	"	0.15	0.92	1.84	1.18
5	"	0.17	2.63	0.83	0.70
6	"	0.17	2.54	0.96	0.72
7	"	0.17	2.47	1.00	0.79
8	Invention	0.06	2.47	1.85	1.59
9	"	0.05	2.46	1.83	1.60
10	"	0.05	2.41	1.87	1.62

As is clear from the results shown in Table 2, it can be seen that Comparison Sample No. 1 shows no reversal characteristics, Comparison Sample Nos. 2 to 4 show low Dmax and high Dmin, and Comparison Sample Nos. 5 to 7 show high Dmin and small $\Delta\log E_{0.2}$.

Also, when the amounts of the additives in Sample Nos. 2 to 7 were changed to some extents, no remarkable improvements were observed.

On the other hand, Sample Nos. 8 to 10, which are the embodiments of this invention, show very excellent photographic characteristics in terms of Dmax, Dmin, Sp-df, and $\Delta\log E_{0.2}$ as compared to the comparison samples.

Example 2

The same procedure as in Example 1 was followed except that the combination of the nucleating agent, the nucleation accelerator and the sensitizing dye was changed as shown in Table 3 below and further a polyethylene terephthalate film base having a subbing layer containing 300 mg/m^2 of tin oxide (SnO_2) (having an electric conductivity of 10^8 Ω/□ at relative humidity of 10%) was used as the support.

The results obtained are shown in Table 4.

Table 3

Sample No.		Nucleating Agent		Nucleating Accelerator		Sensitizing Dye	
		Kind	Amount*	Kind	Amount*	Kind	Amount*
1	Comparison Sample	-	0	-	0	-	0
2	"	N-1-15	2.5×10^{-6}	-	"	-	"
3	"	"	"	II-1	8.8×10^{-4}	-	"
4	"	"	"	II-11	"	-	"
5	"	"	"	II-2	"	-	"
6	"	"	"	II-40	"	-	"
7	Invention	"	"	II-1	"	I-12	1.2×10^{-3}
8	"	"	"	II-11	"	"	"
9	"	"	"	II-2	"	"	"
10	"	"	"	II-40	"	"	"

(*) Mol/Mol-Ag

Table 4

Sample No.		Dmin	Dmax	Sp-df	$\Delta\log E_{0.2}$
1	Comparison Sample	No Reversal Characteristics			
2	"	0.15	0.92	1.84	1.18
3	"	0.17	2.47	1.00	0.79
4	"	0.17	2.45	1.02	0.78
5	"	0.17	2.48	0.99	0.79
6	"	0.20	2.30	0.95	0.77
7	Invention	0.05	2.41	1.87	1.62
8	"	0.05	2.39	1.89	1.63
9	"	0.05	2.42	1.87	1.59
10	"	0.10	2.40	1.85	1.58

As is clear from the Table 4, it can be seen that Comparison Sample No. 1 shows no reversal characteristics, Comparison Sample No. 2 shows low Dmax and high Dmin, and Comparison Sample Nos. 3 to 6 show high Dmin and small $\Delta\log E_{0.2}$.

When the addition amounts of the additives in Comparison Sample Nos. 2 to 6 were changed to some extent, no remarkable improvement was observed.

On the other hand, it can be seen that Sample Nos. 7 to 10, which are the embodiments of this invention, show very excellent photographic performance in terms of Dmax, Dmin, Sp-fd, and $\Delta\log E_{0.2}$ although Dmin in Sample No. 10 may be slightly high.

Example 3

The same procedure as Example 1 was followed except that the combination of the nucleating agent, the nucleation accelerator and the sensitizing dye was changed as shown in Table 5 below. The results obtained are shown in Table 6.

