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(54) Silver halide color photographic lightsensitive material.

(57) In a silver halide color photographic light-sensitive material which comprises a photographic layer having at least one silver halide emulsion layer on a support, fine silver halide grains having an average grain size of less than 0.15 µm, adsorbing a compound for forming a silver salt having a solubility lower than that of silver bromide thereon, and having a silver chloride content of 50 mol% or more are contained in the photographic layer.

Silver halide color photographic light-sensitive material

The present invention relates to a silver halide color photographic light-sensitive material and, more particularly, to a silver halide color photographic light-sensitive material having a high image quality, high sensitivity, and improved storage stability.

Recently, although photographic properties such as a sensitivity and image quality of a color photographic light-sensitive material have been significantly improved, a demand for a further improvement is strong. Therefore, efforts have been made to provide a light-sensitive material satisfying this demand.

Many studies have been made to improve photographic properties by adding fine silver halide grains to a silver halide color photographic light-sensitive material. JP-A-50-23228, JP-A-59-69754, and JP-A-59-160135 ("JP-A" means unexamined published Japanese patent application) disclose an use of a fine grain emulsion. Although these patent applications describe that a composition of halogens in fine grains can be arbitrarily selected, a silver iodobromide emulsion containing a small amount of silver iodide is used in most of their examples. JP-B-49-26134 ("JP-B" means examined Japanese patent application) discloses an use of very fine grains having a grain size of 0.2 µm or less in order to improve sharpness. While this patent application does not define a composition of halogens, it discloses that fine grains having a minimum grain size of 0.07 µm are added in the case of silver iodobromide fine grains, and fine grains having a minimum grain size of 0.15 µm are added in the case of silver chloride. Since grains having a high silver chloride content have high solubility, it is conventionally difficult to form fine grains of 0.15 µm or less. That is, even if grains are fine in a grain formation process, it is difficult to prevent precipitating onto grains in the following processes for forming a light-sensitive material such as desalting, dispersing, and dissolving processes. For these reasons, it is very difficult to manufacture a very fine grain emulsion having a high silver chloride content. In addition, when a fine grain emulsion containing a large amount of silver chloride, having high solubility and unstable is used to a color photographic light-sensitive material, light-sensitive silver halide grains in the same or another layer are adversely affected. As a result, for example, a fog density is undesirably increased. Furthermore, when a color photographic light-sensitive material containing an emulsion having a high silver chloride content is stored for a long time period, problems such as an increase in fog density arise. Therefore, no practical color photographic light-sensitive material containing a very fine grain emulsion having a high silver chloride content has been proposed.

In order to improve image quality, efforts have been made to improve graininess, sharpness, and color reproduction.

In a conventional method of improving sharpness and color reproduction, a compound which releases a development inhibitor in correspondence with an image density upon development is added beforehand to a silver halide color photographic light-sensitive material.

A known example of such a compound is a so-called DIR compound for forming a coupling product by a coupling reaction with an oxide of an aromatic primary amine-based color developing agent and releasing a development inhibitor, as disclosed in each of British Patent 953,454 and U.S. Patents 3,227,554 and 4,095,984. So-called DIR hydroquinones for releasing a development inhibitor by an alternate oxidization reaction with an oxide of developing agent are also known (to be generally referred to as a "DIR compound" hereinafter).

A DIR compound releases a development inhibitor to improve sharpness by an edge effect, prevents formation of large developed silver grains to improve graininess, and improves color reproduction by an interlayer effect. A DIR compound, however, has an essential drawback in which when a large amount of a DIR compound is added, the sensitivity of a silver halide emulsion of a layer to which the compound is added is decreased. For this reason, in a color sensitive layer constituted by a plurality of emulsion layers having different sensitivities, a large amount of a DIR compound is added to layers having lower sensitivities so that a sensitivity decrease in a layer having a high sensitivity is minimized. As a method of further improving this effect, a nondiffusible DIR coupler for releasing a development inhibitor having a highly diffusible property during development as described in JP-A-59-131934 has been developed (to be referred to as a "diffusible DIR coupler" hereinafter. Although this diffusible DIR coupler improves the interlayer effect to largely improve image quality, a part of the released inhibitor is diffused and accumulated in a developing solution to change processing properties, causing another problem.

It is a first object of the present invention to provide a color photographic light-sensitive material having a high sensitivity and a low fog.

It is a second object of the present invention to provide a color photographic light-sensitive material in which photographic properties such as a sensitivity and a fog do not change much during storage of the light-sensitive material.

It is a third object of the present invention to provide a color photographic light-sensitive material in which photographic properties do not vary much when a composition of a processing solution changes.

It is a fourth object of the present invention to provide a color photographic light-sensitive material in which a flowing out of an ingredients from the light-sensitive material during development, especially in a color development process is little.

The above objects of the present invention are achieved by a silver halide color photographic light-sensitive material which comprises a photographic light-sensitive layer having at least one silver halide emulsion layer on a support, wherein fine silver halide grains having an average grain size of less than 0.15 µm, having a compound which forms a silver salt having a lower solubility than that of silver bromide and adsorbed thereon, and having a silver chloride content of 50% or more are contained in the photographic layer.

In addition to the above objects, it is a fifth object of the present invention to provide a color photographic light-sensitive material having high image quality.

The above objects of the present invention are achieved by a silver halide color photographic light-sensitive material which comprises at least one silver halide emulsion layer on a support, wherein the silver halide color light-sensitive material contains fine silver halide grains having an average grain size of less than 0.15 µm, having a compound which forms a silver salt having a lower solubility than that of silver bromide adsorbed thereon, and having a silver chloride content of 50 mol% or more, and contains a compound represented by the following general formula (I):

$A\text{-}(TIME)_n\text{-}B$ (I)

wherein A represents a coupler residue for releasing $(TIME)_n\text{-}B$ upon a coupling reaction with an oxide of an aromatic primary amine developing agent, TIME represents a timing group which is bonded to a coupling active position of A and releases B after it is released from A upon the coupling reaction, and B represents an inhibiting group.

Not all reasons why the above objects of the present invention can be achieved by a silver halide color photorgraphic light-sensitive material according to the present invention have become clear. Fine grains having high silver halide content (to be referred to as "high silver chloride fine grains" hereinafter) used in the present invention, however, are assumed to (1) prevent a diffusible inhibitor released from a diffusible DIR compound from flowing into a developing solution during development, (2) rapidly remove an inhibiting substance such as iodine or bromine produced during development, thereby increasing the number of developed grains, and (3) prevent penetration of an inhibiting compound present in a developing solution into silver halide emulsion layers. It is also assumed that since a compound which forms a silver salt having a lower solubility than that of silver bromide is adsorbed in high silver chloride fine grains, the high silver chloride fine grains are prevented from dissolving to degrade the stability of the light-sensitive material during development or storage.

Fine silver halide grains used in the present invention are added to a photographic layer. The photographic layer means one or more layers coated in order to form a photographic image and is a general term of a silver halide emulsion layer and layers such as an interlayer, a protective layer, and a filter layer which are mutually water permeable with the silver halide emulsion layer. A back layer formed on the opposite side of a support is not included in the photographic layer.

The fine silver halide grains used in the present invention must have an average grain size (diameter of a sphere equivalent to a volume) of less than 0.15 µm. If the average grain size is 0.15 µm or more, an optical scattering effect becomes significant to degrade the sharpness of an image. An average grain size of less than 0.13 µm is preferred in the present invention. Very fine grains having an average grain size of less than 0.10 µm are most preferred. The grain size can be determined by a conventional method using an electron microscope. The grain size is a number-average value. Although a grain size distribution is not particularly limited, a so-called mono-dispersed emulsion having a narrow size distribution is preferred in the present invention. A variation coefficient of a size distribution is preferably 20% or less, more preferably, 15% or less, and most preferably, 10% or less. The shape of grains may be a cube having a (100) face, an octahedron having a (111) face, a dodecahedron having a (110) face, or a polyhedron having high-order Miller indices such as an (hh1) or (hk1) face (h, k, 1 > 1). Grains may have a plurality of faces, e.g., may be tetradecahedral grains having both (100) and (111) faces. In addition, grains may be tabular grains having a twinning plane or indefinite potato-like grains. Although the shape of fine grains used in the present invention is not particularly limited, grains mainly having a (100) face which is a crystal face most stable in a halogen composition preferred in the present invention is most preferred.

The silver halide fine grains used in the present invention must mainly contain silver chloride. A silver chloride content must be 50 mol% or more, preferably, 75 mol% or more, and most preferably, 90 mol%. Pure silver chloride is most preferred. Detailed reasons why high sensitivity is realized by a high silver chloride fine grains are currently being analyzed. One of possible mechanisms, however, is that the high silver chloride fine grains prevent a phenomenon in which development of light-sensitive grains is inhibited by an inhibiting substance released from the light-sensitive material or an inhibiting substance present in a developing solution and therefore the grains essentially become dead grains. The reason why the high silver chloride fine grains efficiently reduce an effect of the inhibiting substance is also expected to become clear in future. In the high silver chloride fine grains used in the present invention, a preferable halogen component other than silver chloride is silver bromide. Although it is not preferred to increase a silver iodide content too much, silver iodochlorobromide containing 10 mol% or less of silver iodide can be used. The interior and the surface layer of the high silver chloride fine grain may consist of either a uniform phase or different phases. When the high silver chloride fine grain consists of different phases, a structure may be a core/shell structure or an epitaxial structure.

An emulsion containing the high silver chloride fine grains used in the present invention need not be chemically or spectrally sensitized. Chemical or spectral sensitization, however, may be performed as long as an adverse effect such as a fog does not occur.

The light sensitivity of the high silver chloride fine grains used in the present invention is preferably, relatively decreased. The sensitivity is preferably lower by 1.0 or more in units of log (exposure) than the lowest sensitivity of a silver halide emulsion concerned in formation of a color image.

In a method of preparing the high silver chloride fine grains having an average grain size of less than 0.15 μm, stabilizing produced nuclear grains and producing a large number of nuclear grains in an initial stage of grain formation, i.e., upon first nucleation in adding process of a silver salt and/or halide are basic factors in fine grain formation.

As the number of stable nuclei is increased, the size of grains obtained after addition of a silver halide is completed is decreased since the silver halide added after nucleation is deposited on the nuclei.

In order to obtain stable nuclei, it is important to minimize physical ripening upon grain formation, i.e., to prevent produced nuclei from being dissolved again.

The temperature upon grain formation, therefore, is preferably decreased as low as possible, e.g., 45°C or less. The electric potential (reference electric potential: saturated calomel electrode) upon material charging preferably falls within the range of +80 mV to +600 mV, and especially in nucleation, it preferably falls within the range of +250 mV to +600 mV.

A binder is important to stabilize nuclear grains and its concentration is preferably falls within the range of 0.2% to 4%.

In order to produce a large number of nuclei, it is important to add a high-concentration solution (e.g., 1 to several mol/ℓ) into a reaction vessel within a short time period. For this purpose, an addition time is preferably 30 minutes or less, more preferably, 20 minutes or less, and most preferably 15 minutes or less.

Although a stirring method is not particularly limited, it is preferred to efficiently and uniformly perform stirring.

Grain formation may be performed by any method such as a single jet method, a double jet method, a combination of these two methods, or a controlled double jet method.

In order to stabilize nuclei or to inhibit precipitation onto grain or physical ripening, it is preferred to add a tetrazaindene compound before, during, or after grain formation. More preferably, a tetrazaindene compound is added immediately after grain formation. An addition amount is 0.1 to 10 g, and preferably, 0.2 to 8 g per mol of Ag.

The pH during grain formation is 2.0 or more, and preferably, 4.0 or more in order to allow adsorption of a tetrazaindene compound.

A silver halide emulsion is normally subjected to a desalting process for removing an unnecessary salt after grain formation. In this desalting process, physical ripening of high silver chloride fine grains having an average grain size of less than 0.15 μm is accelerated to increase the grain size or deform the grains. Therefore, not only the manufacture becomes unstable, but also required photographic properties cannot be obtained.

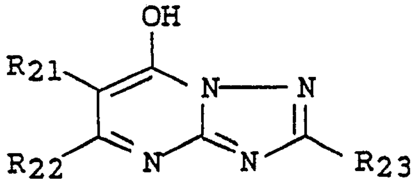
Especially when the pH in the sedimentation/washing process is less than 3.1, the grain size and shape largely change. When, however, the pH value is larger than that, the changes are small. Especially when a tetrazaindene compound is added in a pre-ripening stage, the changes are further decreased.

The pH in the desalting process is preferably 3.2 to 4.8, and more preferably, 3.4 to 4.8.

Gelatin used in preperation of the high silver chloride fine grain emulsion of the present invention may be any of, e.g., lime-treated gelatin, acid-treated gelatin, phthalated gelatin, or a combination thereof.

In order to remove soluble salts from an emulsion after grain formation or physical ripening (desalting process), it is preferred to perform a sedimentation method using an anionic surfactant, an anionic polymer (e.g., polystyrene sulfonic acid), or a gelatin derivative (e.g., acylated gelatin or carbamoylated gelatin), i.e., flocculation method.

A tetrazaindene compound used in the present invention is preferably a compound represented by general formula (II) below:



... (II)

wherein each of R_{21}, R_{22}, and R_{23} independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, an amino group or its derivative, a halogen atom, a substituted or unsubstituted aryl group, or -CONH-R_{24} wherein R_{24} represents a hydrogen atom, a substituted or unsubstituted alkyl group, an amino group or its derivative, a halogen atom, a substituted or unsubstituted aryl group.

