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(54) **Silver halide photographic emulsion and silver halide photographic materials**

Photographische Silberhalogenidemulsion und photographische Silberhalogenidmaterialien

Emulsion photographique à l'halogénure d'argent et matériaux photographiques à l'halogénure d'argent

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EP-A- 0 264 954

EP 0 337 370 B1

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Description

This invention concerns silver halide photographic emulsions and photographic materials which are excellent in respect of high speed, low fogging, and graininess.

The basic features required of a silver halide emulsion for photographic purposes are high speed, low fogging level, fine graininess and high development activity. Grains which have a distinct layer structure with regions which have different halogen compositions within the grains are known which improve these basic features by improving light absorption, improving quantum sensitivity by preventing the occurrence of recombination, increasing the progression of development, and improving graininess by preventing development from proceeding too far (JP-A-60-143331) (The term "JP-A" as used herein means an "unexamined published Japanese patent application"). Grains which have a distinct layer structure are useful when the grain size is large or when they are isotropic grains with a low aspect ratio, and they have contributed to the development of ultra-high speed material. However, they are inadequate in respect of high picture quality at high speeds, and conventional tabular grains which have a high iodine content and a high aspect ratio, and which have a distinct layer structure, are unsatisfactory.

EP-A-264954 which is prior art according to Article 54(3) EPC discloses silver halide emulsions comprising a dispersion of silver halide grains in a binder which has an aspect ratio of 3 to 10 and a core and a shell portion.

The iodide content of the core portion is from 10 to 40 mol% and the silver halide of the surface region of the shell portion contains at least 5 mol% silver iodide.

It is the object of the invention to provide silver halide photographic emulsions and photographic materials which are excellent in respect of high speed, low fogging level, and graininess which have high light absorbing efficiency and which have a high development activity.

Said object is attained by a silver halide photographic emulsion comprising a dispersion of silver halide grains in a binder, at least 60% by the total projected area of the grains being chemically sensitized tabular grains having an aspect ratio of 3 to 10, the grains having a distinct layer structure comprising at least one silver iodobromide layer in which the silver iodide content is from 15 to 45 mol%, wherein the silver halide composition of the outermost layer contains less than 5 mol% silver iodide.

The present invention also provides a silver halide photographic material comprising a support having thereon at least one of said silver halide photographic emulsion.

A "distinct layer structure" as used herein is determined using the X-ray diffraction method. An example of the application of X-ray diffraction methods to silver halide grains has been described by H. Hersch on pages 129 et seq. of volume 10 of the *Journal of Photographic Science* (1962). Thus, if the lattice constant is determined by the halogen composition then diffraction peaks will be produced at diffraction angles which satisfy the Bragg condition ($2d \sin \theta = n\lambda$).

Details of the X-ray diffraction measurement procedure have been described, for example, in Basic Analytical Chemistry Course No. 24, "X-Ray Diffraction" (published by Kyoritsu Shuppan), and "A Guide to X-Ray Diffraction" (published by Rigaku Denki K.K.). The standard method of measurement involves using a copper target and obtaining the diffraction curve of the (220) plane of the silver halide with the copper KB line as source (tube voltage 40 kV, tube current 60 mA). The width of the slits (dispersion slit, light receiving slit), the time constant of the apparatus, the goniometer scanning rate, and the recording speed are selected appropriately to increase the resolution of the measuring apparatus, and it is necessary to verify the measurement accuracy using a standard sample, of silicon for example.

The presence of a "distinct", essentially double layer structure as the term is used in this invention is confirmed by the appearance on the diffraction intensity against diffraction angle curve of the (220) plane of the silver halide obtained using the copper KB line in the range of diffraction angle (2θ) from 38° to 42° of at least two diffraction maxima, namely a diffraction peak corresponding to a high iodide layer which contains from 5 to 45 mol% silver iodide and a diffraction peak corresponding to a low iodide layer which has a silver iodide content of not more than 8 mol%, with a single minimum between them, and by the fact that the ratio of the diffraction intensity of the peak corresponding to the high iodide layer with respect to the diffraction intensity of the peak corresponding to the low iodide layer has a value of from 1/5 to 10/1. The value of the ratio of the diffraction intensities is preferably from 1/3 to 5/1, and most desirably from 1/3 to 3/1.

The silver iodide in the high iodide layer is 17 to 23 mol% or 30 to 45 mol%, preferably 18 to 22 mol% or 34 to 42 mol% in order to stably form the high iodide layer.

The emulsions of the invention which have a distinct essentially double layer structure are preferably such that the diffraction intensity of the minimum value between the two peaks is not more than 90% of the diffraction intensity of the weaker of the two (or more) diffraction maxima (peaks).

Moreover, the minimum value is more desirably not more than 80%, and most desirably not more than 60%, of this value. Methods of analyzing diffraction curves made up of two diffraction components are well known, and they are explained, for example, in "Experimental Physics Course 11, Lattice Defects", published by Kyoritsu Shuppan.

It is useful to assume that the curve is a Gaussian function or a Lorentz function and to make the analysis using a curve analyzer such as that made by DuPont Co.

Two peaks also appear in the above mentioned X-ray diffraction curve in cases where the emulsion contains two types of grains which have different halogen compositions but which do not have a distinct layer structure.

The excellent photographic performance obtained with this present invention cannot be realized with an emulsion of this type. The EPMA (electron probe microanalyser) method can be used as well as the X-ray diffraction method in order to ascertain whether a silver halide emulsion is an emulsion of this invention or an emulsion which contains two types of silver halide grains as described above.

With this method, a sample in which the emulsion grains are well dispersed so that there is no contact between them is prepared and irradiated with an electron beam. An elemental analysis of very small parts can then be carried out by X-ray diffraction with electron beam excitation.

It is possible, in this way, to determine the halogen composition of individual grains by obtaining the characteristic X-ray intensities of the silver and iodine which are radiated from each grain.

If the halogen composition of at least 50 grains is checked using the EPMA method it can be ascertained whether or not the emulsion is an emulsion of this invention.

The iodine content is preferably uniform from grain to grain in an emulsion of this invention.

The relative standard deviation when the distribution of iodine contents between grains is measured using the EPMA method is preferably not more than 50%, and most desirably less than 35%.

Another desirable inter-grain iodine distribution is such that there is a positive correlation between a logarithm of the grain size and the iodine content. There are cases where the iodine content increases as the grain size increases and cases where the iodine content falls as the grain size decreases. Cases in which the correlation coefficients for the correlations are at least 40% are preferred.

The silver halide other than silver iodide in the core part may be silver chlorobromide or silver bromide, but a high proportion of silver bromide is preferred.

The silver halide composition of the outermost layer contains less than 5 mol% of silver iodide.

The silver halide other than silver iodide in the outermost layer may be silver chloride, silver chlorobromide or silver bromide, but a high proportion of silver bromide is preferred.

The effect of this present invention is pronounced in cases where the overall halogen composition includes at least 8 mol% of silver iodide.

Moreover, the overall silver iodide content is preferably at least 10 mol%, and most preferably at least 12 mol%.

No particular limitation is imposed on the size of the silver halide grains which have a distinct layer structure of this invention, but in terms of the volume weight equivalent diameter they are preferably not more than 1.7 μm , more desirably not more than 1.5 μm , and most desirably not more than 1.3 μm .

The emulsions of this invention which contain tabular grains are emulsions in which the tabular grains of which the ratio of the diameter of the circle corresponding to the projected area of the grain and the grain thickness (known as the aspect ratio) has a value of from 3 to 10 account for at least 60%, calculated in terms of the projected area, of all the silver halide grains present in the emulsion.

Emulsions in which tabular grains of an aspect ratio from 3 to 10 account for at least 75%, and preferably at least 90%, of the total projected area are especially desirable.

The mean aspect ratio of the tabular grains is from 3 to 10, more desirably from 3 to 8, and most desirably from 5 to 8.

The color sensitized speed is low when large numbers of grains which have an aspect ratio of less than 3 are present, while the rate of development is slow and practical difficulties with pressure sensitivity arise when large numbers of grains which have an aspect ratio greater than 10 are present.

The average diameter of the tabular silver halide grains used in this invention is preferably from 0.5 to 3.0 μm .

Furthermore, the average thickness is not more than 0.5 μm , and preferably less than 0.35 μm .

In general, the tabular silver halide grains are of a tabular form which has two parallel surfaces, and the term "thickness" as used in this invention signifies the distance between these two parallel surfaces which form the tabular silver halide grain.

The tabular grains used in this invention are preferably grains which have at least 70% of the surface area in the form of a (111) plane. Moreover, grains in which this proportion is at least 80% are most desirable. The area ratio of the (111) plane can be determined using the Kubelka-Munk dye adsorption method. In this method a dye which is adsorbed preferentially on either the (111) plane or the (100) plane and which has a different light spectrum when associated with the (111) plane than that observed when it is associated with the (100) plane is selected. This dye is added to the emulsion and the area proportion of the (111) plane can be determined by investigating, in detail, the light spectrum with respect to the amount of dye which has been added.

The emulsions used in the invention may have a wide grain size distribution, but emulsions which have a narrow grain size distribution are preferred.

A variation coefficient of not more than 40% is preferred, while a value of less than 30% is more desirable, and most desirably the value is less than 25%.

The shape of the tabular grains used in this invention is preferably hexagonal. The lengths of the six sides may

differ, but the lengths of the parallel sides are preferably the same. Moreover, grains of an essentially regular hexagonal shape are the most desirable.

Here, the term, "grains of an essentially regular hexagonal shape" signifies grains the variation coefficient for the lengths of the six sides of which is within 25%. The angle of a hexagon is precisely 120° according to the rule of fixed crystal planes and angles. However, when observed on a micro-scale, the corner parts may have a normal rounded band. Moreover, grains which have a positive rounding are also desirable as tabular grains used in this invention.

The emulsions of this invention which have a distinct layer structure can be prepared by selecting and combining various methods which are known in the field of silver halide photographic materials.

Thus, methods such as the acidic method, the neutral method or the ammonia method can be used to prepare the core grains, and single sided mixing methods, simultaneous mixing methods, and combinations of these methods, can be selected for the system by which the soluble halide is reacted with the soluble silver salt.

Thus, the method in which the pAg value in the liquid phase in which the silver halide is being formed is held constant, which is to say the controlled double jet method, can be used as one system involving a simultaneous mixing procedure. The triple jet method in which a soluble halide of different composition is added independently (for example, for mixing a soluble silver salt with soluble bromide and a soluble iodide) can also be used as another system involving a simultaneous mixing procedure. A silver halide solvent, such as ammonia, a thiocyanate, a thiourea, a thioether or an amine, can be selected and used during the preparation of the core. Emulsions in which the grain size distribution of the core grains is narrow are preferred. The mono-disperse core emulsions as mentioned earlier are especially desirable. Emulsions in which the halogen composition, and especially the iodide content, of the individual grains is uniform at the core stage are preferred.

Whether or not the halogen compositions of the individual grains is uniform can be assessed using the techniques of X-ray diffraction and EPMA as described earlier. Emulsions in which the halogen composition of the core grains is uniform give narrower X-ray diffraction widths.

The preferred conditions during nuclei formation used in this invention are as follows:

1) A gelatin concentration of from 0.8 to 20 wt%, preferably of from 1.0 to 15 wt% and, most desirably, of from 1.0 to 6 wt%, is effective, and any gelatin normally used for photographic purposes can be used. However, gelatin solutions of high concentration (1.6 to 20 wt%) set at temperatures of 35°C and below, and, thus, are difficult to use, and the use of low molecular weight gelatins (of molecular weight from 2,000 to 100,000) and modified gelatins, such as phthalated gelatins and gelatins made from the skins of fish which live in cold seas, which do not set at low temperatures below 35°C is especially desirable.

2) The use of in-liquid addition and mixing apparatus for the reaction liquid, as disclosed in U.S. Patent 3,785,777 (1974) and German Patent Application (OLS) No. 2,556,888, is preferred for providing thorough agitation.

3) The rate of addition of the silver salt and halide is preferably between 6×10^{-4} mol/minute and 2.9×10^{-1} mol/minute, per liter of gelatin solution.

4) The gelatin which is added to the aqueous solution of silver salt or halide which is being added may be any gelatin normally used for photographic purposes, and it can be added in any amount such that these aqueous solutions do not set, and the amount added is normally from 0.05 to 1.6 wt%, but it can be added at higher concentration (about 20 wt% if these solutions are provided with a heating apparatus).

Furthermore, the use of low molecular weight (molecular weight from 2,000 to 100,000) gelatins or modified gelatins is especially desirable because these are not prone to setting.

When gelatin is added to the aqueous solution of silver salt or halide which is being added, the type and concentration of the gelatin, and the temperature, are preferably the same as the type of gelatin, the gelatin concentration and the temperature in the reactor so as to maintain uniform super-saturation factors in the vicinity of the addition ports so that uniform nuclei formation can be achieved.

5) A bromide ion concentration such that the pBr value is from 1.0 to 2.5 can be used in the reaction solution.

6) An unrelated salt concentration of from 1.0×10^{-2} mol/liter, and preferably of from 1×10^{-1} to 1 mol/liter, can be used in the reaction liquid.

Uniform silver iodobromides can be obtained after forming seed crystals of silver iodobromide which have a high silver iodide concentration using methods in which the rates of addition are accelerated with the passage of time as disclosed in JP-B-48-36890 by Irie and Suzuki, or by increasing the addition concentration with the passage of time as disclosed in U.S. Patent 4,242,445 by Saito, and especially good results can be obtained using these methods (The term "JP-B" as used herein means an "examined Japanese patent publication".) In the method of Irie et al. sparingly soluble inorganic crystals for photographic purposes are prepared by adding at least two types of inorganic salt solutions simultaneously in more or less equal quantities in the presence of a protective colloid and carrying out a double de-

composition reaction. The aqueous inorganic salt solutions which are reacted are added at least at a fixed rate of addition and at a rate of addition Q which is not greater than the rate of addition which is proportional to the total surface area of the sparingly soluble inorganic salt crystals during growth, which is to say at a rate $\gamma \leq Q \leq \alpha t^2 + \beta t + \gamma$.

On the other hand, with the Saito method, when silver halide crystals are prepared by the simultaneous addition of at least two types of aqueous inorganic salt solutions in the presence of a protective colloid, the concentrations of the aqueous inorganic salts which are reacted are increased during crystal growth in such a way that virtually no new crystal nuclei are formed during this period. To prepare silver halide grains which have a distinct layer structure the shell may be attached after forming the core grains without any other treatment, but the shell is preferably formed after washing the core emulsion with water for desalting purposes.

The shell can be affixed using various methods known in the field of silver halide photographic materials, but simultaneous mixing methods are preferred. The methods of Irie and Saito described above are preferred for the preparation of emulsions which have a distinct layered structure.

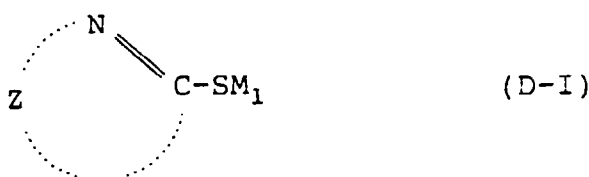
In the case of fine grain emulsions, known methods can be used to prepare grains which have a distinct layered structure, but these methods alone are unsatisfactory for completing the layer structure. Thus, in the first place it is necessary to fix the halogen composition of the high iodide layer very carefully. Silver iodide and silver bromide form a variety of different thermodynamically stable crystal structures and it is known that mixed crystals are not always formed with the given composition ratio. The mixed crystal composition ratio depends on the temperature at the time the grains are being prepared, and it is important that the best composition ratio should be selected between 15 and 25 mol% or 30 and 45 mol%. The stable mixed crystal ratio depends on the environments, such as temperature, pH, pAg, concentration of gelatin solution, etc., but it is considered that it is within the range from 15 to 25 mol% or from 30 to 45 mol%. When a low iodide layer is being grown on the outside of a high iodide layer it is important that the conditions, such as the temperature, pH, pAg and agitation conditions, should be selected appropriately. Moreover, careful selection of the protective colloid when growing the low iodide layer, and growing the low iodide layer in the presence of compounds which are adsorbed on the surface of the silver halide, such as spectrally sensitizing dyes, anti-fogging agent, and stabilizers for example, are desirable. Methods in which fine grains of silver halide are added instead of adding aqueous solutions of silver salts and aqueous solutions of alkali metal halides are also effective when growing the low iodide layer.

The dyes which can be used when growing the low iodide layer include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar-cyanine dyes, hemi-cyanine dyes, styryl dyes and hemi-oxonol dyes. Cyanine dyes, merocyanine dyes and complex merocyanine dyes are especially useful. Any of the nuclei normally used in cyanine dyes can be used as the basic heterocyclic nucleus in these dyes. That is to say, a pyrroline nucleus, oxazoline nucleus, thiazoline nucleus, pyrrole nucleus, oxazole nucleus, thiazole nucleus, selenazole nucleus, imidazole nucleus, tetrazole nucleus or a pyridine nucleus, a nucleus obtained by fusing an aliphatic hydrocarbyl ring with these nuclei, or a nucleus obtained by fusing an aromatic hydrocarbyl ring with these nuclei, for example, an indolenine nucleus, benzindolenine nucleus, indole nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, benzimidazole nucleus or a quinoline nucleus can be used. These nuclei may be substituted on the carbon atoms.

Five or six membered heterocyclic nuclei, such as the pyrazolin-5-one nucleus, the thiohydantoin nucleus, the 2-thio-oxazolidin-2,4-dione nucleus, the thiazolidin-2,4-dione nucleus, the rhodanine nucleus and the thiobarbituric acid nucleus, can be used as the nucleus which has a ketomethylene structure in the merocyanine dyes and complex merocyanine dyes.

For example, the compounds disclosed in Research Disclosure, Item 17643, page 23, paragraph IV (December 1978) and the compounds disclosed in the publications cited therein can be used for this purpose.

The compounds disclosed in JP-A-63-212932 are typical examples. Anti-fogging agents and stabilizers are also useful compounds when growing low iodide layers. These can be selected from the compounds disclosed in the above Research Disclosure. However, there are compounds which are not preferred, such as the tetraazaindenes, shown in the illustrative examples. The addition of mercapto compounds is preferred in this invention, including those represented by formula (D-I).



In this formula, M_1 represents hydrogen, a cation, or a protective group for the mercapto group which is cleaved in alkaline condition, and Z represents an atomic group necessary for forming a five or six membered heterocyclic ring. This heterocyclic ring may have substituent groups, or it may be a condensed ring. In greater detail, M_1 represents hydrogen, a cation (for example, sodium ion, potassium ion, ammonium ion) or a protective group for the mercapto group which is cleaved in alkaline conditions (for example, $-COR$, $-COOH$, or $-CH_2CH_2COR'$, where R' represents hydrogen, an alkyl group, an aralkyl group or an aryl group.

Z represents a group of atoms which is required to form a five or six membered heterocyclic ring. The heterocyclic rings may contain, for example, sulfur atoms, selenium atoms, nitrogen atoms and oxygen atoms as hetero-atoms. They may be condensed rings, and there may be substituent groups on the heterocyclic rings or on the condensed rings.

Examples of Z include tetrazole, triazole, imidazole, oxazole, thiaziazole, pyridine, pyrimidine, triazine, azabenzimidazole, purine, tetraazaindene, triazaindene, pentaazaindene benzotriazole, benzimidazole, benzoxazole and naphthimidazole. Furthermore, these may be substituted, for example, with alkyl groups (for example, methyl, ethyl, n-hexyl, hydroxyethyl, carboxyethyl), alkenyl groups (for example, allyl), aralkyl groups (for example, benzyl, phenethyl), aryl groups (for example, phenyl, naphthyl, p-acetamidophenyl), p-carboxyphenyl, m-hydroxyphenyl, p-sulfamoylphenyl, p-acetylphenyl, o-methoxyphenyl, 2,4-diethylaminophenyl, 2,4-dichlorophenyl), alkylthio groups (for example, methylthio, ethylthio, n-butylthio), arylthio groups (for example, phenylthio, naphthylthio), aralkylthio groups (for example, benzylthio), and mercapto groups. Furthermore, in addition to the substituent groups described above, the condensed rings may be substituted with, for example, nitro groups, amino groups, halogen atoms, carboxyl groups, sulfo groups and hydroxyl groups.

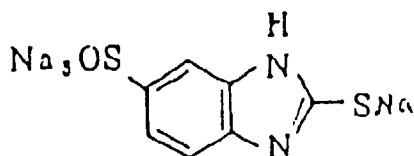
The quantity of these mercapto group containing compounds used is preferably not more than 10^{-3} mol per mol of silver halide.

Among the substituents, carboxyl groups, sulfo groups and hydroxyl are most preferred.

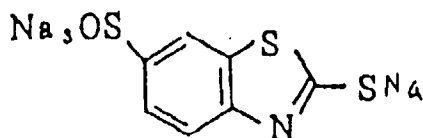
Examples of preferred nitrogen containing heterocyclic compounds which have a mercapto group have been disclosed in JP-A-63-212932, JP-A-62-89952 (corresponding to B.P. 2,176,304A) and JP-A-61-282841 (corresponding to EP-208,146A).

Examples of preferable compounds are as follows:

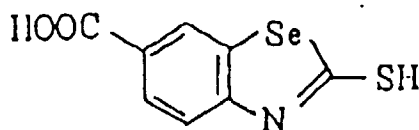
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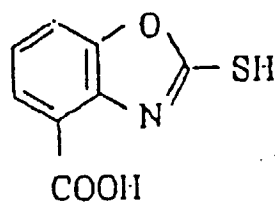
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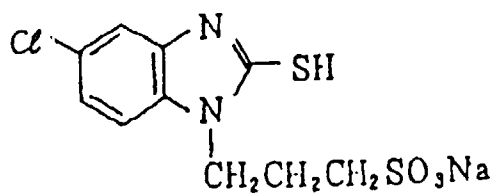
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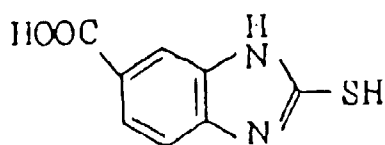
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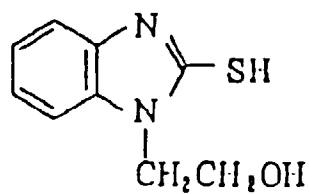
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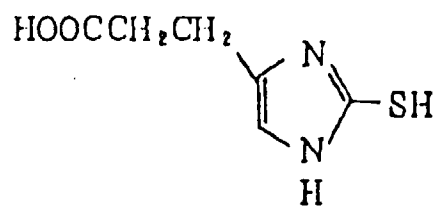
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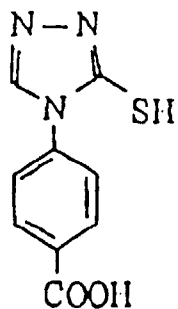


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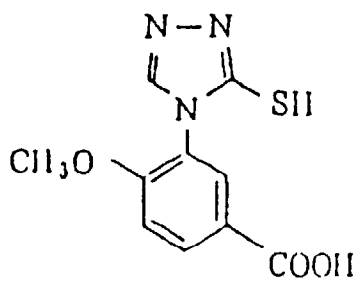


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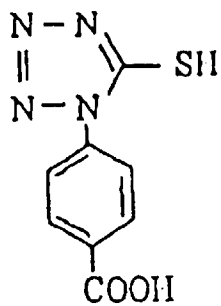


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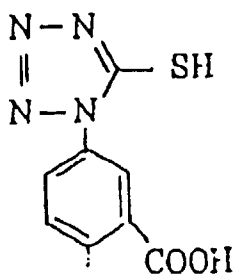


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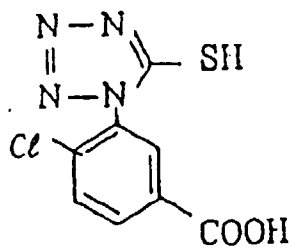
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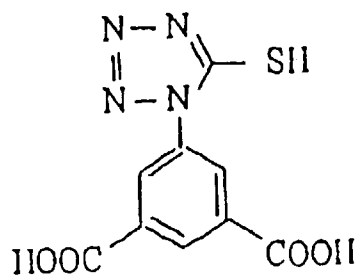


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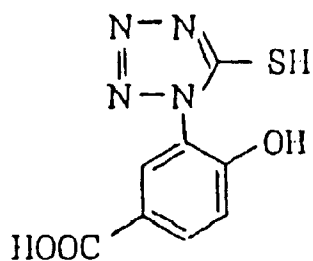


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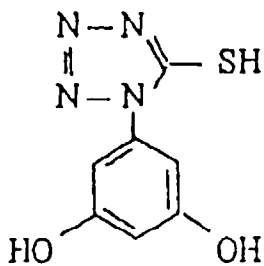


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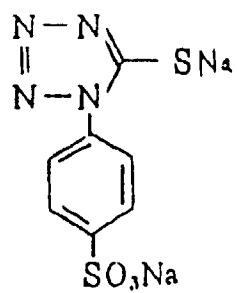
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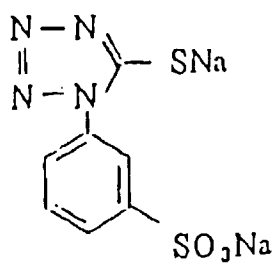
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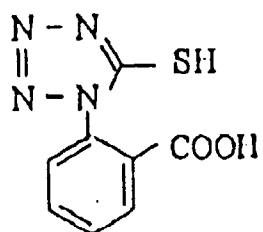
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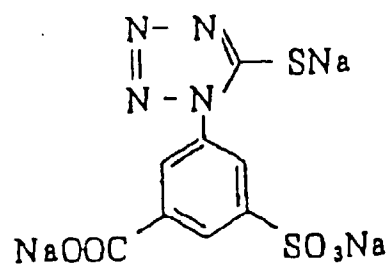
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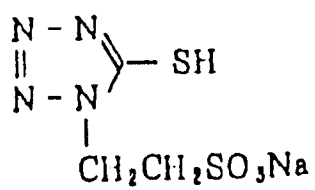
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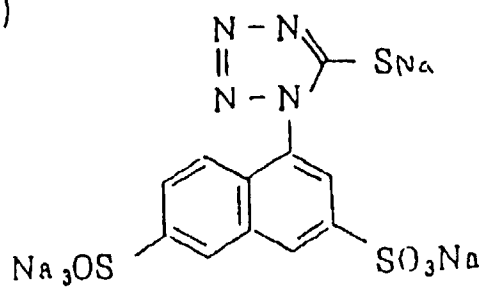
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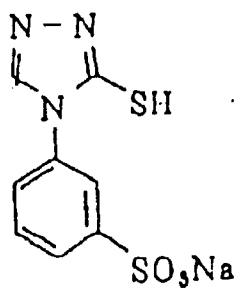
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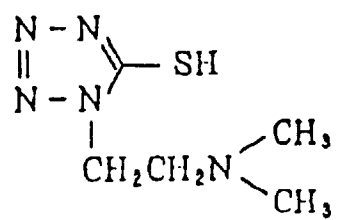
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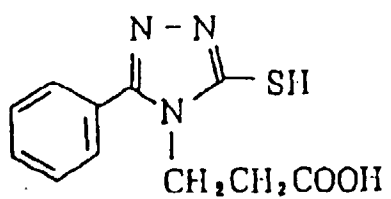
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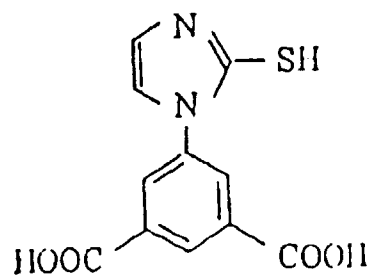
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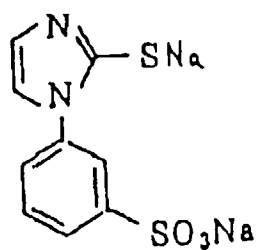
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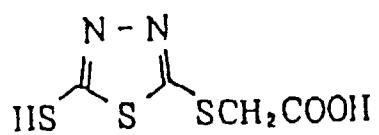
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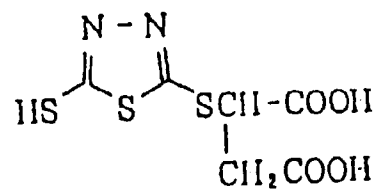
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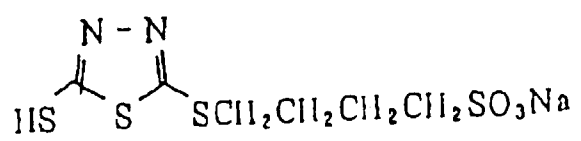
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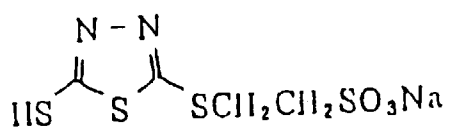
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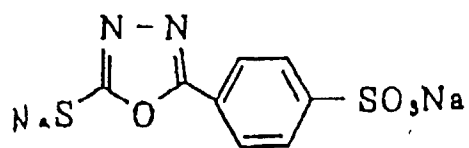


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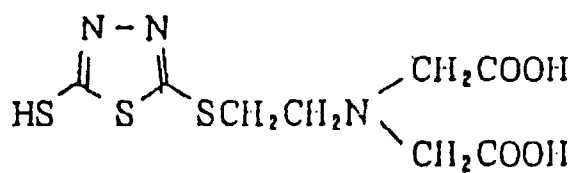


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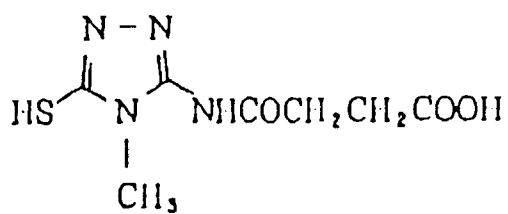
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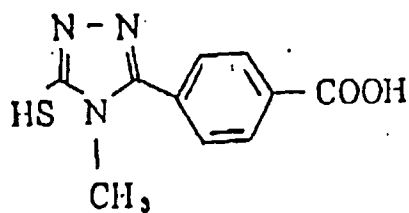
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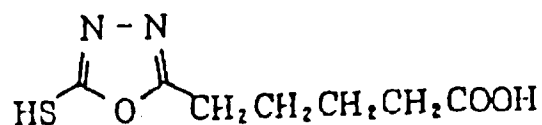


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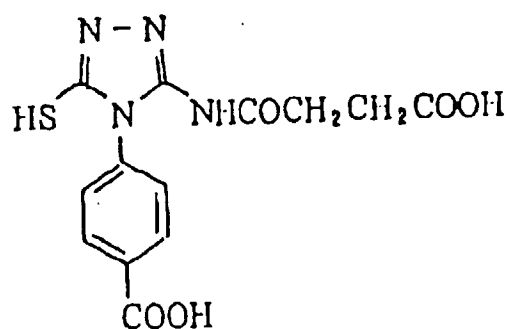
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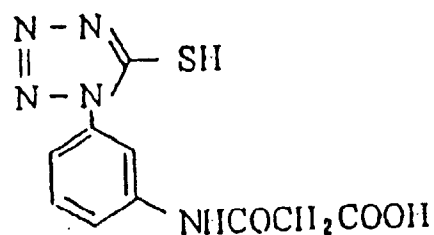


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45 In cases where, as in this invention, the silver halide grains have a distinct layer structure as described above, there are essentially two or more regions which have different halogen compositions present within the grains, and the interior of the grain is described herein as "the core" and the surface part is described herein as the "shell".

The term "essentially two or more" as used herein signifies there may be a third region present as well as the shell.

50 For example, there may be an intermediate layer between the core in the inner part and the outermost layer which constitutes the shell. Such an intermediate layer may have a silver iodide content intermediate between those of the core and the shell, or it may take the form of a layer which has a high silver chloride content. There are also cases where the third layer forms a separate region in the center on the interior core. In such a case the third layer may have a low iodide content or high iodide content (or it may consist of silver iodide) relative to that of the core, depending on the intended purpose of the layer. Moreover, the third layer may be a separate region which is present on the outside

55 of the shell. In this case the third layer may be a silver bromide layer which contains no iodide, a layer which has a higher silver iodide content than the shell or a layer which contains silver chloride, for example, depending on its intended purpose.

However, when such a third region is present it should have essentially no effect on the form of the two peaks (the

two peaks corresponding to the high iodide part and the low iodide part) when the X-ray diffraction pattern is obtained in the way described earlier.

That is to say, the silver halide grains have an essentially distinct double layer structure, and even in cases where there is a high iodide content core, an intermediate part and a low iodide content shell, there are two peaks on the X-ray diffraction pattern with a single minimum between the two peaks, the diffraction intensity corresponding to the high iodide part is from 1/5 to 10/1 times, preferably from 1/3 to 5/1 times, and most desirably from 1.3 to 3/1 times, that of the low iodide part, and the minimum is not more than 90%, preferably not more than 80%, and most desirably not more than 70%, of the smaller of the two peaks.

The silver halides of different composition may be joined with an epitaxial junction in an emulsion of this invention, or they may be joined with a compound other than silver halide, such as silver thiocyanate or lead oxide, for example.

Grains of various crystalline forms may be used in combination with the tabular grains.

The silver halide emulsions which are used have normally been subjected to physical ripening, chemical ripening and spectral sensitization. Additives used in such processes have been disclosed in Research Disclosure Nos. 17643 and 18716, and the locations of these items are summarized in the table below.

Known photographically useful additives which can be used in this invention are also disclosed in the two Research Disclosures mentioned above, as shown in the table below.