Table 5

Sample No.		Nucleating Agent		Nucleating Accelerator		Sensitizing Dye	
		Kind	Amount*	Kind	Amount*	Kind	Amount*
1	Comparison Sample	-	0	-	0	-	0
2	"	N-1-21	2.5×10^{-6}	-	"	-	"
3	"	"	"	II-1	8.8×10^{-4}	-	"
4	"	"	"	II-11	"	-	"
5	"	"	"	II-2	"	-	"
6	Invention	"	"	II-1	"	I-13	1.2×10^{-3}
7	"	"	"	II-11	"	I-13	"
8	"	"	"	II-2	"	I-13	"
9	"	"	"	II-1	"	I-12	"
10	"	"	"	II-11	"	I-12	"
11	"	"	"	II-2	"	I-12	"

(*) Mol/Mol-Ag

Table 6

Sample No.		Dmin	Dmax	Sp-df	$\Delta\log E_{0.2}$
1	Comparison Sample	No Reversal Characteristics			
2	"	0.15	0.93	1.85	1.12
3	"	0.17	2.54	0.96	0.72
4	"	0.17	2.60	0.88	0.70
5	"	0.17	2.50	0.90	0.65
6	Invention	0.07	2.48	1.75	1.32
7	"	0.07	2.53	1.77	1.31
8	"	0.07	2.45	1.73	1.29
9	"	0.05	2.46	1.83	1.60
10	"	0.05	2.50	1.82	1.58
11	"	0.05	2.40	1.85	1.62

As is clear from the results shown above, it can be seen that Comparison Sample No. 1 shows no reversal characteristics, Comparison Sample No. 2 shows low Dmax and high Dmin, and Comparison Sample Nos. 3 to 5 show high Dmin and small $\Delta\log E_{0.2}$.

When the addition amounts of the additives in Comparison Sample Nos. 2 to 5 were changed to some extent, no remarkable change was observed.

On the other hand, Sample Nos. 6 to 11, which are the embodiments of this invention, show very excellent photographic performance in terms of Dmax, Dmin, Sp-fd, and $\Delta\log E_{0.2}$ as compared to Comparison Sample Nos. 1 to 5. In these samples, Sample Nos. 9 to 11 give particularly excellent results.

Example 4

A silver halide emulsion (Emulsion B) was prepared as follows.

Emulsion B

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to a 3% aqueous gelatin solution in the presence of thioether with vigorously stirring at 75° C over a period of 5 minutes to provide an octahedral silver bromide emulsion having a mean grain size of 0.15 µm.

After adjusting the pAg of the emulsion to 8.20, 38 mg of sodium thiosulfate and 38 mg of chloroauric acid (tetra-hydrate) per mol of silver were added to the emulsion followed by heating to 75° C for 50 minutes to perform chemical sensitization.

The crystal growing procedure as above was further followed using the silver bromide grains thus obtained as the cores for 40 minutes under the same precipitation condition as above while controlling the pAg of the emulsion to 8.20 or 7.70 to provide an octahedral or tetradecahedral mono-dispersed core/shell silver bromide emulsion, respectively, each having a mean grain size of 0.25 µm.

After washing with water and desalting the emulsion, 6.0 mg of sodium thiosulfate and 6.0 mg of chloroauric acid (tetra-hydrate) per mol of silver were added to the emulsion and the emulsion was heated to 75° C for 60 minutes to perform chemical sensitization, whereby internal latent image type silver halide emulsions (Emulsions B-1 and B-2) were obtained.

The ratio of plane (100) in the surfaces of the entire grains contained in each emulsion was measured by the method described in Journal of Imaging Science, 29, 165(1985). Also, the another plane was plane (111).

The results obtained are shown below.

Emulsion	Ratio of plane (100)
B-1	85%
B-2	15%

By following the same procedures as Examples 1 to 3 except that the aforesaid Emulsion B-1 or B-2 was used in place of Emulsion A, almost the same results as in Examples 1 to 3 were obtained. That is, it can be seen that the samples containing the nucleating agent, the nucleation accelerator, and the sensitizing dye defined in this invention show excellent direct positive characteristics as high Dmax, low Dmin, high Sp-df, and large $\Delta \log E_{0.2}$ in both the cases of the octahedral grains and the tetradecahedral grains as compared with the comparison samples.

Example 5

The samples as used in Examples 1 to 4 were prepared. Each of the samples was light-exposed as in Example 1, developed using each of the developers shown below for 30 seconds at 35° C, and then stopped, fixed and washed in the conventional manner. Thus, excellent positive characteristics as in Examples 1 to 4 were obtained.