R_{21} may form a ring together with R_{22}. In addition, any of R_{21} to R_{24} may be a multivalent group to form a bis or tris structure. A preferable example of an alkyl group of each of R_{21} to R_{24} is a lower alkyl group having 1 to 10, and preferably, 1 to 4 carbon atoms. One or more substituents may be present in this alkyl group. Examples of the substituent are a halogen atom, OH, SH, CN, NO_2, a sulfo group, a carboxyl group, an alkoxy group, an aryl group, and alkyl-, aryl-, or a heterocyclic-sulfonyl group. Examples of a derivative of an amino group of each of R_{21} to R_{24} are an acyl-substituted derivative and a derivative which is hydrolyzed into an amino group under alkaline conditions upon development. An aryl group of each of R_{21} to R_{24} has 6 to 20, and preferably, 6 to 10 carbon atoms, and is preferably a substituted or unsubstituted phenyl group. One or more substituents may be present in this aryl group. Typical examples of the substituent are an alkyl group, a halogen atom, NH_2, OH, CN, NO_2, and an alkoxy group.

Examples of a tetrazaindene compound preferred in the present invention will be listed in Table 11 to be presented later.

A color photographic light-sensitive material directly containing a high silver chloride fine grain emulsion is easily fogged. This tendency is significant especially when the light-sensitive material is stored for a long time period. As means for preventing the fog, a method in that a compound which forms a low-solubility salt together with silver ions is adsorbed on the surface of a high silver chloride fine grain is found to be effective. In order to achieve the effects of the present invention, a solubility product of a silver salt of an adsorbate must be lower than that of silver bromide. In this case, the solubility product must be smaller than a solubility product of silver bromide (pK_{sp}, the logarithm of its reciprocal = 12.3), on the basis of a value obtained in water at about 25°C. In particular, a compound which forms a slightly soluble silver salt having a solubility product closer to or less than that of silver iodide achieves preferable effects. An adsorbate may be added upon preparation of a coating solution or upon preparation of an emulsion.

A compound which forms a slightly soluble silver salt is preferably a compound having a sulfur atom which is bonded to a silver ion and adsorbed on the surface of a silver halide crystal. Examples of such a compound are mercaptotetrazoles, mercaptotriazoles, mercaptothiadiazoles, and benzthiazole-2-thions.

Of the above preferable compounds containing sulfur, a compound having a mercapto group is represented by the following general formula (III):

Z-SH (III)

wherein Z represents an aliphatic hydrocarbon group, an aromatic group, or a heterocyclic group which may have one or more substituents. The aliphatic hydrocarbon group may be saturated or unsaturated and may be straight-chain, branched, or cyclic. Examples of this group are an alkyl group, an alkenyl group, and an alkinyl group. The aromatic group may be a monocyclic ring or a condensed ring. The heterocyclic group is a 3- to 8-membered ring containing at least one of O, N, S, and Se and one or more carbon atoms. A substituent allowed in these groups is not particularly limited. Typical examples of the substituent are -COOH, $-SO_3H$, -OH, $-NH_2$, $-N(CH_3)_3$, a halogen atom, alkoxy, and CN-. A compound represented by formula (III) may be a salt of alkali metal such as Na^+ or K^+, or NH_4^+.

Of these groups, a 5-membered heterocyclic residue (preferably having 30 or less, and more preferably, 18 or less carbon atoms) containing one or more nitrogen atoms in a ring is preferred.

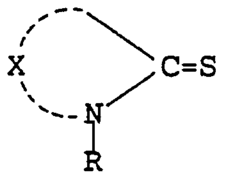
The heterocyclic residue represented by Z may be further condensed. Preferable examples of the group are imidazole, triazole, tetrazole, thiazole, oxazole, selenazole, benzimidazole, benzoxazole, benzthiazole, thiadiazole, oxadiazole, benzselenazole, pyrazole, pyrimidine, triazine, pyridine, naphthothiazole, naphthoimidazole, naphthoxazole, azabenzimidazole, purine, and azaindene (e.g., triazaindene, tetrazaindene, and pentazaindene).

These heterocyclic residues and condensed rings may be substituted with a proper substituent.

Examples of the substituents are an alkyl group (e.g., methyl, ethyl, hydroxyethyl, trifluoromethyl, sulfopropyl, dipropylaminoethyl, and adamantane), an alkenyl group (e.g., allyl), an aralkyl group (e.g., benzyl and p-chlorophenethyl), an aryl group (e.g., phenyl, naphthyl, p-carboxyphenyl, 3,5-dicarboxyphenyl, m-sulfophenyl, p-acetoamidophenyl, 3-capramidephenyl, p-sulfamoylphenyl, m-hydroxyphenyl, p-nitrophenyl, 3,5-dichlorophenyl, and 2-methoxyphenyl), a heterocyclic residue (e.g., pyridine), a halogen atom (fluorine, chlorine, bromine, and iodine), a mercapto group, a cyano group, a carboxyl group, a sulfo group, a hydroxyl group, a carbamoyl group, a sulfamoyl group, an amino group, a nitro group, an alkoxy group (e.g., methoxy and ethoxy), an aryloxy group (e.g., phenoxy), an acyl group (e.g., acetyl), an acylamino group (e.g., acetylamino, capramide, and methylsulfonylamino), a substituted amino group (e.g., diethylamino and hydroxyamino), an alkyl- or arylthio group (e.g., methylthio, carboxyethylthio, and sulfobutylthio), an alkoxycarbonyl group (e.g., methoxycarbonyl), and an aryloxycarbonyl group (e.g., phenoxycarbonyl).

In addition, a disulfide (Z-S-S-Z) which easily cleaves into formula (III) above in an emulsion may be used.

Of the compounds which form a slightly soluble silver salt, a compound having a thioketone group is represented by general formula (IV) below:



... (IV)

wherein R represents an alkyl group, an aralkyl group, an alkenyl group, or an aryl group. These groups may be substituted.

In the above general formula (IV), X represents an atom group required to form a 5- or 6-membered ring. This atom group may be condensed.

Examples of a heterocyclic ring formed by X are thiazoline, thiazolidine, selenazoline, oxazoline, oxazolidine, imidazoline, imidazolidine, thiadiazoline, oxadiazoline, triazoline, tetrazoline, and pyrimidine. Other examples are benzthiazoline, naphthothiazoline, tetrahydrobenzthiazoline, benzimidazoline, and benzoxazoline which are formed by condensing a carbon ring or heterocyclic ring to the above heterocyclic ring.

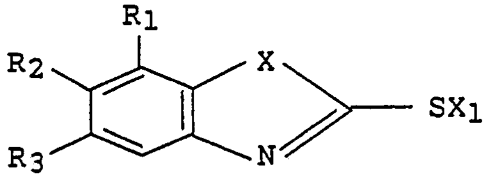
These heterocyclic rings may be substituted with the substituents enumerated above for a compound represented by general formula (III).

Examples of R are an alkyl group (e.g., methyl, propyl, sulfopropyl, and hydroxyethyl), an alkenyl group (e.g., allyl), an aralkyl group (e.g., benzyl), an aryl group (e.g., phenyl, p-tolyl, and o-chlorophenyl), and a heterocyclic group (e.g., pyridyl).

Typical examples of compounds represented by general formulas (III) and (IV) will be listed in Table 12 to be presented later.

These compounds can be prepared by referring to literatures cited in E.J. Birr, "Stabilization of Photographic Silver Halide Emulsions", Focal Press, 1974, C.G. Barlow et. al., Rer. Prog. Appl. Chem. Vol. 59, P. 159, (1974), Research Disclosure 17643 (1978), JP-B-48-34169, JP-B-47-18008, JP-B-49-23368, and Chemical Magazine 74 1365 to 1369 (1954), Beilstein XII, 394, IV, No. 121.

An adsorbate most preferred in the present invention is a compound represented by general formula (V):



... (V)

wherein X represents -O-, -NH-, or -S-, and each of R_1, R_2, R_3, and R_4 independently represents a hydrogen atom or a group substitutable with a hydrogen atom. At least one of R_1, R_2, R_3, and R_4 is bonded directly or via a divalent connecting group, and is a substituted or unsubstituted alkyl or aryl group having 13 or less carbon atoms. X_1 represents a hydrogen atom or a cation for neutralizing molecule.

General formula (V) will be described in detail below.

X is preferably -NH-.

Preferable examples of R_1, R_2, R_3, and R_4 are a hydrogen atom, a halogen atom (F, Cl, Br, and I), a substituted or unsubstituted alkyl group (e.g., methyl, trifluoromethyl, ethyl, n-octyl, and benzyl), a substituted or unsubstituted aryl group (e.g., phenyl and p-chlorophenyl), a substituted or unsubstituted alkoxy group, an aryloxy group (e.g., methoxy, n-hexyloxy, phenoxy, n-octyloxy, and 2-ethylhexyloxy), a sulfonyl group (e.g., methanesulfonyl and p-toluenesulfonyl), a sulfonamide group (e.g., n-octanesulfonamide and p-toluenesulfonamide), a sulfamoyl group (e.g., diethylsulfamoyl and 4-chlorophenylsulfamoyl), a carbamoyl group (e.g., n-butylcarbamoyl, 4-cyanophenylcarbamoyl, and 2-ethylhexylcarbamoyl), an amide group (e.g., n-hexaneamide, n-decaneamide, benzamide, and 2-ethylhexaylamino), an ureido group (e.g., 3-butylureido and morpholinocarbonylamino), an aryl- or alkoxycarbonylamino group (e.g., ethoxycarbonylamino, iso-butylcarbonylamino, and phenoxycarbonylamino), an aryl- or alkoxycarbonyl group (e.g., ethoxycarbonyl and phenoxycarbonyl), an aryl- or alkylaminocarbonyloxy group (e.g., phenylaminocarbonyloxy and iso-butylaminocarbonyloxy), a cyano group, and an alkyl- or arylthio group (e.g., n-octylthio and 2-methoxycarbonylphenylthio). The number of carbon atoms of these substitutable groups is preferably 13 or less, and more preferably 11 or less.

At least one of R_1, R_2, R_3, and R_4 is bonded directly or via a divalent connecting group, and a substituted or unsubstituted alkyl- or aryl group having 13 or less carbon atoms, and preferably, a substituted or unsubstituted alkyl group having 5 to 11 carbon atoms. Most preferable examples of the divalent connecting group are an amide bond, a sulfonamide bond, an ureido bond, an ether bond, a thioether bond, a sulfonyl bond, a carbonyl bond, an urethane bond, a carbamoyl bond, and a sulfamoyl bond.

Examples of the cation represented by X_1 for neutralizing a molecule are Na^+, K^+, and NH_4^+.

Although typical examples of a compound represented by general formula (V) for use in the present invention will be listed in Table 13 to be presented later, the present invention is not limited to those examples.

A compound represented by general formula (V) for use in the present invention can be synthesized by a method similar to those described in J. Van Allan., B.D. Deacon, Ore. Synth. IV, 569 (1963), J. Bunner Ber., 9, 465 (1876), L.B. Sebrell. C.E. Boord. Am. Chem. Soc., 45 2390 (1923), and JP-A-62-133448.

A compound represented by general formula (V) of the present invention can be used in an amount essentially falling within the range of 1×10^{-3} to 10 mol%, and preferably, 1×10^{-2} to 1 mol% per mol of a silver halide grain present in a non-light-sensitive silver halide emulsion. An addition amount is most preferably close to a saturated absorption amount with respect to the surface of a silver halide fine grain of the present invention. A compound may be directly dispersed in a hydrophilic colloid or dissolved in an organic solvent such as methanol or ethyleneglycol and then added.

A high silver chloride fine grain emulsion for use in the present invention can be contained in any layer included in a color photographic light-sensitive material such as a protective layer, a blue-sensitive layer, a yellow filter layer, a green-sensitive layer, an interlayer, a red-sensitive layer, and an antihalation layer. When silver halide emulsion layers essentially having the same color sensitivity are to be separated into two or more layers such as a high-speed layer and a low-speed layer, a high silver chloride fine grain emulsion can be contained in either only one or two or more of high-, low-, and medium-speed layers. In addition, a non-light-sensitive layer is sometimes inserted between light-sensitive layers having essentially the same color sensitivity (e.g., green-sensitive high-speed layer/non-light-sensitive interlayer/green-sensitive low-speed layer). This non-light-sensitive layer may preferably contain the fine grain emulsion. Generally, an interlayer between different light-sensitive layers preferably contains the fine grain emulsion used in the present invention. More preferably, a protective layer furthest from a support, an antihalation layer closest to the support, and a non-light-sensitive layer adjacent to either of the two layers contain the fine grain emulsion.

The high silver chloride fine grain emulsion used in the present invention is effective in not only a normal layer arrangement but also a layer arrangement such as blue-sensitive layer/green-sensitive high-speed layer/red-sensitive high-speed layer/green-sensitive low-speed layer/red-sensitive low-speed layer, blue-sensitive layer/red-sensitive high-speed layer/green-sensitive high-speed layer/green-sensitive low-speed layer/red-sensitive low-speed layer, blue-sensitive layer/green-sensitive high-speed layer/red-sensitive high-speed layer/red-sensitive low-speed layer/green-sensitive low-speed layer, or blue-sensitive high-speed layer/green-sensitive high-speed layer/red-sensitive high-speed layer/blue-sensitive low-speed layer/green-sensitive low-speed layer/red-sensitive low-speed layer.

Although effects of the present invention can be sufficiently achieved by adding the high silver chloride fine grain emulsion used in the present invention to only one layer, the emulsion can be added to two or more layers. In addition, a layer containing a fine grain emulsion having a high silver bromide content may be present together with the high silver chloride fine grain emulsion used in the present invention.

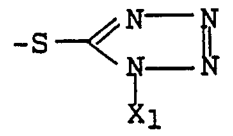
A coating silver amount of the high silver chloride fine grain emulsion used in the present invention is preferably 0.01 to 3 g/m^2, more preferably, 0.05 to 1.5 g/m^2, and most preferably, 0.1 to 0.8 g/m^2.