<u>Type of Additives</u>	<u>RD 17643</u>	<u>RD 18716</u>
1. Chemical Sensitizers	Page 23	Page 648, right column
2. Speed Increasing Agents		- ditto -
3. Spectral Sensitizers and Supersensitizers	Pages 23 to 24	Page 648, right column to page 649, right column
4. Whiteners	Page 24	
5. Antifoggants and Stabilizers	Pages 24 to 25	Page 649, right column
6. Light-Absorbers, Filter Dyes and UV Absorbers	Pages 25 to 26	Page 649, right column to page 650, left column

5	7. Antistaining Agents	Page 25, right column	Page 650, left column to right column
	8. Dye Image Stabilizers	Page 25	
10	9. Film Hardening Agents	Page 26	Page 651, left column
	10. Binders	Page 26	- ditto -
15	11. Plasticizers and Lubricants	Page 27	Page 650, right column
	12. Coating Promotors and Surfactants	Pages 26 to 27	- ditto -
20	13. Antistatic Agents	Page 27	- ditto -

Various color couplers can be used in this invention, and examples are disclosed in the patents disclosed in Research Disclosure (RD) No. 17643, sections VII C to G.

25 Those disclosed, for example, in U.S. Patents 3,933,501, 4,022,620, 4,326,024 and 4,401,752, JP-B-58-10739, and British Patents 1,425,020 and 1,476,760 are preferred as yellow couplers.

The 5-pyrazolone and pyrazoloazole based compounds are preferred as magenta couplers, and those disclosed, for example, in U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,064, Research Disclosure No. 24220 (June 1984), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-4365, and U.S. Patents 4,500,630 and 4,540,654 are especially desirable.

30 Phenol and naphthol based couplers are used as cyan couplers, and those disclosed, for example, in U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011 and 4,327,173, West German Patent (OLS) 3,329,729, European Patent 121,365A, U.S. Patents 3,446,622, 4,333,999, 4,451,559 and 4,427,767, and European Patent 161,626A are preferred.

35 The colored couplers for correcting the unwanted absorptions of colored dyes disclosed, for example, in Research Disclosure No. 17643 section VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,136,258, and British Patent 1,146,368, are preferred.

The couplers of which the colored dyes have a suitable degree of diffusibility disclosed in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570 and West German Patent (OLS) 3,234,533 are preferred.

40 Typical examples of polymerized dye forming couplers have been disclosed, for example, in U.S. Patents 3,451,820, 4,080,211 and 4,367,282, and British Patent No. 2,102,173.

The use of couplers which release photographically useful groups on coupling is preferred in this invention. The DIR couplers which release development inhibitors disclosed in the patents disclosed in the aforementioned Research Disclosure No. 17643, section VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, and U.S. Patent 4,248,962 are preferred.

45 The couplers disclosed in British Patents 2,097,140 and 2,131,188, JP-A-59-157638 and JP-A-59-170840 are preferred as couplers which release nucleating agents or development accelerators in the form of the image during development.

50 Other couplers which can be used in the photosensitive materials of this invention include the competitive couplers disclosed, for example, in U.S. Patent 4,130,427, the multi-equivalent couplers disclosed, for example, in U.S. Patents 4,283,472, 4,338,393 and 4,310,618, the DIR redox compound releasing couplers, DIR coupler releasing couplers, DIR redox compound releasing couplers or DIR coupler releasing redox compounds disclosed, for example, in JP-A-60-185950 and JP-A-62-24252, the couplers which release a dye to which color is restored after elimination as disclosed in European Patent 173,302A, the bleach accelerator releasing couplers disclosed, for example, in Research Disclosure Nos. 11449 and 242412, and JP-A-61-201247, and the ligand releasing couplers disclosed, for example, 55 in U.S. Patent 4,553,477.

The use of compounds which release diffusible development inhibitors, or precursors thereof, by means of a coupling reaction with the oxidized form of a developing agent as DIR compound is especially desirable in this invention.

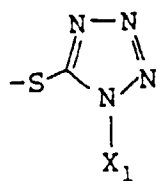
Compounds of this type are represented by formula (I):



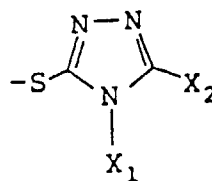
(I)

In this formula, A represents a coupler group capable of releasing (LINK)_n-B by means of a coupling reaction with an oxidized primary aromatic amine developing agent; LINK represents a groups which is bonded to the active coupling position of A and which is capable of releasing B after being released from A by the coupling reaction; B is a group represented by formulae (IIa), (IIb), (IIc), (IIe), (IIe), (IIe), (IIg), (IIh), (IIi), (IIj), (IIk), (III), (IIIm), (IIIn), (IIo), or (IIp) indicated below; and n is 0 or 1. Moreover, when n is zero, B is bonded directly to A.

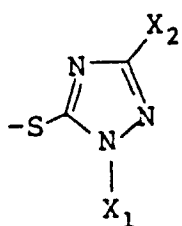
Formula (IIa)



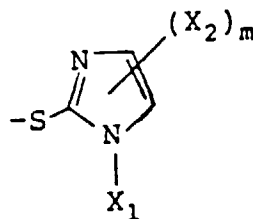
Formula (IIb)



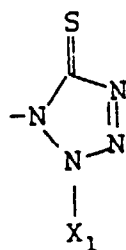
Formula (IIc)



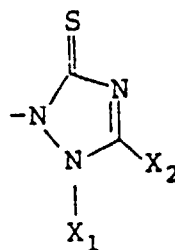
Formula (IId)



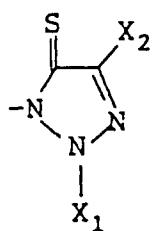
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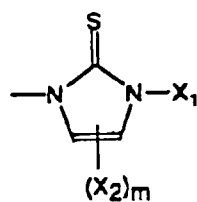
Formula (IIe)



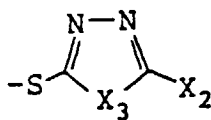
Formula (IIg)



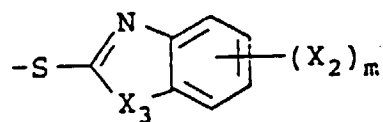
Formula (IIh)



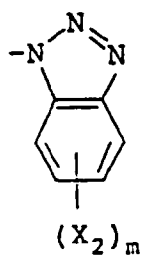
Formula (IIi)



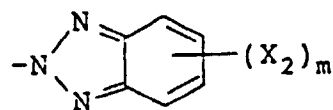
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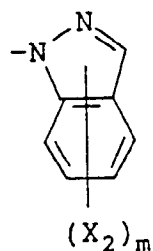
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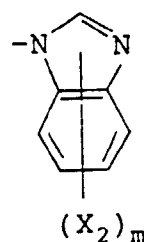
Formula (III)



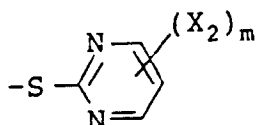
Formula (IIIm)



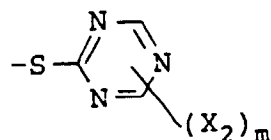
Formula (IIIn)



Formula (IIo)



Formula (IIp)



In these formulae, X_1 represents a substituted or unsubstituted aliphatic group which has from 1 to 4 carbon atoms (the substituent groups being selected from alkoxy groups, alkoxy carbonyl groups, hydroxyl groups, acylamino groups, carbamoyl groups, sulfonyl groups, sulfonamido groups, sulfamoyl groups, amino groups, acyloxy groups, cyano groups, ureido groups, acyl groups, halogen atoms and alkylthio groups, and the number of carbon atoms contained in these substituent groups is not more than 3) or a substituted phenyl group which preferably has from 6 to 20 carbon atoms (the substituent groups being selected from among hydroxyl groups, alkoxy carbonyl groups, acylamino groups, carbamoyl groups, sulfonyl groups, sulfonamido groups, sulfamoyl groups, acyloxy groups, ureido groups, carboxyl groups, cyano groups, nitro groups, amino group and acyl group, and the number of carbon atoms contained in these substituent groups is not more than 3). X_2 represents hydrogen, an aliphatic group, a halogen atom, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxy carbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a cyano group, a nitro group, an amino group, an alkoxy carbonylamino group, an aryloxy carbonyl group or an acyl group, in which these organic groups preferably have from 1 to 20 carbon atoms. X_3 represents hydrogen, sulfur or an imino group which has not more than 4 carbon atoms, and m is a integer of 1 or 2. However, the total number of carbon atoms in all of the m X_2 groups is not more than 8 and, when m is 2, the two X_2 groups may be the same or different.

The compounds represented by formula (I) are described in detail below.

Coupler residual groups which form dyes (for example, yellow, magenta and cyan dyes) on undergoing a coupling reaction with the oxidized form of a primary aromatic amine developing agent and coupler residual groups which provide coupling reaction products which have essentially no absorbance in the visible region are included among the coupler residual groups represented by A in formula (I).

Examples of yellow image forming coupler residual groups represented by A include coupler residual groups of the pivaloylacetanilide type, the benzoylacetanilide type, the malonic acid diester type, the malonic acid diamide type, the benzoylmethane type, the benzothiazolylacetamide type, the malonic acid ester monoamide type, the benzothiazolylacetate type, the benzoxazolylacetamide type, the benzoxazolylacetate type, the benzimidazolylacetamide type and the benzimidazolylacetate type, the coupler residual groups derived from heterocyclic substituted acetamides and heterocyclic substituted acetates included in U.S. Patent 3,841,880, the coupler residual groups derived from acylacetamides disclosed in U.S. Patent 3,770,446, British Patent 1,459,171, West German Patent (OLS) 2,503,099, JP-A-50-139738, and Research Disclosure No. 15737, and the heterocyclic type coupler residual groups disclosed in U.S. Patent 4,046,574.

Preferred examples of magenta image forming coupler residual groups represented by A include the coupler re-

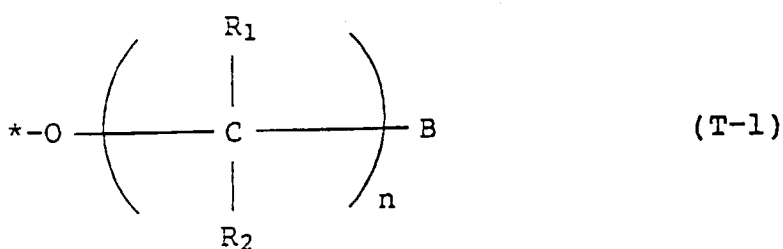
sidual groups which have a 5-oxo-2-pyrazoline nucleus, a pyrazolo-[1,5-a]-benzimidazole nucleus, a pyrazoloimidazole nucleus, a pyrazolotriazole nucleus or a pyrazolotetrazole nucleus, and the cyanoacetophenone type coupler residual groups.

Preferred examples of cyan image forming coupler residual groups represented by A include coupler residual groups which have a phenol nucleus or an α -naphthol nucleus.

Moreover, couplers which undergo a coupling reaction with the oxidized form of the developing agent and release a development inhibitor but which subsequently form no dye at all have the same effect as DLR couplers. Coupler residual groups of this type represented by A include those disclosed in U.S. Patents 4,052,213, 4,088,491, 3,632,345, 3,958,993 and 3,961,959. Moreover, A may be the coupler residual group of a polymerized coupler as disclosed in U.S. Patents 3,451,820, 4,080,211 and 4,367,282, and British Patent 2,102,173.

Preferred examples of LINK in general formula (I) are indicated below.

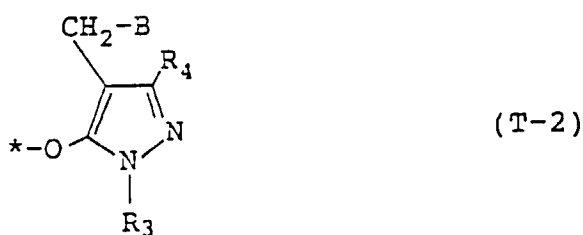
(1) Groups which make use of a hemi-acetal cleavage reaction. For example, those disclosed in U.S. Patent 4,146,396 and JP-A-60-249148, JP-A-60-249149 and JP-A-60-218645, and groups represented by the formula (T-1):



In this formula, * indicates the position which is bonded to the coupling position of A, R_1 and R_2 represent hydrogen or substituents n is 1 or 2, R_1 and R_2 each represents hydrogen, alkyl group which has from 1 to 4 carbon atoms, or aryl group which has from 6 to 10 carbon atoms, preferably hydrogen, and when n is 2, the two R_1 groups and the two R_2 groups may be the same or different, and any two of the R_1 and R_2 groups may be joined together to form a ring. B is as defined in formula (I).

(2) Groups which undergo a cleavage reaction by an intramolecular nucleophilic substitution reaction, for example, the timing groups disclosed in U.S. Patent 4,248,962.

(3) Groups which undergo a cleavage reaction by an electron transfer reaction along a conjugated system, for example, the groups disclosed in U.S. Patent 4,409,323, or groups which can be represented by formula (T-2) below (the groups disclosed in British Patent 2,096,783A).



In this formula, * indicates the position which is bonded to the coupling position of A, R_3 and R_4 represent hydrogen or substituent groups, and B is as defined in formula (I). Examples of the groups represented by R_3 include alkyl groups which have from 1 to 24 carbon atoms (for example, methyl, ethyl, benzyl, dodecyl) and aryl groups which have from 6 to 24 carbon atoms (for example, phenyl, 4-tetradecyloxyphenyl, 4-methoxyphenyl, 2,4,6-trichlorophenyl, 4-nitrophenyl, 4-chlorophenyl, 2,5-dichlorophenyl, 4-carboxyphenyl, p-tolyl), and examples of the groups represented by R_4 include hydrogen, alkyl groups which have from 1 to 24 carbon atoms (for example, methyl, ethyl, undecyl, pentadecyl), aryl groups which have from 6 to 36 carbon atoms (for example, phenyl, 4-methoxyphenyl), cyano groups, alkoxy groups which have from 1 to 24 carbon atoms (for example, methoxy, ethoxy, dodecyloxy), amino groups which have from 0 to 36 carbon atoms (for example, amino, dimethylamino, piperidino, dihexylamino anilino), carbonamido groups which have from 1 to 24 carbon atoms (for example, acetamido, benzamido, tetradecanamido), sulfonamido groups

which have from 1 to 24 carbon atoms, for example, methylsulfonamido, phenylsulfonamido), carboxyl groups, alkoxycarbonyl groups which have from 2 to 24 carbon atoms (for example, methoxycarbonyl, ethoxycarbonyl, dodecyloxy-carbonyl) and carbamoyl groups which have from 1 to 24 carbon atoms (for example, carbamoyl, dimethylcarbamoyl, pyrrolidinocarbonyl).

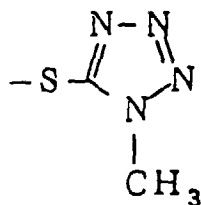
5 Examples of the substituent groups X_1 , X_2 and X_3 in the groups represented by the general formulae (IIa) to (IIp) are indicated below.

Thus, X_1 may be, for example, methyl, ethyl, propyl, butyl, methoxyethyl, ethoxyethyl, iso-butyl, allyl, dimethylaminoethyl, propargyl, chloroethyl, methoxycarbonylmethyl, methylthioethyl, 4-hydroxyphenyl, 3-hydroxyphenyl, 4-sulfamoylphenyl, 3-sulfamoylphenyl, 4-carbamoylphenyl, 3-carbamoylphenyl, 4-dimethylaminophenyl, 3-acetamidophenyl, 10 4-propanamidophenyl, 4-methoxyphenyl, 2-hydroxyphenyl, 2,5-dihydroxyphenyl, 3-methoxycarbonylaminoethyl, 3-(3-methylureido)phenyl, 3-(3-ethylureido)phenyl, 4-hydroxyethoxyphenyl or 3-acetamido-4-methoxyphenyl; X_2 may be, for example, hydrogen, methyl, ethyl, benzyl, n-propyl, iso-propyl, n-butyl, iso-butyl, cyclohexyl, fluorine, chlorine, bromine iodine, hydroxymethyl, hydroxyethyl, hydroxyl, methoxy, ethoxy, butoxy, allyloxy, benzyloxy, methylthio, ethylthio, methoxycarbonyl, ethoxycarbonyl, acetamido, propanamido, butanamido, octanamido, benzamido, dimethylcarbamoyl, methylsulfonyl, methylsulfonamido, phenylsulfonamido, dimethylsulfamoyl, acetoxyl, ureido, 3-methylureido, 15 cyano, nitro amino, 1-methyl-2-benzthiazolylideneamino, dimethylamino, methoxycarbonylamino, ethoxycarbonylamino, phenoxycarbonyl, methoxyethyl or acetyl; and X_3 may be, for example, hydrogen sulfur, imino, methylimino, ethylimino, propylimino or allylimino.

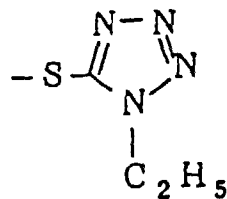
Those groups represented by formulae (IIa) to (IIp) which are represented by the general formulae (IIa), (IIb), (IIi), (IIj), (IIk), and (III) are preferred, and of these groups, those represented by the general formulae (IIa), (IIi), (IIj) and (IIk) are especially preferred.

Examples of groups which can be represented by B in general formula (I) are indicated below.

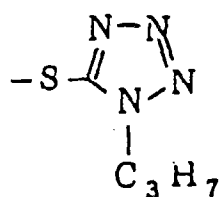
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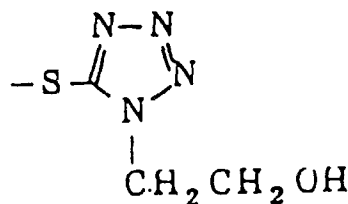
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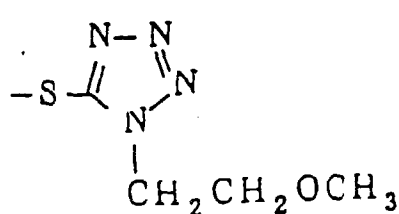
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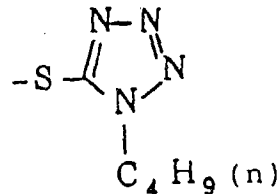
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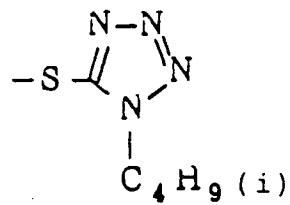
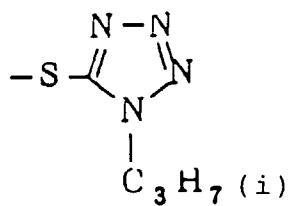
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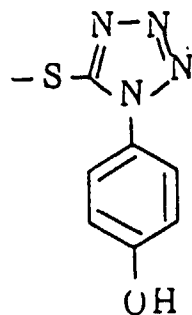
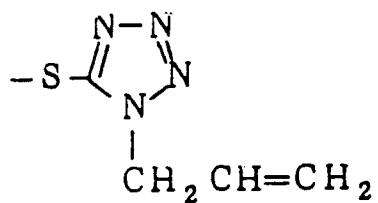


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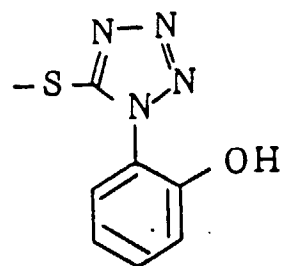
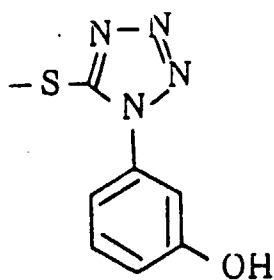
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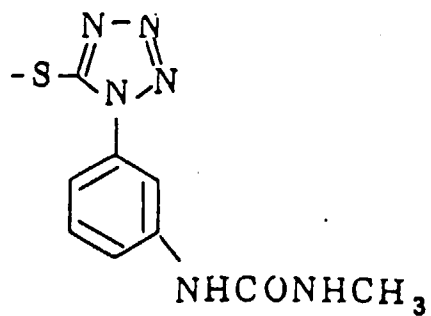
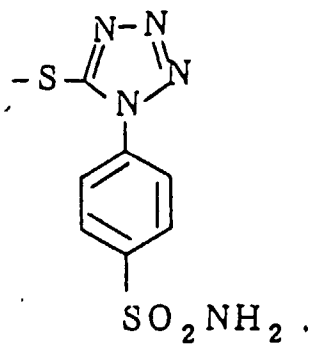
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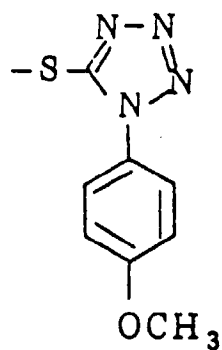
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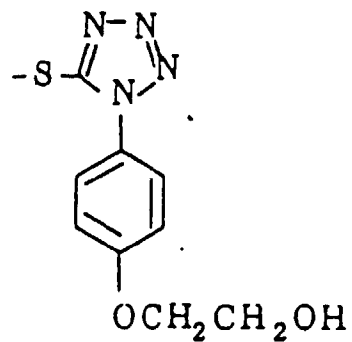
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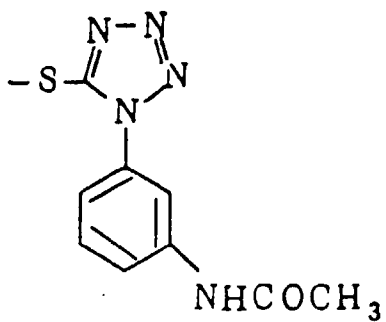


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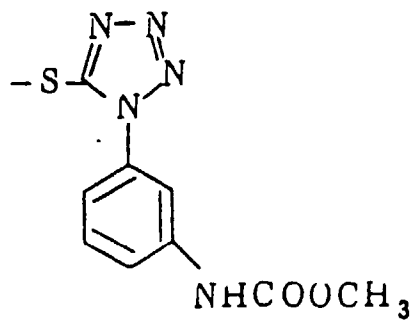


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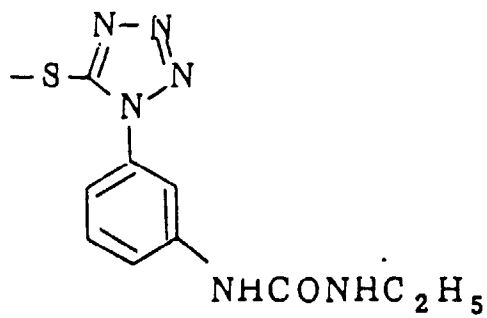


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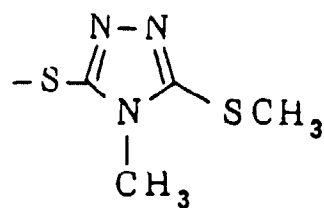


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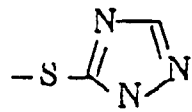
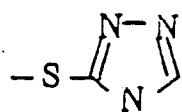
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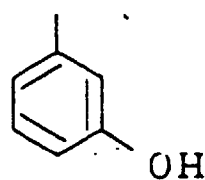
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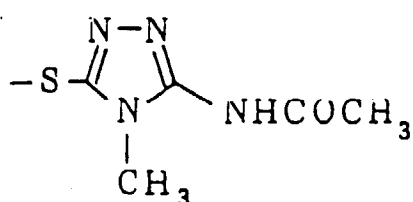
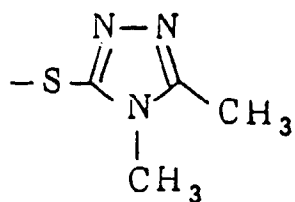


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OH

OH

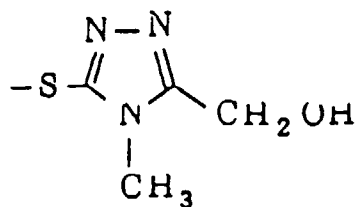
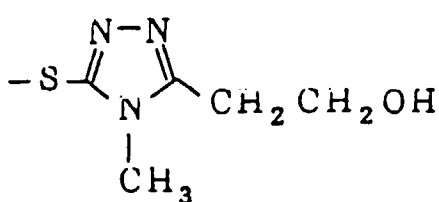
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CH₃NHCOCH₃CH₃CH₃

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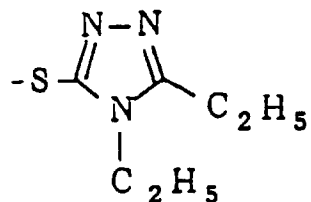
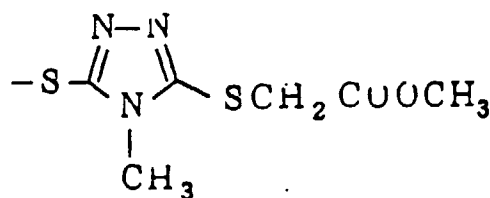


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CH₂CH₂OHCH₂OHCH₃CH₃

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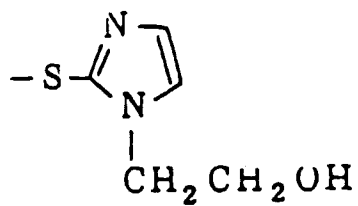


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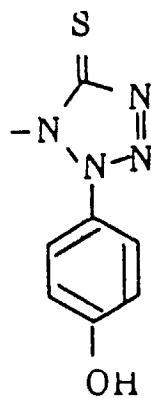
SCH₂COOCH₃C₂H₅CH₃C₂H₅

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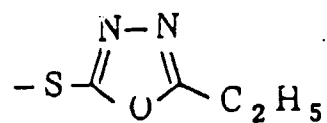
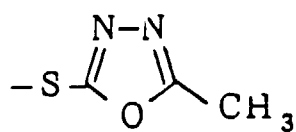


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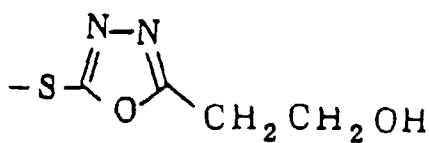
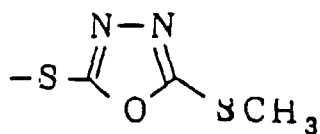
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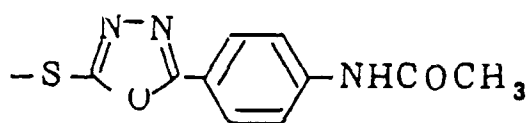
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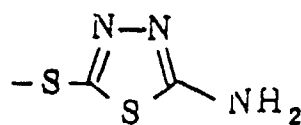
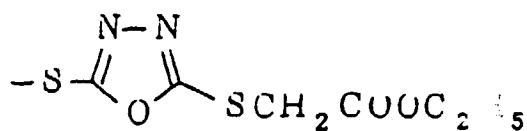
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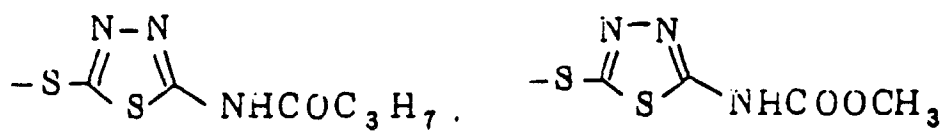
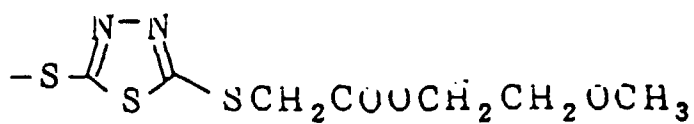
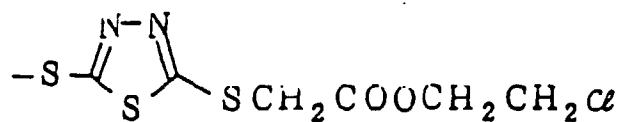
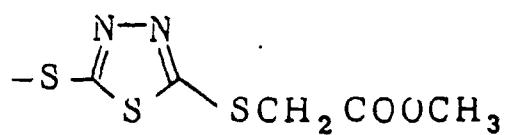
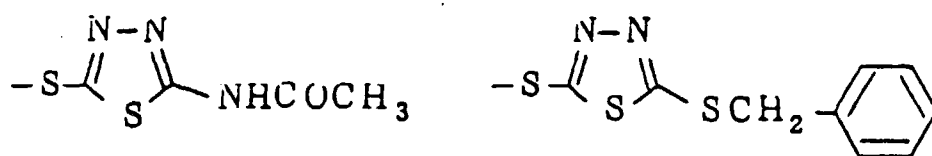


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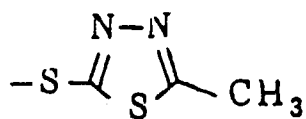
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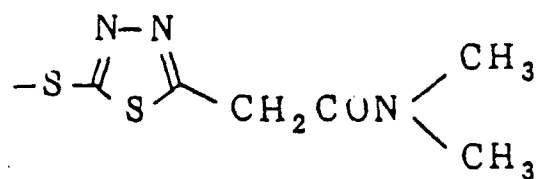
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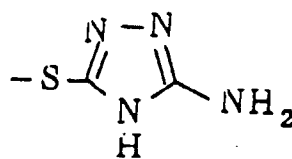
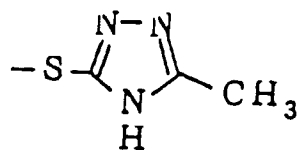
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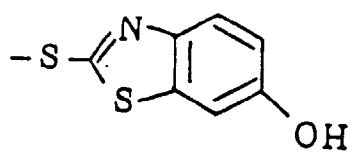
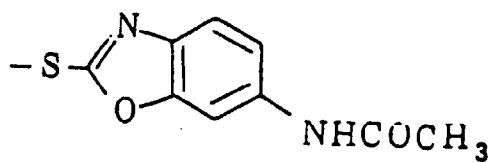
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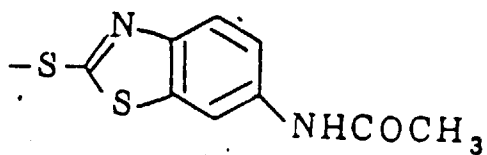
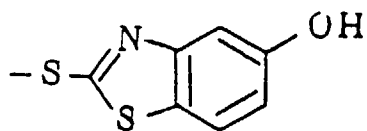
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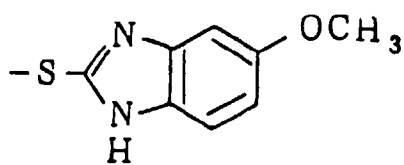
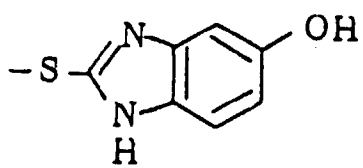
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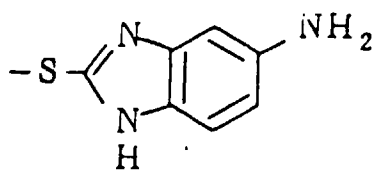
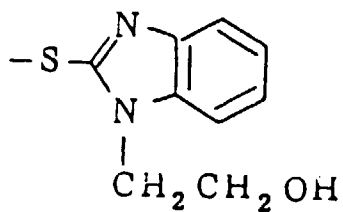
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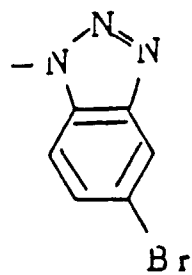
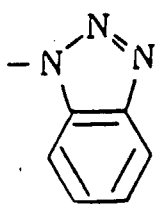
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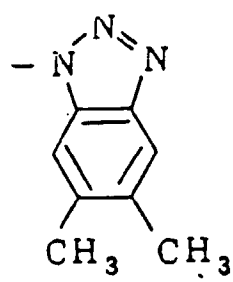
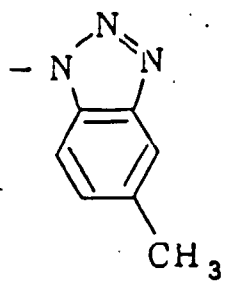
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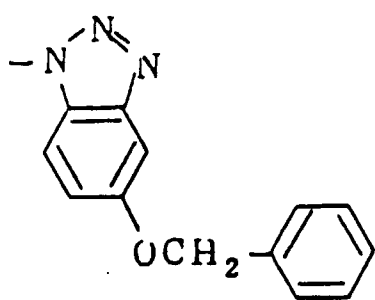


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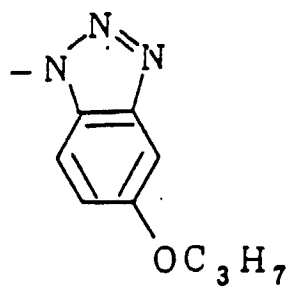
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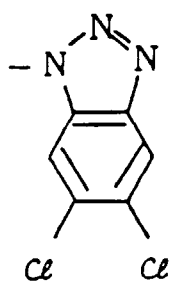


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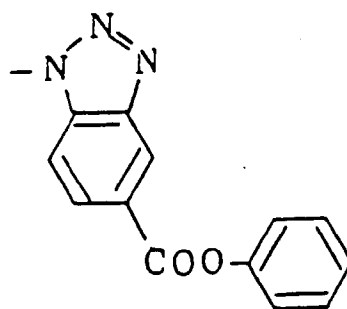


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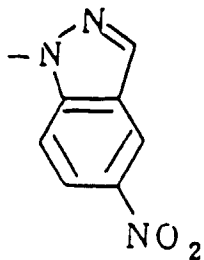


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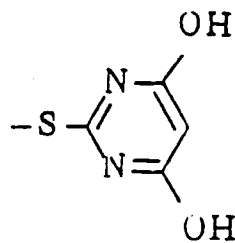


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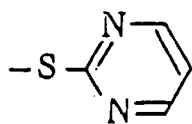
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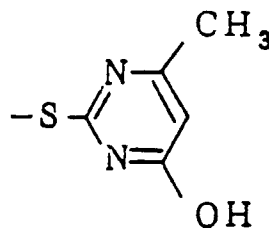
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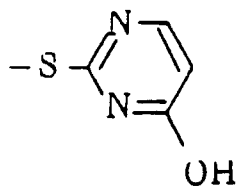


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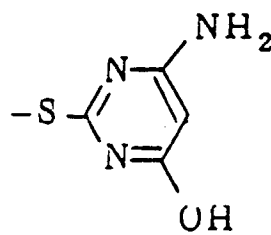


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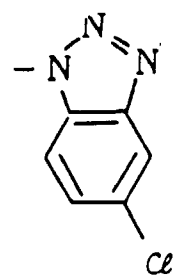
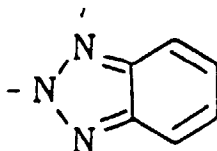
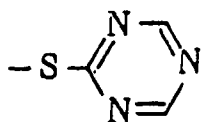
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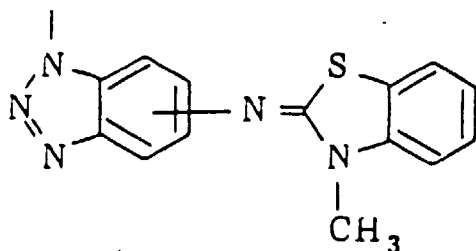
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Examples of couplers used in this invention are indicated below.