Developers

FR Data Com-Pak Negative (made by FR Co.)
Datagraphic Auto Pos Chem Kit (made by ALTA Co.)

Thus, it can be seen that he direct positive silver halide photographic elements of this invention have excellent aptitude for the processing solution.

Example 6

By following the same procedures as Example 1, an internal latent image type silver halide emulsion (Emulsion A) was prepared.

The emulsion was split into 7 portions and the polyethylene oxide compound shown in Table 7 below was added to each portion as shown in Table 7. Furthermore, 2.5×10^{-6} mol/mol-Ag of the nucleating agent (N-I-15), 8.8×10^{-4} mol/mol-Ag of the nucleation accelerator (II-1), and 1.2×10^{-3} mol/mol-Ag of the sensitizing dye (I-12) were added to each portion. Also, 5×10^{-4} mol/mol-Ag of 4-hydroxy-6-methyl-1,3,3,3a-tetraazaindene and 1×10^{-3} mol/mol-Ag of 5-methylbenzotriazole as stabilizers and 80 mg/m^2 of 1,3-divinylsulfonyl 2-propanol as a hardening agent were added thereto.

On the other hand, to 1000 mg/m^2 of an aqueous gelatin solution for surface protective layer were added 30 mg/m^2 of barium strontium sulfate having a mean particle size of 1.0 μm as a matting agent, 50 mg/m^2 of hydroquinone, 20 mg/m^2 of a compound having the structural formula (1) used in Example 1, and 25 mg/m^2 of sodium p-dodecylbenzenesulfonate and 5 mg/m^2 of the surface active agent having the structural formula (2) used in Example 1 as coating aids.

The aforesaid silver halide emulsion and the aforesaid aqueous gelatin solution were simultaneously coated on a polyethylene terephthalate film at a silver coverage of 1.6 g/m^2. Thus, Samples 1 to 7 were prepared.

Each of the sample was exposed to xenon flash light of 3.75×10^5 lux through a continuous wedge for 10^{-4} second, developed using a Proster Plus developer, made by Eastman Kodak Company for 30 seconds at 35° C, and stopped, fixed, and washed in the conventional manner to provide positive images.

The results obtained are shown in Table 8 below.

Table 7

Sample No.		Polyethylene Oxide	
		Kind	Amount (mg/m^2)
1	Comparison Sample	XI-2	0
2	Invention	"	10
3.	"	"	17
4	"	"	35
5	"	XI-17	10
6	"	"	17
7	"	"	35

Table 8

Sample No.		Dmax	Dmin
1	Comparison Sample	2.0	0.05
2	Invention	2.2	"
3	"	2.5	"
4	"	2.9	"
5	"	2.1	"
6	"	2.4	"
7	"	2.7	"

As is clear from the above results, it can be seen that the polyethylene oxide compound for use in this invention increased Dmax without increasing Dmin, that is, greatly improves the discrimination.

Example 7

The same procedure as Example 6 was followed except that two kinds of the nucleating agents as shown in Table 9 below were used together and further a polyethylene terephthalate film base having a subbing layer containing 300 mg/m^2 of tin oxide (SnO_2) (having an electric conductivity of 10^8 Ω/□ at relative humidity of 10%) was used as the support.

The results obtained are shown in Table 10 below.

Table 9

Sample No.		Polyethylene Oxide		Nucleating Agent	
		Kind	Amount (mg/m^2)	Kind	Amount (mol/mol-Ag)
1	Comparison Sample	XI-2	0	N-I-21 N-II-16	1.8×10^{-6} 3.0×10^{-4}
2	Invention	"	10	" "	" "
3	"	"	17	" "	" "
4	"	"	35	" "	" "

Table 10

Sample No.		Dmax	Dmin
1	Comparison Sample	2.2	0.05
2	Invention	2.4	"
3	"	2.7	"
4	"	3.1	"

As is clear from the above results, it can be seen that the polyethylene oxide compound for use in this invention increases Dmax without increasing Dmin, that is greatly improves the discrimination even in the system of using two kinds of nucleating agents together.