A compound represented by general formula (I) used in the present invention will be described below:

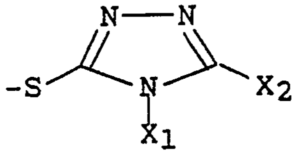
A-(TIME)$_n$-B (I)

wherein A represents a coupler residue for releasing (TIME)$_n$-B upon a coupling reaction with an oxide of an aromatic primary amine developing agent, TIME represents a timing group which is bonded to a coupling active position of A and releases B after it is released from A upon the coupling reaction, and B represents a group represented by general formula (Ia), (Ib), (Ic), (Id), (Ie), (If), (Ig), (Ih), (Ii), (Ij), (Ik), (Il), (Im), (In), (Io), or (Ip), and n represents an integer of 0 or 1. Note that when n is 0, B is directly bonded to A.

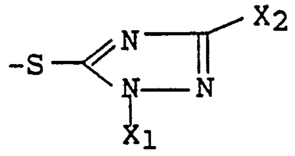
Formula (Ia)



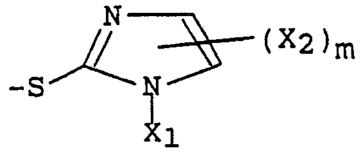
Formula (Ib)



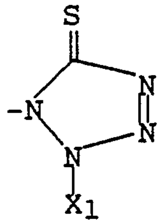
Formula (Ic)



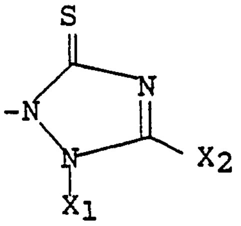
Formula (Id)



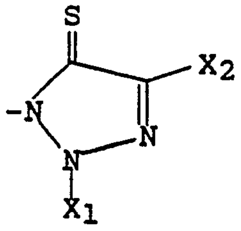
Formula (Ie)



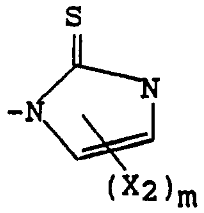
Formula (If)



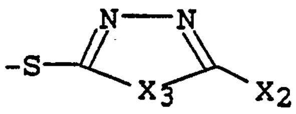
Formula (Ig)



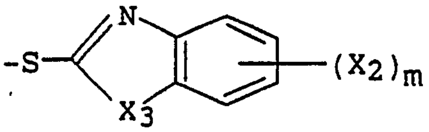
Formula (Ih)



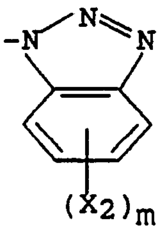
Formula (Ii)



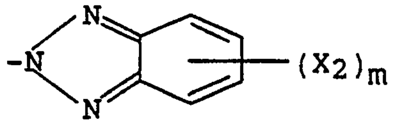
Formula (Ij)



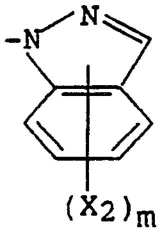
Formula (Ik)



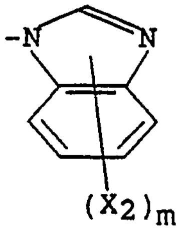
Formula (Iℓ)



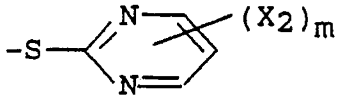
Formula (Im)



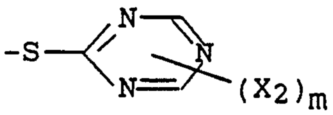
Formula (In)



Formula (Io)



Formula (Ip)



wherein X_1 represents a substituted or unsubstituted aliphatic hydrocarbon group having 1 to 4 carbon atoms wherein a substituent is, for example, selected from the group consisting of an alkoxy group, an alkoxycarbonyl group, a hydroxyl group, an acylamino group, an albamoyl group, a sulfonyl group, a sulfonamide group, sulfamoyl group, an amino group, an acyloxy group, a cyano group, an ureido group, an acyl group, a halogen atom, and an alkylthio group, and the number of carbon atoms constained in these substituents is 3 or less (to be referred to as an "aliphatic group" hereinafter), or a substituted phenyl group wherein a substituent is, for example, selected from the group consisting of a hydroxyl group, an alkoxycarbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamide group, a sulfamoyl group, an acyloxy group, an ureido group, a carboxyl group, a cyano group, a nitro group, an amino group, and an acyl group, and the number of carbon atoms contained in these substituents is 3 or less; X_2 represents a hydrogen atom, an aliphatic group, a halogen atom, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxycarbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamide group, a sulfamoyl group, an acyloxy group, an ureido group, a cyano group, a nitro group, an amino group, an alkoxycarbonylamino group, an aryloxycarbonyl group, or an acyl group; X_3 represents an oxygen atom, a sulfur atom, or an imino group having 4 or less carbon atoms; and m represents an integer of 1 or 2. Note that a total number of carbon atoms contained in m X_2s is 8 or less. When m is 2, two X_2s may be the same or different.

A compound represented by general formula (I) will be described in detail below.

A coupler residue represented by A in general formula (I) includes a coupler residue which forms a dye (e.g., yellow, magenta, or cyan) by a coupling reaction with an oxide of an aromatic primary amine developing agent and a coupling residue for forming a coupling reaction product essentially not causing absorption of light in a visible light range.

Examples of a yellow-image forming coupler residue represented by A are coupler residues of a pivaloylacetanilide type, a benzoylacetanilide type, a malondiester type, a malondiamide type, a dibenzoylmethane type, a benzothiazolylacetoamide type, a malonestermonoamide type, a benzothiazolylacetate type, a benzoxazolylacetoamide type, a benzoxazolylacetate type, a malondiester type, a benzimidazolylacetoamide type and a benzimidazolylacetate type; a coupler residue derived from heterocyclic ring-substituted acetoamide or heterocyclic ring-substituted acetate described in U.S. Patent 3,841,880; a coupler residue derived from an acylacetamide described in U.S. Patent 3,770,446, British Patent 1,459,171, West German Patent (OLS) 2,503,099, JP-A-50-139738, or Research Disclosure No. 15737; and a heterocyclic coupler residue described in U.S. Patent 4,046,574.

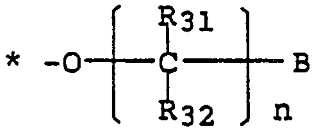
A preferable example of a magenta-image forming coupler residue represented by A is a coupler residue having a 5-oxo-2-pyrazoline nucleus, a pyrazolo-[1,5-a]benzimidazole nucleus, a pyrazoloimidazole nucleus, a pyrazolotriazole nucleus (pyrazolo[1,5-b][1,2,4]triazole nucleus or pyrazolo[5,1-c][1,2,4]triazole nucleus), pyrazolotetrazole nucleus, or a cyanoacetophenone type coupler residue.

A preferable example of a cyan-image forming coupler residue represented by A is a coupler residue having a phenol nucleus or an α-naphthol nucleus.

Even when a coupler does not essentially form a dye after it is coupled with an oxide of a developing agent and releases a development inhibitor, an effect as a DIR coupler remains unchanged. Examples of a coupler residue of this type represented by A are coupler residues described in U.S. Patents 4,052,213, 4,088,491, 3,632,345, 3,958,993, and 3,961,959.

Preferable examples of TIME in formula (I) are as follows.

(1) A group which utilizes a cleavage reaction of hemiacetal. Examples of this group are described in U.S. Patent 4,146,396, Japanese Patent Application Nos. 59-106223, 59-106224, and 59-75475 and represented by the following formula:

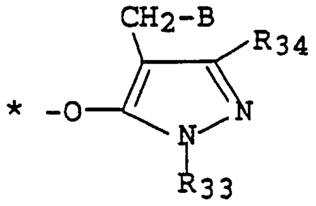


$$* -O\left(\begin{array}{c} R_{31} \\ | \\ C \\ | \\ R_{32} \end{array}\right)_n B$$

wherein symbol * represents a position bonded to a coupling position of A, each of R_{31} and R_{32} independently represents a hydrogen atom or substituent, and n represents 1 or 2. When n is 2, R_{31} and R_{32} may be the same or different. In addition, two arbitrary R_{31} and R_{32} may be coupled to form a cyclic structure. B represents a group defined by general formula (I).

(2) A group which utilizes an intramolecular nucleophilic substitution reaction to cause a cleavage reaction. An example of this group is a timing group described in U.S. Patent 4,248,962.

(3) A group which utilizes an electron transfer reaction along a conjugated unsaturated system to cause a cleavage reaction. Examples of this group are a group described in U.S. Patent 4,409,323 and a group represented by the following general formula (described in British Patent 2,096,783A):



wherein symbol * represents a position bonded to a coupling position of A, each of R_{33} and R_{34} independently represents a hydrogen atom or a substituent, and B represents a group defined by general formula (I). Examples of R_{33} are an alkyl group having 1 to 24 carbon atoms (e.g., methyl, ethyl, benzyl, and dodecyl), and an aryl group having 6 to 24 carbon atoms (e.g., phenyl, 4-tetradecyloxyphenyl, 4-methoxyphenyl, 2,4,6-trichlorophenyl, 4-nitrophenyl, 4-chlorophenyl, 2,5-dichlorophenyl, 4-carboxyphenyl, and p-tolyl). Examples of R_{34} are a hydrogen atom, an alkyl group having 1 to 24 carbon atoms (e.g., methyl, ethyl, undecyl, and pentadecyl), an aryl group having 6 to 36 carbon atoms (e.g., phenyl and 4-methoxyphenyl), a cyano group, an alkoxy group having 1 to 24 carbon atoms (e.g., methoxy, ethoxy, and dodecyloxy), an amino group having 0 to 36 carbon atoms (e.g., amino, dimethylamino, piperidino, dihexylamino, and anilino), a carboxylic acid amide group having 1 to 24 carbon atoms (e.g., acetamide, benzamide, and tetradecanamide), a sulfonamide group having 1 to 24 carbon atoms (e.g., methylsulfonamide and phenylsulfonamide), a carboxyl group, an alkoxycarbonyl group having 2 to 24 carbon atoms (e.g., methoxycarbonyl, ethoxycarbonyl, and dodecyloxycarbonyl), and a carbamoyl group having 1 to 24 carbon atoms (e.g., carbamoyl, dimethylcarbamoyl, and pyrrolidinocarbonyl).

Examples of substituents X_1, X_2, and X_3 in groups represented by general formulas (Ia) to (Ip) will be described below.

Examples of X_1 are methyl, ethyl, propyl, butyl, methoxyethyl, ethoxyethyl, isobutyl, allyl, dimethylaminoethyl, propargyl, chloroethyl, methoxycarbonylmethyl, methylthioethyl, 4-hydroxyphenyl, 3-hydroxyphenyl, 4-sulfamoylphenyl, 3-sulfamoylphenyl, 4-carbamoylphenyl, 3-carbamoylphenyl, 4-dimethylaminophenyl, 3-acetamidophenyl, 4-propaneamidophenyl, 4-methoxyphenyl, 2-hydroxyphenyl, 2,5-dihydroxyphenyl, 3-methoxycarbonylaminophenyl, 3-(3-methylureido)phenyl, 3-(3-ethylureido)phenyl, 4-hydroxyethoxyphenyl, and 3-acetamido-4-methoxyphenyl. Examples of X_2 are a hydrogen atom, methyl, ethyl, benzyl, n-propyl, i-propyl, n-butyl, i-butyl, cyclohexyl, a fluorine atom, a chlorine atom, a bromine atom, an iodine atom, hydroxymethyl, hydroxyethyl, hydroxyl, methoxy, ethoxy, butoxy, allyloxy, benzyloxy, methylthio, ethylthio, methoxycarbonyl, ethoxycarbonyl, acetamide, propaneamide, butaneamide, octaneamide, benzamide, dimethylcarbamoyl, methylsulfonyl, methylsulfonamide, phenylsulfonamide, dimethylsulfamoyl, acetoxy, ureido, 3-methylureido, cyano, nitro, amino, dimethylamino, methoxycarbonylamino, ethoxycarbonylamino, phenoxycarbonyl, methoxyethyl, and acetyl. Examples of X_3 are an oxygen atom, a sulfur atom, imino, methylimino, ethylimino, propylimino, and allylimino.

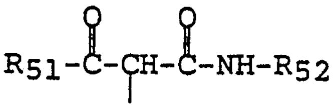
Of groups represented by formulas (Ia) to (Ip), a group represented by formula (Ia), (Ib), (Ii), (Ij), (Ik), or (Il) is preferred, and a group represented by formula (Ia), (Ii), (Ij), or (Ik) is most preferred.

Examples of a group represented by B in general formula (I) will be listed in Table 14 to be presented later.

A DIR coupler represented by general formula (I) (to be referred to as a "coupler of the present invention" hereinafter) is mixed in a so-called main coupler which forms a color image without releasing an inhibiting group. A mixing ratio of the coupler of the present invention with respect to the main coupler is 0.1 mol% to 100 mol%, and preferably, 1 mol% to 50 mol%. An addition amount of the coupler of the present invention is 0.01 mol% to 20 mol%, and preferably, 0.5 mol% to 10 mol% with respect to a silver halide present in the same or adjacent layer.