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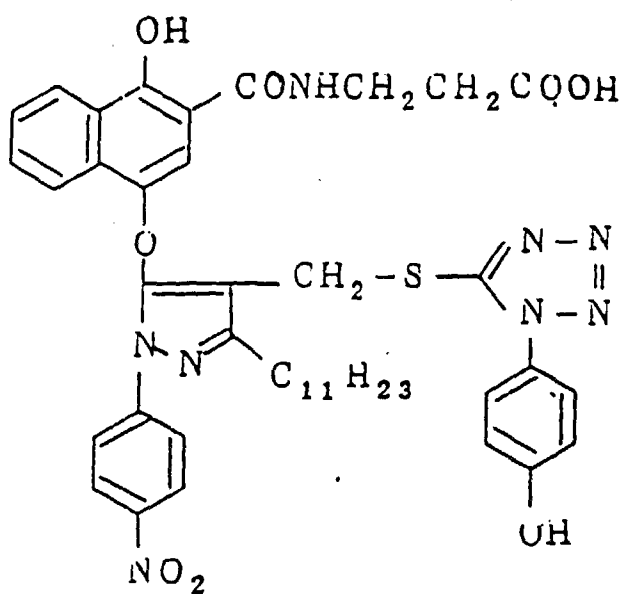
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(D-2)

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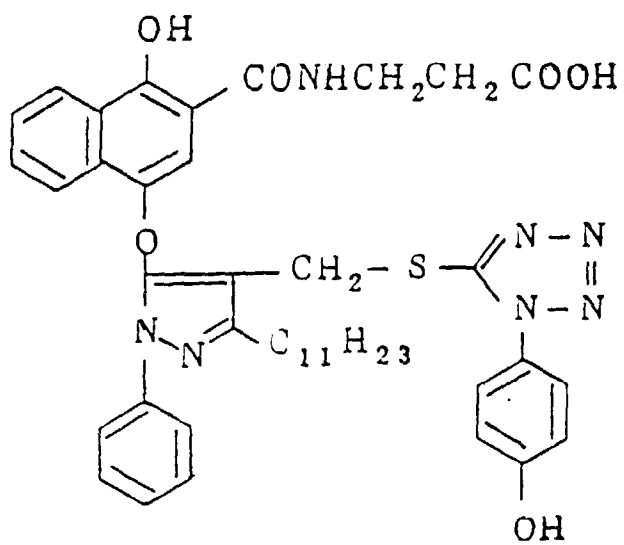
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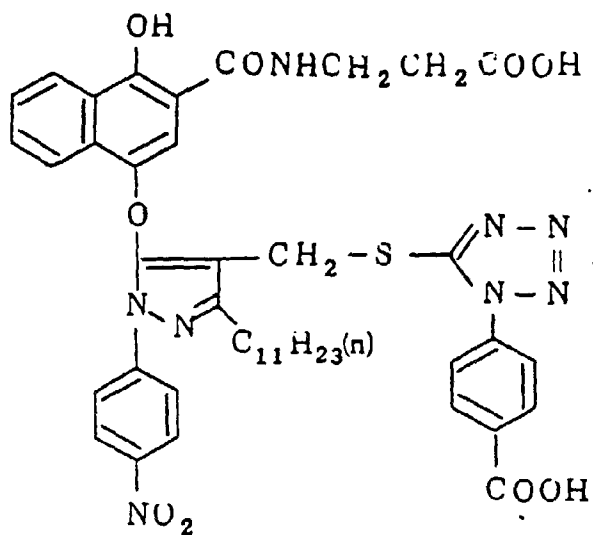
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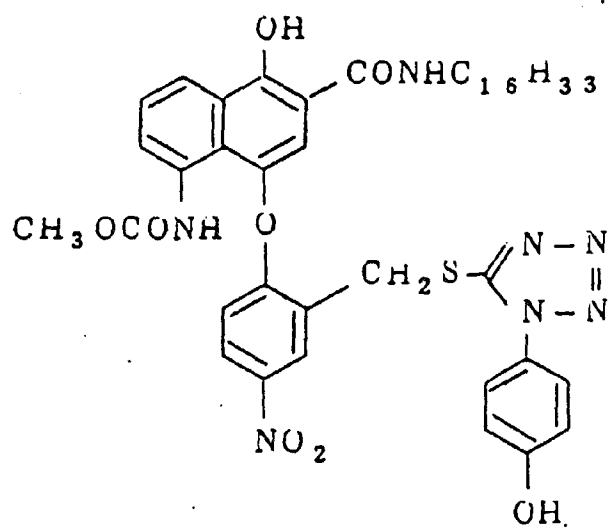
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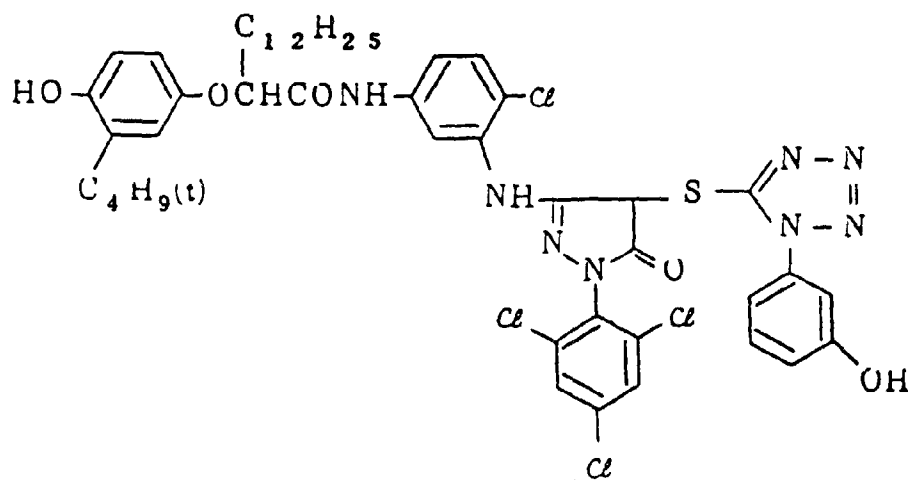
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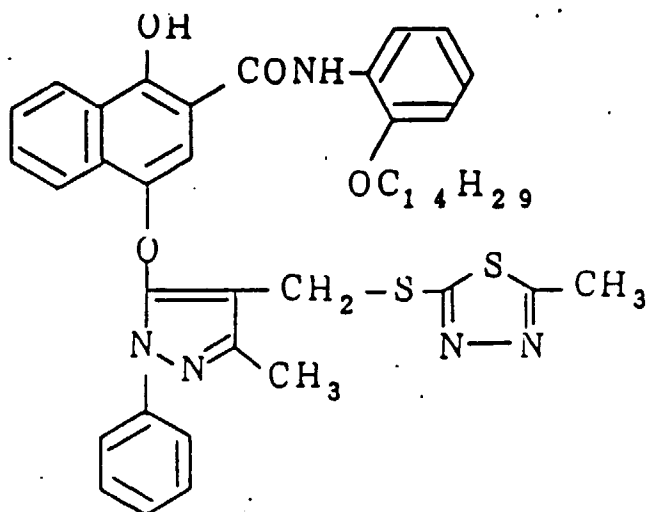
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(D-5)



(D-6)



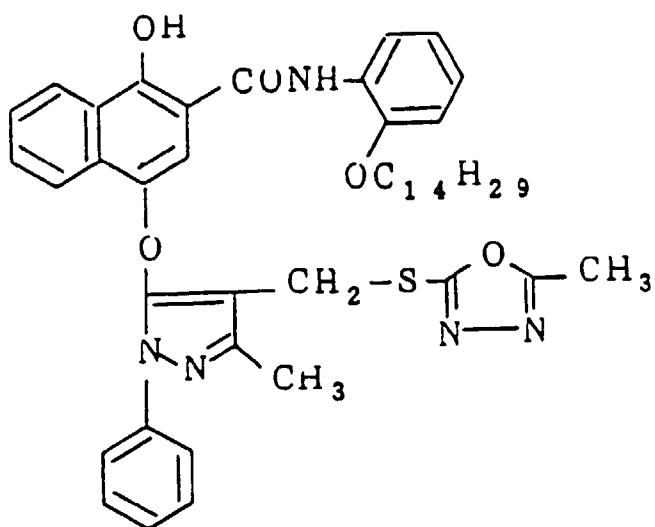
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(D-8)

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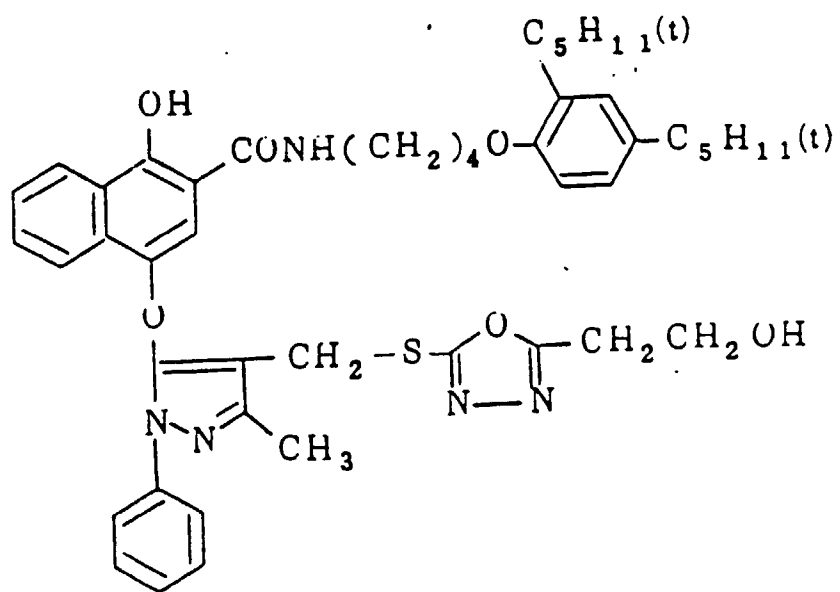
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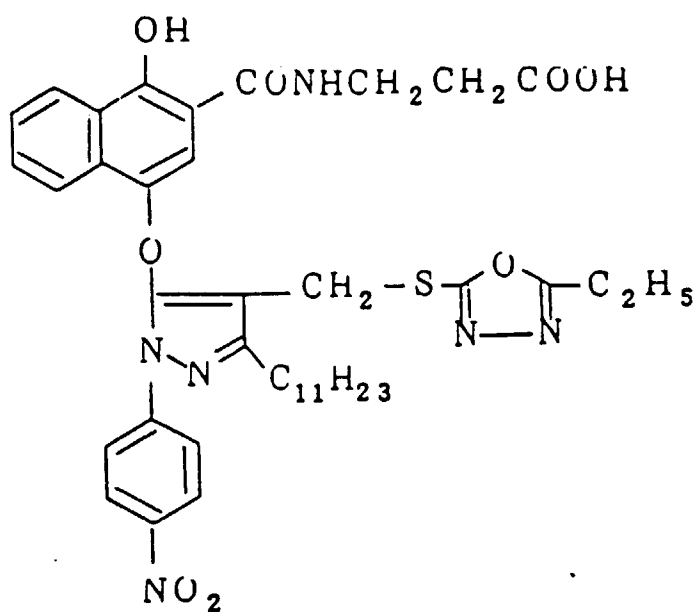
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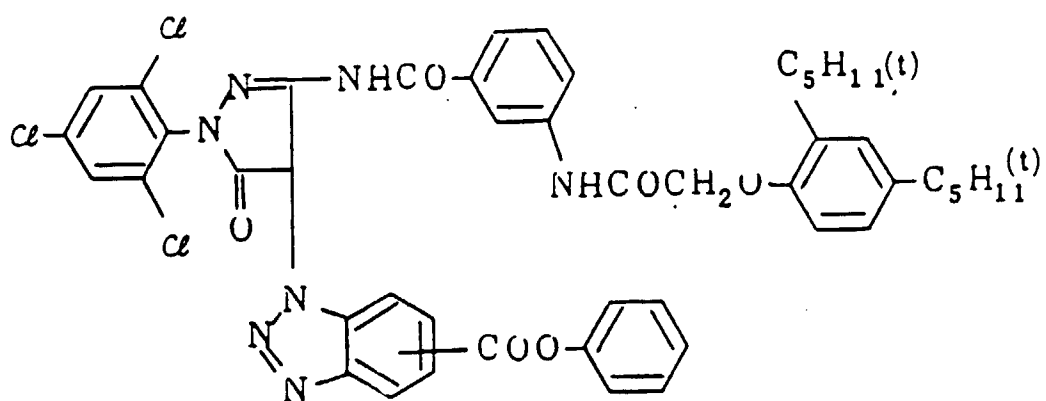
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(D-9)



(D-10)



(D-11)

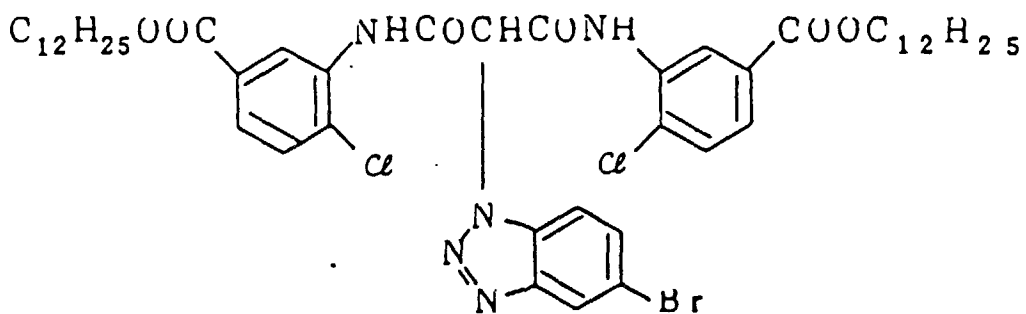
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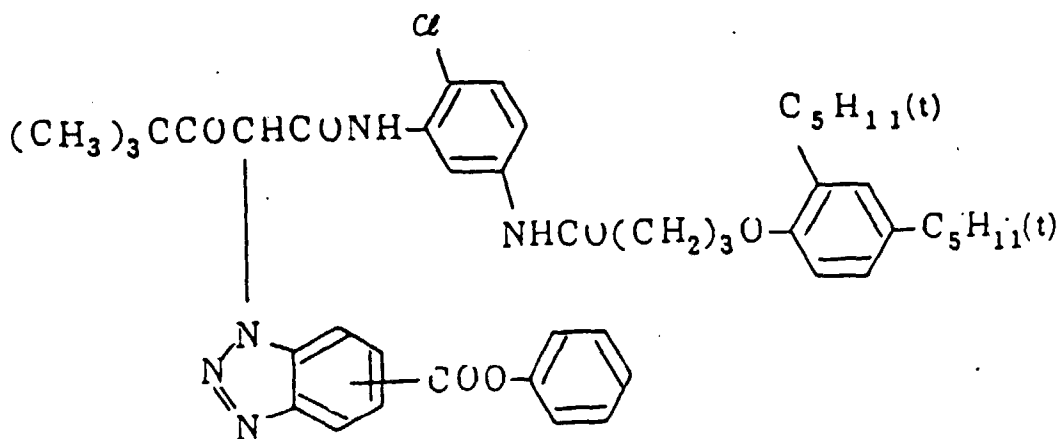
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(D-12)

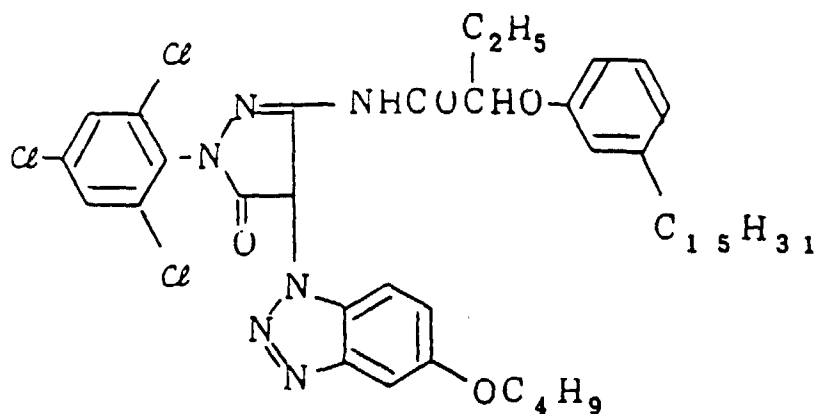


(D-13)

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(D-14)

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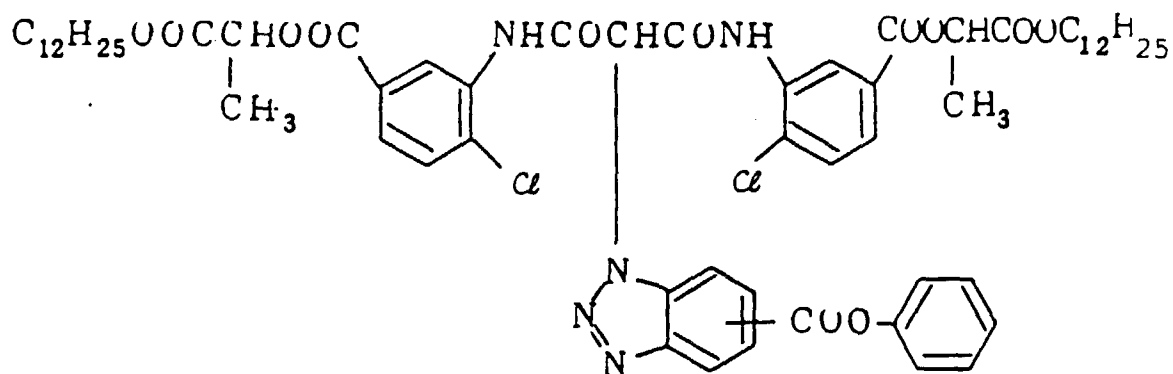
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(D-15)

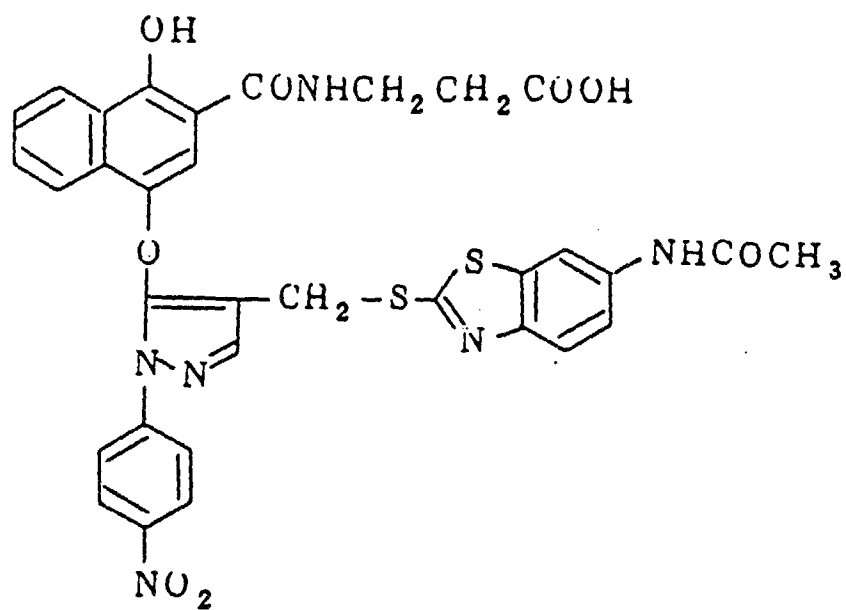
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(D-16)

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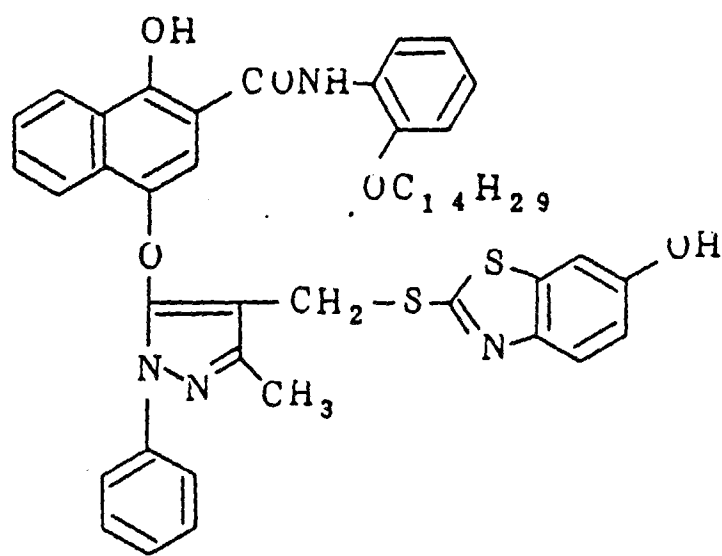
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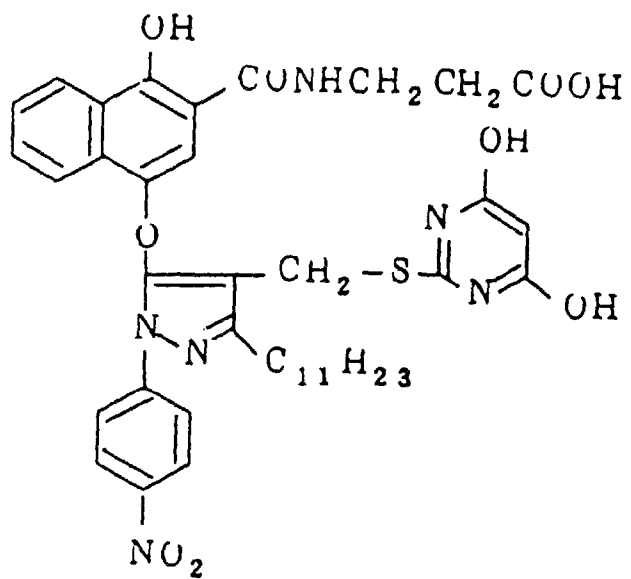
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(D-18)

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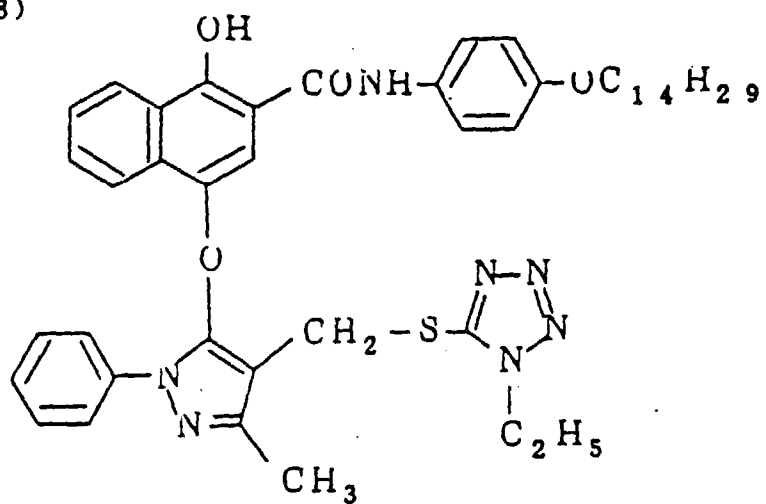
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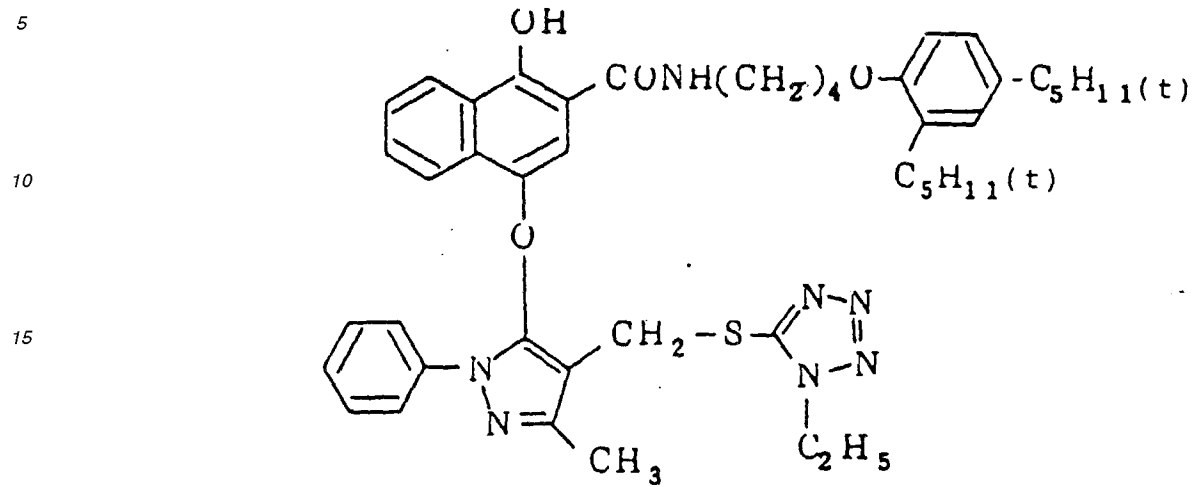
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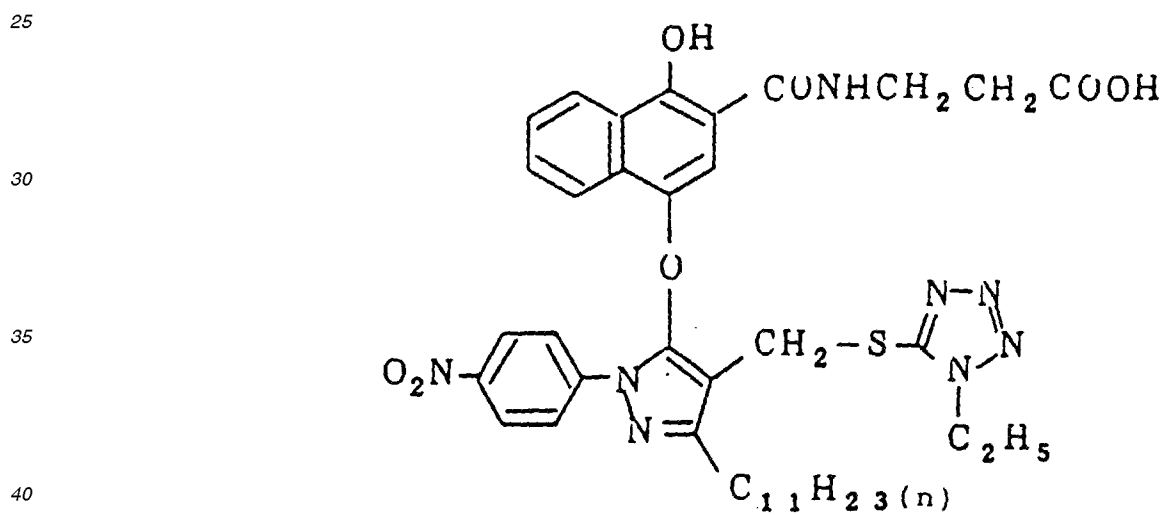
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(D-19)



(D-20)



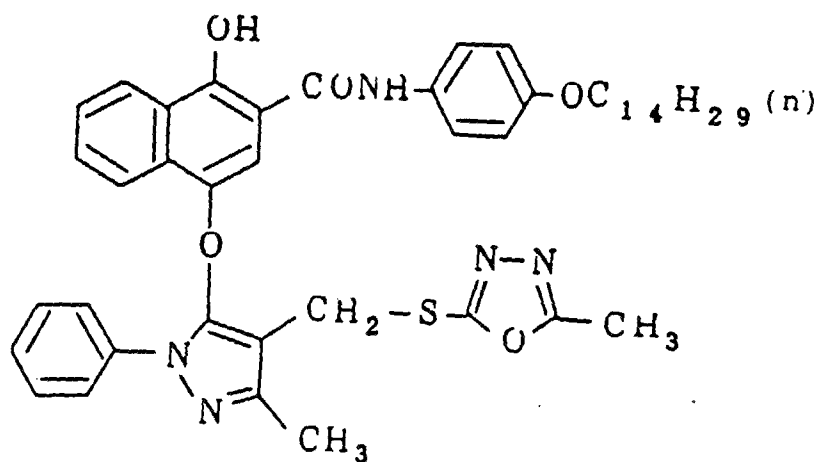
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(D-21)

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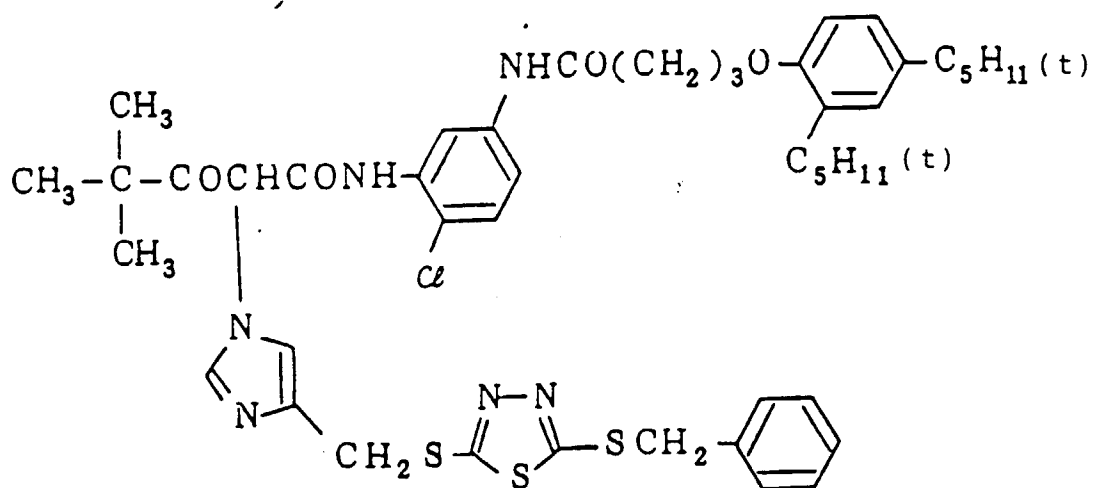
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(D-21) (sic)

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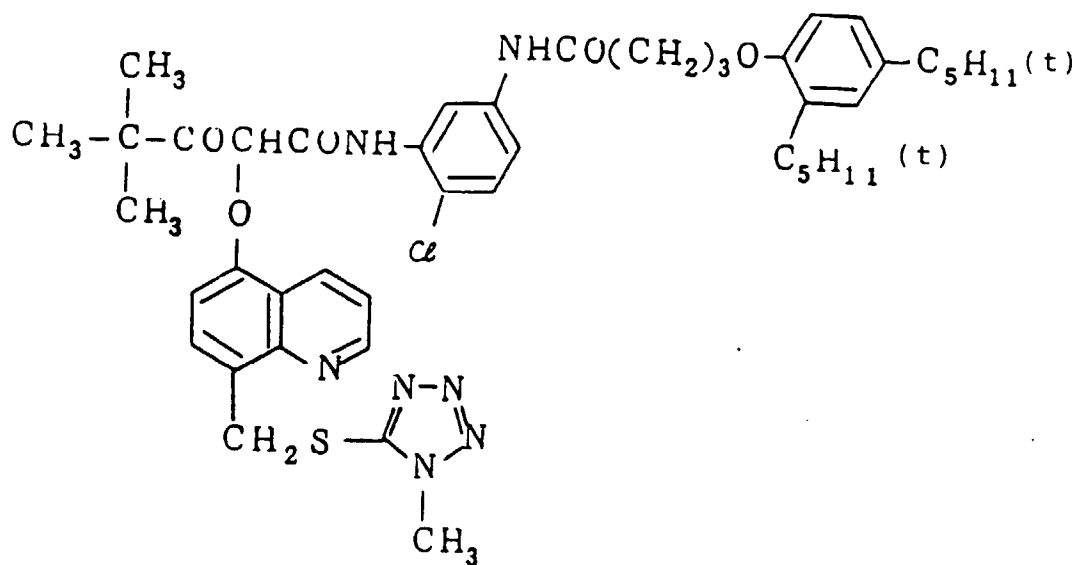