Example 8

By following the same procedures as in Examples 6 and 7 except that Emulsion B-1 or B-2 as used in Example 4 in place of Emulsion A, almost the same results as in Examples 6 and 7 were obtained. That is, it can be seen that the samples containing the polyethylene oxide compound, the nucleating agent, the nucleation accelerator, and the sensitizing dye defined in this invention show direct positive characteristics excellent in discrimination in both cases of octahedral grains and tetradecahedral grains as compared with the comparison samples.

Example 9

The samples as in Examples 6 to 8 were prepared. Each of the samples was light exposure as in Example 6, developed using each of the following developers for 30 seconds at 35 °C, and stopped, fixed, and washed in the conventional manner. In this example, excellent positive characteristics as in Examples 6 to 8 were obtained.

Developers

FR Data Com-Pak Negative (made by FR Co.)

Detagraphic Auto Pos Chem Kit (made by ALTA Co.)

From the results, it can be seen that the direct positive silver halide photographic elements of this invention have an excellent aptitude for the processing solution.

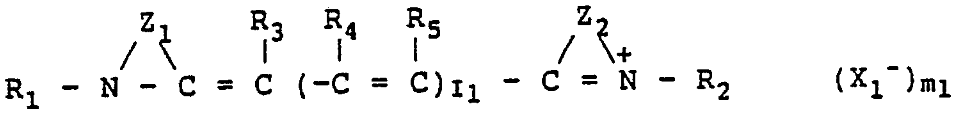
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A process of forming direct positive images comprising;

(A) imagewise exposing a silver halide photographic element comprising a support having provided thereon at least one photographic emulsion layer containing previously unfogged internal latent image type silver halide grains, and,

(B) developing the resulting photographic element, wherein said photographic element contains a nucleating agent in said photographic emulsion layer or another hydrophilic colloid layer and contains a sensitizing dye represented by formula (I) in said photographic emulsion layer and wherein development is performed in the presence of a nucleating accelerator;



$$R_1-\overset{Z_1}{N}-C=\overset{R_3}{C}(-\overset{R_4}{C}=\overset{R_5}{C})_{l_1}-C=\overset{Z_2}{\overset{+}{N}}-R_2 \qquad (X_1^-)_{m_1}$$

(I)

wherein Z_1 and Z_2, which may be the same or different, each represents an atomic group forming a 5- or 6-membered nitrogen-containing heterocyclic nucleus; l_1 represents 0 or 1; R_1 and R_2, which may be the same or different, each represents a substituted or unsubsti tuted alkyl group having from 1 to 10 carbon atoms or a substituted or unsubstituted alkenyl group having from 1 to 10 carbon atoms; R_3 and R_5 represents a hydrogen atom, said R_3 and R_1 or said R_5 and R_2 may combine each other to form a 5- or 6-membered ring; R_4 represents a hydrogen atom or a substituted or unsubstituted lower alkyl group; X_1 represents an acid anion; and m_1 represents 0 or 1, when the dye of the formula forms an intramolecular salt, m_1 is 0.

2. The process of forming direct positive images as claimed in claim 1, wherein the nucleation accelerator represented by formula (II)

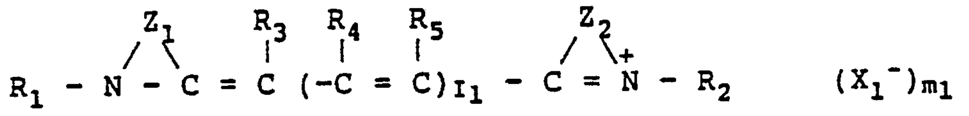
$A[\{Y_1\}_{n_1}R]_{m_1}$ (II)

wherein A represents a group adsorbing to silver halide; Y_1 represents a divalent linkage group composed of an atom or an atomic group selected from a hydrogen atom, a carbon atom, nitrogen atom, oxygen atom, and sulfur atom; R represents an organic group containing at least one of a thioether group, an amino group, an ammonium group, an ether group, and a heterocyclic group; m_1 represents 1 or 2; and n_1 represents 0 or 1.