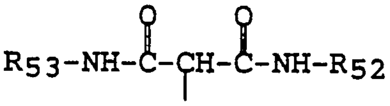
The present invention can achieve its effects especially when A in general formula (I) is a coupler residue represented by the following general formula (Cp-1), (Cp-2), (Cp-3), (Cp-4), (Cp-5), (Cp-6), (Cp-7), (Cp-8), (Cp-9), (Cp-10), or (Cp-11). These couplers are preferable because their coupling rates are high:

Formula (Cp-1)



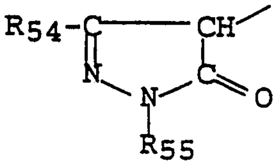
$$R_{51}-\overset{\overset{O}{\|}}{C}-\underset{|}{C}H-\overset{\overset{O}{\|}}{C}-NH-R_{52}$$

Formula (Cp-2)

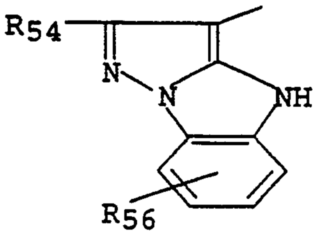


$$R_{53}-NH-\overset{\overset{O}{\|}}{C}-\underset{|}{C}H-\overset{\overset{O}{\|}}{C}-NH-R_{52}$$

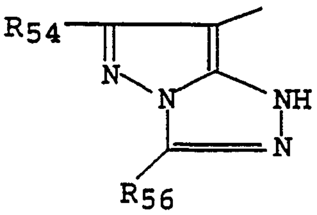
Formula (Cp-3)



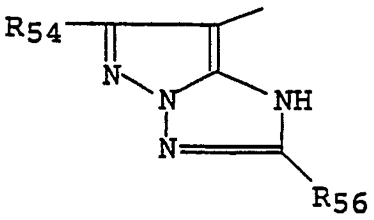
Formula (Cp-4)



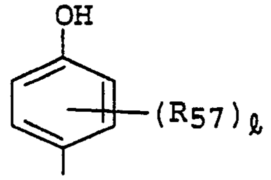
Formula (Cp-5)



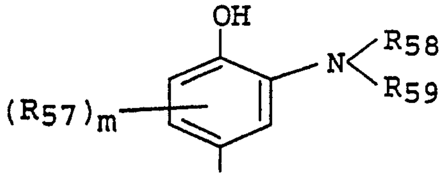
Formula (Cp-6)



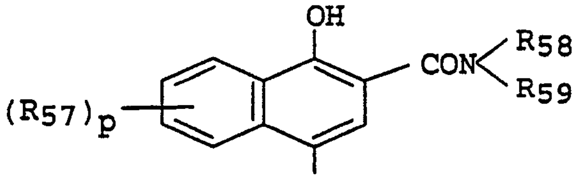
Formula (Cp-7)



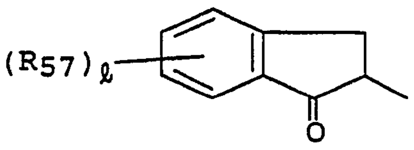
Formula (Cp-8)



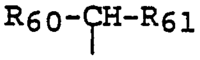
Formula (Cp-9)



Formula (Cp-10)



Formula (Cp-11)



$$R_{60}\text{-}\underset{|}{C}H\text{-}R_{61}$$

In the above formulas, a nonbonded branch extending from a coupling position represents a bonding position of a coupling split-off group. In the above formulas, when R_{51}, R_{52}, R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{59}, R_{60}, or R_{61} contain an anti-diffusion group, a total number of carbon atoms is 8 to 32, and preferably, 10 to 22. Otherwise, the total number of carbon atoms is preferably 15 or less.

R_{51} to R_{61}, ℓ, m, and p in general formulas (Cp-1) to (Cp-11) will be described below.

R_{51} represents an aliphatic group, an aromatic group, an alkoxy group, or a heterocyclic group. Each of R_{52} and R_{53} independently represents an aromatic group or a heterocyclic group.

An aliphatic group represented by R_{51} preferably has 1 to 22 carbon atoms, and may be substituted or unsubstituted and a chain or a ring. Preferable examples of a substituent for an alkyl group are an alkoxy group, an aryloxy group, an amino group, an acylamino group, and a halogen atom. These groups may also have substituents. Examples of an aliphatic group effective as R_{51} are isopropyl, isobutyl, tert-butyl, isoamyl, tert-amyl, 1,1-dimethylbutyl, 1,1-dimethylhexyl, 1,1-diethylhexyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, 2-methoxyisopropyl, 2-phenoxyisopropyl, 2-p-tert-butylphenoxyisopropyl, α-aminoisopropyl, α-(diethylamino)isopropyl, α-(succinimido)isopropyl, α -(phthalimido)isopropyl, and α-(benzenesulfonamido)-isopropyl.

When R_{51}, R_{52}, or R_{53} represents an aromatic group, especially a phenyl group, this aromatic group may be substituted. The aromatic group such as a phenyl group may be substituted with, e.g., an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, alkoxycarbonylamino group, an aliphatic amide group, an alkylsulfamoyl group, an alkylsulfonamide group, an alkylureido group, or an alkyl-substituted succinimide group. These substituents have 32 or less carbon atoms. In this case, an aromatic group such as phenylene may be present in a chain of the alkyl group. The phenyl group may be substituted with, e.g., an aryloxy group, an aryloxycarbonyl group, an arylcarbamoyl group, an arylamide group, an arylsufamoyl group, an arylsulfonamide group, or an arylureido group. An aryl group of these substituents may be further substituted with one or more alkyl groups each having 1 to 22 carbon atoms.

A phenyl group represented by R_{51}, R_{52}, or R_{53} is further substituted with an amino group including an amino group substituted with a lower alkyl group having 1 to 6 carbon atoms, a hydroxyl group, a carboxy group, a sulfo group, a nitro group, a cyano group, a thiocyano group, or a halogen atom.

In addition, R_{51}, R_{52}, or R_{53} may represent a substituent obtained by condensation of a phenyl group and another ring, such as a naphthyl group, a quinolyl group, an isoquinolyl group, a chromanyl group, a coumaranyl group, or a tetrahydronaphtyl group. These substituents may also have another substituents.

When R_{51} represents an alkoxy group, an alkyl portion of the alkoxy group represents a straight-or branched-chain alkyl group having 1 to 32, and preferably, 1 to 22 carbon atoms, or a cyclic alkyl group. The alkyl portion may includes a straight-chain or branched alkenyl group having 1 to 32, and preferably, 1 to 22 carbon atoms, or a cyclic alkenyl group. These groups may be substituted with a halogen atom, an aryl group, or an alkoxy group.

When R_{51}, R_{52}, or R_{53} represents a heterocyclic group, this heterocyclic group is bonded to a carbon atom of a carbonyl group of an acyl group or a nitrogen atom of an amide group in α-acylacetamide via one of carbon atoms forming a heterocyclic ring. Examples of such a heterocyclic ring are thiophene, furan, pyran, pyrrole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, imidazole, thiazole, oxazole, triazine, thiadiazine, and oxazine. These rings may have substituents thereon.

In general formula (Cp-3), R_{55} represents a straight- or branched-chain alkyl group having 1 to 32, and preferably, 1 to 22 carbon atoms (e.g., methyl, isopropyl, tert-butyl, hexyl, and dodecyl), an alkenyl group (e.g., allyl), a cyclic alkyl group (e.g., cyclopentyl, cyclohexyl, and norbornyl), an aralkyl group (e.g., benzyl and β-phenylethyl), or a cyclic alkenyl group (e.g., cyclopentenyl and cyclohexenyl). These groups may be substituted with a halogen atom, a nitro group, a cyano group, an aryl group, an alkoxy group, an aryloxy group, a carboxyl group, an alkylthiocarbonyl group, an arylthiocarbonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a sulfo group, a sulfamoyl group, a carbamoyl group, an acylamino group, a diacylamino group, an ureido group, an urethane group, a thiourethane group, a sulfonamide group, a heterocyclic group, an arylsulfonyl group, an alkylsulfonyl group, an arylthio group, an alkylthio group, an alkylamino group, a dialkylamino group, an anilino group, an N-arylanilino group, an N-alkylanilino group, an N-acylanilino group, a hydroxyl group, or a mercapto group.

R_{55} may also represent an aryl group (e.g., phenyl and α- or β-naphtyl). This aryl group may have one or more substituents. Examples of the substituent are alkyl, alkenyl, cyclic alkyl, aralkyl, cyclic alkenyl, a halogen atom, nitro, cyano, aryl, alkoxy, aryloxy, carboxyl, alkoxycarbonyl, aryloxycarbonyl, sulfo, sulfamoyl, carbamoyl, acylamino, diacylamino, ureido, urethane, sulfonamide, a heterocyclic ring, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylamino, dialkylamino, anilino, N-alkylanilino, N-arylanilino, N-acylanilino, and hydroxyl.

R_{55} may also represent a heterocyclic group (e.g., a 5- or 6-membered heterocyclic or condensed heterocyclic group containing a nitrogen atom, an oxygen atom, or a sulfur atom as a hetero-atom, such as pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, and naphthoxazolyl), a heterocyclic group substituted by a substituent enumerated above for the aryl group, an aliphatic or aromatic acyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkylcarbamoyl group, an arylcarbamoyl group, an alkylthiocarbamoyl group, or an arylthiocarbamoyl group.

R_{54} represents a hydrogen atom, straight- or branched-chain alkyl, straight- or branched-chain alkenyl, cyclic alkyl, aralkyl, and cyclic alkenyl groups (these groups may have the substituents enumerated above for R_{55}), an aryl group and a heterocyclic group (these groups may have the substituents enumerated above for R_{55}), an alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl, and stearyloxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl and naphthoxycarbonyl), an aralkyloxycarbonyl group (e.g., benzyloxycarbonyl), an alkoxy group (e.g., methoxy, ethoxy, and heptadecyloxy), aryloxy (e.g., phenoxy and tolyloxy), an alkylthio group (e.g., ethylthio and didecylthio), an arylthio group (e.g., phenylthio and α-naphthylthio), a carboxyl group, an acylamino group (e.g., acetylamino, 3-[(2,4-di-tert-amylphenoxy)-acetamide]benzamide), a diacylamino group, an N-alkylacylamino group (e.g., N-methylpropionamide), an N-arylacylamino group (e.g., N-phenylacetamide), an ureido group (e.g., ureido, N-arylureido, and N-alkylureido), an urethane group, a thiourethane group, an arylamino group (e.g., phenylamino, N-methylanilino, diphenylamino, N-acetylanilino, and 2-chloro-5-tetradecaneamideanilino), an alkylamino group (e.g., n-butylamino, methylamino, and cyclohexylamino), a cycloamino group (e.g., piperidino and pyrrolidino), a heterocyclic amino group (e.g., 4-pyridylamino and 2-benzoxazolylamino), an alkylcarbonyl group (e.g., methylcarbonyl), an arylcarbonyl group (e.g., phenylcarobonyl), a sulfonamide group (e.g., alkylsulfonamide and arylsulfonamide), a carbamoyl group (e.g., ethylcarbamoyl, dimethylcarbamoyl, N-methyl-phenylcarbamoyl, and N-phenylcarbamoyl), a sulfamoyl group (e.g., N-alkylsulfamoyl, N,N-dialkylsulfamoyl, N-arylsulfamoyl, N-alkyl-N-arylsulfamoyl, and N,N-diarylsulfamoyl), a cyano group, a hydroxyl group, or a sulfo group.

R_{56} represents a hydrogen atom, a straight- or branched-chain alkyl group having 1 to 32, and preferably, 1 to 22 carbon atoms, a alkenyl group, a cyclic alkyl group, an aralkyl group, or a cyclic alkenyl group. These groups may have the substituents enumerated above for R_{55}.

R_{56} may represent an aryl group or a heterocyclic group. These groups may have the substituents enumerated above for R_{55}.

R_{56} may also represent a cyano group, an alkoxy group, an aryloxy group, a halogen atom, a carboxyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, a sulfo group, a sulfamoyl group, a carbamoyl group, an acylamino group, a diacylamino group, an ureido group, an urethane group, a sulfonamide group, an arylsulfonyl group, an alkylsulfonyl group, an arylthio group, an alkylthio group, an alkylamino group, a dialkylamino group, an anilino group, an N-arylanilino group, an N-alkylanilino group, an N-acylanilino group, or a hydroxyl group.

Each of R_{57}, R_{58}, and R_{59} independently represents a group used in an ordinary 4-equivalent phenol or α-naphthol coupler. Examples of R_{57} are a hydrogen atom, a halogen atom, an alkoxycarbonylamino group, an aliphatic hydrocarbon residue, an N-arylureido group, an acylamino group, and -O-R_{62} or -S-R_{62} - (wherein R_{62} represents an aliphatic hydrocarbon residue). When two or more R_{57}s are present in the same molecule, the two or more R_{57}s may be the same or different groups. The aliphatic hydrocarbon residue includes a group having a substituent.

When these substituents contain an aryl group, the aryl group may have the substituents enumerated above for R_{55}.

Each of R_{58} and R_{59} may be independently selected from the group consisting of an aliphatic hydrocarbon residue, an aryl group, and a heterocyclic residue. Otherwise one of R_{58} and R_{59} may be a hydrogen atom. These groups include a group having substituents. In addition, R_{58} may form a nitrogen-containing heterocyclic nucleus together with R_{59}.

The aliphatic hydrocarbon residue may be saturated or unsaturated, and may be straight- or branched-chain or cyclic. Preferable examples of the aliphatic hydrocarbon residue are an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, t-butyl, isobutyl, dodecyl, octadecyl, cyclobutyl, and cyclohexyl), and an alkenyl group (e.g., allyl and octenyl). Examples of the aryl group are phenyl and naphthyl. Typical examples of the heterocyclic residue are pyridinyl, quinolyl, thienyl, piperidyl, and imidazolyl. Examples of a substituent to be introduced to the aliphatic hydrocarbon residue, the aryl group, and the heterocyclic residue are a halogen atom and groups of nitro, hydroxyl, carboxyl, amino, substituted amino, sulfo, alkyl, alkenyl, aryl, a heterocyclic ring, alkoxy, aryloxy, arylthio, arylazo, acylamino, carbamoyl, ester, acyl, acyloxy, sulfonamide, sulfamoyl, sulfonyl, and morpholino.

$\underline{\ell}$ represents an integer from 1 to 4, $\underline{m}$ represents an integer from 1 to 3, and $\underline{p}$ represents an integer from 1 to 5.