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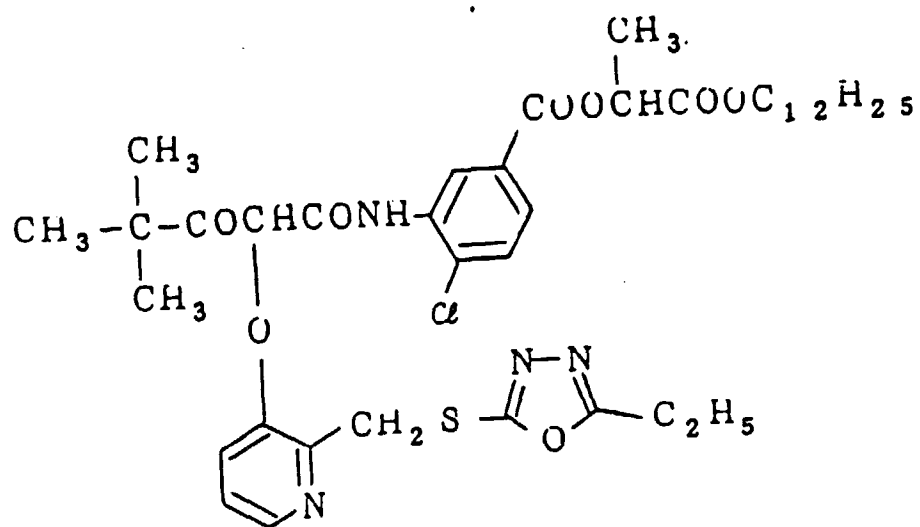
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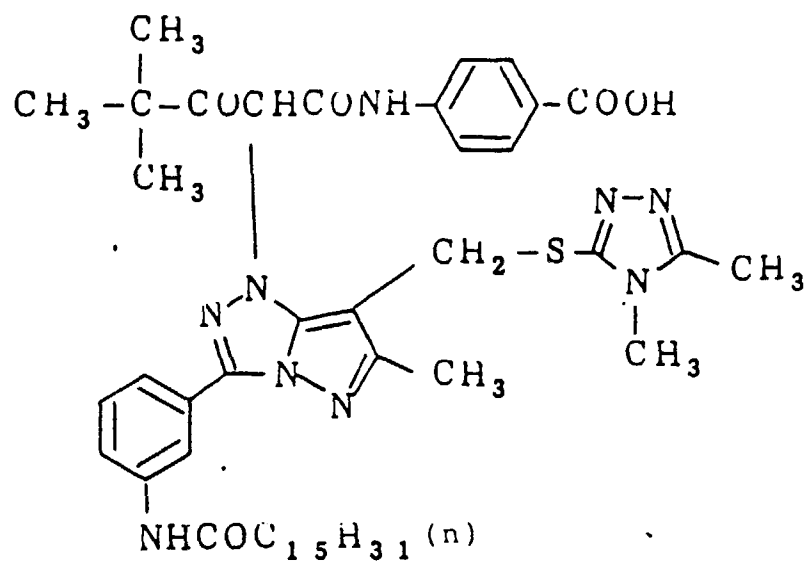
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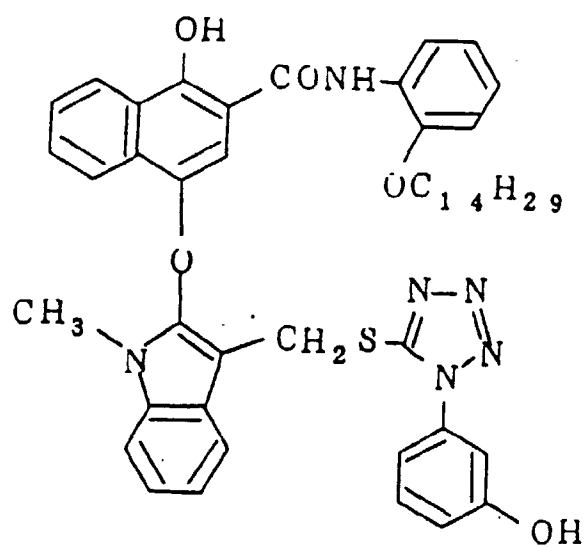
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(D-24)



(D-25)



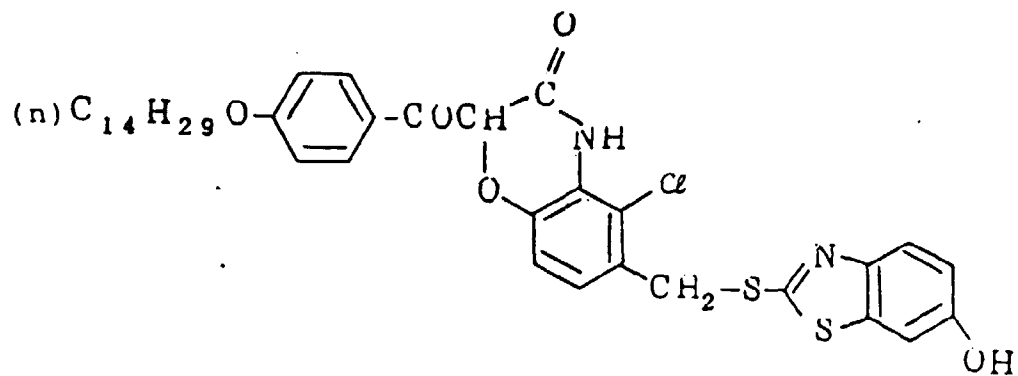
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(D-26)

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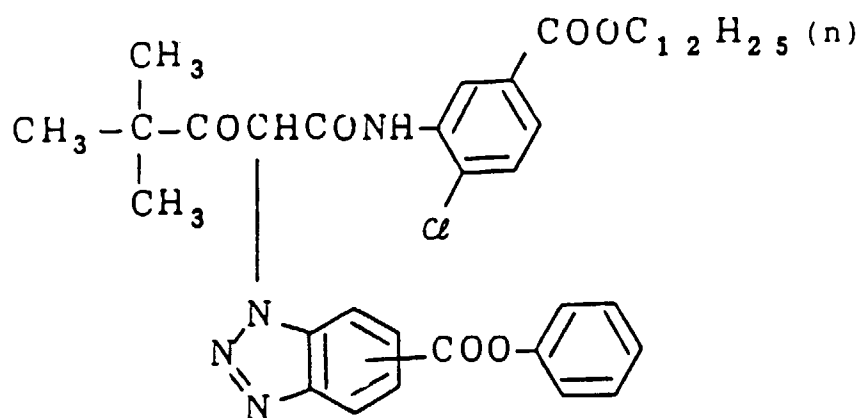
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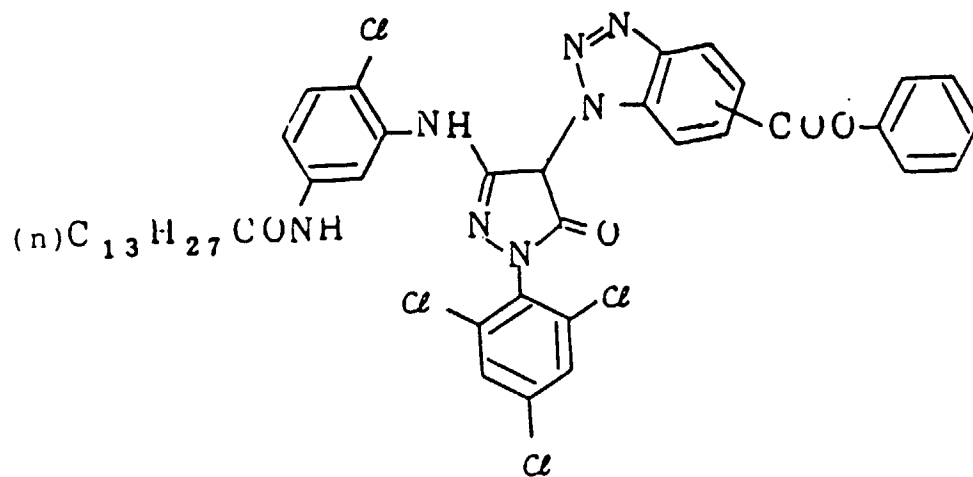


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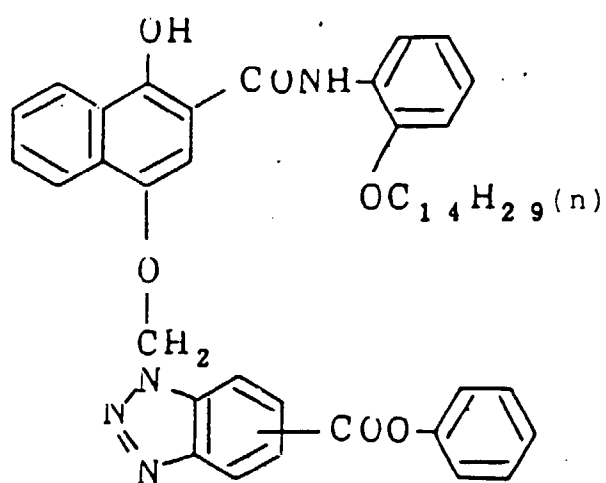
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(D-28)



(D-29)



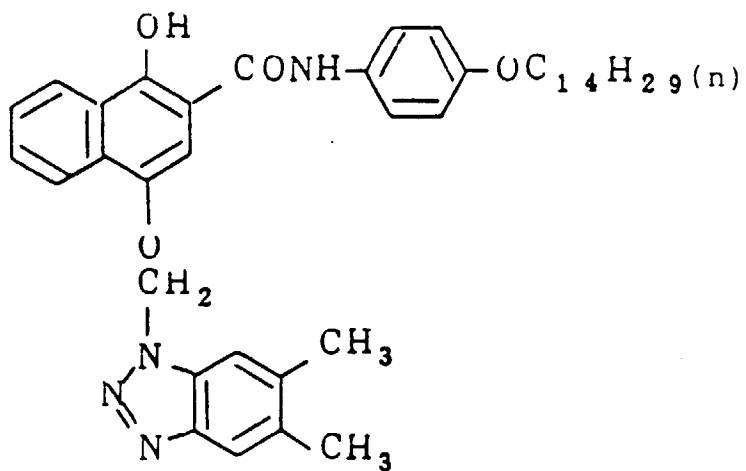
(D-30)

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(D-31)

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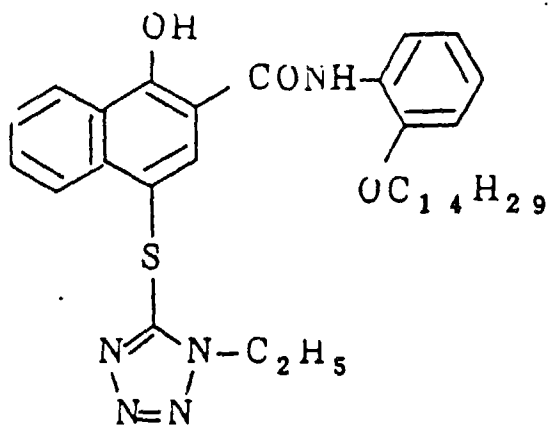
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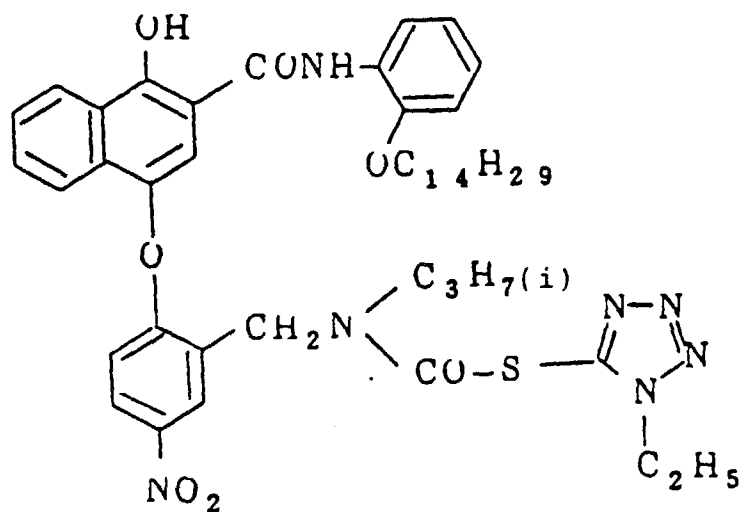
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(D-32)



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(D-33)

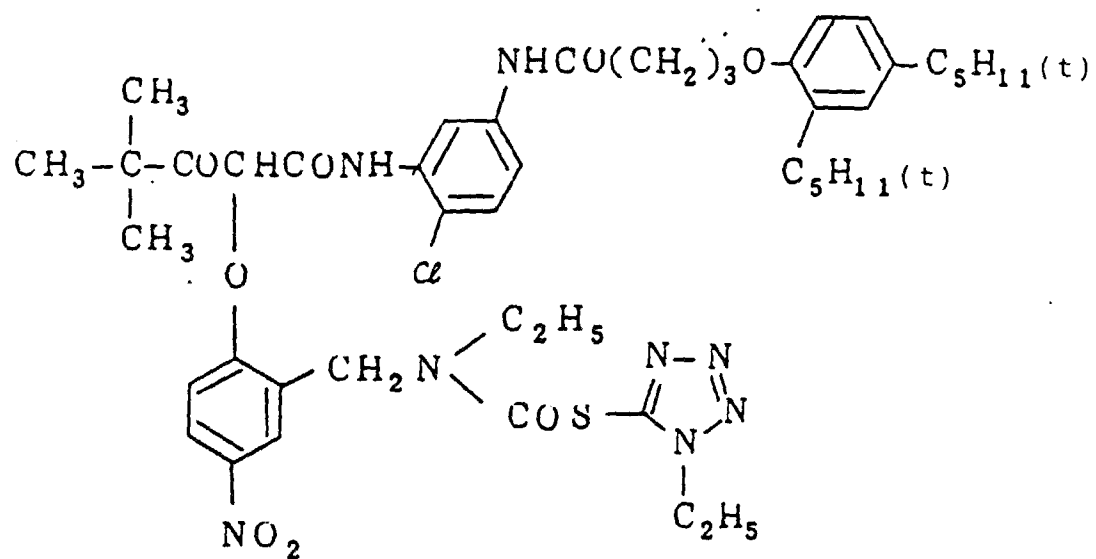
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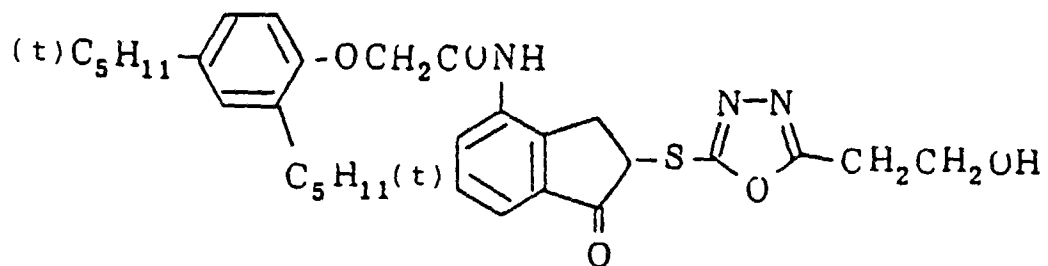


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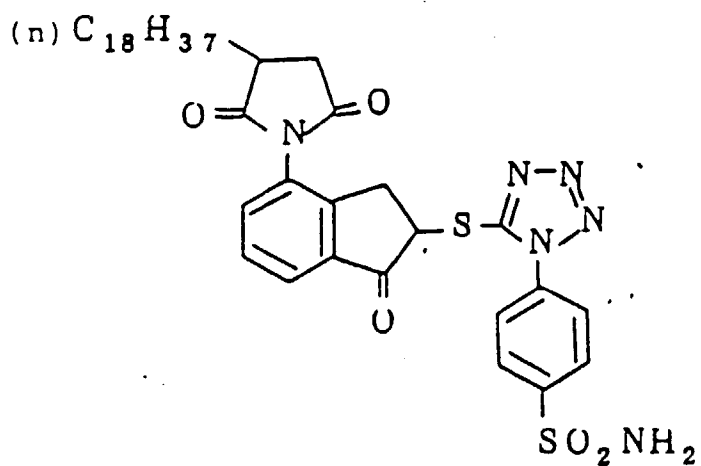
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(D-35)

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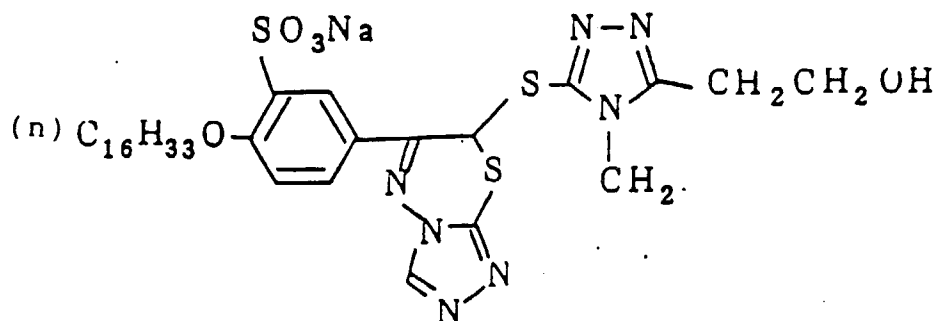
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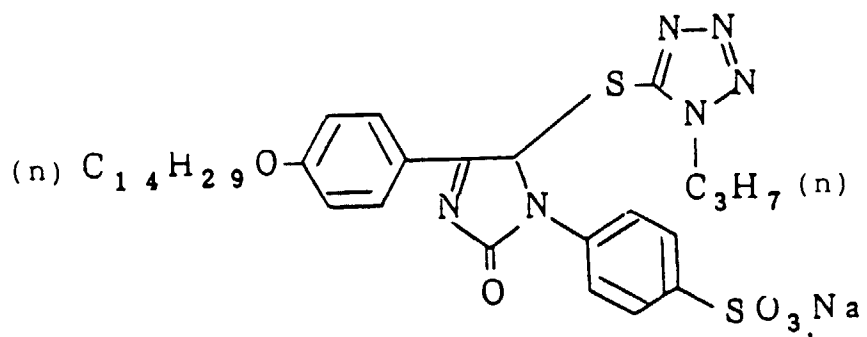
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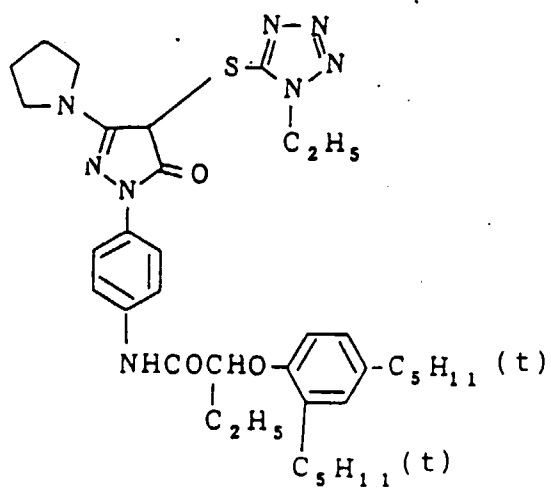
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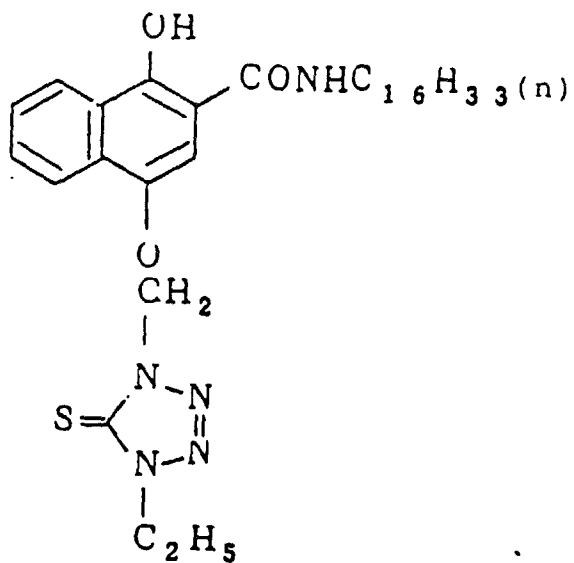
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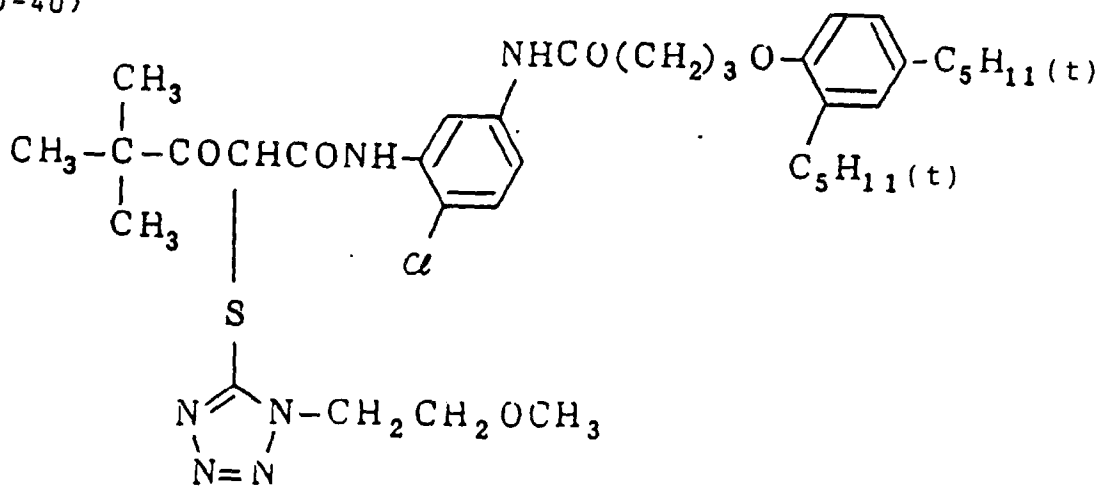
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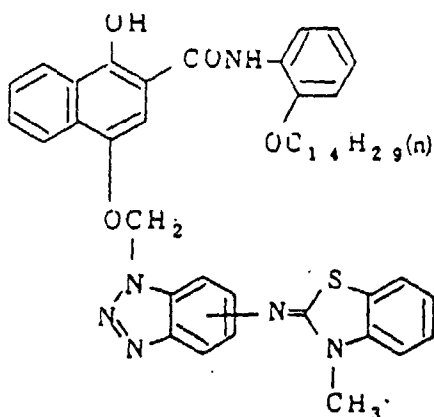
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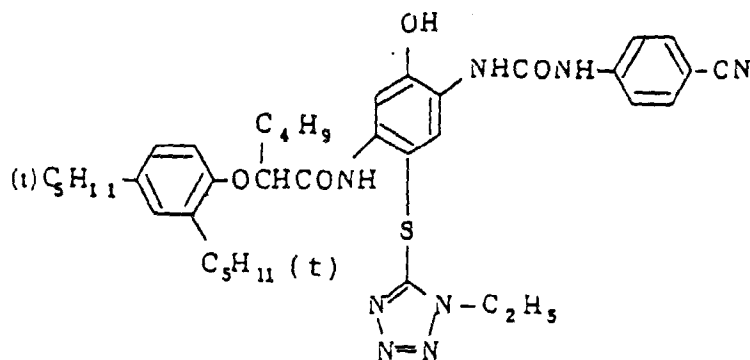
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(D-43)



(D-44)



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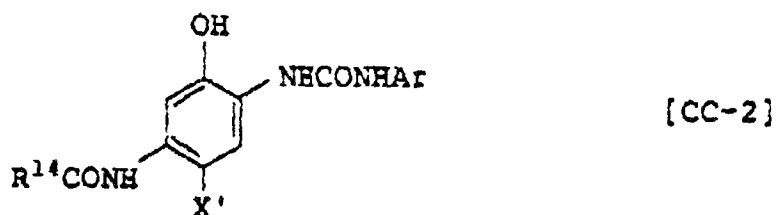
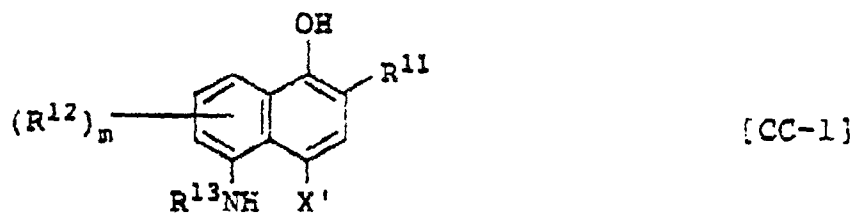
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These compounds represented by formula (I) can be prepared using the methods disclosed in U.S. Patents 4,174,966, 4,183,752, 4,421,845 and 4,477,563, JP-A-54-145135, JF-A-57-151944, JF-A-57-154234, JP-A-57-188035, JP-A-58-98728, JP-A-58-162949, JP-A-58-209736, JP-A-58-209737, JP-A-58-209738 and JP-A-58-209740.

The compounds represented by formula (I) are included in the photosensitive material in at least one of the silver halide emulsion layers, intermediate layers, filter layers (yellow filter layer, magenta filter layer), undercoating layers, anti-halation layers, protective layers or other auxiliary layers, but they are preferably included in the photosensitive silver halide emulsion layers or in photosensitive layers which are adjacent thereto and, most desirably, they are included in layers which contain emulsion grains used this invention or in layers of the same color sensitivity which are adjacent thereto.

The compounds represented by formula (I) can be included in the photosensitive material using the same methods as used for the dispersion of couplers as described below. The total quantity of these compounds added is from 10⁻⁶ to 10⁻³ mol/m², preferably from 3×10⁻⁶ to 5×10⁻⁴ mol/m², and most desirably from 5×10⁻⁶ to 2×10⁻⁴ mol/m².

The use of compounds represented by the formulae (CC-1), (CC-2) and (CC-5) below as cyan couplers is preferred in this invention.



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R¹¹ in these formulae represents -CONR¹⁵R¹⁶, -NHCOR₁₅, -NHCOOR¹⁷, -SO₂NR¹⁵R¹⁷, -NHSO₂R¹⁷, -NHCONR¹⁵R¹⁶ or -NHSO₂NR¹⁵R¹⁶.

R¹⁵, R¹⁶ and R¹⁷, which may be the same or different, each represents an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms, or a heterocyclic group which has from 2 to 30 carbon atoms.

R¹² represents a halogen atom, a hydroxyl group, an amino group, a carboxyl group, a sulfonic acid group, a cyano group, an aromatic group, a heterocyclic group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a ureido group, an acyl group, an acyloxy group, an aliphatic oxy group, an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an aliphatic sulfonyl group, an aromatic sulfonyl group, a sulfamoylamino group, a nitro group, or an imido group, and the number of carbon atoms contained in R¹² is from 0 to 30. Moreover, m is 0 or an integer from 1 to 3.

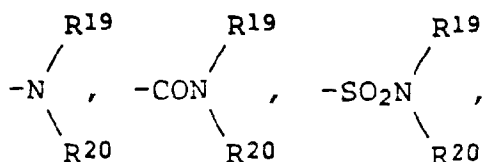
The dioxymethylene group is an example of a cyclic R¹² when m is 2.

R¹³ is represented by formula (CC-3) indicated below.



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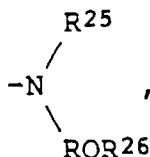
Here, Y represents >NH, >CO or >SO₂, n is 0 or 1, and R¹⁸ represents hydrogen, an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms, a heterocyclic group which has from 3 to 30 carbon atoms, -OR¹⁹, -SR¹⁹, -COR¹⁹,



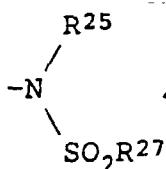
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-CO₂R²¹, -SO₂R²¹ or -SO₂OR²¹, -SO₂R²¹ or -SO₂OR²¹. Here R¹⁹, R²⁰ and R²¹ which may be the same or different, each has the same definition as R¹⁵.

R¹⁵ and R¹⁶ in

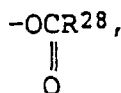


-SO₂R²⁷, -SOR²⁷, -OCOR²⁷ and

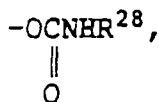
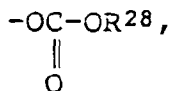


R²⁵ and R²⁶, which may be the same or different, each represents hydrogen, an aliphatic group, aromatic group or heterocyclic group; and R²⁷ represents an aliphatic group, aromatic group or heterocyclic group. The number of carbon atoms in Ar is from 6 to 30, and phenyl groups substituted with the aforementioned substituent groups are preferred.

X' represents hydrogen or a group which is eliminated on coupling (including the leaving atom, same below) a "coupling-off group". Typical examples of groups which are eliminated on coupling include halogen atoms, -OR²⁸, -SR²⁸,



-NHCOR²⁸, -NHSR²⁸,

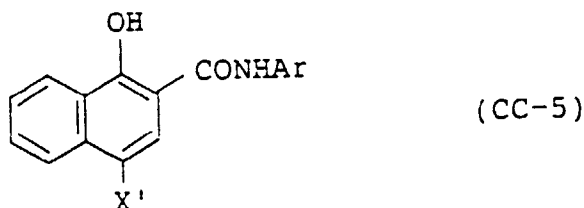


aromatic oxo groups which have from 6 to 30 carbon atoms and heterocyclic groups which have from 1 to 30 carbon atoms which are bonded to the active coupling position of the coupler via a nitrogen atom (for example, succinimido group, phthalimido group, hydantoinyl group, pyrazolyl group, 2-benzotriazolyl group). Here, R²⁸ represents an aliphatic group which has from 1 to 30 carbon atoms, an aromatic group which has from 6 to 30 carbon atoms, or a heterocyclic group which has from 2 to 30 carbon atoms.

The aliphatic groups in the compounds used in this invention can, as mentioned before, be saturated or unsaturated, substituted or unsubstituted, linear chain, branched chain or cyclic groups, and some typical examples include a methyl group, ethyl group, butyl group, cyclohexyl group, allyl group, propargyl group, methoxyethyl group, n-decyl group, n-dodecyl group, n-hexadecyl group, trifluoromethyl group, pentafluoropropyl group, dodecyloxypropyl group, 2,4-di-tert-amylphenoxypropyl group and 2,4-di-tert-amylphenoxybutyl group.

Furthermore, the aromatic groups may also be substituted or unsubstituted groups, and typical examples include a phenyl group, tolyl group, 2-tetradecyloxyphenyl group, pentafluorophenyl group, 2-chloro-5-dodecyloxyphenyl group, 4-chlorophenyl group, 4-cyanophenyl group and 4-hydroxyphenyl group.

The heterocyclic groups may also be substituted or unsubstituted groups, and typical examples include a 2-pyridyl group, 4-pyridyl group, 2-furyl group, 4-thienyl group and quinolinyl group.

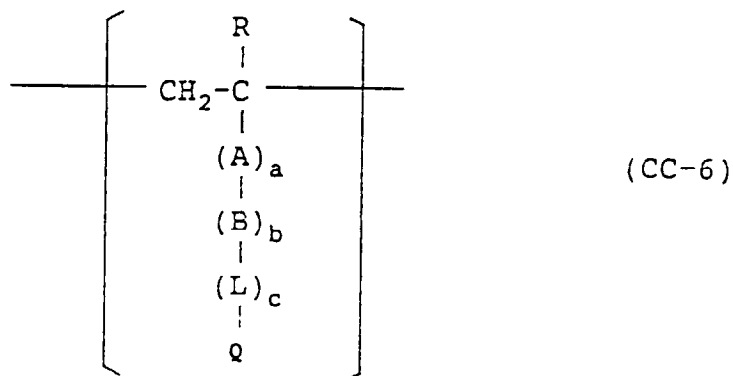


15 Ar and X' in the above formula have the same definition as in formula (CC-2).

Ar in general formula (CC-5) represents an aromatic group which has from 6 to 30 carbon atoms, and the preferred substituent groups include alkyl groups, alkoxy groups, halogen atoms, alkoxy carbonyl groups, carbonamido groups, sulfonamido groups, alkoxy carbonamino groups and alkylthio groups, and the most desirable substituent groups are alkoxy groups (for example, methoxy, ethoxy, propyloxy, butoxy, benzyloxy, methoxyethoxy, 2-ethylhexyloxy, decyloxy, dodecyloxy, tetradecyloxy, 2-hexadecyloxy, 2-dodecyloxyethoxy, 2-dodecylthiopropoxy) and halogen atoms (fluorine, chlorine, bromine, iodine).

20 Couplers represented by the general formula (CC-1) can be joined at the substituent groups R¹¹, R¹², R¹³ or X', and couplers represented by the general formulae (CC-2) and (CC-5) can be joined at the substituent groups Ar, via divalent groups or groups which have a valency of more than two to form dimers, oligomers or larger units. In this case, 25 the number of carbon atoms may be outside the ranges specified for each substituent group as described earlier.

30 Homopolymers or copolymers of addition polymerizable ethylenic type unsaturated compounds which have cyan dye forming coupler residual groups (cyan color forming monomers) are typical examples in which couplers represented by the general formulae (CC-1), (CC-2) and (CC-5) form oligomers. In this case, the oligomer contains repeating units of general formula (CC-6), and one or more types of cyan color forming repeating unit represented by formula (CC-6) may be included in the oligomer, or the oligomer may take the form of a copolymer which contains one or more non-color forming ethylenic monomer as a copolymerization component.



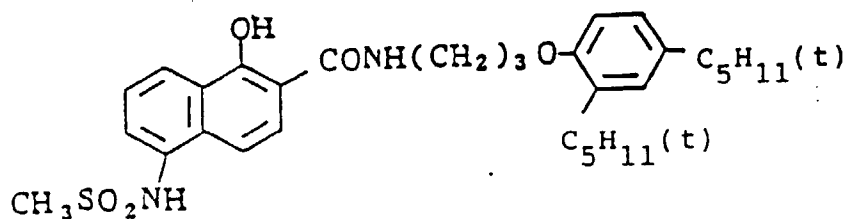
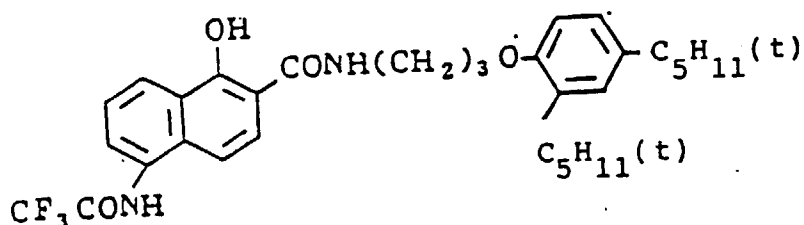
50 R in this formula represents an alkyl group which has from 1 to 4 carbon atoms, or a chlorine atom; A represents -CONH-, -COO- or a substituted or unsubstituted phenylene group; B represents a substituted or unsubstituted alkylene group, phenylene group or aralkylene group, and L represents -CONH-, -NHCONH-, -NHCOO-, -NHCO-, -OCONH-, -NH-, -COO-, -OCO-, -CO-, -O-, -S-, -SO₂-, NHSO₂- or SO₂NH-. Moreover a, b and c each is 0 or 1. Q represents a cyan coupler residual group in which a hydrogen atom other than that of the hydroxyl group in the 2-position has been eliminated from a compound represented by formula (CC-1), (CC-2) or (CC-5).