3. The process of forming direct positive images as claimed in claim 1, wherein the photographic element further contains a polyalkylene oxide compound in the photographic emulsion layer or another hydrophilic colloid layer.

4. The process of forming direct positive images as claimed in claim 1, wherein the nucleation accelerator exists in the photographic emulsion layer or other hydrophilic colloid layer of the photographic element.

5. A direct positive silver halide photographic element comprising a support having provided thereon at least one photographic emulsion layer containing previously unfogged internal latent image type silver halide grains, wherein the photographic element contains a nucleating agent in said photographic emulsion layer or another hydrophilic colloid layer, and contains a sensitizing dye represented by formula (I) in said photographic emulsion layer;



$$R_1-\overset{Z_1}{N-C}=\overset{R_3}{C}(-\overset{R_4}{C}=\overset{R_5}{C})_{l_1}-\overset{Z_2}{C=N^+}-R_2 \qquad (X_1^-)_{m_1}$$

(I)

wherein Z_1 and Z_2, which may be the same or different, each represents an atomic group forming a 5- or 6-membered nitrogen-containing heterocyclic nucleus; l_1 represents 0 or 1; R_1 and R_2, which may be the same or different, each represents a substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms or a substituted or unsubstituted alkenyl group having from 1 to 10 carbon atoms; R_3 and R_5 each represents a hydrogen atom, said R_3 and R_1 or said R_5 and R_2 may combine with each other to form a 5- or 6-membered ring; R_4 represents a hydrogen atom or a substituted or unsubstituted lower alkyl group; X_1 represents an acid anion group; m_1 represents 0 or 1, when the dye of the formula forms an intramolecular salt, m_1 is 0.

6. The direct positive silver halide photographic element as claimed in claim 5, wherein the photographic emulsion layer or another hydrophilic colloid layer of the photographic element further contains a nucleation accelerator.

7. The direct positive silver halide photographic element as claimed in claim 6, wherein the nucleation accelerator is shown by formula (II);

$A[(Y_1)_{n_1}R]_{m_1}$ (II)

wherein A represents a group adsorbing to silver halide; Y_1 represents an atom or an atomic group selected from a hydrogen atom, a carbon atom, nitrogen atom, oxygen atom, and sulfur atom; R represents an organic group having at least one of a thioether group, an amino group, an ammonium group, an ether group, and a heterocyclic group; m_1 represents 1 or 2; and n_1 represents 0 or 1.

8. The process as claimed in claim 1, wherein said nucleating agent is employed in an amount of from about 1×10^{-8} mol to 1×10^{-2} mol/mol of silver in the silver halide emulsion layer.

9. The process as claimed in claim 8, wherein said nucleating agent is employed in an amount of from about 1×10^{-7} mol to 1×10^{-3} mol/mol of silver in the silver halide emulsion layer.

10. The process as claimed in claim 4, wherein said nucleation accelerator is employed in an amount of from 10^{-6} to 10^{-2} mol/mol of silver.

11. The process as claimed in claim 10, wherein said nucleation accelerator is employed in an amount of from 10^{-5} to 10^{-2} mol/mol of silver halide.

12. The process as claimed in claim 1, wherein said nucleation accelerator is added to a processing solution in an amount of from 10^{-8} to 10^{-3} mol/liter of the processing solution.

13. The process as claimed in claim 12, wherein said nucleation accelerator is added to a processing solution in an amount of from 10^{-7} to 10^{-4} mol/liter of the processing solution.

14. The process as claimed in claim 3, wherein said polyalkylene oxide is employed in an amount of from 5 to 500 mg/m^2 of said photographic light-sensitive element.

15. The process as claimed in claim 14, wherein said polyalkylene oxide is employed in an amount of from 10 to 300 mg/m^2 of said photographic light-sensitive element.

16. The direct positive silver halide photographic element as claimed in claim 5, wherein said photographic element further contains a polyalkylene oxide compound in the photographic emulsion layer or another hydrophilic colloid layer.