R_{60} represents an arylcarbonyl group, an alkanoyl group having 2 to 32, and preferably, 2 to 22 carbon atoms, an arylcarbamoyl group, an alkanecarbamoyl group having 2 to 32, and preferably, 2 to 22 carbon atoms, an alkoxycarbonyl group having 1 to 32, and preferably, 1 to 22 carbon atoms, or an aryloxycarbonyl group. These groups may have substituents. Examples of the substituent are an alkoxy group, an alkoxycarbonyl group, an acylamino group, an alkylsulfamoyl group, an alkylsulfonamide group, an alkylsuccinimide group, a halogen atom, a nitro group, a carboxyl group, a nitrile group, an alkyl group, and an aryl group.

R_{61} represents an arylcarbonyl group, an alkanoyl group having 2 to 32, and preferably, 2 to 22 carbon atoms, an arylcarbamoyl group, an alkanecarbamoyl group having 2 to 32, and preferably, 2 to 22 carbon atoms, an alkoxycarbonyl or aryloxycarbonyl group having 1 to 32, and preferably, 1 to 22 carbon atoms, an alkylsulfonyl group having 1 to 32, and preferably, 1 to 22 carbon atoms, an arylsulfonyl group, an aryl group, or a 5- or 6-membered heterocyclic group (a hetero-atom is selected from a nitrogen atom, an oxygen atom, and a sulfur atom, and the group is e.g., a triazolyl group, an imidazolyl group, a phthalimide group, a succinimide group, a furyl group, a pyridyl group, and a benzotriazolyl group). These groups may have substituents enumerated above for R_{60}.

Of the above coupler residues, as a yellow coupler residue, it is preferred that R_{51} represents a t-butyl group or a substituted or unsubstituted aryl group and R_{52} represents a substituted or unsubstituted aryl group in general formula (Cp-1) or R_{52} and R_{53} represent a substituted or unsubstituted aryl group in general formula (Cp-2).

As a magenta coupler residue, it is preferred that R_{54} represents an acylamino group, an ureido group, or an arylamino group and R_{55} represents a substituted aryl group in general formula (Cp-3), R_{54} represents an acylamino group, an ureido group, or an arylamino group and R_{56} represents a hydrogen atom in general formula (Cp-4), or R_{54} and R_{56} represent a straight- or branched-chain alkyl group, an alkenyl group, a cyclic alkyl group, an aralkyl group, or a cyclic alkenyl group in general formulas (Cp-5) and (Cp-6).

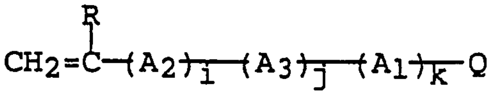
As a cyan coupler residue, it is preferred that R_{57} represents an acylamino or ureido group at 2-site, an acylamino or alkyl group at 5-site, a hydrogen atom or chlorine atom at 6-site in general formula (Cp-7), or R_{57} represents a hydrogen atom, an acylamino group, a sulfonamide group, or an alkoxycarbonyl group at 5-site, R_{58} represents a hydrogen atom, and R_{59} represents a phenyl group, an alkyl group, an alkenyl group, a cyclic alkyl group, an aralkyl group, or a cyclic alkenyl group in general formula (Cp-9).

As a colorless compound forming coupler, it is preferred that R_{57} represents an acylamino group, a sulfonamide group, or a sulfamoyl group in general formula (Cp-10) or R_{60} and R_{61} represent an alkoxycarbonyl group in general formula (Cp-11).

In addition, any of R_{51} to R_{61} may form a polymer having, e.g., a bis structure or may be a polymer obtained from a monomer having an ethylenically unsaturated group at any site of the monomer or a copolymer thereof with a non-coloring monomer.

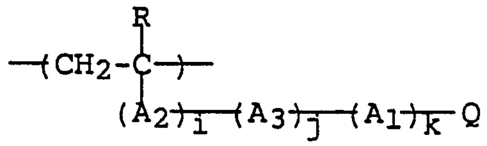
When an above described coupler residue represents a polymer, it is a polymer derived from a monomeric coupler represented by general formula (Cp-12) and having a repeating unit represented by general formula (Cp-13), or a copolymer with at least one type of non-coloring monomer containing at least one ethylene group which cannot be coupled to an oxide of an aromatic primary amine developing agent. In this case, two or more types of monomeric coupler may be simultaneously polymerized:

Formula (Cp-12)



$$CH_2{=}\overset{\displaystyle R}{\overset{|}{C}}-(A_2)_I-(A_3)_J-(A_1)_K-Q$$

Formula (Cp-13)



$$-\!\!\left(CH_2-\overset{\displaystyle R}{\overset{|}{\underset{\displaystyle (A_2)_I-(A_3)_J-(A_1)_K-Q}{C}}}\right)\!\!-$$

wherein R represents a hydrogen atom, a lower alkyl group having 1 to 4 carbon atoms, or a chlorine atom, A_1 represents -CONR′-, -NR′CONR′-, -NR′COO-, -COO-, $-SO_2-$, -CO-, -NRCO-, $-SO_2NR'-$, $-NR'SO_2-$, -OCO-, -OCONR′-, -NR′-, or -O-, A_2 represents -CONR′- or -COO-, and R′ represents a hydrogen atom, an aliphatic group, or an aryl group. If two or more Rs are present in one molecule, they may be the same or different. A_3 represents a substituted or unsubstituted alkylene group having 1 to 10 carbon atoms, an aralkylene group, or a substituted or unsubstituted arylene group. An alkylene group may be a straight- or branched-chain group. Examples of an alkylene group as A_3 are methylene, methylmethylene, dimethylmethylene, dimethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, and decylmethylene. An example of an aralkylene group as A_3 is benzilidene. Examples of an arylene group as A_3 are phenylene and naphthylene.

Q represents a group to be bonded to general formula (Cp-12) or (Cp-13) at any position of R_{51} to R_{61} in formulas (Cp-1) to (Cp-11).

Each of i, j, and k independently represents 0 or 1, but they do not simultaneously represent 0.

Examples of a substituent of an alkylene group, an aralkyl group, or an arylene group represented by

A_3 are an aryl group (e.g., phenyl), a nitro group, a hydroxyl group, a cyano group, a sulfo group, an alkoxy group (e.g., methoxy), an aryloxy group (e.g., phenoxy), an acyloxy group (e.g., acetoxy), an acylamino group (e.g., acetylamino), a sulfonamide group (e.g., methanesulfonamide), a sulfamoyl group (e.g., methylsulfamoyl), a halogen atom (e.g., fluorine, chlorine, and bromine), a carboxyl group, a carbamoyl group (e.g., methylcarbamoyl), an alkoxycarbonyl group (e.g., methoxycarbonyl), and a sulfonyl group (e.g., methylsulfonyl). If two or more substituents are present, they may be the same or different.

Examples of a non-coloring ethylenical monomer which cannot be coupled to an oxide of an aromatic primary amine developing agent are acrylic acid, α-chloroacrylic acid, α-alkylacrylic acid, an ester or amide derived from these acrylic acids, methylenebisacrylamide, vinylester, acrylonitrile, an aromatic vinyl compound, a maleic acid derivative, and vinylpyridines. Two or more types of these non-coloring ethylenically unsaturated monomers can be simultaneously used.

When the coupler of the present invention is used in combination with a technique of thinning a photographic layer, especially sharpness is preferably improved. Examples of the layer-thinning technique are decreasing a silver amount by using a 2-equivalent coupler, decreasing a coating amount of a coupler by using a bis type coupler or a polymer coupler to enhance color formation from couplers per unit weight, and decreasing an addition amount of a coupler by using a coupler which can efficiently form an image forming dye with less side reaction upon the coupler coloring reaction (2-equivalent magenta coupler). These techniques are all known to those skilled in the art as a method of decreasing the film thickness of an emulsion layer in order to improve sharpness. When the coupler of the present invention was used, especially, in combination with the above techniques, obtained sharpness significantly differed from that obtained by using a known DIR coupler. The above-enumerated couplers effective to thin a layer are used in a layer containing the coupler of the present invention or layers at levels upper (farther from a support) than that layer. Most preferably, in a color photographic light-sensitive material containing at least one type of 2-equivalent yellow coupler in a blue-sensitive emulsion layer and at least one type of 2-equivalent magenta coupler or polymer magenta coupler (2-equivalent or 4-equivalent) in a green-sensitive emulsion layer, the coupler of the present invention is contained in at least one of the green-sensitive emulsion layer and a red-sensitive emulsion layer. In this case, the coupler of the present invention may or may not be contained in the blue-sensitive emulsion layer.

Examples of the coupler of the present invention will be listed in Table 15 to be presented later. The couplers, however, are not limited to those in Table 15.

These compounds can be synthesized by methods described in, e.g., U.S. Patents 4,174,966, 4,183,752, 4,421,845, and 4,477,563, JP-A-54-145135, JP-A-57-151944, JP-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-58-209749.

These compounds are preferably added in a light-sensitive silver halide emulsion layer or a layer adjacent to that layer in a light-sensitive material. An addition amount of the compounds is 1×10^{-6} to 1×10^{-3} mol/m^2, and preferably, 3×10^{-6} to 5×10^{-4} mol/m^2.

A compound represented by general formula (I) of the present invention can be added in the same manner as a conventional coupler as will be described later.

In the color photographic light-sensitive material of the present invention, at least one of silver halide emulsion layers of blue-, green-, and red-sensitive layers need only be formed on a support. The number and order of the silver halide emulsion layer and non-light-sensitive layers are not particularly limited. A typical example is a silver halide photographic light-sensitive material having at least one light-sensitive layer unit consisting of a plurality of silver halide emulsion layers having essentially the same color sensitivity and different speeds. This light-sensitive layer is a unit light-sensitive layer having a color sensitivity to blue, green, or red light. In a multi-layered silver halide color photographic light-sensitive material having unit light-sensitive layers consisting of a plurality of emulsion layers, the unit light-sensitive layers are generally arranged in an order of red-, green-, and blue-sensitive layers from a support. This arrangement order, however, may be reversed or modified such that a light-sensitive layer is inserted between layers having the same color sensitivity in accordance with an application, as described above.

Various non-light-sensitive layers such as interlayers may be formed between the above silver halide light-sensitive layers, the uppermost layer, and the lowermost layer.

The interlayers may contain, e.g., couplers or DIR compounds as described in, e.g., JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037, and JP-A-61-20038. The interlayers may also contain a color mixing inhibitor as in normal use.

A plurality of silver halide emulsion layers constituting each unit light-sensitive layer preferably have a two-layered structure having high- and low-speed emulsion layers as described in West German Patent 1,121,470 or British Patent 923,045. Generally, layers are preferably arranged from those having higher sensitivities toward a support, and a non-light-sensitive layer may be formed between the silver halide emulsion layers. In addition, as described in, e.g., JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, low-speed emulsion layers may be arranged farther from a support while high-speed emulsion layers are arranged closer to the support.

More specifically, the layers can be arranged from a farthest position from a support in the order of low-speed blue-sensitive layer (BL)/high-speed blue-sensitive layer (BH)/high-speed green-sensitive layer (GH)-/low-speed green-sensitive layer (GL)/high-speed red-sensitive layer (RH)/low-speed red-sensitive layer (RL), BH/BL/GL/GH/RH/RL, or BH/BL/GH/GL/RL/RH.

As described in JP-B-55-34932, the layers can also be arranged in the order of blue-sensitive layer/GH/RH/GL/RL from a farthest position from a support. Alternatively, as described in JP-A-56-25738 and JP-A-62-63936, the layers can be arranged in the order of blue-sensitive layer/GL/RL/GH/RH from a farthest position from a support.

In addition, as described in JP-B-49-15495, a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having a sensitivity lower than that of the upper layer is arranged as an intermediate layer, and a silver halide emulsion layer having a sensitivity lower than that of the intermediate layer is arranged as a lower layer, thereby forming a structure in which three layers having different sensitivities are arranged such that a sensitivity is decreased toward a support. When three layers having different sensitivities are formed in this manner, medium-, high-, and low-speed emulsion layers may be arranged in one color-sensitive layer in the order named from a farthest position from a support, as described in JP-A-59-202464.

As described above, various layer arrangements and orders can be selected in accordance with an application of the light-sensitive material.

Effects of the present invention are significant when high silver chloride fine grains for use in the present invention are used in combination with a light-sensitive material containing an emulsion layer having a high silver iodide content (to be referred to as "high iodide layer" hereinafter). More specifically, the high silver chloride fine grains are preferably combined with a light-sensitive material including at least one emulsion layer containing 8 to 30 mol%, preferably, 10 to 25 mol%, and more preferably, 12 to 20 mol% of silver iodide. More preferably, these high iodide layers have a structure partially having a high iodide layer in a silver halide grain. A silver halide grain preferably has a 15- to 42-mol% of layer as a high iodide layer in the grain. The presence of these layers can be easily detected by analyzing means such as an X-ray diffraction method. More preferably, a silver halide grain contains 2 to 10 mol% of silver iodide at a portion close to the grain surface. The silver iodide content at a portion close to the surface can be easily detected by a surface analyzing method according to ESCA.

The silver halide photographic emulsion for use in the present invention can be prepared by using methods described in, for example, Research Disclosure (RD), No. 17643 (1978, December), PP. 22 and 23, "I. Emulsion Preparation and Types", and RD No. 18716 (1979, November), P. 648; P. Glafkides, "Chimie et Physique Photographique" Paul Montel, 1967; G.F. Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966; and V.L. Zelikman et al., "Making and Coating Photographic Emulsion", Focal Press, 1964.

Monodispersed emulsions described in, e.g., U.S. Patents 3,574,628 and 3,655,394, and British Patent 1,413,748 are also preferable.

A tabular grain having an aspect ratio of about 5 or more can be used in the present invention. The tabular grain can be easily prepared by methods described in, e.g., Gutoff, "Photographic Science and Engineering", Vol. 14, PP. 248 to 257 (1970); U.S. Patents 4,434,226, 4,414,310, 4,433,048, and 4,439,520, and British Patent 2,112,157.