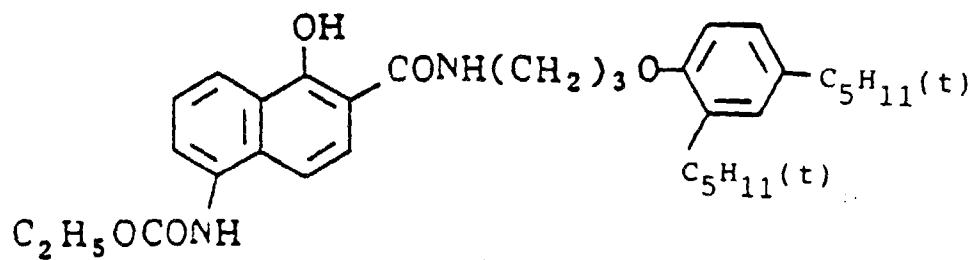
55 Copolymers of the cyan color forming monomer which provides repeating units of general formula (CC-6) and the non-color forming ethylenic monomers described below are preferred as oligomers. A weight ratio of the comonomer is preferably from 0 to 80 wt%, the most preferably from 20 to 70 wt%. A molecular weight of the polymer is from 5.0 × 10² to 1.0 × 10⁶, preferably from 1.0 × 10³ to 1.0 × 10⁵. The polymer preferably constitutes with a linear polymer.

Examples of non-color forming ethylenic monomers which do not couple with the oxidation products of a primary aromatic amine developing agent include acrylic acid, α -chloroacrylic acid and β -alkylacrylic acids (for example, methacrylic acid), esters and amides derived from these acrylic acids (for example, acrylamide, methacrylamide, n-butylacrylamide, tert-butylacrylamide, diacetoneacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, iso-butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and β -hydroxyethyl methacrylate), vinyl esters (for example, vinyl acetate, vinyl propionate and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (for example, styrene and derivatives thereof, for example, vinyltoluene, divinylbenzene, vinylacetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (for example, vinyl ethyl ether), maleic acid esters, N-vinyl-2-pyrrolidone, N-vinyl pyridine, and 2- and 4-vinylpyridines.

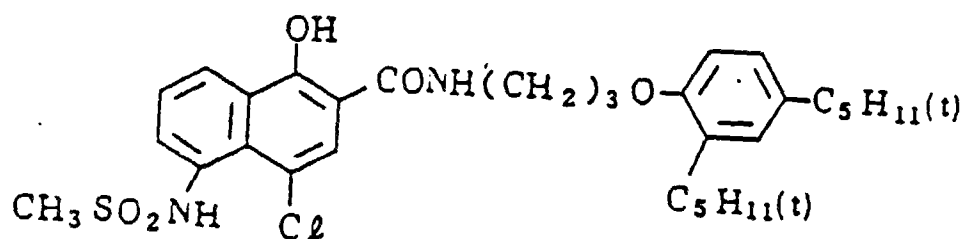
The acrylic acid esters, methacrylic acid esters, aromatic vinyl compounds and maleic acid esters are especially desirable. Two or more of the non-color forming ethylenic monomers used here can be used conjointly. For example, use can be made of methyl acrylate and butyl acrylate, butyl acrylate and styrene, butyl methacrylate and methacrylic acid, and methyl acrylate and diacetoneacrylamide.

Examples of couplers represented by formulae (CC-1), (CC-2), (CC-5) and (CCC-6) are indicated below. In these formulae the group (t) C_5H_{11} is a $-C(CH_3)_2CH_2C(CH_3)_3$ group.

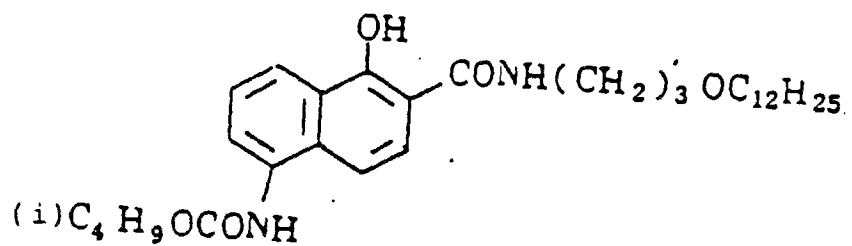




(1-3)



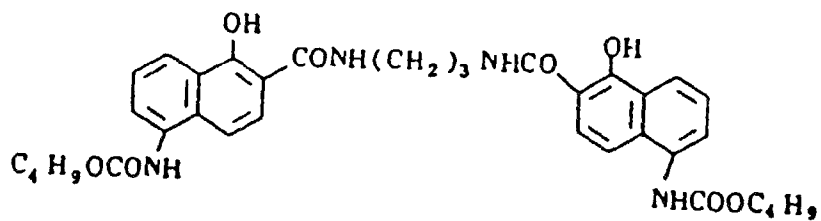
(1-4)



(1-5)

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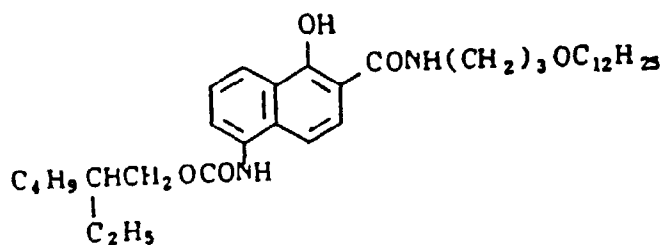


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(1-6)

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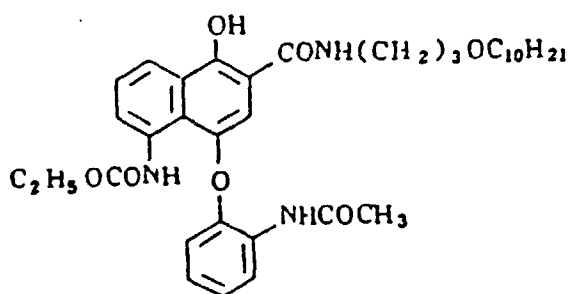


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(1-7)

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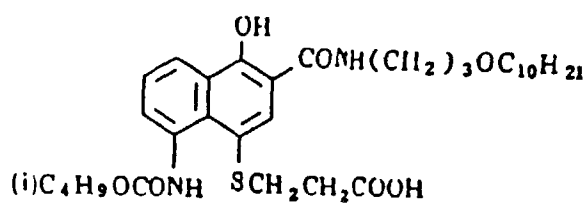
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(1-8)

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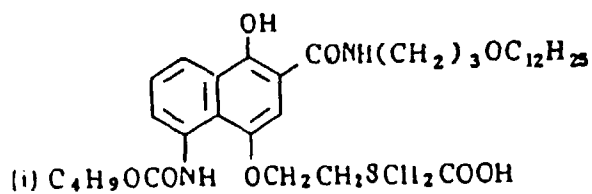


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(I-9)

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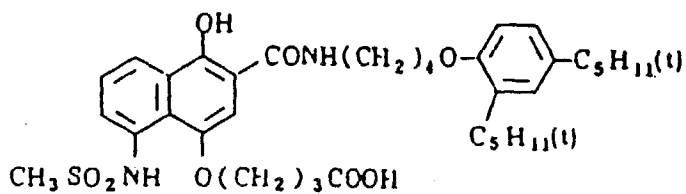


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(I-10)

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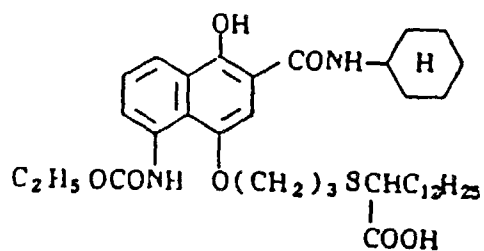


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(I-11)

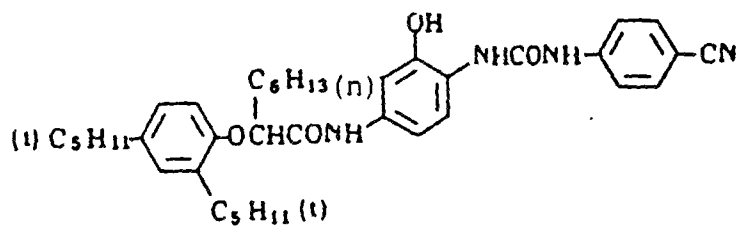
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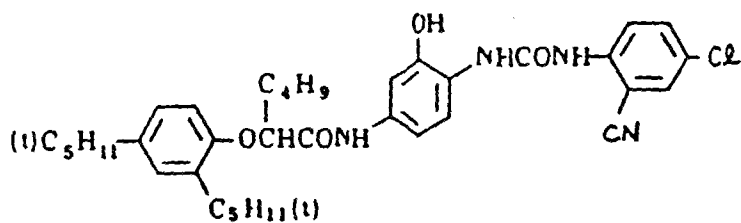


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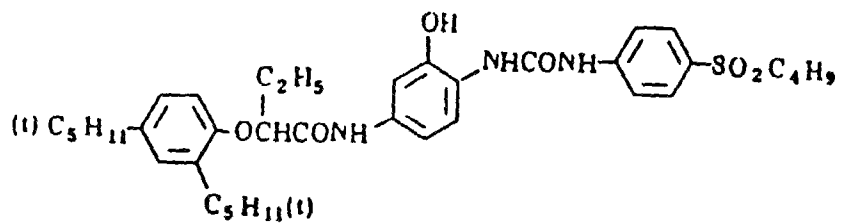
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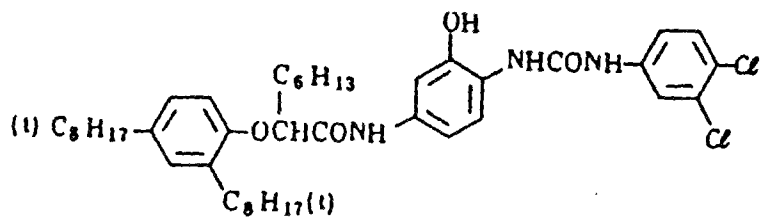
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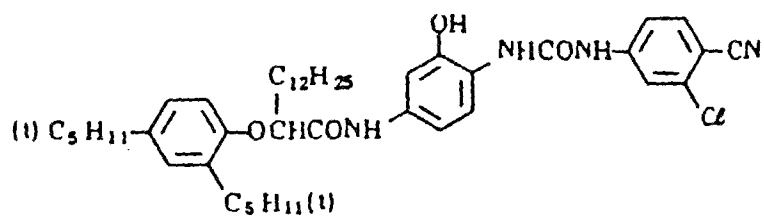
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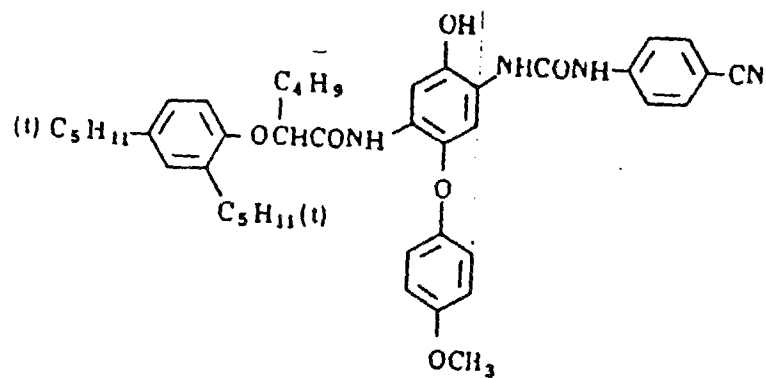
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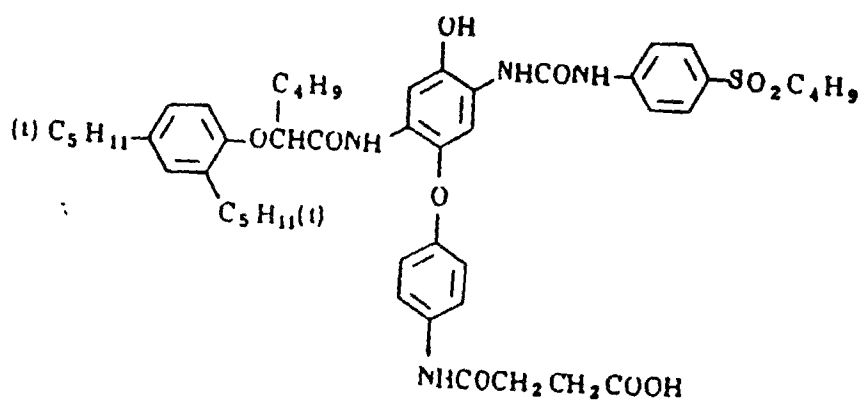
(I-19)



(I-20)



(I-21)

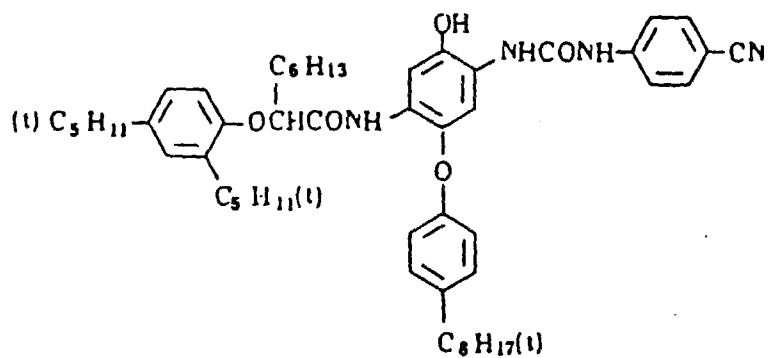


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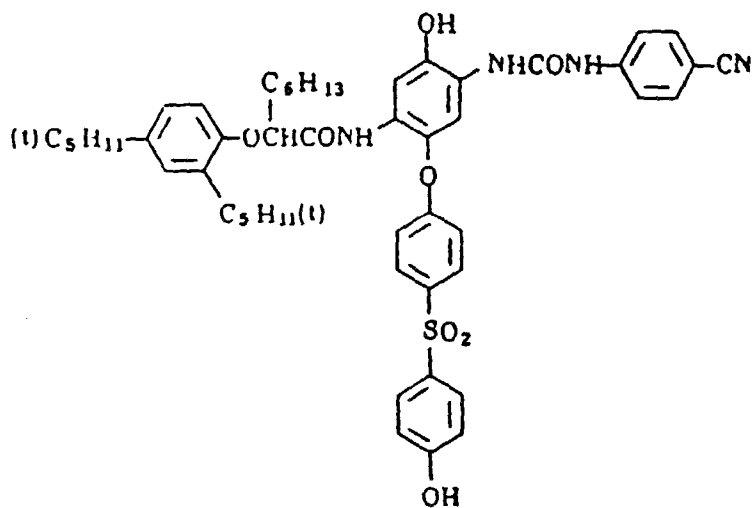
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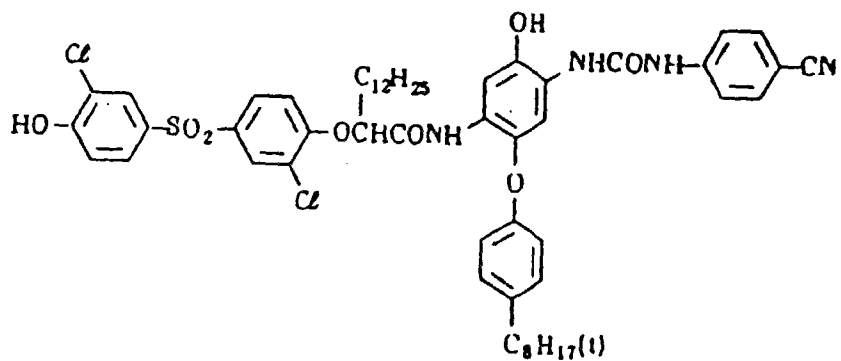
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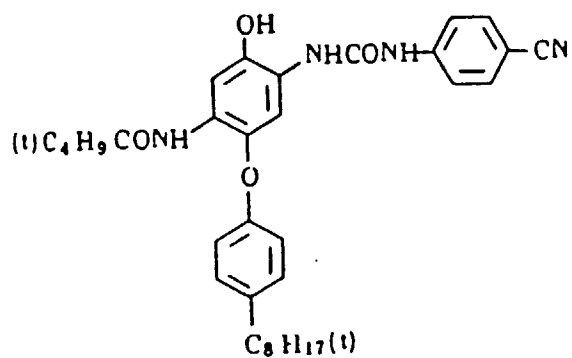


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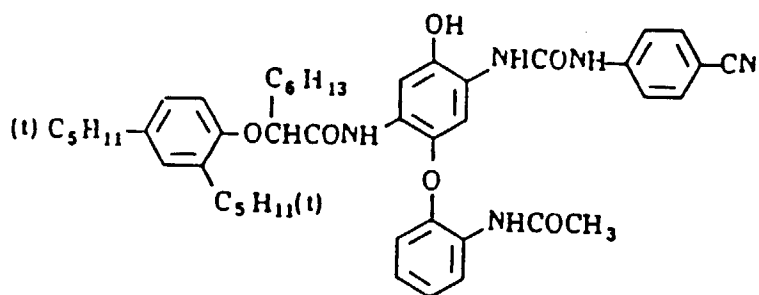


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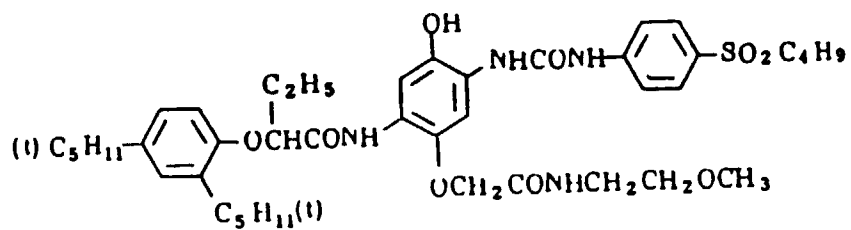
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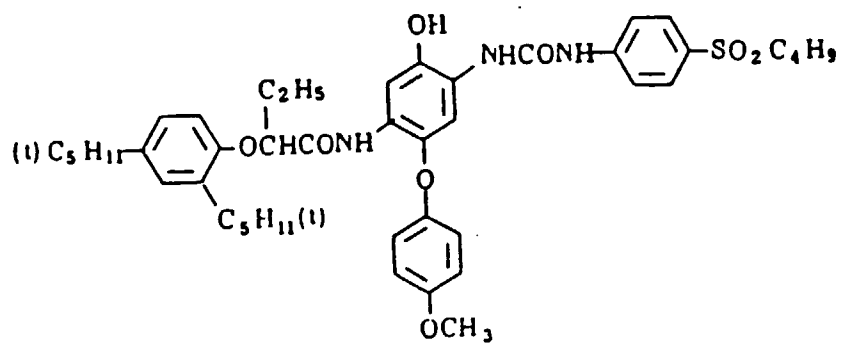


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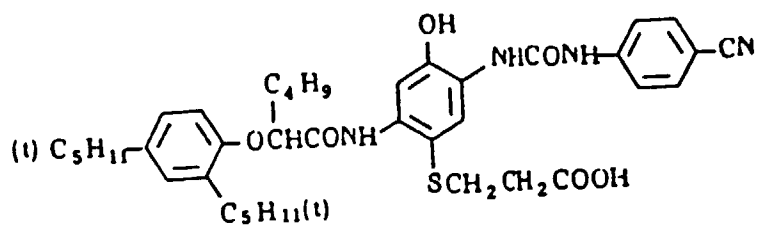
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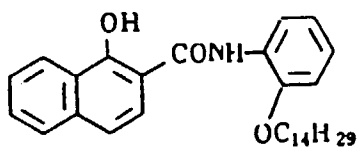
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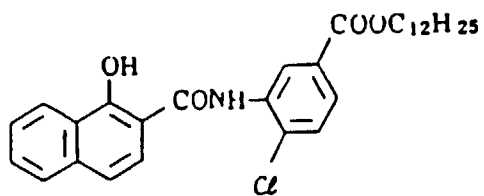
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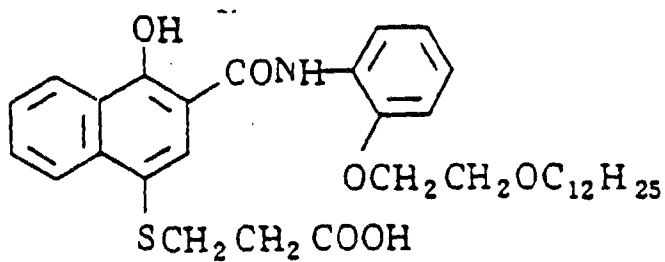


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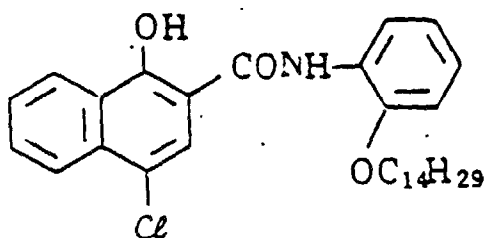


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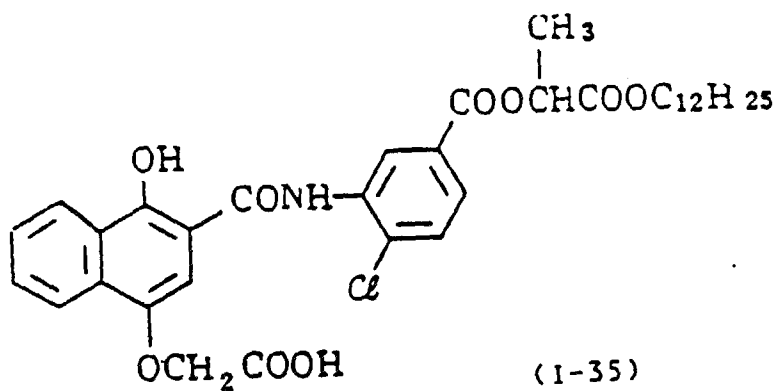
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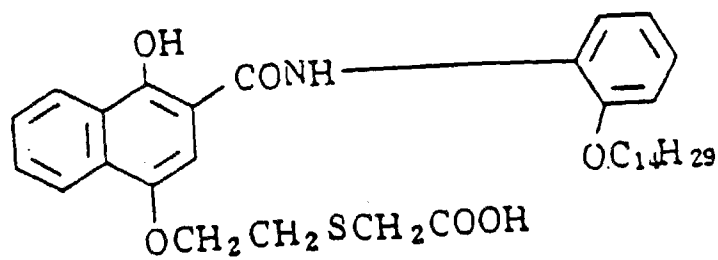
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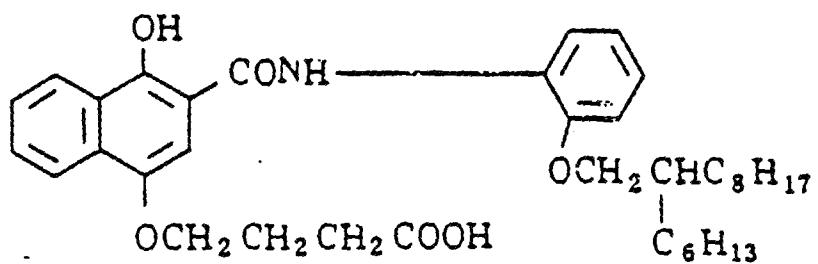
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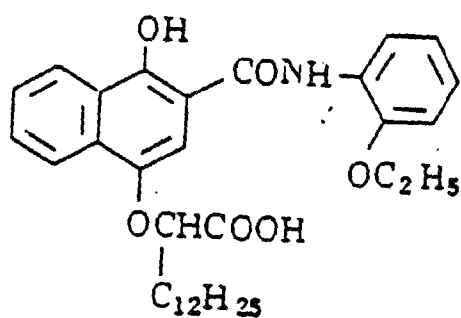


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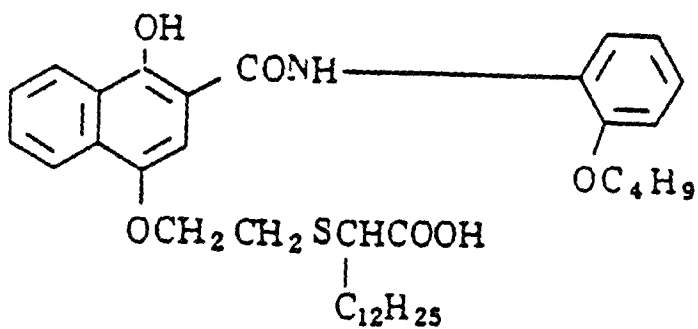
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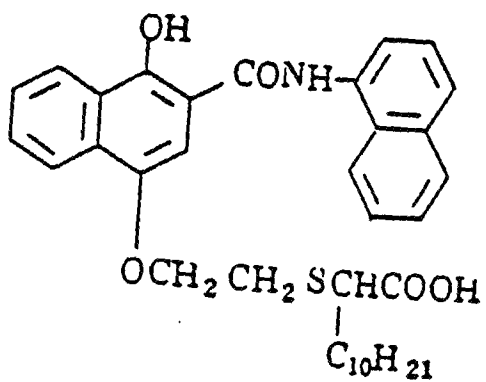
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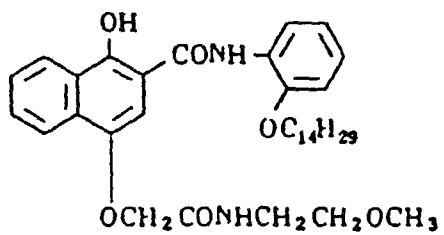


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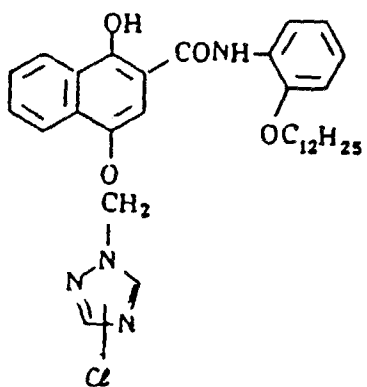


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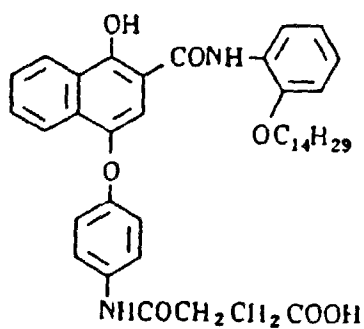
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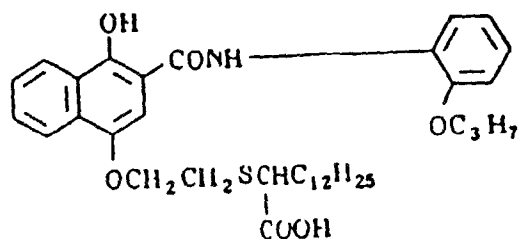


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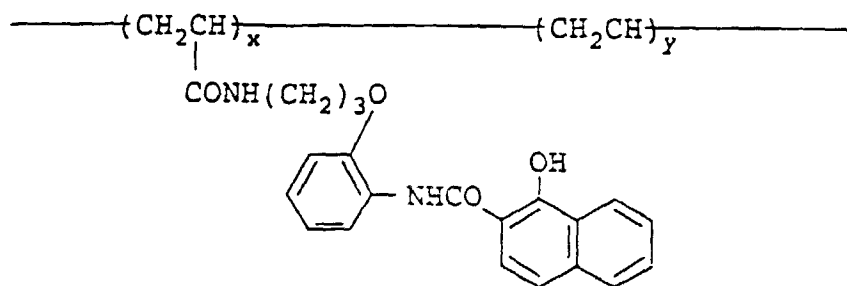
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$x:y=70:30$
(mol. wt ratio)

(I-45)

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Couplers represented by formula (CC-1) can be prepared using the methods disclosed in JP-A-60-237448, JP-A-61153640 and JP-A-61-145557.

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Couplers represented by formula (CC-2) can be prepared using the methods disclosed, for example, in U.S. Patent 3,488,193, JP-A-48-15529, JP-A-50-117422, JP-A-52-18315, JP-A-52-90932, JP-A-53-52423, JP-A-54-48237, JP-A-54-66129, JP-A-55-32071, JP-A-55-65957, JP-A-55-105226, JP-A-56-1938, JP-A-56-12643, JP-A-56-27147, JP-A-56-126832 and JP-A-58-95346.

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Couplers represented by formula (CC-5) can be prepared using the methods disclosed, for example, in U.S. Patents 4,254,212, 4,296,199 and 3,488,193, British Patent 914,507, and JP-B-54-378232.

The total amount of the couplers represented by formulae (CC-1), (CC-2) and (CC-5) added is at least 30 mol%, preferably at least 50 mol%, more desirably at least 70 mol%, and most desirably at least 90 mol% of the total amount of cyan coupler.

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The use of combinations of two or more of the couplers represented by the general formulae (CC-1), (CC-2) and (CC-5) is preferred and, in cases where a layer is divided into two layers of the same color sensitivity but of different speeds, the use of two-equivalent couplers in the high speed layer and four-equivalent couplers in the low speed layer is preferred. In cases where there are three or more layers of the same color sensitivity but different speeds, two-equivalent couplers are preferably used in the highest speed layer and four-equivalent couplers are preferably used in the slowest layer, and either type may be used in the layers of intermediate speed, or both types of coupler can be used conjointly.

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The couplers used in the invention can be introduced into the photosensitive materials using various known methods of dispersion.

Examples of high boiling point solvents which can be used in oil in water dispersion methods have been disclosed,

for example, in U.S. Patent 2,322,027.

Examples of high boiling point organic solvents of boiling point above 175°C at normal pressure which can be used in the oil in water dispersion method include phthalic acid esters (for example, dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl) phthalate, bis(2,4-di-tert-amylphenyl) isophthalate and bis(1,1-diethylpropyl)phthalate), esters of phosphoric acid or phosphonic acid (for example, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tri-dodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate and di-2-ethylhexylphenyl phosphonate), benzoic acid esters (for example, 2-ethylhexyl benzoate, dodecyl benzoate and 2-ethylhexyl p-hydroxybenzoate), amides (for example, N,N-diethyldodecanamide, N,N-diethyl laurylamide and N-tetradecylpyrrolidone), alcohols or phenols (for example, isostearyl alcohol and 2,4-di-tert-amylphenol), aliphatic carboxylic acid esters (for example, bis(2-ethylhexyl) sebacate, dioctyl azelate, glycerol tributyrates, isostearyl lactate and trioctyl citrate), aniline derivatives (for example, N,N-dibutyl-2-butoxy-5-tertoctylaniline), and hydrocarbons (for example, paraffins, dodecylbenzene and di-isopropyl naphthalene). Organic solvents of a boiling point above about 30°C, and preferably above 50°C, but below about 160°C, can be used as auxiliary solvents, and typical examples of such solvents include ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

The processes and effects of the latex dispersion method, and examples of latexes for loading, have been disclosed, for example, in U.S. Patent 4,199,363, and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

The color photosensitive materials of the present invention may contain various antiseptics or antifungal agents such as benzoisothiazolone, n-butyl p-hydroxybenzoate, phenol, or 1-(4-thiazolyl) benzimidazole, which are disclosed in JP-A-63-157747, JP-A-62-272248, and Japanese Patent Application No. 62-238096.

The invention can be applied to various types of color photosensitive materials. Typical examples include color negative films for general and cinematographic purposes, color reversal films for slide and television purposes, color papers, color positive films and color reversal papers.

Suitable supports which can be used in the invention have been disclosed, for example, on page 28 of Research Disclosure No. 17643, and from the right hand column on page 647 to the left hand column on page 648 of Research Disclosure No. 18716.

Color photographic materials according to this invention can be developed and processed using the normal methods disclosed on pages 28-29 of Research Disclosure No. 17643 and in the left and right hand columns of page 651 of Research Disclosure No. 18716.

The color development baths used in the development processing of photosensitive materials of this invention are preferably aqueous alkaline solutions which contain primary aromatic amine based color developing agents as the principal components. Aminophenol based compounds are useful as color developing agents, but the use of p-phenylenediamine based compounds is preferred. Typical examples of these compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethyl aniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, and the sulfate, hydrochloride and p-toluenesulfonate salts of these compounds. Two or more of these compounds can be used conjointly, depending on the intended purpose.

The color development baths generally contain pH buffers, such as alkali metal carbonates, borates or phosphates, and development inhibitors or anti-fogging agents, such as bromides, iodides, benzimidazoles, benzothiazoles or mercapto compounds. They may also contain, as required, various preservatives, such as hydroxylamine, diethylhydroxylamine, hydrazine sulfite, phenylsemicarbazides, triethanolamine, catechol sulfonic acids, triethylenediamine(1,4-diazabicyclo[2,2,2]octane), organic solvents, such as ethylene glycol and diethylene glycol, development accelerators, such as benzyl alcohol, poly(ethylene glycol), quaternary ammonium salts and amines, dye forming couplers, competitive couplers, fogging agents such as sodium borohydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, viscosity imparting agents, various chelating agents, as typified by the aminopolycarboxylic acids, aminopolymethacrylic acids, alkylphosphonic acids and phosphonocarboxylic acids, typical examples of which include ethylenediamine tetraacetic acid, nitrilo triacetic acid, diethylenetriamine pentaacetic acid, cyclohexanediamine tetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-disphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N-tetramethylenephosphonic acid, ethylenediamine di(o-hydroxyphenylacetic acid), and salts of these compounds.

Color development is carried out after a normal black and white development in the case of reversal processing. The known black-and-white developing agents, for example, dihydroxybenzenes such as hydroquinone, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, and aminophenols such as N-methyl-p-aminophenol, can be used individually, or in combinations, in the black and white development bath.

The pH of these color developers and black and white developers is generally within the range from 9 to 12. Furthermore, the replenishment rate of these development baths depends on the color photographic material which is being processed, but it is generally less than 3 liters per square meter of photosensitive material, and it is possible,

by reducing the bromide ion concentration in the replenisher, to use a replenishment rate of less than 500 ml per square meter of photosensitive material. The prevention of loss of liquid by evaporation, and aerial oxidation, by minimizing the contact area with the air in the processing tank is desirable in cases where the replenishment rate is low. The replenishment rate can be reduced further by suppressing the accumulation of bromide ion in the developer. The color development processing time is normally set between 2 and 5 minutes, but it is possible to arrange shorter processing times by using higher temperatures, higher pH levels, and higher concentrations of the color developing agent.