A crystal structure may be uniform, may have different compositions of halogen in its inner and outer portions, or may be a layered structure. Alternatively, a silver halide having a different composition may be bonded by an epitaxial junction, or a compound other than a silver halide such as silver rhodanate or zinc oxide may be bonded.

In addition, a mixture of grains having various crystal shapes can be used.

The silver halide emulsion is normally subjected to physical ripening, chemical ripening, and spectral sensitization, and then used. Additives used in these steps are described in Research Disclosure Nos. 17643 and 18716, and they are summarized as follows.

Conventional photographic additives for use in the present invention are also described in above two RDs and listed in the Table below.

Additives	RD No.17643	RD No.18716
1. Chemical sensitizers	page 23	page 648, right column
2. Sensitivity increasing agents		page 648, right column
3. Spectral sensitizers super sensitizers	pages 23-24	page 648, right column to page 649, right column
4. Brighteners	page 24	
5. Antifoggants and stabilizers	pages 24-25	page 649, right column
6. Light absorbent, filter dye, ultraviolet absorbents	pages 25-26	page 649, right column to page 650, left column
7. Stain preventing agents	page 25, right column	page 650, left to right columns
8. Dye image stabilizer	page 25	
9. Hardening agents column	page 26	page 651, left
10. Binder	page 26	page 651, left
11. Plasticizers, lubricants	page 27	page 650, right column
12. Coating aids, surface active agents	pages 26-27	page 650, right column
13. Antistatic agents	page 27	page 650, right column

In order to prevent degradation in photographic properties caused by formaldehyde gas, a compound which can react with and set formaldehyde described in U.S. Patent 4,411,987 or 4,435,503 is preferably added to a light-sensitive material.

In this invention, various color couplers can be used in the light-sensitive material. Specific examples of these couplers are described in above-described Research Disclosure, No. 17643, VII-C to VII-G as patent references.

Preferred examples of a yellow coupler are described in, e.g., U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752, and 4,248,961 JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023, and 4,511,649, and EP 249,473A.

Examples of a magenta coupler are preferably 5-pyrazolone and pyrazoloazole compounds, and more preferably, compounds described in, e.g., U.S. Patents 4,310,619 and 4,351,897, EP 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-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, and JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654, and 4,556,630, and WO (PCT) 88/04795.

Examples of a cyan coupler are phenol and naphthol couplers, and preferably, those described in, e.g., 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 Application (OLS) No. 3,329,729, EPs 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,753,871, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199, and JP-A-61-42658.

Preferable examples of a colored coupler for correcting additional, undesirable absorption of a colored dye are those described in Research Disclosure No. 17643, VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368.

Preferable examples of a coupler capable of forming colored dyes having proper diffusibility are those described in U.S. Patent 4,366,237, British Patent 2,125,570, EP 96,570, and West German Patent Application (OLS) No. 3,234,533.

Typical examples of a polymerized dye-forming coupler are described in U.S. patents 3,451,820, 4,080,211, 4,367,282, 4,409,320, and 4,576,910, and British Patent 2,102,173.

Couplers releasing a photographically useful residue upon coupling are preferably used in the present invention. DIR couplers, i.e., couplers releasing a development inhibitor are described in the patents cited in the above-described Research Disclosure No. 17643, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, and JP-A-63-37346, and U.S. Patent 4,248,962.

Preferable examples of a coupler imagewise releasing a nucleating agent or a development accelerator upon development are those described in British Patents 2,097,140 and 2,131,188, and JP-A-59-157638 and JP-A-59-170840.

Examples of a coupler which can be used in the light-sensitive material of the present invention are competing couplers described in, e.g., U.S. Patent 4,130,427; poly-equivalent couplers described in, e.g., U.S. Patents 4,283,472, 4,338,393, and 4,310,618; a DIR redox compound releasing coupler, a DIR coupler releasing coupler, a DIR coupler releasing redox compound, or a DIR redox releasing redox compound described in, e.g., JP-A-60-185950 and JP-A-62-24252; couplers releasing a dye which turns to a colored form after being released described in EP 173,302A; bleaching accelerator releasing couplers described in, e.g., RD. Nos. 11449 and 24241 and JP-A-61-201247; a legand releasing coupler described in, e.g., U.S. Patent 4,553,477; and a leuco dye releasing coupler described in JP-A-63-75747.

The couplers for use in this invention can be introduced in the light-sensitive materials by various known dispersion methods.

Examples of a high-boiling solvent used in an oil-in-water dispersion method are described in, e.g., U.S. Patent 2,322,027.

Examples of a high-boiling organic solvent to be used in the oil-in-water dispersion method and having a boiling point of 175 °C or more at normal pressure are phthalic esters (e.g., dibutylphthalate, dicyclohexylphthalate, di-2-ethylhexylphthalate, decylphthalate, bis(2,4-di-t-amylphenyl)phthalate, bis(2,4-di-t-amylphenyl)isophthalate, and bis(1,1-di-ethylpropyl)phthalate), phosphates or phosphonates (e.g., triphenylphosphate, tricresylphosphate, 2-ethylhexyldiphenylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, tributoxyethylphosphate, trichloropropylphosphate, and di-2-ethylhexylphenylphosphonate), benzoates (e.g., 2-ethylhexylbenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide, and N-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearylalcohol and 2,4-di-tert-amylphenol), aliphatic carboxylates (e.g., bis(2-ethylhexyl)sebacate, dioctylazelate, glyceroltributylate, isostearyllactate, and trioctylcitrate), an aniline derivative (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), and hydrocarbons (e.g., paraffin, dodecylbenzene, and diisopropylnaphthalene). An organic solvent having a boiling point of about 30 °C or more, and preferably, 50 °C to about 160 °C can be used as a co-solvent. Typical examples of the co-solvent are ethyl acetate, butyl acetate, ethyl propionate, methylethylketone, cyclohexanone, 2-ethoxyethylacetate, and dimethylformamide.

Steps and effects of a latex dispersion method and examples of an impregnating latex are described in, e.g., U.S. Patent 4,199,363 and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

The present invention can be applied to various color light-sensitive materials. Examples of the material are a color negative film for a general purpose or a movie, a color reversal film for a slide or a television, color paper, a color positive film, and color reversal paper.

Examples of a support suitable for use in this invention are described in the above-mentioned RD. No. 17643, page 28 and ibid., No. 18716, page 647, right column to page 648, left column.

The color photographic light-sensitive materials of this invention can be developed by the ordinary processes as described, for example, in the above-described Research Disclosure, No. 17643, pages 28 and 29 and ibid., No. 18716, page 651, left to right columns.

A color developer used in developing of the light-sensitive material of the present invention is an aqueous alkaline solution mainly consisting of, preferably, an aromatic primary amine-based color developing agent. As the color developing agent, although an aminophenol-based compound is effective, a p-phenylenediamine-based compound is preferably used. Typical examples of the p-phenylenediamine-based compound are 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-β-methoxyehtylaniline, and sulfates, hydrochlorides and p-toluenesulfonates thereof. These compounds can be used in a combination of two or more thereof in accordance with applications.

In general, the color developer contains a pH buffering agent such as a carbonate, a borate or a phosphate of an alkali metal, and a development restrainer or antifoggant such as a bromide, an iodide, a benzimidazole, a benzothiazole or a mercapto compound. If necessary, the color developer may also contain a preservative such as hydroxylamine, diehtylhydroxylamine, a hydrazine sulfite, a phenylsemicarbazide, triethanolamine, a catechol sulfonic acid or a triethylenediamine(1,4-diazabicyclo[2,2,2]octane); an organic solvent such as ethyleneglycol or diethyleneglycol; a development accelerator such as benzylalcohol, polyethyleneglycol, a quaternary ammonium salt or an amine; a dye forming coupler; a competing coupler; a fogging agent such as sodium boron hydride; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a viscosity imparting agent; and a chelating agent such as an aminopolycarboxylic acid, an aminopolyphosphonic acid, an alkylphosphonic acid or a phosphonocarboxylic acid. Examples of the chelating agent are ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′,N′-tetramethylenephosphonic acid and ethylenediamine-di(o-hydroxyphenylacetic acid), and salts thereof.

In order to perform reversal development, black-and-white development is performed and then color development is performed. As a black-and-white developer, well-known black-and-white developing agents, e.g., a dihydroxybenzene such as hydroquinone, a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone, and an aminophenol such as N-methyl-p-aminophenol can be used singly or in a combination of two or more thereof.

The pH of the color and black-and-white developers is generally 9 to 12. Although a quantity of replenisher of the developer depends on a color photographic light-sensitive material to be processed, it is generally 3 liters or less per m^2 of the light-sensitive material. The quantity of replenisher can be decreased to be 500 mℓ or less by decreasing a bromide ion concentration in a replenisher. In order to decrease the quantity of replenisher, a contact area of a processing solution in a processing tank with air is preferably decreased to prevent evaporation and oxidation of the solution upon contact with air. The quantity of replenisher can be decreased by using a means capable of suppressing an accumulation amount of bromide ions in the developer.

A color development time is normally set between 2 to 5 minutes. The processing time, however, can be shortened by setting a high temperature and a high pH and using the color developing agent at a high concentration.

The photographic emulsion layer is generally subjected to bleaching after color development. The bleaching may be performed either simultaneously with fixing (bleach-fixing) or independently thereof. In addition, in order to increase a processing speed, bleach-fixing may be performed after bleaching. Also, processing may be performed in a bleach-fixing bath having two continuous tanks, fixing may be performed before bleach-fixing, or bleaching may be performed after bleach-fixing, in accordance with applications. Examples of the bleaching agent are a compound of a multivalent metal such as iron (III), cobalt (III), chromium (VI) and copper (II); a peroxide; a quinone; and a nitro compound. Typical examples of the bleaching agent are a ferricyanide; a dichromate; an organic complex salt of iron (III) or cobalt (III), e.g., a complex salt of an aminopolycarboxylic acid such as ehtylenediaminetetraacetic acid, diehtylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, and glycoletherdiaminetetraacetic acid, or a complex salt of citric acid, tartaric acid or malic acid; a persulfate; a bromate; a permanganate; and a nitrobenzene. Of these compounds, an iron (III) complex salt of aminopolycarboxylic acid such as an iron (III) complex salt of ethylenediaminetetraacetic acid, and a persulfate are preferred because they can increase a processing speed and prevent an environmental contamination. The iron (III) complex salt of aminopolycarboxylic acid is effective in both the bleaching and bleach-fixing solutions. The pH of the bleaching or bleach-fixing solution containing the iron (III) complex salt of aminopolycarboxylic acid is normally 5.5 to 8. In order to increase the processing speed, however, processing can be performed at a lower pH.

A bleaching accelerator can be used in the bleaching solution, the bleach-fixing solution and their pre-bath, if necessary. Effective examples of the bleaching accelerator are compounds having a mercapto group or a disulfide group described in, e.g., 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, and JP-A-53-28426, and RD No. 17129 (July, 1978); a thiazolidine derivative described in JP-A-50-140129; thiourea derivatives described in JP-B-45-8506, JP-A-52-20832 and JP-A-53-32735, and U.S. Patent 3,706,561; iodide salts described in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds described in West German Patents 966,410 and 2,748,430; a polyamine compound described in JP-B-45-8836; compounds described 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 a bromide ion. The compounds having a mercapto or disulfide group are preferred since they have a good accelerating effect. In particular, the compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630 are preferred. The compound described in U.S. Patent 4,552,834 is also preferred. These bleaching accelerators may be added in the light-sensitive material. These bleaching accelerators are effective especially in bleach-fixing of a color light-sensitive material for picture taking with camera.

Examples of the fixing agent are a thiosulfate, a thiocyanate, a thioether-based compound, a thiourea and a large amount of an iodide. Of these compounds, a thiosulfate, especially, ammonium thiosulfate can be used in a widest range of applications. As a preservative of the bleach-fixing solution, a sulfite, a bisulfite or a carbonyl bisulfite adduct is preferred.

The photographic light-sensitive material of the present invention is normally subjected to washing and/or stabilizing steps after desilvering. An amount of water used in the washing step can be arbitrarily determined over a broad range in accordance with the properties of the light-sensitive material (e.g., a property determined by use of a coupler), the application of the material, the temperature of the water, the number of water tanks (the number of stages), a replenishing scheme representing a counter or forward current, and other conditions. The relationship between the amount of water and the number of water tanks in a multi-stage counter-current scheme can be obtained by a method described in "Journal of the Society of Motion Picture and Television Engineers", Vol. 64, PP. 248 - 253 (May, 1955).

According to the above-described multi-stage counter-current scheme, the amount of water used for washing can be greatly decreased. Since washing water stays in the tanks for a long period of time, however, bacteria multiply and floating substances may be undesirably attached to the light-sensitive material. In order to solve this problem in the process of the color photographic light-sensitive material of the present invention, a method of decreasing calcium and magnesium ions can be effectively utilized, as described in JP-A-62-288838. In addition, a germicide such as an isothiazolone compound and cyabendazole described in JP-A-57-8542, a chlorine-based germicide such as chlorinated sodium isocyanurate, and germicides such as benzotriazole described in Hiroshi Horiguchi, "Chemistry of Antibacterial and Antifungal Agents", Eiseigijutsu-Kai ed., "Sterilization, Antibacterial, and Antifungal Techniques for Microorganisms", and Nippon Bokin Bobabi Gakkai ed., "Dictionary of Antibacterial and Antifungal Agents".

The pH of the water for washing the photographic light-sensitive material of the present invention is 4 to 9, and preferably, 5 to 8. The water temperature and the washing time can vary in accordance with the properties and applications of the light-sensitive material. Normally, the washing time is 20 seconds to 10 minutes at a temperature of 15° C to 45° C, and preferably, 30 seconds to 5 minutes at 25° C to 40° C. The light-sensitive material of the present invention can be processed directly by a stabilizer in place of washing. All known methods described in JP-A-57-8543, JP-A-58-14834, and JP-A-60-220345 can be used in such stabilizing processing.