The photographic emulsion layers are normally subjected to a bleaching process after color development. The bleaching process may be carried out at the same time as the fixing process (in a bleach-fix process) or it may be carried out as a separate process. Moreover, a bleach-fix process can be carried out after a bleaching process in order to speed up processing. Moreover processing can be carried out in two connected bleach-fix baths, a fixing process can be carried out before carrying out a bleach-fix process, or a bleaching process can be carried out after a bleach-fix process, according to the intended purpose of the processing. Compounds of poly-valent metals, such as iron(III), cobalt(III), chromium(VI) and copper(II), peracids, quinones and nitro compounds, for example, can be used as bleaching agents. Typical bleaching agents include ferricyanides; dichromates; organic complex salts of iron(III) or cobalt(III), for example, complex salts with aminopolycarboxylic acids, such as ethylenediamine tetraacetic acid, diethylenetriaminepentaacetic acid, cylohexanediamine tetraacetic acid, methylimino diacetic acid, 1,3-diaminopropane tetraacetic acid and glycol ether diamine tetraacetic acid, citric acid, tartaric acid, or malic acid; persulfates; bromates; permanganates and nitrobenzenes. Of these materials, the use of the aminopolycarboxylic acid iron(III) complex salts, principally ethylenediamine tetraacetic acid iron(III) complex salts, and persulfates, is preferred both for rapid processing and the prevention of environmental pollution. Moreover, the amino polycarboxylic acid iron(III) complex salts are especially useful in both bleach baths and bleach-fix baths. The pH of the bleach or bleach-fix baths in which aminopolycarboxylic acid iron(III) complex salts are being used is normally from 5.5 to 8, but processing can be speeded up by using a lower pH.

Bleach accelerators can be used, as required, in the bleach baths, bleach-fix baths, or bleach or bleach-fix pre-baths. Examples of useful bleach accelerators have been disclosed in the following publications. Thus, there are the compounds which have a mercapto group or a disulfide group disclosed, for example, in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, and Research Disclosure No. 17129 (July 1978); the thiazolidine derivatives disclosed in JP-A-50-140129; the thiourea derivatives disclosed in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735, and U.S. Patent 3,706,561; the iodides disclosed in West German Patent 1,127,715 and JP-A-58-16235; the polyoxyethylene compounds disclosed in West German Patents 966,410 and 2,748,430; the polyamine compounds disclosed in JP-B-45-8836; the other compounds disclosed in JP-A-49-42434, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506 and JP-A-58-163940; and bromide ions. Among these compounds, those which have a mercapto group or a disulfide group are preferred in view of their large accelerating effect, and the use of the compounds disclosed in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 is especially desirable. Moreover, the use of the compounds disclosed in U.S. Patent 4,552,834 is also desirable. These bleach accelerators may be added to the sensitive material. These bleach accelerators are especially effective when bleach-fixing camera color photosensitive materials.

Thiosulfates, thiocyanates, thioether based compounds, thioureas, and large quantities of iodides can be used as fixing agents, but thiosulfates are generally used for for this purpose and ammonium thiosulfate, in particular, can be used in the widest range of applications. Sulfites or bisulfites, or carbonylbisulfite addition compounds, are the preferred preservatives for bleach-fix baths.

The silver halide color photographic materials of this invention are generally subjected to a water washing and/or stabilizing process after the desilvering process. The amount of water used in the water washing process can be fixed within a wide range according to the nature of the photosensitive material (depending on the materials, such as couplers, which are being used), the wash water temperature, the number of washing tanks (the number of washing stages), the replenishment system, i.e. whether a counter-flow or a sequential-flow system is used, and various other conditions. The relationship between the amount of water used and the number of water washing tanks in a multi-stage counter-flow system can be obtained using the method outlined on pages 24S-253 of Journal of the Society of Motion Picture and Television Engineers, Volume 64 (May 1955).

The amount of wash water can be greatly reduced by using the multi-stage counter-flow system described in this article but bacteria proliferate due to the increased residence time of the water in the tanks and problems arise as a result of the sediments which are formed becoming attached to the photosensitive material. The method in which the calcium ion and manganese ion concentrations are reduced as disclosed in JP-A-62-288838 can be used very effectively to overcome problems of this sort in the processing of color photosensitive materials of this invention. Furthermore, the isothiazolone compounds and cyabendazoles disclosed in JP-A-57-8542, and chlorine based disinfectants such as chlorinated sodium isocyanurate, and benzotriazoles, and the disinfectants disclosed in "Chemistry of Biocides and Fungicides" by Horiguchi, "Killing Microorganism, Biocidal and Fungicidal Techniques", published by the Health

and Hygiene Technical Society, and in "A Dictionary of Biocides and Fungicides", published by the Japanese Biocide and Fungicide Society, can be used for this purpose.

The pH value of the wash water used in the processing of the photosensitive materials of the invention is within the range from 4 to 9, and preferably within the range from 5 to 8. The wash water temperature and the washing time can be set variously according to the nature of the photosensitive material and the application, but, in general, washing conditions of from 20 seconds to 10 minutes at a temperature of from 15°C to 45°C, and preferably of from 30 seconds to 5 minutes at a temperature of from 25°C to 40°C, are selected. Moreover, the photosensitive materials of this invention can be processed directly in a stabilizing bath instead of being subjected to a water wash as described above. The known methods disclosed in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345 can all be used for this purpose.

Furthermore, there are cases in which a stabilization process is carried out following the aforementioned water washing process, and the stabilizing baths which contain formalin and surfactant which are used as a final bath for camera color photosensitive materials are an example of such a process. Various chelating agents and fungicides can be added to these stabilizing baths.

The overflow which accompanies replenishment of the above mentioned wash water and/or stabilizer can be re-used in other processes such as the desilvering process.

A color developing agent may also be incorporated into the silver halide color photosensitive materials of this invention in order to simplify and speed up processing. The incorporation of various color developing agent precursors is preferred. For example, the indoaniline based compounds disclosed in U.S. Patent 3,342,597, the Schiff's base type compounds disclosed in U.S. Patent 3,342,599 and Research Disclosure Nos. 14850 and 15159, the aldol compounds disclosed in Research Disclosure No. 13924, the metal salt complexes disclosed in U.S. Patent 3,719,492, and the urethane based compounds disclosed in JP-A-53-135628, can all be used for this purpose.

Various 1-phenyl-3-pyrazolidones can be incorporated as required, into the silver halide color photosensitive materials of this invention to accelerate color development. Typical compounds of this type have been disclosed, for example, in JP-A-56-64339, JP-A-57-144547 and JP-A-58-115438.

The various processing baths in this invention are used at a temperature of from 10°C to 50°C. The standard temperature is normally from 33°C to 38°C, but processing is accelerated and the processing time is shortened at higher temperatures and, conversely, increased image quality and improved stability of the processing baths can be achieved at lower temperatures. Furthermore, processes using hydrogen peroxide intensification or cobalt intensification as disclosed in West German Patent 2,226,770 or U.S. Patent 3,674,499 can be carried out in order to economize on silver in the photosensitive material.

Furthermore, silver halide photosensitive materials of this invention can also be used as heat developable photosensitive materials as disclosed, for example, in U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056, and European Patent 210,660A2.

The present invention is now described in greater detail with reference to the following specific examples. Unless otherwise indicated, all parts, percents and ratios are by weight.

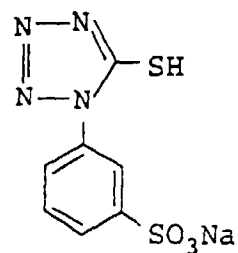
EXAMPLE 1

An aqueous solution (100 ml) which contained 5.0 g of silver nitrate and 100 ml of an aqueous solution which contained potassium bromide and potassium iodide were mixed simultaneously over a period of 3 minutes, with stirring, in an aqueous solution obtained by dissolving 10 g of inert gelatin and 3.0 g of potassium bromide in 1000 ml of distilled water at a temperature of 60°C, after which an excess of potassium bromide and inert gelatin were added and the emulsion was physically ripened for 20 minutes. Moreover, 0.2 mol/l, 0.67 mol/l and 2 mol/l aqueous silver nitrate solution and aqueous potassium halide (a mixture of potassium bromide and potassium iodide) solution were then added using a simultaneous mixing method in accordance with the method disclosed in U.S. Patent 4,242,445, to prepare silver iodobromide core grains. The silver iodide content was varied to 13.3, 20, 30 and 40 mol% by adjusting the mixing ratio of the potassium bromide and the potassium iodide. The size of the core grains was adjusted to from 0.82 to 1.13 µm by means of the amount of silver halide added after physical ripening. The core grains were washed with water to remove the soluble salts.

Silver bromide shells were then grown by selecting the core grains and the amount of silver halide so as to provide the core iodide contents and core/shell ratios indicated in Table 1 and adding a 1.0 mol/l silver nitrate solution and a 1.03 mol/l potassium bromide solution using a simultaneous mixing method. The shell solution using a simultaneous mixing method. The shell was formed after adsorbing compound (1) of which the structural formula is indicated below when preparing emulsions 4 to 9.

Compound (1)

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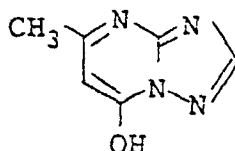
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15 Mainly potato shaped grains of low aspect ratio were used for the core grains in the preparation of emulsion 9. The shell was formed after adsorbing compound (2) of which the structural formula is indicated below when preparing emulsion 10.

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Compound (2)

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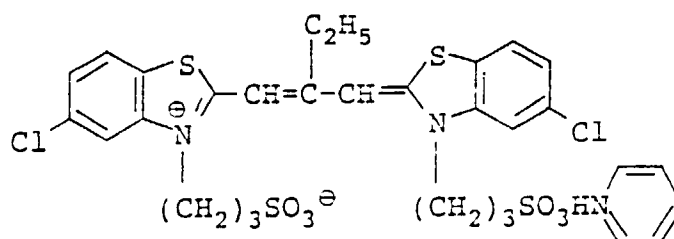


30 The structures of emulsions 1 to 10 are summarized in Table 1. Those which are indicated as having a distinct layer structure had a layer structure in which the presence of silver iodobromide which has a silver bromide content of 15 to 45 mol% as specified in this patent could be confirmed using the X-ray diffraction method. The form of the grains is indicated by the value, expressed as a percentage, obtained by dividing the sum of the projected areas of grains which had an aspect ratio (the value obtained by dividing the corresponding projected area diameter by the thickness of the grain) of from 3 to 10 by the sum of the projected area of all of the grains. The grain size is indicated by the volume equivalent sphere diameter for the volume weight. Emulsions 1 to 10 were adjusted to pH 6.5, pAg 8.4, after desalting, and chemically sensitized in the presence of compound (3) the structural formula of which is indicated below using sodium thiosulfate, chloroauric acid and potassium thiocyanate. The optimum quantities of each additive were selected for each emulsion.

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Compound (3)

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Table 1

	Iodide Content Core	Iodide Content Shell	Core/Shell Ratio	Overall Iodide Content	Distinct Double Layer Structure of the Invention	Projected Area of Aspect Ratio 3 - 10	Grain Size (μm)
1	13.3	0	3/2	10	No	90%	1.25 Comparative Ex.
2	30	0	1/2	10	No	70	1.20 Comparative Ex.
3	40	0	1/2	13.3	No	65	1.21 Comparative Ex.
4	20	0	1/2	6.7	Yes	70	1.26 Comparative Ex.
5	20	0	1/1	10	Yes	80	1.22 This Invention
6	20	0	2/1	13.3	Yes	85	1.24 This Invention
7	20	0	3/1	15	Yes	90	1.20 This Invention
8	20	0	2/1	14.3	Yes	90	1.22 This Invention
9	20	0	2/1	13.3	Yes	30	1.20 Comparative Ex.
10	20	0	2/1	13.3	No	70	1.27 Comparative Ex.

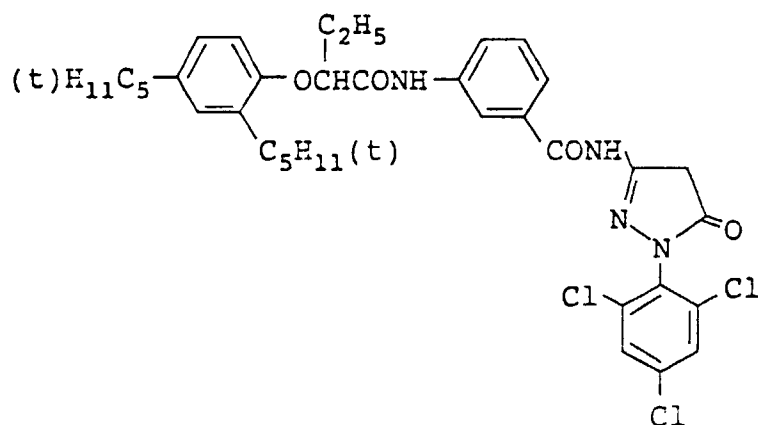
These emulsions and protective layers were coated at the rates showing in Table 2 onto triacetylcellulose film supports on which an under-layer had been provided.

Table 2

(1) Emulsion Layer

Emulsion: Emulsions 1-8 as indicated in Table 1, as silver $2.1 \times 10^{-1} \text{ mol/m}^2$

Coupler $1.5 \times 10^{-3} \text{ mol/m}^2$



ExY-3 $1.0 \times 10^{-4} \text{ mol/m}^2$

Tricresyl phosphate 1.10 g/m^2

Gelatin 2.30 g/m^2

(2) Protective Layer

2,4-Dichlorotriazine-6-hydroxy-s-triazine, sodium salt 0.08 g/m^2

Gelatin 1.80 g/m^2

These samples were given a sensitometric exposure and color developed and processed in the way indicated below.

The processed samples were subjected to density measurements using a green filter. The results obtained in Table 3.

The development processing used was carried out at 38°C under the conditions indicated below.

1. Color Development 2 minutes 45 seconds
2. Bleaching 6 minutes 30 seconds
3. Water Wash 3 minutes 15 seconds
4. Fixing 6 minutes 30 seconds

EP 0 337 370 B1

- 5. Water Wash 3 minutes 15 seconds
- 6. Stabilization 3 minutes 15 seconds

The compositions of the processing baths used in each process were as indicated below.

5

Color Development Bath

10

15

Sodium nitrilotriacetate	1.0 g
Sodium sulfite	4.0 g
Sodium carbonate	30.0 g
Potassium bromide	1.4 g
Hydroxylamine sulfate	2.4 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g
Water	to make up to 1 ℓ

Bleach Bath

20

25

Ammonium bromide	160.0 g
Aqueous ammonia (28%)	25.0 ml
Ethylenediamine tetra-acetic acid, sodium iron salt	130 g
Glacial acetic acid	14 ml
Water	to make up to 1 ℓ

Fixer Bath

30

35

Sodium tetrapolyphosphate	2.0 g
Sodium sulfite	4.0 g
Ammonium thiosulfate (70%)	175.0 ml
Sodium bisulfite	4.6 g
Water	to make up to 1 ℓ

Stabilizer Bath

40

Formalin	8.0 ml
Water	to make up to 1 ℓ

45

Table 3

50

55

Emulsion	Fog	Speed	RMS Value at Density 1.0	
1	0.10	65	0.035	Comparative Ex.
2	0.08	100	0.038	Comparative Ex.
3	0.07	80	0.038	Comparative Ex.
4	0.09	100	0.042	Comparative Ex.
5	0.08	120	0.035	This Invention
6	0.07	120	0.033	This Invention
7	0.07	110	0.032	This Invention
8	0.07	115	0.032	This Invention
9	0.12	90	0.033	Comparative Ex.
10	0.13	60	0.039	Comparative Ex.

EP 0 337 370 B1

It is clear from Table 3 that the emulsions of this invention exhibited desirable speed and graininess characteristics.

EXAMPLE 2

5 Samples 101 to 106, multi-layer color photosensitive materials consisting of layers the compositions of which are indicated below, were prepared on undercoated cellulose triacetate film supports.

Composition of the Photosensitive Layers

10 The amounts coated are shown in units of g/m² of silver in the case of silver halides and colloidal silver, in units of g/m² in the case of couplers, and in units of mol per mol of silver halide in the same layer in the case of sensitizing dyes.

First Layer: Anti-halation Layer

15

Black colloidal silver	0.2 as silver
Gelatin	2.2
UV-1	0.1
UV-2	0.2
Cpd-1	0.05
Solv-1	0.01
Solv-2	0.01
Solv-3	0.08

20

25

Second Layer: Intermediate Layer

30

Fine grain silver bromide (corresponding sphere diameter (0.07 μm))	0.15 as silver
Gelatin	1.0
Cpd-2	0.2

Third Layer: First Red Sensitive Emulsion Layer

35

Silver iodobromide emulsions 0.26
(10 mol% AgI, high internal AgI type, as silver
corresponding sphere diameter 0.7 μm,
variation coefficient of corresponding
40 sphere diameter 15%, tetradecahedral
grains)

45

50

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5	Silver iodobromide emulsions (4 mol% AgI, high internal AgI type, corresponding sphere diameter 0.4 μm, variation coefficient of corresponding sphere diameter 22%, tetradecahedral grains)	0.2 as silver
10	Gelatin	1.0
	ExS-1	4.5×10 ⁻⁴ mol
15	ExS-2	1.5×10 ⁻⁴ mol
	ExS-3	0.4×10 ⁻⁴ mol
	ExS-4	0.3×10 ⁻⁴ mol
20	ExC-1	0.33
	ExC-2	0.009
25	ExC-3	0.023
	ExC-6	0.14

Fourth Layer: Second Red Sensitive Emulsion Layer

30

Silver iodobromide emulsion	0.55 as silver
Gelatin	0.7
ExS-1	4.0×10 ⁻⁴
ExS-2	1.2×10 ⁻⁴
Exs-3	0.35×10 ⁻⁴
ExS-4	0.25×10 ⁻⁴
ExC-6	0.08
ExC-3	0.05
ExC-4	0.10

35

40

Fifth Layer: Third Red Sensitive Emulsion Layer

45

Silver iodobromide emulsion	0.9 as silver
Gelatin	0.6
ExS-1	3.0×10 ⁻⁴
ExS-2	1.0×10 ⁻⁴
Exs-3	0.3×10 ⁻⁴
ExC-4	0.07
ExC-5	0.06
Solv-1	0.12
Solv-2	0.12

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EP 0 337 370 B1

Sixth Layer: Intermediate Layer

5

Gelatin	1.0
Cpd-4	0.1

Seventh Layer: First Green Sensitive Emulsion Layer

10

Silver iodobromide emulsion 0.2
 (10 mol% AgI, high internal AgI as silver
 type, corresponding sphere diameter
 0.7 μ m, variation coefficient of
 corresponding sphere diameter 14%,
 tetradecahedral grains)

15

Silver iodobromide emulsion 0.1
 (4 mol% AgI, high internal AgI as silver
 type, corresponding sphere diameter
 0.4 μ m, variation coefficient of
 corresponding sphere diameter 22%,
 tetradecahedral grains)

20

25

Gelatin 1.2

ExS-5 5×10^{-4} mol

ExS-6 2×10^{-4} mol

30

ExS-7 1×10^{-4} mol

35

ExM-1 0.41

ExM-2 0.10

40

ExM-5 0.03

Solv-1 0.2

45

Eighth Layer: Second Green Sensitive Emulsion Layer

50

Silver iodobromide emulsion	0.4 as silver
Gelatin	0.35
ExS-5	3.5×10^{-4}
ExS-6	1.5×10^{-4}
ExS-7	0.8×10^{-4}
ExM-1	0.09
ExM-3	0.01
Solv-1	0.15

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EP 0 337 370 B1

Ninth Layer: Intermediate Layer

Gelatin	0.5
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5

Tenth Layer: Third Green Sensitive Emulsion Layer

10	Silver iodobromide emulsion	1.0 as silver
	Gelatin	0.8
15	ExS-5	2.5×10^{-4}
	ExS-6	1.0×10^{-4}
	ExS-7	0.5×10^{-4}
20	ExM-1	0.04
	ExM-3	0.01
25	ExC-4	0.05
	Solv-1	0.2

30

Eleventh Layer: Yellow Filter Layer

Cpd-3	0.05
Gelatin	0.5
Solv-1	0.1

35

Twelfth Layer: Intermediate Layer

Gelatin	0.5
Cpd-2	0.1

40

Thirteenth Layer: First Blue Sensitive Layer

45

50	Silver iodobromide emulsion (10 mol% AgI, high internal AgI type, corresponding sphere diameter 0.7 μm , variation coefficient of corresponding sphere diameter 14%, tetradecahedral grains)	0.1 as silver
	Silver iodobromide emulsion (4 mol% AgI, high internal AgI type, corresponding sphere diameter 0.4 μm , variation coefficient of corresponding sphere diameter 22%, tetradecahedral grains)	0.05 as silver
55	Gelatin	1.0
	ExS-8	3×10^{-4} mol
	ExY-1	0.53

EP 0 337 370 B1

(continued)

ExY-2	0.02
Solv-1	0.15

5

Fourteenth Layer: Second Blue Sensitive Emulsion Layer

10 Silver iodobromide emulsion 0.19
 (19.0 mol% AgI, high internal AgI as silver
 type, corresponding sphere diameter

15 1.0 μm, variation coefficient of
 corresponding sphere diameter 16%,
 tetradecahedral grains)

20 Gelatin 0.3
 ExS-8 2×10⁻⁴ mol
 ExY-1 0.22
 25 Solv-1 0.07

Fifteenth Layer: Intermediate Layer

30

Fine grain silver iodobromide emulsion (2 mol% AgI, uniform type, corresponding sphere diameter 0.13 μm)	0.2 as silver
Gelatin	0.36

35

Sixteenth Layer: Third Blue Sensitive Emulsion Layer

Silver iodobromide emulsion (14.0 mol% AgI, high internal AgI type, corresponding sphere diameter 1.5 μm, variation coefficient of corresponding sphere diameter 28%, plate like grains, diameter/thickness ratio 5.0)	1.0 as silver
Gelatin	0.5
ExS-8	1.5×10 ⁻⁴ mol
ExY-1	0.2
45 Solv-1	0.07

Seventeenth Layer: First Protective Layer

50

Gelatin	1.8
UV-1	0.1
UV-2	0.2
Solv-1	0.01
55 Solv-2	0.01

EP 0 337 370 B1

Eighteenth Layer: Second Protective Layer

5
10

Fine grain silver bromide emulsion (corresponding sphere diameter 0.07 μm)	0.18 as silver
Gelatin	0.7
Poly(methyl methacrylate) particles (diameter 1.5 μm)	0.2
W-1	0.02
H-1	0.4
Cpd-5	1.0

In each layer, about 400 ppm in average of benzisothiazolone and about 1,000 ppm in average of n-butyl p-hydroxybenzoate based on an amount of gelatin, were added.

15

The emulsions 11 to 18 shown in Table 4 were prepared using the method of grain formation described in Example 1. Each emulsion was chemically sensitized with sodium thiosulfate and chloroauric acid in the presence of spectrally sensitizing dye. The amounts of each added were selected optimally. The emulsions used in Examples 101 to 106 are shown in Table 4.

Table 4

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Sample No.	4th Layer	5th Layer	8th Layer	10th Layer
101*	11	13	15	17
102	11	14	15	17
103	12	14	15	17
104	11	13	15	18
105	11	13	16	18
106	12	14	16	18

*: For comparison

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Samples 101 to 106 all had about the same speed. It was confirmed that granularity was improved when emulsions of this invention were used. Moreover, it was confirmed that the use of emulsions of this invention was particularly desirable with combinations of more than one layer.

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Table 5

<u>Layer No.</u>	<u>Emulsion No.</u>	<u>Iodide Content Core</u>	<u>Iodide Content Shell</u>	<u>Core/Shell</u>	<u>Overall Iodide Content</u>	<u>Distinct Layer Structure of the Invention</u>	<u>Projected Area of Aspect Ratio 3-10</u>	<u>Grain Size (µm)</u>	
4	1	30	0	1/2	10	No	50%	1.05	Comparative Ex.
4	12	20	0	1/1	10	Yes	70	1.00	This Invention
5	13	40	0	1/3	10	No	70	1.53	Comparative Ex.
5	14	20	0	2/1	13.2	Yes	80	1.25	This Invention
8	15	30	0	1/2	10	No	45	0.95	Comparative Ex.
8	16	20	0	1/1	10	Yes	75	0.90	This Invention
10	17	40	0	1/3	10	No	70	1.45	Comparative Ex.
10	18	20	0	2/1	13.3	Yes	90	1.20	This Invention

EP 0 337 370 B1

EXAMPLE 3

Sample 301, a multi-layer color photosensitive material, was prepared by the lamination coating of the layers of which the compositions are indicated below on an undercoated cellulose triacetate film support.

Photosensitive Layer Compositions

The numerical value for each component indicates the amount coated in units of g/m², calculated as silver in the case of the silver halides. However, the amounts coated are indicated in units of mol per mol of silver halide in the same layer in the case of the sensitizing dyes.

Sample 301

First Layer: Anti-halation Layer

Black colloidal silver	0.20 as silver
Gelatin	0.40

Second Layer: Intermediate Layer

2,5-Di-tert-pentadecylhydroquinone	0.18
ExM-6	0.07
ExC-3	0.02
Cpd-6	0.002
U-1	0.06
U-2	0.08
U-3	0.10
Solv-1	0.10
Solv-2	0.02
Gelatin	1.04

Third Layer: First Red Sensitive Layer

Emulsion A	0.25 as silver
Emulsion B	0.25 as silver
ExS-1	6.9×10 ⁻⁵
ExS-4	1.6×10 ⁻⁵
ExS-2	1.8×10 ⁻⁵
ExS-3	3.1×10 ⁻⁴
ExC-1	0.335

EP 0 337 370 B1

(continued)

ExC-7	0.020
Gelatin	0.87

5

Fourth Layer: Second Red Sensitive Emulsion Layer

10

Emulsion C	1.0 as silver
ExS-1	5.1×10^{-5}
ExS-2	1.4×10^{-5}
ExS-3	2.3×10^{-4}
ExC-1	0.400
ExC-3	0.050
ExC-7	0.015
Gelatin	1.30

15

Fifth Layer: Third Red Sensitive Emulsion Layer

20

Emulsion D	1.60 as silver
ExS-1	5.4×10^{-5}
ExS-2	1.4×10^{-5}
ExS-3	2.4×10^{-4}
ExS-4	1.2×10^{-5}
ExC-3	0.010
ExC-1	0.080
ExC-6	0.097
Solv-4	0.22
Solv-1	0.10
Gelatin	1.63

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Sixth Layer: Intermediate Layer

40

Cpd-7	0.040
Solv-3	0.020
Gelatin	0.80

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EP 0 337 370 B1

Seventh Layer: First Green Sensitive Emulsion Layer

5	Emulsion A	0.15 as silver
	Emulsion B	0.15 as silver
10	ExS-5	3.0×10^{-5}
	ExS-6	1.0×10^{-4}
	ExS-7	3.8×10^{-4}
15	ExM-1	0.260
20	ExM-6	0.021
	ExM-3	0.030
25	ExY-2	0.025
	Solv-1	0.100
	Cpd-8	0.010
30	Gelatin	0.63

Eighth Layer: Second Green Sensitive Emulsion Layer

35	Emulsion C	0.45 as silver
	ExS-5	2.1×10^{-5}
	ExS-6	7.0×10^{-5}
40	ExS-7	2.6×10^{-4}
	ExM-1	0.094
	ExY-3	0.018
	ExM-8	0.020
	ExM-3	0.026
45	Solv-2	0.160
	Cpd-8	0.008
	Gelatin	0.50

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EP 0 337 370 B1

Ninth Layer: Third Green Sensitive Emulsion Layer

5	Emulsion E	1.2 as silver
	ExS-5	3.5×10^{-5}
10	ExS-6	8.0×10^{-5}
	ExS-7	3.0×10^{-4}
	ExM-1	0.015
15		
	ExM-7	0.100
20	ExM-8	0.050
	ExM-3	0.025
25	Solv-1	0.25
	Solv-4	0.10
30	Gelatin	1.54

Tenth Layer: Yellow Filter Layer

35	Yellow colloidal silver	0.05 as silver
	Cpd-7	0.08
	Solv-4	0.03
	Gelatin	0.60

Eleventh Layer: First Blue Sensitive Emulsion Layer

45	Emulsion A	0.08 as silver
	Emulsion B	0.07 as silver
	Emulsion F	0.07 as silver
	ExS-8	3.5×10^{-5}
	ExY-1	0.721
50	ExC-7	0.020
	ExY-3	0.015
	Solv-1	0.28
	Gelatin	1.10

Twelfth Layer: Second Blue Sensitive Emulsion Layer

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EP 0 337 370 B1

5

Emulsion G	0.45 as silver
ExS-8	9.5×10^{-4}
ExY-1	0.154
ExC-7	0.007
ExY-2	0.010
Solv-3	0.05
Gelatin	0.78

10

Thirteenth Layer: Third Blue Sensitive Emulsion Layer

15

Emulsion H	0.77 as silver
ExS-8	2.2×10^{-4}
ExY-1	0.20
ExC-7	0.005
Solv-1	0.07
Gelatin	0.69

20

Fourteenth Layer: First Protective Layer

25

1 mol% AgI silver iodobromide emulsion (average grain size 0.07 μm)	0.25 as silver
UN-1	0.11
UN-2	0.17
Solv-4	0.05
Gelatin	1.00

30

Fifteenth Layer: Second Protective Layer

35

Poly(methyl methacrylate) particles (diameter about 1.5 μm) 0.54 as silver

40

Cpd-5 0.10
Cpd-9 0.10
Gelatin 1.20

45

About 400 ppm, in average, of benzothiazolone, about 1,000 ppm, in average, of n-butyl p-hydroxybenzoate, based on an amount of gelatin, gelatin hardening agent H-1 and surfactants were added to each layer in addition to the components indicated above.

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Samples 302 to 311

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Samples 302 to 311 were prepared in the same way except that Emulsion D in the fifth layer and Emulsion E in the ninth layer of Sample 301 were replaced as shown in Table 7. Moreover, when Emulsion E was replaced by Emulsion N the amount of ExS-5, ExS-6 and ExS-7 were increased by a factor of 1.15, when it as replaced with Emulsion O these amounts were increased by a factor of 1.40, and when it was replaced with Emulsions P and Q these amounts were increased by a factor of 1.60.

Moreover, the Emulsions A to Q used in these samples were prepared in accordance with the method described earlier. The characteristics of Emulsions A to Q are summarized in Table 6.

EP 0 337 370 B1

The samples were given an imagewise exposure, developed and processed in the way indicated below and the relative speeds of each color sensitive layer were obtained. The relative speeds are indicated as the logarithm of the reciprocal of the exposure required to provide a density of fog + 0.2 for each of the cyan and magenta densities, and the values are expressed as relative values taking the value for Sample 301 to be zero.

Furthermore, the samples were exposed through a wedge for RMS granularity measurement purposes and the RMS values for a 48 μm diameter aperture at cyan (R) and magenta (G) densities of fog + 0.2 were measured.

Processing was carried out as indicated below at 38°C using an automatic processor.

Color Development	3 minutes	15 seconds
Bleaching	1 minute	
Bleach-Fixing	3 minutes	15 seconds
Water Wash (1)		40 seconds
Water Wash (2)	1 minute	
Stabilization		40 seconds
Drying (50°C)	1 minute	15 seconds

In the processes outlined above, water washes (1) and (2) were carried out with a counter-flow washing system from wash (2) to wash (1). The compositions of the processing baths were as indicated below.

Moreover, the replenishment rate for each processing bath was 1200 ml per square meter of color photosensitive material in the case of the color development bath, and 800 ml per square meter of color photosensitive material in all other baths, including the water washing baths. Furthermore, the carry over from the previous bath to the water washing process was 50 ml per square meter of color photosensitive material.

Color Development Bath

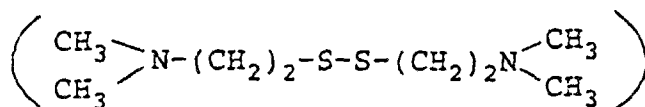
	Solution	Replenisher
Diethylenetriamine pentaacetic acid	1.0 g	1.1 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g	2.2 g
Sodium sulfite	4.0 g	4.4 g
Potassium carbonate	30.0 g	32.0 g
Potassium bromide	1.4 g	0.7 g
Potassium iodide	1.3 mg	-
Hydroxylamine sulfate	2.4 g	2.6 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g	5.0 g
Water	to make up to 1.0 ℓ	1.0 ℓ
pH	10.0	10.05

Bleach Bath (Commonly used for developing solution, and replenisher)

Ethylenediamine tetraacetic acid, 120.0 g
 ferric ammonium salt

EP 0 337 370 B1

Ethylenediamine tetraacetic acid, di-sodium salt	10.0 g
Ammonium nitrate	10.0 g
Ammonium bromide	100.0 g
Bleach accelerator	5×10^{-3} mol



Aqueous ammonia to pH 6.3
Water to make up to 1.0 ℓ

Bleach-Fix Bath (Commonly used for developing solution, and replenisher)

Ethylenediamine tetraacetic acid, ferric ammonium salt	50.0 g
Ethylenediamine tetraacetic acid, di-sodium salt	5.0 g
Sodium sulfite	12.0 g
Aqueous ammonium thiosulfate solution (70%)	240 ml
Aqueous ammonia	to pH 7.3
Water	to make up to 1 ℓ

Water Washing Water

Town water which had a calcium ion content of 32 mg/ℓ and a magnesium ion content of 7.3 mg/ℓ was passed through a column packed with an H-type strongly acidic cation exchange resin and an OH-type strongly basic anion exchange resin, and 20 mg per liter sodium isocyanurate dichloride was added to the treated water which had a calcium ion content of 1.2 mg/ℓ and a magnesium ion content of 0.4 mg/ℓ for use.