Stabilizing is sometimes performed subsequently to washing. An example is a stabilizing bath containing formalin and a surface-active agent to be used as a final bath of the color light-sensitive material for picture taking with camera. Various chelating agents or anti-fungal agents can be added in the stabilizing bath.

An overflow solution produced upon washing and/or replenishment of the stabilizing solution can be reused in another step such as a desilvering step.

The silver halide color photographic light-sensitive material of the present invention may contain a color developing agent in order to simplify processing and increase a processing speed. In order to add the color developing agent, various precursors of the color developing agent are preferably used. Examples of the precursor are an indoaniline-based compound described in U.S. Patent 3,342,597; Schiff base compounds described in U.S. Patent 3,342,599 and Research Disclosure Nos. 14,850 and 15,159; an aldol compound described in RD No. 13,924; a metal complex salt described in U.S. Patent 3,719,492; and a urethane-based compound described in JP-A-53-135628.

The silver halide color light-sensitive material of the present invention may contain various 1-phenyl-3-pyrazolidones in order to accelerate color development, if necessary. Typical examples of the compound are described in JP-A-56-64339, JP-A-57-144547, and JP-A-58-115438.

Each processing solution in the present invention is used at a temperature of 10° C to 50° C. Although a normal processing temperature is 33° C to 38° C, processing may be accelerated at a high temperature to shorten a processing time, or image quality or stability of a processing solution may be improved at a lower temperature. In order to save silver for the light-sensitive material, processing using cobalt intensification or hydrogen peroxide intensification described in West German Patent No. 2,226,770 or U.S. Patent 3,674,499 may be performed.

The silver halide light-sensitive material of the present invention can also be applied to thermal development light-sensitive materials described in, e.g., U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056, and EP 210,660A2.

Example 1

An aqueous silver nitrate solution (B) and an aqueous sodium chloride solution (C) were added in an aqueous gelatin solution (A) maintained at 38° C by a simultaneous mixing method over 12 minutes to the end of addition of the solution (B), while an electric potential was controlled as follows. The electric potential was measured by using a metal silver electrode and a double junction type saturated calomel reference electrode, and electric potential was controlled by detecting a difference with respect to a set electric potential and automatically controlling an addition amount of the solution (C).

After a compound represented by general formula (II) was added in an amount of 1.0 g per mol of $AgNO_3$ immediately after grain formation, the solution mixture was left to stand for about ten minutes. Thereafter, a formalin condensate of sodium naphthalenesulfonate was added as a settling agent, a pH was adjusted to 3.8, and then a desalting treatment was performed twice. Thereafter, NaOH, gelatin, and H_2O were added and dispersed to adjust the pH to be 6.0 and a pAg to be 7.2. No chemical sensitization was performed. Grain sizes and grain shapes of these emulsions were observed by an electron microscope (Table 1).

(A) Lime-Treated Gelatin	10 g
NaCℓ	0.2 g
H_2O	1,000 cc
(B) $AgNO_3$	150 g
H_2O	300 cc
(C) NaCℓ	54 g
H_2O	300 cc

Table 1

Addition Time / Emulsion No.	Addition Time and Set Potential		Average Grain Size (µm)	Grain Shape	
	0~4'	4'~12'			
1-a	+600 mV	+600 mV	0.09	Cube	Present Invention
b		+450	0.085	"	"
c		+ 80	0.085	"	"
d		+ 50	0.19	Slightly Rounded Cube	Comparative Example
e	+500 mV	+600	0.085	Cube	Present Invention
f		+450	0.075	"	"
g		+ 80	0.075	"	"
h		+ 50	0.18	Slightly Rounded Cube	Comparative Example
i	+450 mV	+600	0.08	Cube	Present Invention
j		+450	0.07	"	"
k		+ 80	0.07	"	"
l		+ 50	0.16	Slightly Rounded Cube	Comparative Example
1-m	+250 mV	+600	0.09	Cube	Present Invention
n		+450	0.08	"	"
o		+ 80	0.08	"	"
p		+ 50	0.18	Slightly Rounded Cube	Comparative Example
q	+ 80 mV	+600	0.12	Cube	Present Invention
r		+450	0.10	"	"
s		+ 80	0.10	"	"
t		+ 50	0.19	"	Comparative Example
u	+ 50 mV	+600	0.18	"	"
v		+ 80	0.18	"	"
w		+ 50	0.20	"	"

As is apparent from Table 1, silver chloride grains having a grain size of 0.15 µm or less can be obtained by controlling the electric potential from +80 to +600 mV during grain formation and using a compound II-1. In particular, fine grains can be obtained by setting a high electric potential in the first half of addition.

Example 2

A sample 201 as a multilayered color photographic light-sensitive material consisting of layers having the following compositions and formed on an undercoated cellulose triacetate film support was prepared.

Compositions of Light-Sensitive Layers

The coating amounts of a silver halide, colloidal silver, and couplers are represented in units of g/m^2 of silver, and that of sensitizing dyes is represented by the number of mols per mol of the silver halide in the same layer. Note that formulas of compounds presented in the following compositions are listed in Table 16.

Layer 1: Antihalation Layer	
Black Colloidal Silver coating silver amount	0.2
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

Layer 2: Interlayer	
Fine Grain Silver Bromide (sphere-equivalent diameter = 0.07 μm) coating silver amount	0.15
Gelatin	1.0
Cpd-2	0.2

Layer 3: 1st Red-Sensitive emulsion Layer

Silver Iodobromide Emulsion (AgI = 10.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.7 µm, variation coefficient of sphere-equivalent diameter = 14%, tetradecahedral grain) coating silver amount	0.26
Silver Iodobromide Emulsion (AgI = 4.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.4 µm, variation coefficient of sphere-equivalent diameter = 22%, tetradecahedral grain) coating silver amount	0.2
Gelatin	1.0
ExS-1	4.5×10^{-4}
ExS-2	1.5×10^{-4}
ExS-3	0.4×10^{-4}
ExS-4	0.3×10^{-4}
ExC-1	0.33
ExC-2	0.009
ExC-3	0.023
ExC-6	0.14

Layer 4: 2nd Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 16 mol%, internally high AgI type, sphere-equivalent diameter = 1.0 µm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 4.0) coating silver amount	0.55
Gelatin	0.7
ExS-1	3×10^{-4}
ExS-2	1×10^{-4}
ExS-3	0.3×10^{-4}
ExS-4	0.3×10^{-4}
ExC-3	0.05
ExC-4	0.10
ExC-6	0.08

Layer 5: 3rd Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10.0 mol%, internally high AgI type, sphere-equivalent diameter = 1.2 µm, variation coefficient of sphere-equivalent diameter = 28%, tabular grain, diameter/thickness ratio = 6.0) coating silver amount	0.9
Gelatin	0.6
ExS-1	2×10^{-4}
ExS-2	0.6×10^{-4}
ExS-3	0.2×10^{-4}
ExC-4	0.07
ExC-5	0.06
Solv-1	0.12
Solv-2	0.12

Layer 6: Interlayer	
Gelatin	1.0
Cpd-4	0.1

Layer 7: 1st Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.7 µm, variation coefficient of sphere-equivalent diameter = 14%, tetradecahedral grain) coating silver amount	0.2
Silver Iodobromide Emulsion (AgI = 4.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.4 µm, variation coefficient of sphere-equivalent diameter = 22%, tetradecahedral grain) coating silver amount	0.1
Gelatin	1.2
ExS-5	5×10^{-4}
ExS-6	2×10^{-4}
ExS-7	1×10^{-4}
ExM-1	0.41
ExM-2	0.10
ExM-5	0.03
Solv-4	0.2
Solv-5	0.03

Layer 8: 2nd Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10 mol%, internally high iodide type, sphere-equivalent diameter = 1.0 µm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 3.0) coating silver amount	0.4
Gelatin	0.35
ExS-5	3.5×10^{-4}
ExS-6	1.4×10^{-4}
ExS-7	0.7×10^{-4}
ExM-1	0.09
ExM-3	0.01
Solv-1	0.15
Solv-5	0.03

Layer 9: Interlayer	
Gelatin	0.5

Layer 10: 3rd Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10.0 mol%, internally high AgI type, sphere-equivalent diameter = 1.2 µm, variation coefficient of sphere-equivalent diameter = 28%, tabular grain, diameter/thickness ratio = 6.0) coating silver amount	1.0
Gelatin	0.8
ExS-5	2×10^{-4}
ExS-6	0.8×10^{-4}
ExS-7	0.8×10^{-4}
ExM-3	0.01
ExM-4	0.04
ExC-4	0.005
Solv-1	0.2

Layer 11: Yellow Filter Layer	
Cpd-3	0.05
Gelatin	0.5
Solv-1	0.1

Layer 12: Interlayer	
Gelatin	0.5
Cpd-2	0.1

Layer 13: 1st Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10 mol%, internally high iodide type, sphere-equivalent diameter = 0.7 μm, variation coefficient of sphere-equivalent diameter = 14%, tetradecahedral grain) coating silver amount	0.1
Silver Iodobromide Emulsion (AgI = 4.0 mol%, internally high iodide type, sphere-equivalent diameter = 0.4 μm, variation coefficient of sphere-equivalent diameter = 22%, tetradecahedral grain) coating silver amount	0.05
Gelatin	1.0
ExS-8	3×10^{-4}
ExY-1	0.53
ExY-2	0.02
Solv-1	0.15

Layer 14: 2nd Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 19.0 mol%, internally high AgI type, sphere-equivalent diameter = 1.0 μm, variation coefficient of sphere-equivalent diameter = 16%, tetradecahedral grain) coating silver amount	0.19
Gelatin	0.3
ExS-8	2×10^{-4}
ExY-1	0.22
Solv-1	0.07

Layer 15: Interlayer	
Fine Grain Silver Iodobromide (AgI = 2 mol%, homogeneous type, sphere-equivalent diameter = 0.13 μm) coating silver amount	0.2
Gelatin	0.36

Layer 16: 3rd Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 14.0 mol%, internally high AgI type, sphere-equivalent diameter = 1.5 μm, variation coefficient of sphere-equivalent diameter = 28%, tabular grain, diameter/thickness ratio = 5.0) coating silver amount	1.0
Gelatin	0.5
ExS-8	1.5×10^{-4}
ExY-1	0.2
Solv-1	0.07

Layer 17: 1st Protective Layer	
Gelatin	1.8
UV-1	0.1
UV-2	0.2
Solv-1	0.01
Solv-2	0.01

Layer 18: 2nd Protective Layer	
Fine Grain Silver Bromide (sphere-equivalent diameter = 0.07 μm) coating silver amount	0.18
Gelatin	0.7
Polymethylmethacrylate Grain (diameter = 1.5 μm)	0.2
W-1	0.02
H-1	0.4
Cpd-5	1.0

Following the same procedures as for emulsions j (0.07 μm) and w (0.20 μm) in Example 1, grain formation and settling/desalting were performed, and then a compound V-12 for forming a slightly soluble silver salt was added in a dispersion process. The compound was added in an amount of 8×10^{-3} mol/mol of $AgNO_3$ for the emulsion j and 2.8×10^{-3} mol/mol of $AgNO_3$ for the emulsion w, thereby preparing emulsions j′ and w′, respectively. The emulsions w, w′, j, and j′ were added to the layer 18 (second protective layer) to prepare samples 202, 203, 204, and 205, respectively. The emulsion j′ was added to the layer 2 (interlayer) and the layer 18 to prepare a sample 206. Coating silver amounts were the same as those of the control sample 201.

These samples were exposed and then subjected to treatments listed in Table 2.

Table 2

Processing Method I				
Process	Time	Temperature	Quantity of* Replenisher	Tank Volume
Color Development	3 min. 15 sec.	38°C	15 mℓ	20 ℓ
Bleaching	6 min. 30 sec.	38°C	10 mℓ	40 ℓ
Washing	2 min. 10 sec.	35°C	10 mℓ	20 ℓ
Fixing	4 min. 20 sec.	38°C	20 mℓ	30 ℓ
Washing (1)	1 min. 05 sec.	35°C	Counter flow piping from (2) to (1)	10 ℓ
Washing (2)	2 min. 10 sec.	35°C	20 mℓ	10 ℓ
Stabilization	1 min. 05 sec.	38°C	10 mℓ	10 ℓ
Drying	4 min. 20 sec.	55°C		

*) A quantity of replenisher per meter of a 35-mm wide sample.

In the above treatments, a charging amount of a fixing solution to the washing process was 2 mℓ per meter of a 35-mm wide light-sensitive material.

The compositions of the process solutions will be presented below.

Color Developing Solution:		
	Mother Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetate	1.0	1.1
1-hydroxyethylidene-1,1-diphosphonic Acid	3.0	3.2
Sodium Sulfite	4.0	4.9
Potassium Carbonate	30.0	30.0
Potassium Bromide	1.4	-
Potassium Iodide	1.5 mg	-
Hydroxylamine Sulfate	2.4	3.6
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylalinine Sulfate	4.5	7.2
Water to make	1.0 ℓ	1.0 ℓ
pH	10.05	10.10

Bleaching Solution:		
	Mother Solution (g)	Replenisher (g)
Disodium Ethylenediaminetetraacetate Trihydrate	100.0	140.0
Ammonium Bromide	140.0	180.0
Ammonium Nitrate	30.0	40.0
Ammonia Water (27%)	6.5 mℓ	2.5 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.0	5.5

Fixing Solution:		
	Mother Solution (g)	Replenisher (g)
Disodium Ethylenediaminetetraacetate	0.5	1.0
Sodium Sulfite	7.0	12.0
Sodium Bisulfite	5.0	9.5
Ammonium Thiosulfate Aqeuous Solution (70%)	170.0 mℓ	240.0 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.7	6.6

Washing Solution: Common for mother solution and replenisher

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange regin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type strongly basic anion exchange resin (Amberlite IRA-400) to set concentrations of calcium and magnesium ion to be 3 mg/ℓ or less. Subsequently, 20 mg/ℓ of sodium isocyanuric acid dichloride and 150 mg/ℓ of sodium sulfate were added. The pH of the solution fell within the range of 6.5 to 7.5.