Stabilizer Bath (Solution = Replenisher)

Formalin (37% w.v.)	2.0 g
Polyoxyethylene p-nonylphenyl ether (average degree of polymerization 10)	0.3 g
Ethylenediamine tetraacetic acid, sodium salt	0.05
Water	to make up to 1 ℓ
pH	5.8

Drying

Drying temperature	50°C
--------------------	------

Table 6

Emulsion No.	Formulation		Distinct Layer Structure of This Invention	Projected Area of Aspect Ratio 3 - 10 (%)	Overall Average Iodide Content (%)	Average Corresponding Sphere Diameter (µm)	Variation Coeff. of Corresponding Sphere Diameter (%)
	Iodide Core (mol%)	Content Shell Ratio (mol%)					
A	10	0	NO	7	4.0	0.45	25
B	20	0	NO	5	4.0	0.60	15
C	25	2	NO	20	10.0	0.70	25
D	10	0	NO	76	4.0	1.10	30
E	31	0	YES	32	10.3	1.05	25
F	10	5	NO	10	7.5	0.30	15
G	36	3	YES	40	14.0	0.70	25
H	36	3	YES	50	14.0	1.30	35
I	14	0	NO	74	7.0	1.10	30
J	27	0	YES	76	9.0	1.10	30
K	30	1	YES	76	10.7	1.05	30
L	20	1	YES	75	13.6	1.10	30
M	40	0	YES	78	16.0	1.10	30
N	31	0	YES	51	10.2	1.10	25
O	31	0	YES	70	10.2	1.05	25
P	31	0	YES	88	10.2	1.05	30
Q	40	0	YES	79	13.3	1.10	35

Table 7

Sample	Fifth Layer Emulsion	Ninth Layer Emulsion	Relative Speed		RMS Value x 1000	
			Red Layer	Green Layer	R	G
301 (Comparative Ex.)	D	E	0.00	0.00	19.2	21.5
302 (Comparative Ex.)	I	E	+0.01	0.00	19.1	21.4
303 (This Invention)	J	E	+0.01	-0.01	18.3	21.3
304 (This Invention)	K	E	0.00	0.01	17.9	21.3
305 (This Invention)	L	E	0.00	0.00	17.5	21.3
306 (This Invention)	M	E	+0.01	0.00	17.6	21.3
306' (Comparative Ex.)	D	N	0.00	+0.01	19.1	21.0
307 (This Invention)	D	O	0.00	+0.04	19.0	20.5
308 (This Invention)	D	P	-0.01	+0.06	19.0	20.3
309 (This Invention)	D	Q	-0.01	+0.06	19.0	20.0
310 (This Invention)	L	P	0.00	+0.06	17.3	19.9
311 (This Invention)	M	Q	0.00	+0.06	17.3	19.8

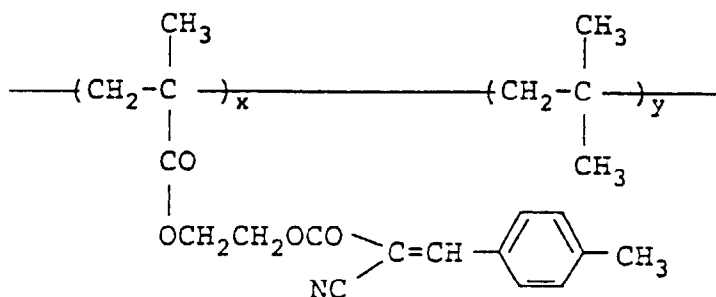
EP 0 337 370 B1

Samples 303 to 306 which contained emulsions J to M of this invention which had a distinct layered structure and a silver iodide content of at least 8 mol% were clearly superior in respect of graininess to the samples 301 and 302 which contained Emulsions D and I which were outside the scope of the present invention.

Furthermore, Samples 307 to 309 which contained Emulsions O to Q in which the fraction of the projected area due to emulsion grains which had an aspect ratio of from 3 to 10 was at least 60% were clearly superior in respect of high speed and graininess to the samples 301 and 306 in which Emulsion E and N which are outside the scope of this invention had been used.

The compounds used in the Examples were as follows:

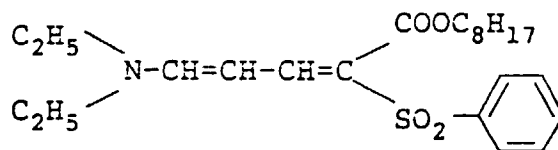
UV-1



$x/y=7/3$ (mol wt.)

(mol. wt. 40,000)

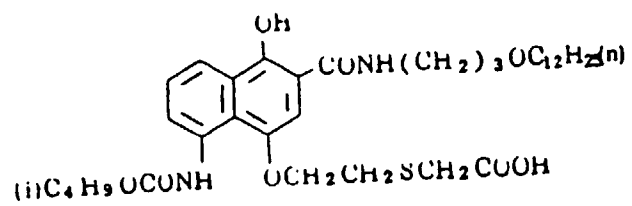
UV-2



Exc-6

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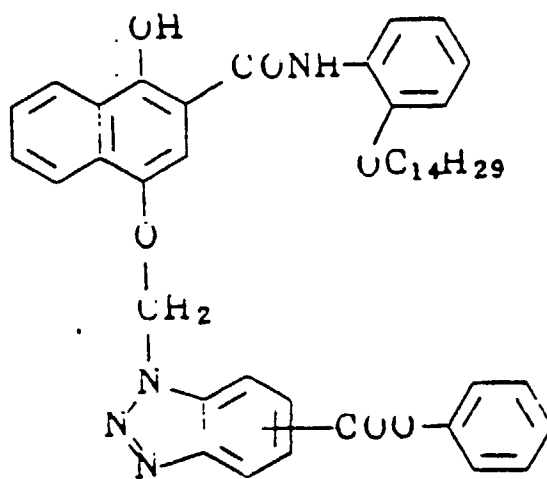
Exc-2

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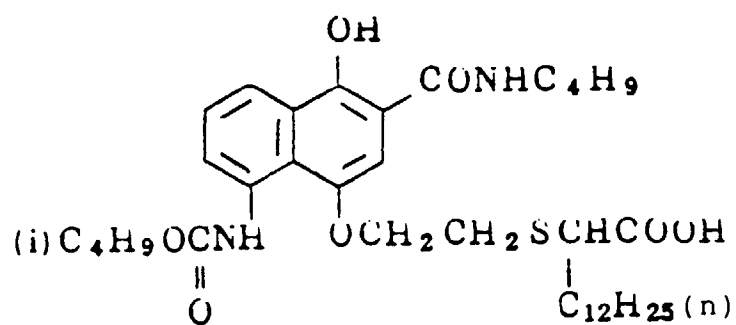
Exc-4

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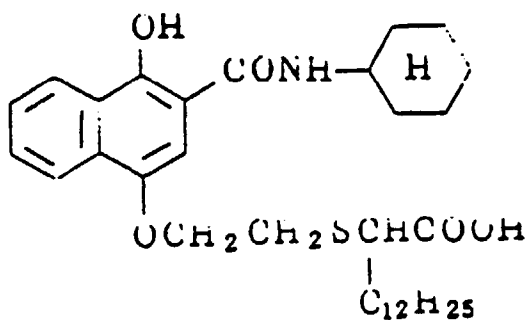
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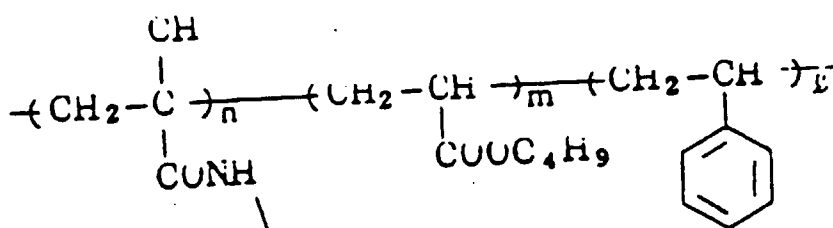
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Exc-5



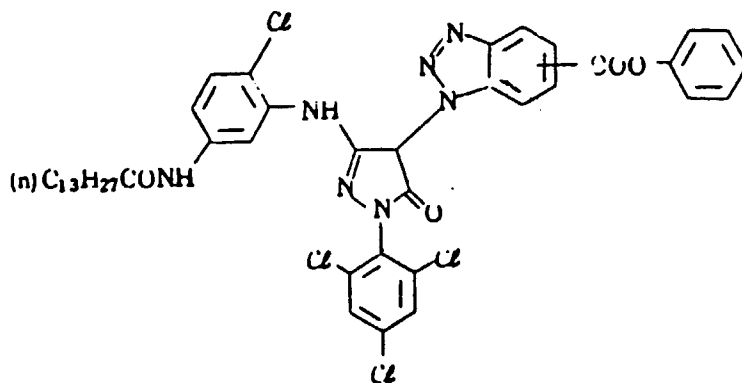
ExM-1



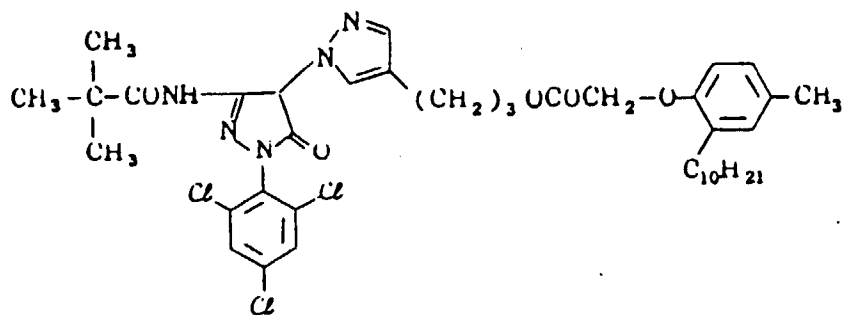
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$n : m : l = 2 : 1 : 1$
 (mol weight ratio)
 Avg. Mol. Wt. 40,000

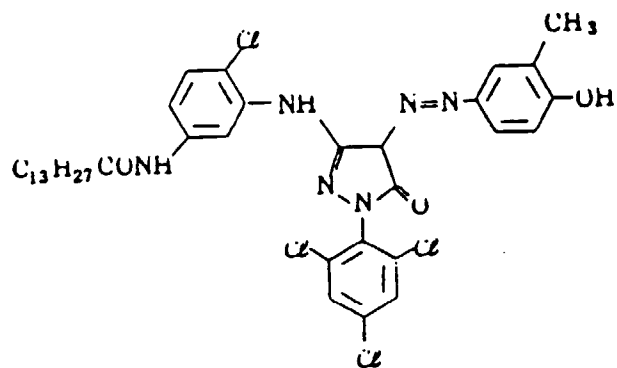
ExM-2



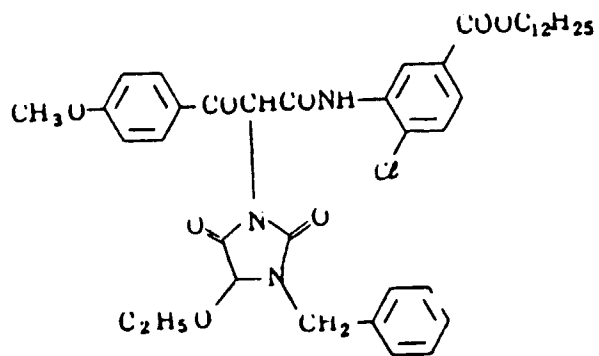
ExM-4



ExM-5



ExY-1

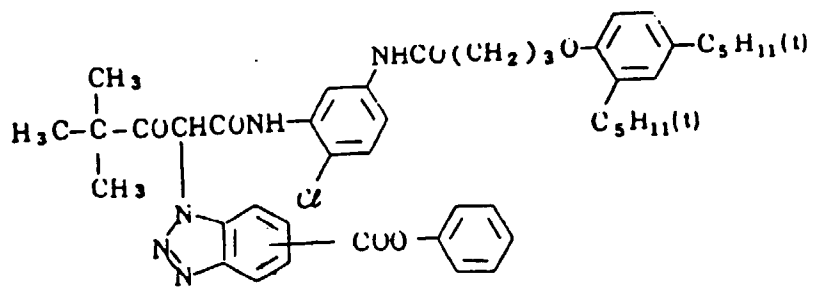


Ex Y-2

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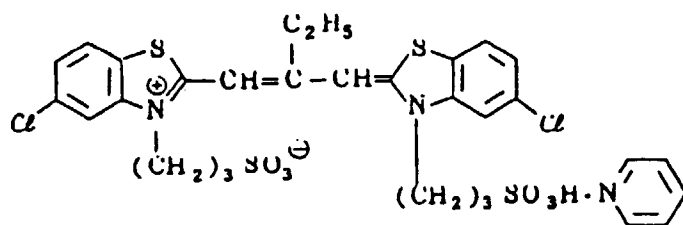
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Ex S-1

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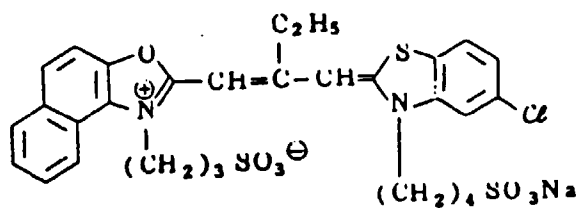


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Ex S-2

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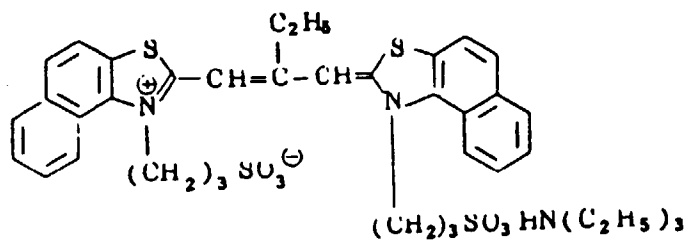


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Ex S-3

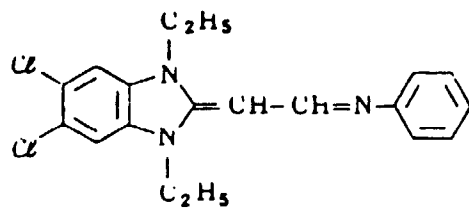
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ExS-4

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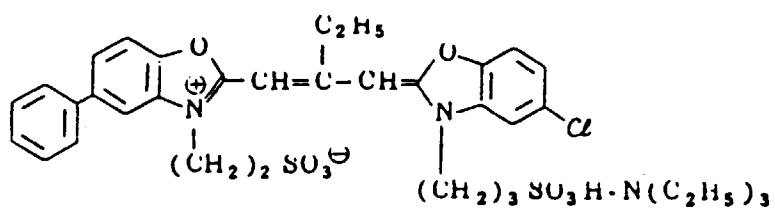


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ExS-5

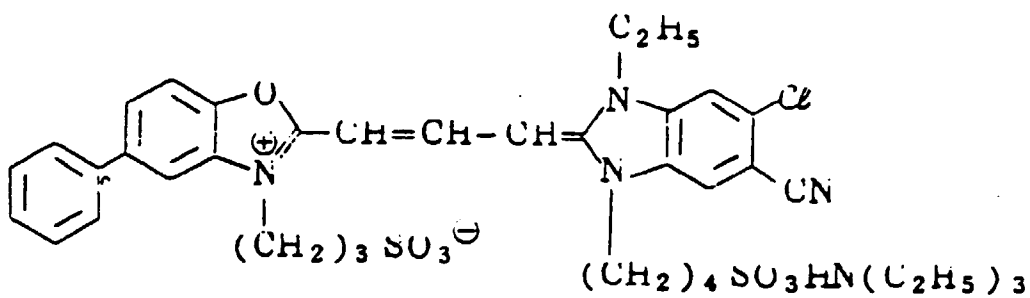
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ExS-6

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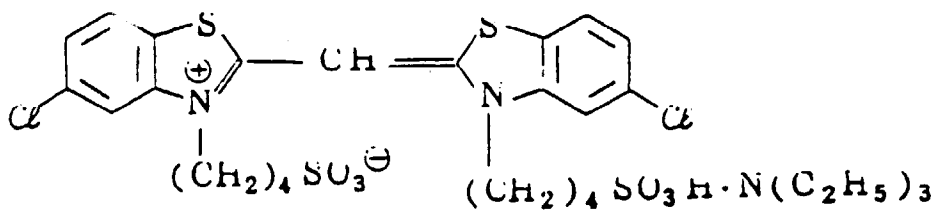


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ExS-8

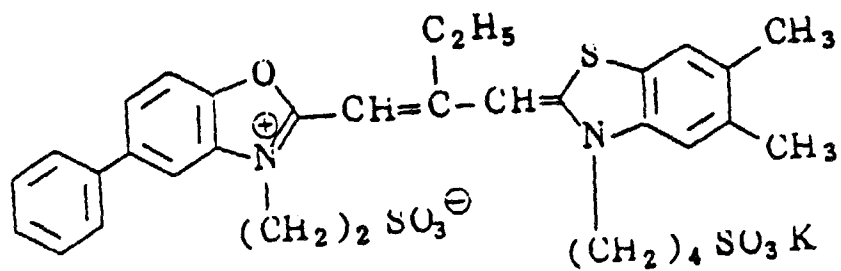
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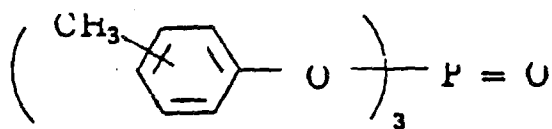
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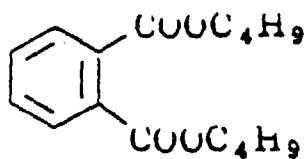
ExS-7



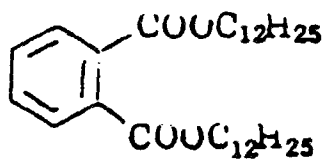
Solv-1



Solv-2



Solv-3

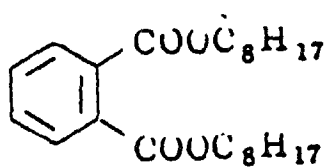


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Solv-4

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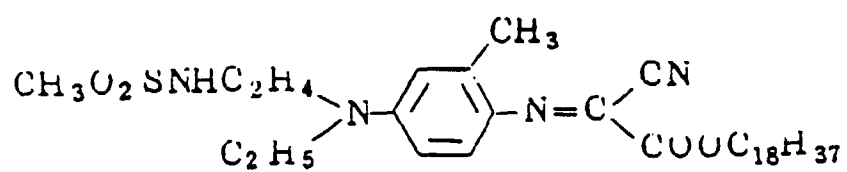


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Cpd-1

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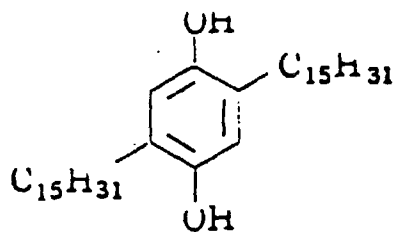


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Cpd-2

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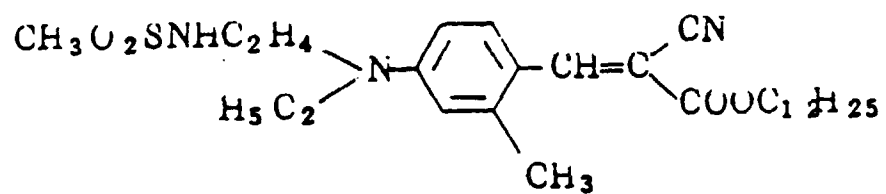


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Cpd-3

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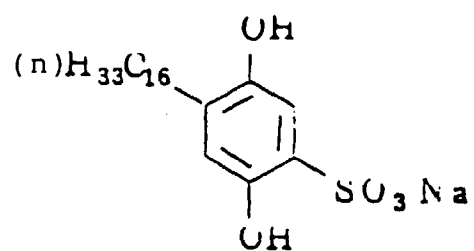
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Cpd-4

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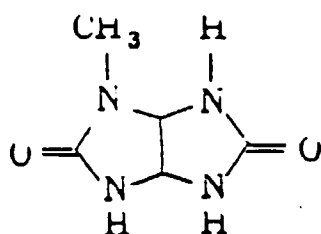


Cpd-5

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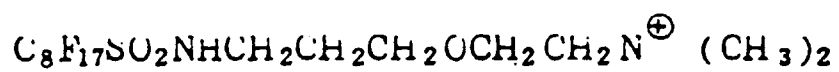
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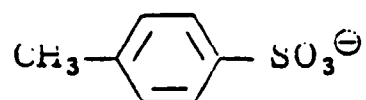


W-1

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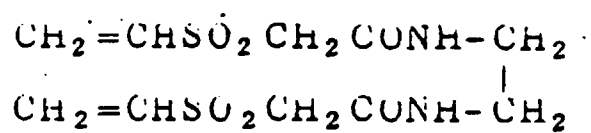
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H-1

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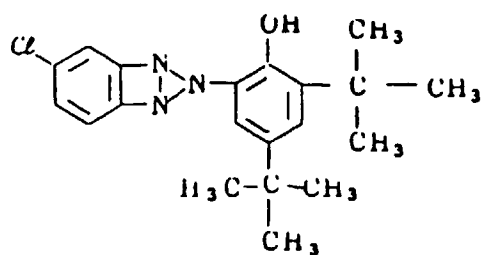
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U-1

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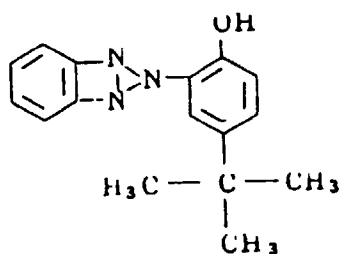


U-2

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U-3

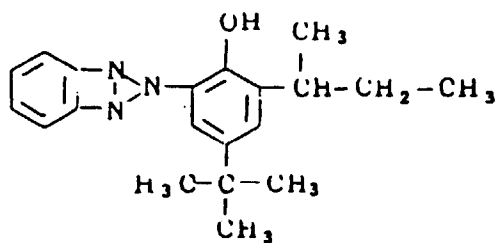
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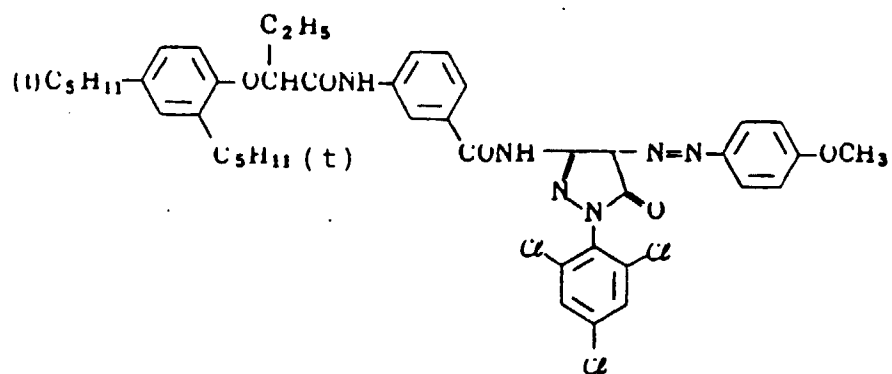
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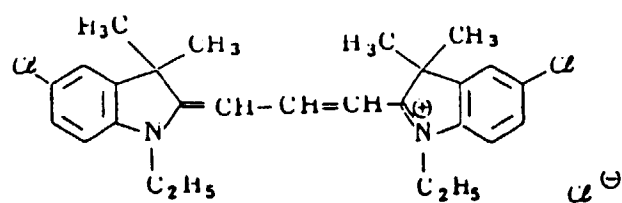
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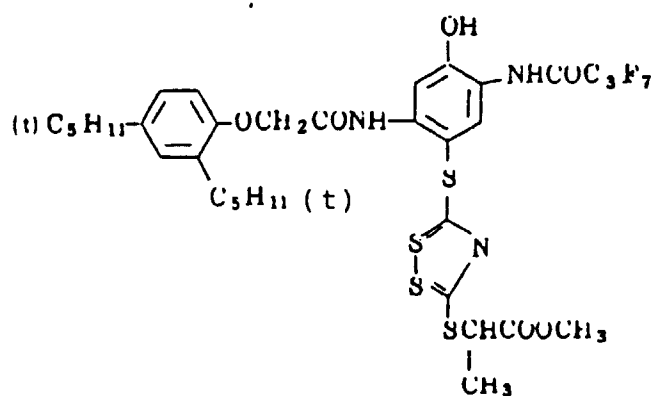
ExM-6



Cpd-6



ExC-7

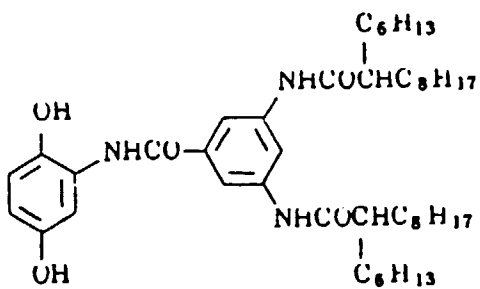


Cpd-7

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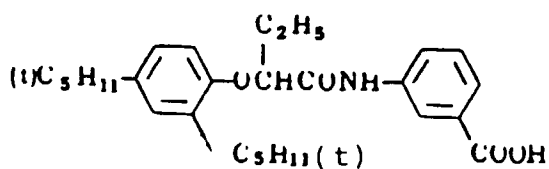


Cpd-8

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ExY-3

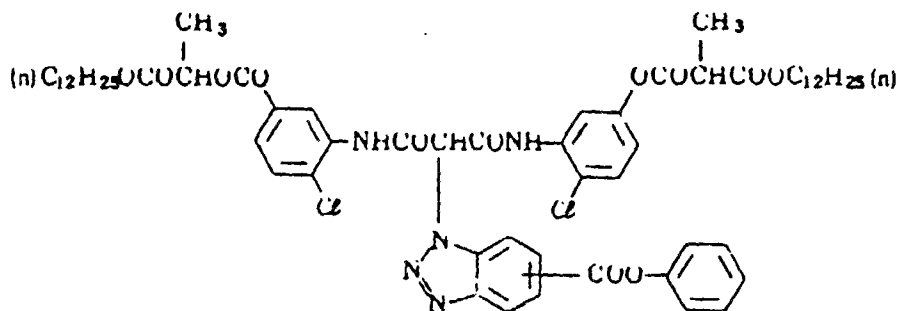
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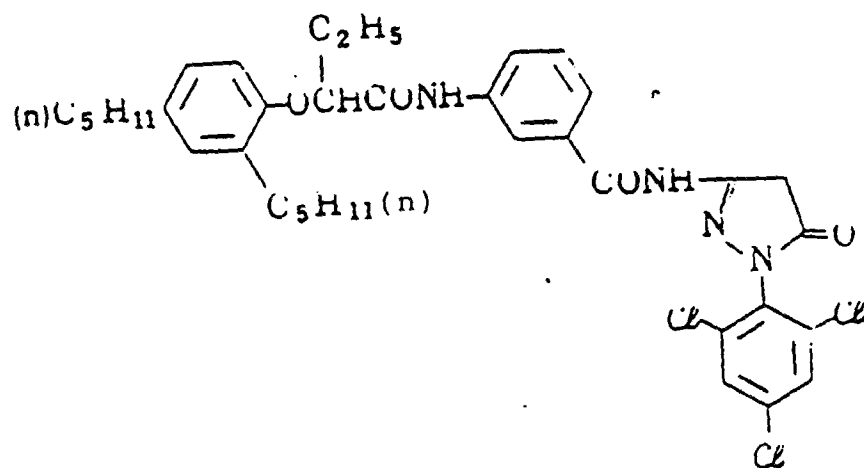
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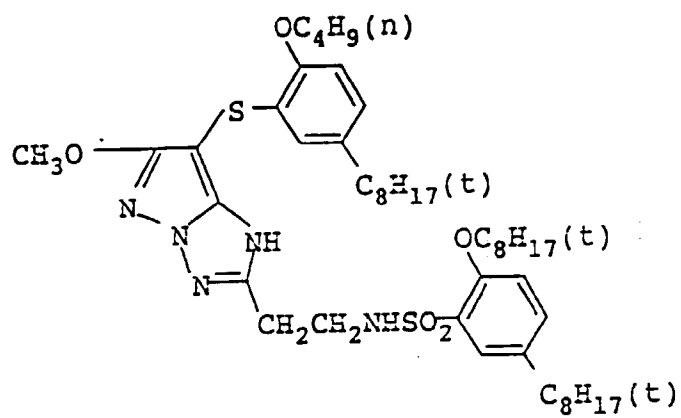
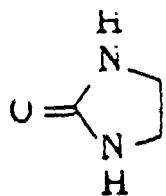
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ExM-7



Cpd-9



Claims

1. A silver halide photographic emulsion comprising a dispersion of silver halide grains in a binder, at least 60% by the total projected area of the grains being chemically sensitized tabular grains having an aspect ratio of 3 to 10, the grains having a distinct layer structure comprising at least one silver iodobromide layer in which the silver iodide content is from 15 to 45 mol%, wherein the silver halide composition of the outermost layer contains less than 5 mol% silver iodide.

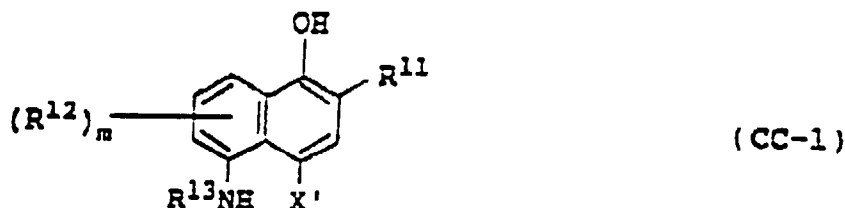
2. The silver halide photographic emulsion of claim 1 further comprising a mercapto compound of formula (D1):



wherein M_1 represents hydrogen, a cation or a protective group for the mercapto group which is cleaved in alkaline condition; and Z represents an atomic group necessary for forming a five or six membered heterocyclic ring.

3. The silver halide photographic emulsion of claim 2, wherein the heterocyclic ring is substituted with at least one substituent, selected from a carboxyl group, a sulfo group or a hydroxyl group.

4. The silver halide photographic emulsion of claim 1, further comprising a cyan coupler of formula (CC-1):



wherein R^{11} represents $-\text{CONR}^{15}\text{R}^{16}$, $-\text{NHCOR}^{15}$, $-\text{NHCOOR}^{17}$, $-\text{SO}_2\text{NR}^{15}\text{R}^{17}$, $-\text{NHSO}_2\text{R}^{17}$, $-\text{NHCONR}^{15}\text{R}^{16}$ or $-\text{NHSO}_2\text{NR}^{15}\text{R}^{16}$; wherein R^{15} , R^{16} and R^{17} , which may be the same or different, each represents an aliphatic group having from 1 to 30 carbon atoms, an aromatic group having from 6 to 30 carbon atoms, or a heterocyclic group having from 2 to 30 carbon atoms;

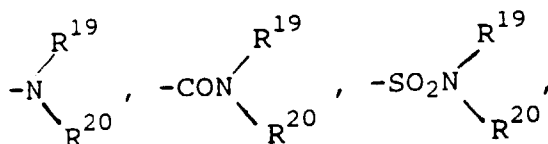
R^{12} represents a halogen atom, a hydroxyl group, an amino group, a carboxyl group, a sulfonic acid group, a cyano group, an aromatic group, a heterocyclic group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a ureido group, an acyl group, an acyloxy group, an aliphatic oxy group, an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an aliphatic sulfonyl group, an aromatic sulfonyl group, a sulfamoylamino group, a nitro group, or an imido group, and the number of carbon atoms contained in R^{12} is from 0 to 30;

m is 0 or an integer from 1 to 3;

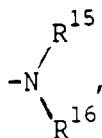
R^{13} is represented by formula (CC-3):



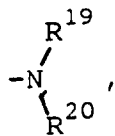
wherein Y represents NH, CO or SO_2 ; n is 0 or 1; and R^{18} represents hydrogen, an aliphatic group having from 1 to 30 carbon atoms, an aromatic group having from 6 to 30 carbon atoms, a heterocyclic group having from 3 to 30 carbon atoms, $-\text{OR}^{19}$, $-\text{SR}^{19}$, $-\text{COR}^{19}$,



-CO₂R²¹, -SO₂R²¹, or -SO₂OR²¹,
 wherein R¹⁹, R²⁰ and R²¹ which may be the same or different, each has the same definition as R¹⁵;
 R¹⁵ and R¹⁶ in

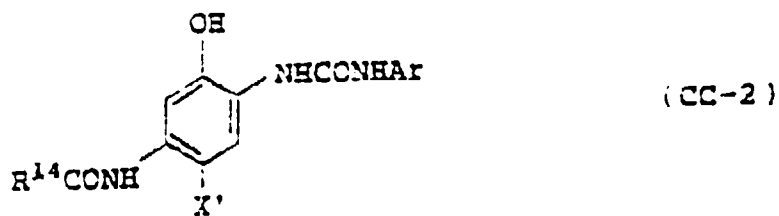


and R¹⁹ and R²⁰ in



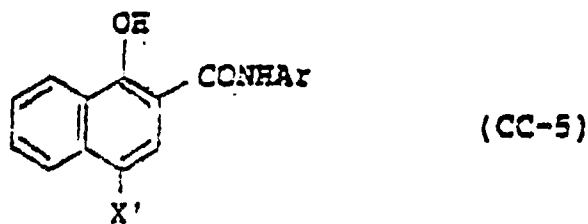
in R¹¹ and R¹⁸ may be joined together to form a nitrogen containing heterocyclic ring;
 and X' represents hydrogen or a group which is eliminated on coupling.

5. The silver halide photographic emulsion of claim 1, further comprising a cyan coupler of formula (CC-2);



wherein R¹⁴ represents an aliphatic group having from 1 to 36 carbon atoms, an aromatic group having from 6 to 36 carbon atoms, or a heterocyclic group which has from 2 to 36 carbon atoms;
 Ar represents an aromatic group having 6 to 30 carbon atoms, which may be substituted by alkyl groups, alkoxy groups, halogen atoms, alkoxy carbonyl groups, carbonamido groups, sulfonamido groups, alkoxy carbonyl amino groups, alkylthio groups, and halogen atoms;
 and X' is as defined in claim 4.

6. The silver halide photographic emulsion of claim 1, further comprising a cyan coupler of formula (CC-5):



10 wherein Ar and X' have the same definition as in formula (CC-2) of claim 5.

- 15
7. The silver halide photographic emulsion of claim 1, wherein the silver iodide content in the silver iodobromide is from 15 to 25 mol%.
- 20
8. The silver halide photographic emulsion of claim 1, wherein the silver iodide content in the silver iodobromide is from 30 to 45 mol%.
9. The silver halide photographic emulsion of claim 1 wherein the total silver iodide content is at least 8 mol%.
- 25
10. A silver halide photographic material comprising a support having thereon at least one silver halide photographic emulsion according to any of claims 1 to 9.
11. The silver halide photographic material of claim 10, at least one layer thereof further comprising at least one coupler represented by formula (I):

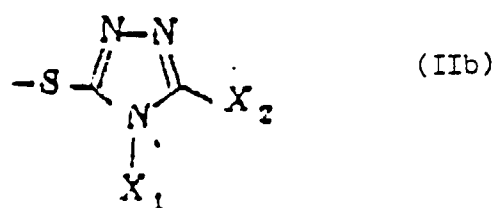
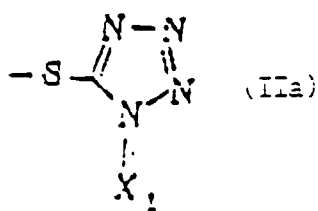


30 wherein

A represents a coupler group capable of releasing $(\text{LINK})_n-B$ by a coupling reaction with an oxidized primary aromatic amine developing agent;

LINK represents a group bonded to the active coupling site of A which is capable of releasing B after being released from A;

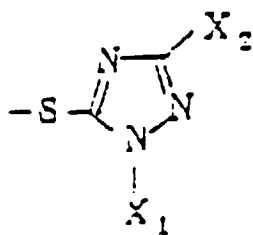
35 B is represented by formulae (IIa), (IIb), (IIc), (IId), (IIe), (IIf), (IIg), (IIh), (IIi), (IIj), (IIk), (IIl), (IIm), (IIn), (IIo) or (Iip); and
n is 0 or 1:



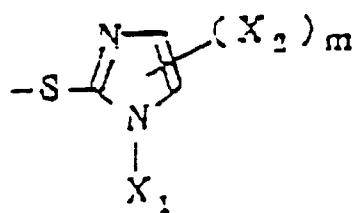
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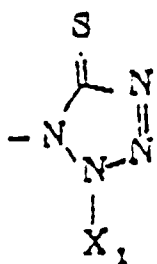
(IIc)



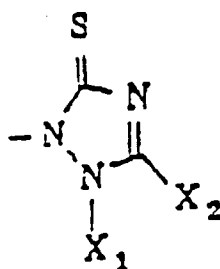
(IIId)

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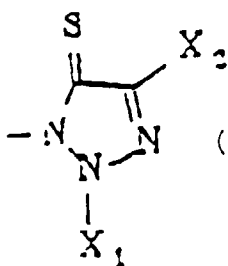
(IIe)



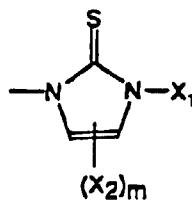
(IIIf)

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(IIg)

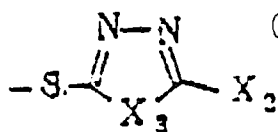


(IIh)

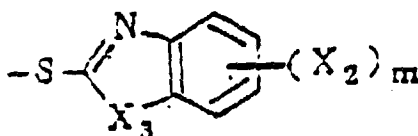
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(IIi)

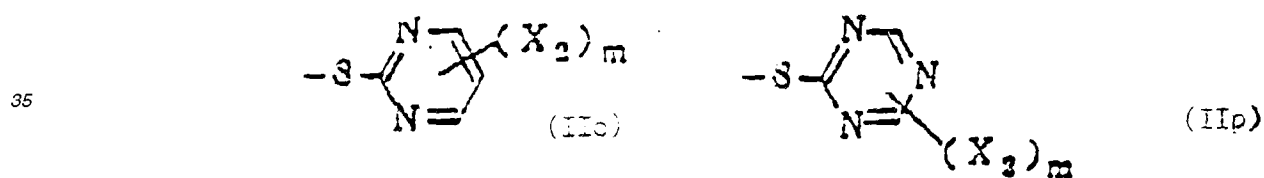
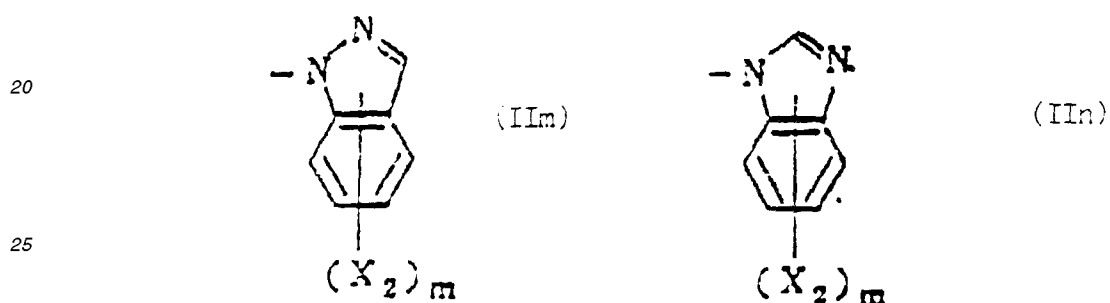
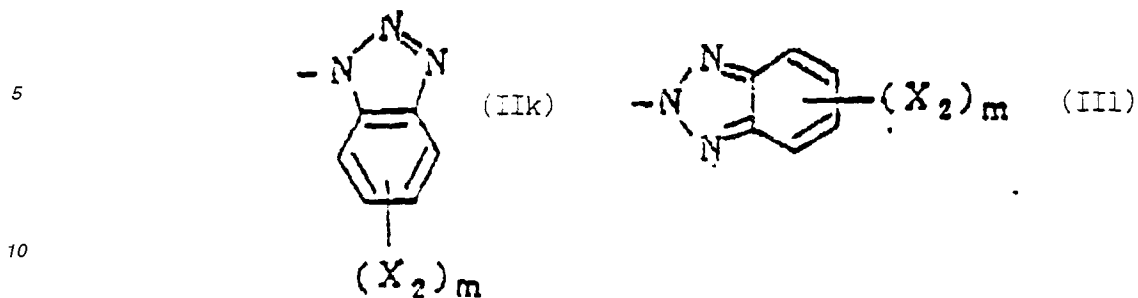


(IIj)

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wherein X₁ represents a substituted or unsubstituted aliphatic group containing from 1 to 4 carbon atoms or a substituted phenyl group;

X₂ represents hydrogen, an aliphatic group, a halogen atom, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxy carbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a cyano group, a nitro group, an amino group, an alkoxy carbonylamino group, an aryloxy carbonyl group or an acyl group;

X₃ represents sulfur or an imino group containing at most 4 carbon atoms or a hydrogen atom (as regards formulae (IIa) to (IIh) and (IIk) to (IIp);

m is 1 or 2; and

the total number of carbon atoms in all X₂ groups is at most 8.

Patentansprüche

- 55 1. Photographische Silberhalogenidemulsion, umfassend eine Dispersion von Silberhalogenidkörnern in einem Bindemittel, wobei mindestens 60% der gesamten Projektionsfläche der Körner chemisch sensibilisierte tafelförmige Körner mit einem Aspektverhältnis von 3 bis 10 sind, wobei die Körner eine unterschiedliche Schichtstruktur besitzen, umfassend mindestens eine Silberiodbromidschicht, in der der Silberiodidgehalt 15 bis 45 Mol-% beträgt,

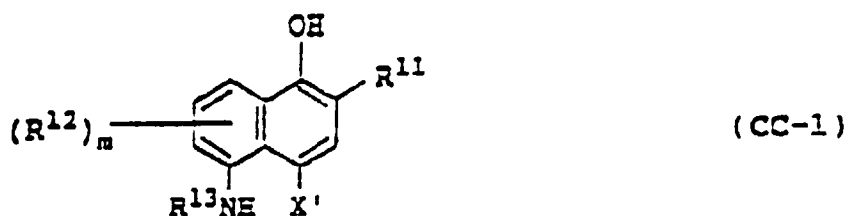
worin die Silberhalogenidzusammensetzung der äußersten Schicht weniger als 5 Mol-% Silberiodid enthält.

2. Photographische Silberhalogenidemulsion nach Anspruch 1, weiterhin umfassend eine Mercaptoverbindung der Formel (D1):



worin M₁ Wasserstoff, ein Kation oder eine Schutzgruppe für die Mercaptoverbindung bedeutet, die in alkalischer Lösung abgespalten wird; und Z bedeutet eine Gruppe aus Atomen, die erforderlich ist, um einen 5- oder 6-gliedrigen heterocyclischen Ring zu bilden.

3. Photographische Silberhalogenidemulsion nach Anspruch 2, worin der heterocyclische Ring mit mindestens einem Substituenten substituiert ist, ausgewählt aus einer Carboxylgruppe, einer Sulfogruppe oder einer Hydroxylgruppe.
4. Photographische Silberhalogenidemulsion nach Anspruch 1, weiterhin umfassend einen Cyankuppler der Formel (CC-1):



worin R¹¹ -CONR¹⁵R¹⁶, -NHCOR¹⁵, -NHCOOR¹⁷, -SO₂NR¹⁵R¹⁷, -NHSO₂R¹⁷, -NHCONR¹⁵R¹⁶ oder -NHSO₂NR¹⁵R¹⁶ bedeutet; worin R¹⁵, R¹⁶ und R¹⁷, die gleich oder verschieden sein können, jeweils eine aliphatische Gruppe mit 1 bis 30 Kohlenstoffatomen, eine aromatische Gruppe mit 6 bis 30 Kohlenstoffatomen oder eine heterocyclische Gruppe mit 2 bis 30 Kohlenstoffatomen bedeuten;

R¹² bedeutet ein Halogenatom, eine Hydroxylgruppe, eine Aminogruppe, eine Carboxylgruppe, eine Sulfonsäuregruppe, eine Cyanogruppe, eine aromatische Gruppe, eine heterocyclische Gruppe, eine Carbonamidogruppe, eine Sufonamidogruppe, eine Carbamoylgruppe, eine Sulfamoylgruppe, eine Ureidogruppe, eine Acylgruppe, eine Acyloxygruppe, eine aliphatische Oxygruppe, eine aromatische Oxygruppe, eine aliphatische Thiogruppe, eine aromatische Thiogruppe, eine aliphatische Sulfonylgruppe, eine aromatische Sulfonylgruppe, eine Sulfamoylaminogruppe, eine Nitrogruppe oder eine Imidogruppe, und die Anzahl der Kohlenstoffatome, die in R¹² enthalten sind, beträgt 0 bis 30;

m ist 0 oder eine ganze Zahl von 1 bis 3;

R¹³ wird durch die Formel (CC-3) dargestellt:



worin Y NH, CO oder SO₂ bedeutet; n ist 0 oder 1;

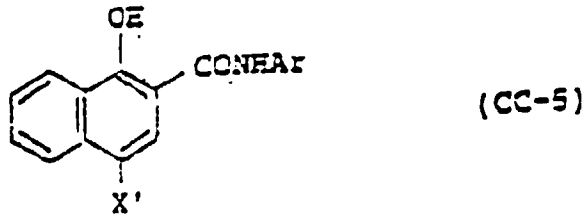
und R¹⁸ bedeutet Wasserstoff, eine aliphatische Gruppe mit 1 bis 30 Kohlenstoffatomen, eine aromatische Gruppe mit 6 bis 30 Kohlenstoffatomen, eine heterocyclische Gruppe mit 3 bis 30 Kohlenstoffatomen, -OR¹⁹,

und X' hat die gleiche Bedeutung wie in Anspruch 4.

6. Photographische Silberhalogenidemulsion nach Anspruch 1, weiterhin umfassend einen Cyankuppler der Formel (CC-5):

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worin Ar und X' die gleiche Bedeutung wie in Formel (CC-2) von Anspruch 5 haben.

7. Photographische Silberhalogenidemulsion nach Anspruch 1, worin der Silberiodidgehalt in dem Silberiodbromid 15 bis 25 Mol-% beträgt.

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8. Photographische Silberhalogenidemulsion nach Anspruch 1, worin der Silberiodidgehalt in dem Silberiodbromid 30 bis 45 Mol-% beträgt.

9. Photographische Silberhalogenidemulsion nach Anspruch 1, worin der gesamte Silberiodidgehalt mindestens 8 Mol-% beträgt.

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10. Photographisches Silberhalogenidmaterial, umfassend einen Träger mit darauf mindestens einer photographischen Silberhalogenidemulsion nach einem der Ansprüche 1 bis 9.

11. Photographisches Silberhalogenidmaterial nach Anspruch 10, worin mindestens eine Schicht des Materials weiterhin mindestens einen Kuppler umfaßt, der durch Formel (I) dargestellt ist:

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worin

A eine Kupplergruppe bedeutet, die $(\text{LINK})_n-B$ bei einer Kupplungsreaktion mit einem oxidierten Entwickler auf der Basis eines primären aromatischen Amins freisetzen kann;

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LINK bedeutet eine Gruppe, die an die aktive Kupplungsstelle von A gebunden ist und die B freisetzen kann, nachdem sie von A freigesetzt worden ist;

B wird durch die Formeln (IIa), (IIb), (IIc), (IId), (IIe), (IIf), (IIg), (IIh), (IIi), (IIj), (IIk), (IIl), (IIm), (IIn), (IIo) oder (IIp) dargestellt; und

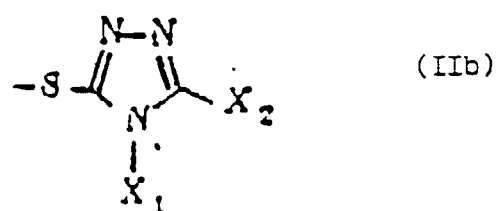
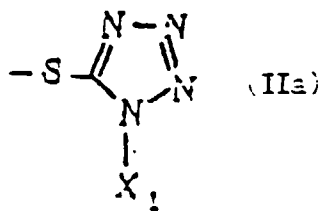
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n ist 0 oder 1;

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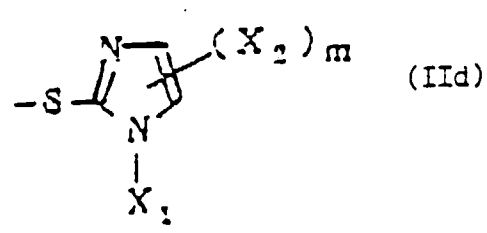
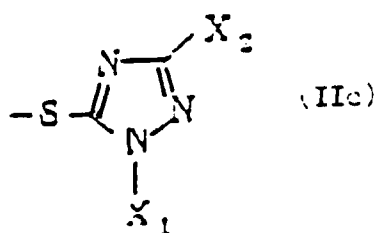
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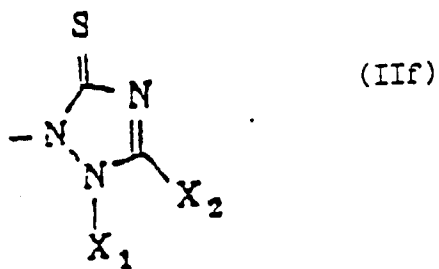
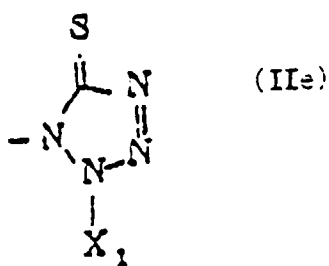
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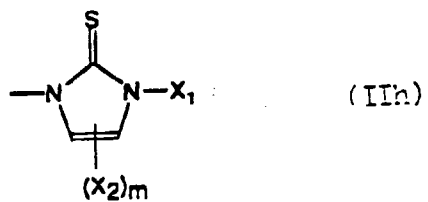
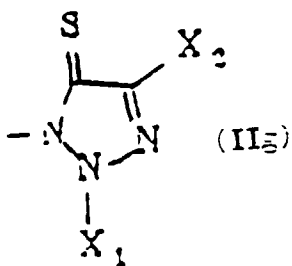
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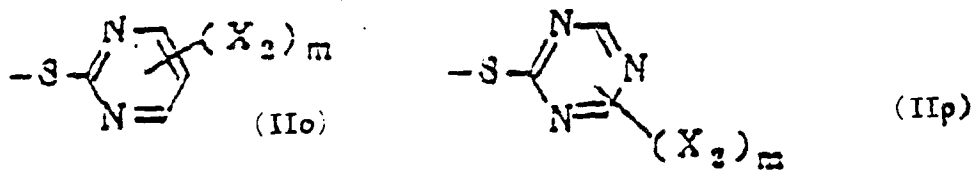
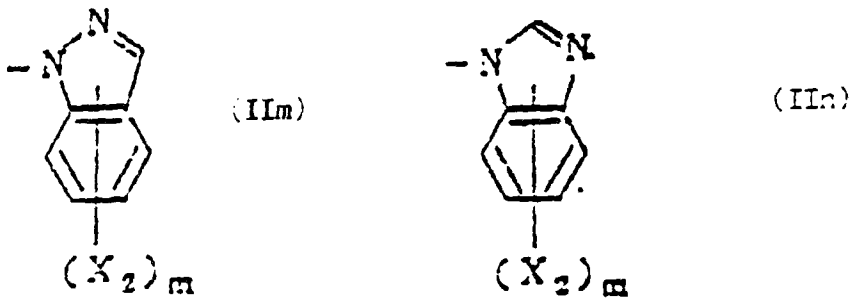
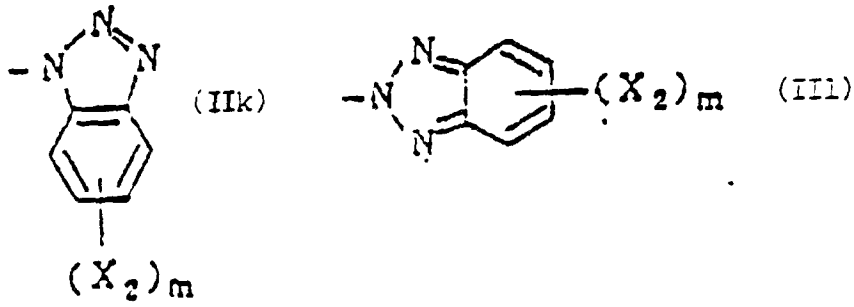
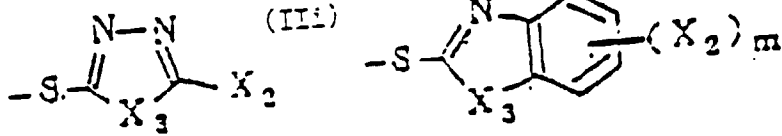


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(IIj)



50 worin X_1 eine substituierte oder unsubstituierte aliphatische Gruppe, enthaltend 1 bis 4 Kohlenstoffatome, oder eine substituierte Phenylgruppe bedeutet;

55 X_2 bedeutet Wasserstoff, eine aliphatische Gruppe, ein Halogenatom, eine Hydroxylgruppe, eine Alkoxygruppe, eine Alkylthiogruppe, eine Alkoxy-carbonylgruppe, eine Acylaminogruppe, eine Carbamoylgruppe, eine Sulfonylgruppe, eine Sulfonamidogruppe, eine Sulfamoylgruppe, eine Acyloxygruppe, eine Ureidogruppe, eine Cyanogruppe, eine Nitrogruppe, eine Aminogruppe, eine Alkoxy-carbonylaminogruppe, eine Aryloxy-carbonylgruppe oder eine Acylgruppe;

X₃ bedeutet Schwefel oder eine Iminogruppe, enthaltend höchstens 4 Kohlenstoffatome, oder ein Wasserstoffatom (was die Formeln (IIa) bis (IIh) und (IIk) bis (IIp) betrifft;

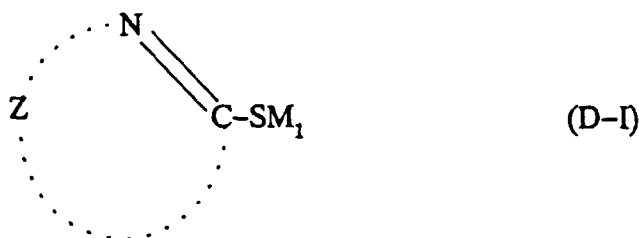
m ist 1 oder 2; und

die Gesamtzahl der Kohlenstoffatome in allen X₂-Gruppen beträgt höchstens 8.

Revendications

1. Une émulsion photographique d'halogénure d'argent comprenant une dispersion de grains d'halogénure d'argent dans un liant, au moins 60 % des grains, par rapport à la surface projetée totale, étant des grains tabulaires sensibilisés chimiquement ayant un rapport d'aspect de 3 à 10, les grains ayant une structure stratifiée distincte comprenant au moins une couche d'iodobromure d'argent dans laquelle la teneur en iodure d'argent est de 15 à 45 mol %, où la composition de l'halogénure d'argent dans la couche extérieure contient moins de 5 mol % d'iodure d'argent.

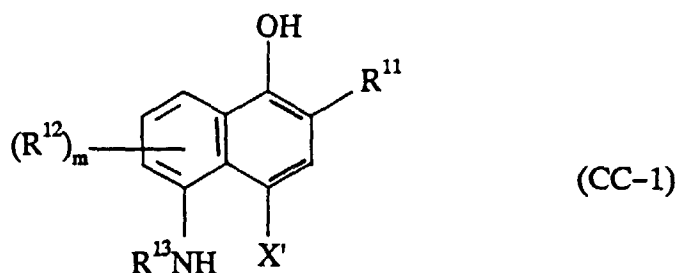
2. L'émulsion photographique d'halogénure d'argent selon la revendication 1, comprenant en outre un composé mercapto de formule (D-I):



dans laquelle M₁ représente l'hydrogène, un cation ou un groupe protecteur du groupe mercapto qui est séparé en conditions alcalines ; et Z représente un groupe atomique nécessaire pour former un noyau hétérocyclique à 5 ou 6 chaînons.

3. L'émulsion photographique d'halogénure d'argent selon la revendication 2, dans laquelle le noyau hétérocyclique est substitué par au moins un substituant, choisi parmi un groupe carboxyle, un groupe sulfo et un groupe hydroxyle.

4. L'émulsion photographique d'halogénure d'argent selon la revendication 1, comprenant en outre un coupleur pour cyan de formule (CC-1):



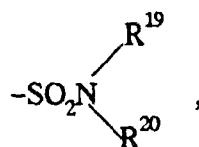
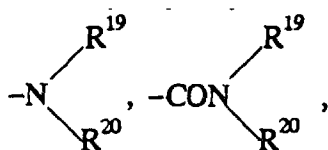
dans laquelle R¹¹ représente -CONR¹⁵R¹⁶, -NHCOR¹⁵, -NHCOOR¹⁷, -SO₂NR¹⁵R¹⁷, -NHCO₂R¹⁷, -NHCONR¹⁵R¹⁶ ou -NHCO₂NR¹⁵R¹⁶; où R¹⁵, R¹⁶ et R¹⁷, qui peuvent être les mêmes ou différents, représentent chacun un groupe aliphatique en C₁-C₃₀, un groupe aromatique en C₆-C₃₀ ou un groupe hétérocyclique ayant de 2 à 30 atomes de carbone; R¹² représente un atome d'halogène, un groupe hydroxyle, un groupe amino, un groupe carboxyle, un groupe acide sulfonique, un groupe cyano, un groupe aromatique, un groupe hétérocyclique, un groupe carbona-

EP 0 337 370 B1

mido, un groupe sulfonamido, un groupe carbamoyle, un groupe sulfamoyle, un groupe uréido, un groupe acyle, un groupe acyloxy, un groupe oxy aliphatique, un groupe oxy aromatique, un groupe thio aliphatique, un groupe thio aromatique, un groupe sulfonyle aliphatique, un groupe sulfonyle aromatique, un groupe sulfanoylamino, un groupe nitro ou un groupe imido et le nombre d'atomes de carbone contenus dans R¹² est de 0 à 30; m est égal à 0 ou à un entier de 1 à 3; R¹³ est représenté par la formule (CC-3):

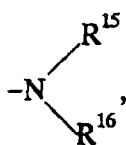


dans laquelle Y représente NH, CO ou SO₂; n est égal à 0 ou 1; et R¹⁸ représente l'hydrogène, un groupe aliphatique ayant de 1 à 30 atomes de carbone, un groupe aromatique ayant de 6 à 30 atomes de carbone, un groupe hétérocyclique ayant de 3 à 30 atomes de carbone, -OR¹⁹, -SR¹⁹, -COR¹⁹,

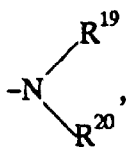


-CO₂R²¹, -SO₂R²¹ ou -SO₂OR²¹,

où R¹⁹, R²⁰ et R²¹, qui peuvent être les mêmes ou différents, ont chacun la même définition que R¹⁵; R¹⁵ et R¹⁶ dans

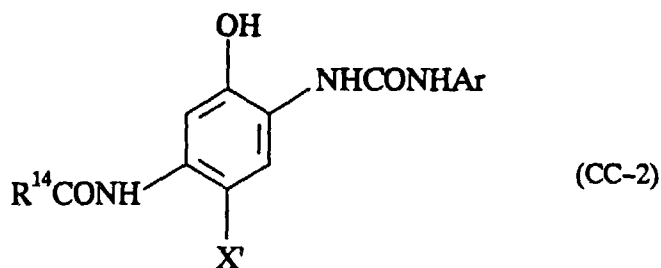


et R¹⁹ et R²⁰ dans



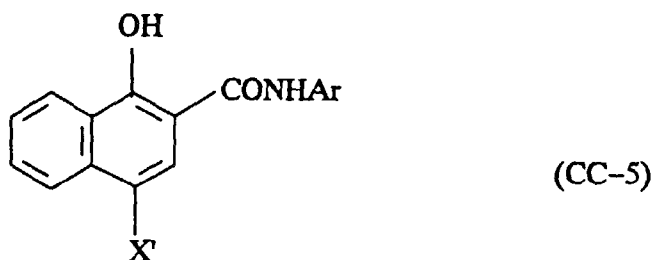
dans R¹¹ et R¹⁸ peuvent être reliés ensemble pour former un noyau hétérocyclique azoté; et X' représente l'hydrogène ou un groupe qui est éliminé par couplage.

5. L'émulsion photographique d'halogénure d'argent selon la revendication 1, comprenant en outre un coupleur pour cyan de formule (CC-2):



15 dans laquelle R¹⁴ représente un groupe aliphatique ayant de 1 à 36 atomes de carbone, un groupe aromatique ayant de 6 à 36 atomes de carbone ou un groupe hétérocyclique qui a de 2 à 36 atomes de carbone; Ar représente un groupe aromatique ayant de 6 à 30 atomes de carbone, qui peut être substitué par des groupes alkyles, des groupes alcoxy, des atomes d'halogènes, des groupes alcoxycarbonyles, des groupes cubonamido, des groupes sulfonamido, des groupes alcoxycarbonamido et des groupes alkylthio; et X' est tel que défini à la revendication 4.

- 20 6. L'émulsion photographique d'halogénure d'argent selon la revendication 1, comprenant en outre un coupleur pour cyan de formule (CC-5):



dans laquelle Ar et X' ont la même définition que dans la formule (CC-2) à la revendication 5.

- 35 7. L'émulsion photographique d'halogénure d'argent selon la revendication 1, dans laquelle la teneur en iodure d'argent dans l'iodobromure d'argent est de 15 à 25 mol %.
- 40 8. L'émulsion photographique d'halogénure d'argent selon la revendication 1, dans laquelle la teneur en iodure d'argent dans l'iodobromure d'argent est de 30 à 45 mol %.
- 45 9. L'émulsion photographique d'halogénure d'argent selon la revendication 1, dans laquelle la teneur totale en iodure d'argent est d'au moins 8 mol %.
10. Un matériau photographique à l'halogénure d'argent comprenant un support portant au moins une émulsion photographique d'halogénure d'argent selon l'une quelconque des revendications 1 à 9.
11. Le matériau photographique à l'halogénure d'argent selon la revendication 10, dont au moins une couche comprend en outre au moins un coupleur représenté par la formule (I):



dans laquelle

55 A représente un groupe de coupleur capable de libérer (LINK)_n-B par une réaction de couplage avec un agent développeur du type amine aromatique primaire oxydé; LINK représente un groupe relié à A du côté du centre de couplage actif, qui est capable de libérer B après

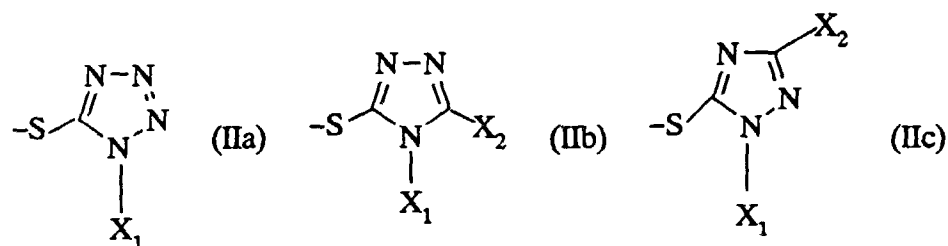
avoir été séparé de A ;

B est représenté par l'une des formules (IIa), (IIb), (IIc), (IId), (IIe), (IIf), (IIg), (IIh), (Iii), (Iij), (Iik), (Iil), (Iim), (Iin), (Iio) et (Iip); et

n est égal à 0 ou 1 :

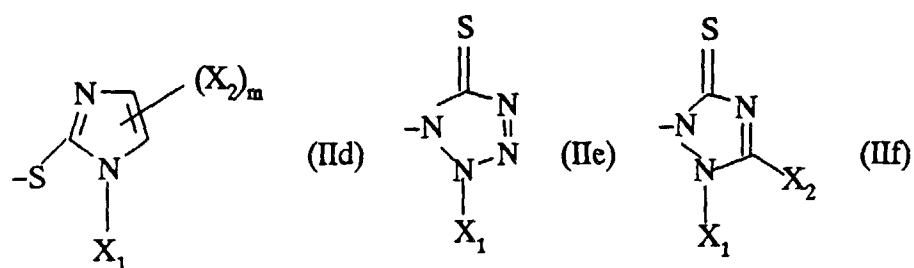
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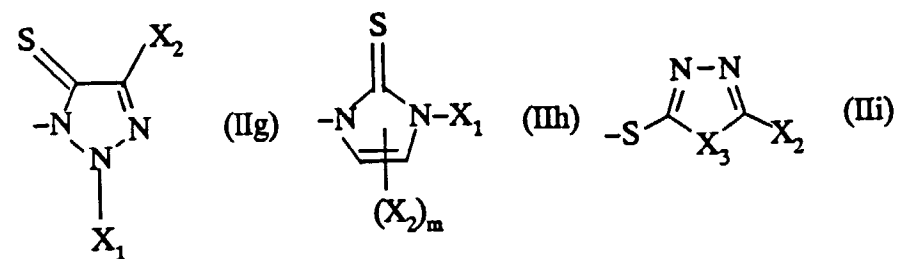
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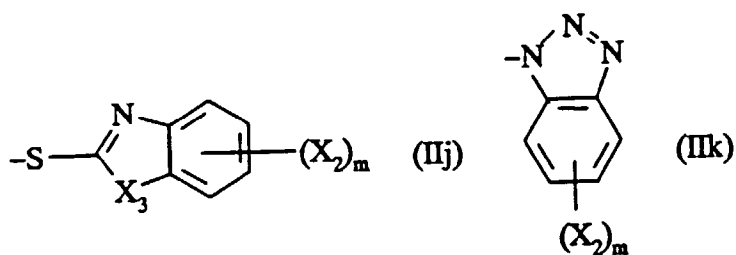
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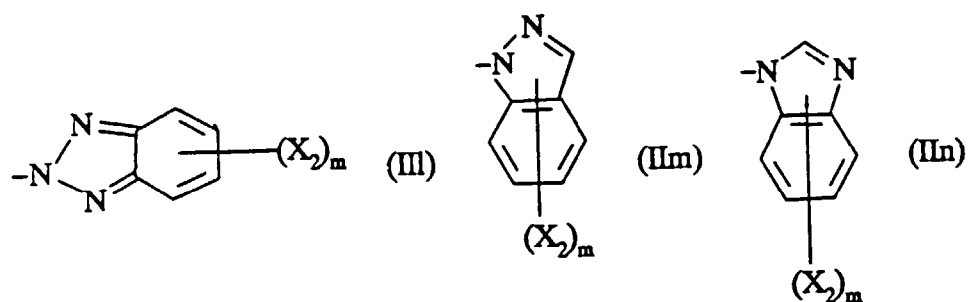
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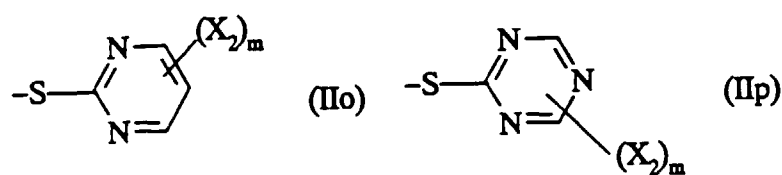
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dans lesquelles X_1 représente un groupe aliphatique contenant de 1 à 4 atomes de carbone substitué ou non ou un groupe phényle substitué;

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X_2 représente l'hydrogène, un groupe aliphatique, un atome d'halogène, un groupe hydroxyle, un groupe alcoxy, un groupe alkylthio, un groupe alcoxycarbonyle, un groupe acylamino, un groupe carbamoyle, un groupe sulfonyle, un groupe sulfonamido, un groupe sulfamoyle, un groupe acyloxy, un groupe uréido, un groupe cyano, un groupe nitro, un groupe amino, un groupe alcoxycarbonylamino, un groupe aryloxycarbonyle ou un groupe acyle ;

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X_3 représente le soufre ou un groupe imino contenant au plus 4 atomes de carbone ou un atome d'hydrogène (pour les formules (IIa) à (IIh) et (IIk) à (IIp));

m est égal à 1 ou 2 ; et

le nombre total d'atomes de carbone dans tous les groupes X_2 est au plus de 8.

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