Stabilizing Solution:		
	Mother Solution (g)	Replenisher (g)
Formalin (37%)	2.0 mℓ	3.0 mℓ
Polyoxyehtylene-p-monononylphenylether (avearage polymerization degree = 10)	0.3	0.45
Disodium Ethylenediaminetetraacetate	0.05	0.08
Water to make	1.0 ℓ	1.0 ℓ
pH	5.0 - 8.0	5.0 - 8.0

Prior to the treatments of the samples of Example, 500 m of a Super HR100 negative film (width = 35 mm) available from Fuji Photo Film Co., Ltd. were treated to obtain steady running solutions.

Table 3 shows results of measuring densities of the treated samples.

Table 3

Layer 2			Layer 18			Sample
Composition	Size	Compound	Composition	Size	Compound	
Fine Grain Silver Bromide	0.07 μ	-	Fine Grain Silver Bromide	0.07	-	201 (Comparative Example)
"	"	-	w Silver Chloride	0.20	-	202 (Comparative Example)
"	"	-	w' Silver Chloride	"	V - 12	203 (Comparative Example)
"	"	-	j Silver Chloride	0.07	-	204 (Comparative Example)
"	"	-	j' Silver Chloride	"	V - 12	205 (Present Invention)
j' Silver Chloride	"	I - 12	"	"	"	206 (Present Invention)

(Continued)

Sample	Blue-Sensitive Layer		Red-Sensitive Layer	
	Sensitivity	Fogging Density	Sensitivity	Fogging Density
201 (Comparative Example)	100	Control	100	Control
202 (Comparative Example)	95	0.10	98	0.03
203 (Comparative Example)	105	0.02	103	± 0
204 (Comparative Example)	80	0.15	95	0.04
205 (Present Invention)	120	0.01	108	± 0
206 (Present Invention)	120	0.01	115	± 0

Example 3

In the first process in Example 2, the amounts of potassium bromide and potassium iodide in the color developing solution as a steady running solution were changed. The mother solution and replenisher were adjusted such that steady values of potassium bromide of the color developing solutions in the second and third processes were set to be 1.2 g/ℓ and 1.7 g/ℓ, respectively, and those of potassium iodide of the color developing solutions in the fourth and fifth processes were set to be 1.0 mg/ℓ and 3.0 mg/ℓ, respectively. The other composition of the color developing solution was the same as the color developing solution in the first process. The samples 201, 205, and 206 prepared in Example 2 were subjected to the second to fifth processes to obtain the sensitivities of red-, and blue-sensitive layers. The sensitivity was obtained as a relative value assuming that sensitivities obtained in the second and fourth processes were 100. The results are listed in Table 4.

Table 4

Sample No.	Sensitivity of Blue-Sensitive Layer		Sensitivity of Red-sensitive Layer	
	Third Process	Fifth Process	Third Process	Fifth Process
201 (Comparative Example)	75	91	91	100
205 (Present Invention)	85	94	89	100
206 (Present Invention)	85	94	93	100

As is apparent from Table 4, a sensitivity variation of each sample of the present invention is small when a bromine or iodine ion density varies.

Example 4

The operations and treatments were performed following the same procedures as in Example 2 except that instead of the compound V-12 used in Example 2, the compounds V-5, V-9, V-10, V-18, V-23, and V-40 were used in an equimolar amount of the compound V-12. As a result, the same effects as obtained by using the compound V-12 were obtained.

Example 5

A sample 501 as a multilayered color photographic light-sensitive material consisting of layers having the following compositions and formed on an undercoated cellulose triacetate film support was prepared.

Compositions of Light-Sensitive Layers

The coating amounts of a silver halide, colloidal silver, and couplers are represented in units of g/m^2 of silver, and that of sensitizing dyes is represented by the number of mols per mol of the silver halide in the same layer.

Note that formulas of compounds presented in the following compositions are listed in Table 17.

Layer 1: Antihalation Layer	
Black Colloidal Silver coating silver amount	0.2
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

Layer 2: Interlayer	
Fine Grain Silver Bromide (sphere-equivalent diameter = 0.07 µm) coating silver amount	0.15
Gelatin	1.0
Cpd-2	0.2

Layer 3: 1st Red-Sensitive emulsion Layer

Silver Iodobromide Emulsion (AgI = 10.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.7 µm, variation coefficient of sphere-equivalent diameter = 14%, tetradecahedral grain) coating silver amount	0.26
Silver Iodobromide Emulsion (AgI = 4.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.4 µm, variation coefficient of sphere-equivalent diameter = 22%, tetradecahedral grain) coating silver amount	0.2
Gelatin	1.0
ExS-1	4.5×10^{-4}
ExS-2	1.5×10^{-4}
ExS-3	0.4×10^{-4}
ExS-4	0.3×10^{-4}
ExC-1	0.33
ExC-2	0.009
ExC-3	0.023
ExC-6	0.14

Layer 4: 2nd Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 16 mol%, internally high AgI type, sphere-equivalent diameter = 1.0 µm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 4.0) coating silver amount	0.55
Gelatin	0.7
ExS-1	3×10^{-4}
ExS-2	1×10^{-4}
ExS-3	0.3×10^{-4}
ExS-4	0.3×10^{-4}
ExC-3	0.05
ExC-4	0.10
ExC-6	0.08

Layer 5: 3rd Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10.0 mol%, internally high AgI type, sphere-equivalent diameter = 1.2 μm, variation coefficient of sphere-equivalent diameter = 28%, tabular grain, diameter/thickness ratio = 6.0) coating silver amount	0.9
Gelatin	0.6
ExS-1	2×10^{-4}
ExS-2	0.6×10^{-4}
ExS-3	0.2×10^{-4}
ExC-4	0.07
ExC-5	0.06
Solv-1	0.12
Solv-2	0.12

Layer 6: Interlayer	
Gelatin	1.0
Cpd-4	0.1

Layer 7: 1st Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.7 μm, variation coefficient of sphere-equivalent diameter = 14%, tetradecahedral grain) coating silver amount	0.2
Silver Iodobromide Emulsion (AgI = 4.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.4 μm, variation coefficient of sphere-equivalent diameter = 22%, tetradecahedral grain) coating silver amount	0.1
Gelatin	1.2
ExS-5	5×10^{-4}
ExS-6	2×10^{-4}
ExS-7	1×10^{-4}
ExM-1	0.41
ExM-2	0.10
ExM-5	0.03
Solv-1	0.2
Solv-5	0.03

Layer 8: 2nd Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10 mol%, internally high iodide type, sphere-equivalent diameter = 1.0 μm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 3.0) coating silver amount	0.4
Gelatin	0.35
ExS-5	3.5×10^{-4}
ExS-6	1.4×10^{-4}
ExS-7	0.7×10^{-4}
ExM-1	0.09
ExM-3	0.01
Solv-1	0.15
Solv-4	0.03

Layer 9: Interlayer	
Gelatin	0.5

Layer 10: 3rd Green-Sensitive Emulsion Layer

Silver Iodobromide emulsion (AgI = 10.0 mol%, internally high AgI type, sphere-equivalent diameter = 1.2 μm, variation coefficient of sphere-equivalent diameter = 28%, tabular grain, diameter/thickness ratio = 6.0) coating silver amount	1.0
Gelatin	0.8
ExS-5	2×10^{-4}
ExS-6	0.8×10^{-4}
ExS-7	0.8×10^{-4}
ExM-3	0.01
ExM-4	0.04
ExC-4	0.005
Solv-1	0.2

Layer 11: Yellow Filter Layer	
Cpd-3	0.05
Gelatin	0.5
Solv-1	0.1

Layer 12: Interlayer	
Gelatin	0.5
Cpd-2	0.1

Layer 13: 1st Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 10 mol%, internally high iodide type, sphere-equivalent diameter = 0.7 µm, variation coefficient of sphere-equivalent diameter = 14%, tetradecahedral grain) coating silver amount	0.1
Silver Iodobromide Emulsion (AgI = 4.0 mol%, internally high iodide type, sphere-equivalent diameter = 0.4 µm, variation coefficient of sphere-equivalent diameter = 22%, tetradecahedral grain) coating silver amount	0.05
Gelatin	1.0
ExS-8	3×10^{-4}
ExY-1	0.53
ExY-2	0.02
Solv-1	0.15

Layer 14: 2nd Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 19.0 mol%, internally high AgI type, sphere-equivalent diameter = 1.0 µm, variation coefficient of sphere-equivalent diameter = 16%, tetradecahedral grain) coating silver amount	0.19
Gelatin	0.3
ExS-8	2×10^{-4}
ExY-1	0.22
Solv-1	0.07

Layer 15: Interlayer	
Fine Grain Silver Iodobromide (AgI = 12 mol%, homogeneous type, sphere-equivalent diameter = 0.13 µm) coating silver amount	0.2
Gelatin	0.36
Cpd-5	0.6

Layer 16: 3rd Blue-Sensitive Emulsion Layer	
Silver Iodobromide Emulsion (AgI = 14.0 mol%, internally high AgI type, sphere-equivalent diameter = 1.5 µm, variation coefficient of sphere-equivalent diameter = 28%, tabular grain, diameter/thickness ratio = 5.0) coating silver amount	1.1
Gelatin	0.5
ExS-8	1.5×10^{-4}
ExY-1	0.2
Solv-1	0.07

Layer 17: 1st Protective Layer	
Gelatin	1.8
UV-1	0.1
UV-2	0.2
Solv-1	0.01
Solv-2	0.01
Cpd-5	0.6

Layer 18: 2nd Protective Layer	
Fine Grain Silver Bromide (sphere-equivalent diameter = 0.07 µm) coating silver amount	0.35
Gelatin	1.4
Polymethylmethacrylate Grain (diameter = 1.5 µm)	0.2
W-1	0.02
H-1	0.4

The fine grain silver bromide emulsion of the layer 18 was changed to the silver chloride fine grain emulsion of the present invention while the silver coating amount was kept unchanged from that of the sample 501, thereby preparing a sample 502.

The fine grain silver chloride emulsion of the present invention was prepared as follows.

An aqueous silver nitrate solution (B) and an aqueous sodium chloride solution (C) were added to an aqueous gelatin solution (A) maintained at 38° C by a simultaneous mixing method over 12 minutes to the end of addition of the solution (B), while an electric potential was controlled to be +450 mV. The electric potential was measured by using a metal silver electrode and a double junction type saturated calomel reference electrode, and electric potential was controlled by detecting a difference with respect to a set electric potential and automatically controlling an addition amount of the solution (C). Immediately after grain formation, a compound V-12 represented by general formula (V) was added in an amount of 8×10^{-3} mol per mol of $AgNO_3$.

Thereafter, the resultant solution mixture was left to stand for about ten minutes, and a formalin condensate of sodium naphthalenesulfonate was added as a settling agent, a pH was adjusted to 3.8, and then a desalting treatment was performed twice. Thereafter, NaOH, gelatin, and H_2O were added and dispersed to adjust the pH to be 6.0 and a pAg to be 7.2. No chemical sensitization was performed. Grain sizes and grain shapes of these emulsions were observed by an electron microscope. As a result, cubic grains having a diameter (of a sphere having a volume which correspond to a volume of the cubic grain) of 0.07 µm were obtained.

(A) Lime-Treated Gelatin	10 g
NaCℓ	0.2 g
H_2O	1,000 cc
(B) $AgNO_3$	150 g
H_2O	300 cc
(C) NaCℓ	54 g
H_2O	300 cc

The compounds ExC-2, ExM-2, and ExY-2 in the samples 501 and 502 were changed to couplers D-30, D-29, and D-12 of the present invention. Equimolar amounts of these couplers were used to prepare samples 503 and 504.

These samples were exposed and then subjected to treatments listed in Table 5 below.

Table 5

Processing Method II				
Process	Time	Temperature	Quantity of* Replenisher	Tank Volume
Color Development	3 min. 15 sec.	38° C	15 mℓ	20 ℓ
Bleaching	6 min. 30 sec.	38° C	10 mℓ	40 ℓ
Washing	2 min. 10 sec.	35° C	10 mℓ	20 ℓ
Fixing	4 min. 20 sec.	38° C	20 mℓ	30 ℓ
Washing (1)	1 min. 05 sec.	35° C	Counter flow piping from (2) to (1)	10 ℓ
Washing (2)	1 min. 05 sec.	35° C	20 mℓ	10 ℓ
Stabilization	1 min. 05 sec.	38° C	10 mℓ	10 ℓ
Drying	4 min. 20 sec.	55° C		

*) A quantity of reprenisher per meter of a 35-mm wide sample.

In the above treatments, a charging amount of a fixing solution to the washing process was 2 mℓ per meter of a 35-mm wide light-sensitive material.

The compositions of the processing solutions will be presented below.

Color Developing Solution:		
	Mother Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetate	1.0	1.1
1-hydroxyethylidene-1,1-diphosphonic Acid	3.0	3.2
Sodium Sulfite	4.0	4.9
Potassium Carbonate	30.0	30.0
Potassium Bromide	1.4	-
Potassium Iodide	1.5 mg	-
Hydroxylamine Sulfate	2.4	3.6
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylalinine Sulfate	4.5	7.2
Water to make	1.0 ℓ	1.0 ℓ
pH	10.05	10.10

Bleaching Solution:		
	Mother Solution (g)	Replenisher (g)
Disodium Ethylenediaminetetraacetate Trihydrate	100.0	140.0
Ammonium Bromide	140.0	180.0
Ammonium Nitrate	30.0	40.0
Ammonia Water (27%)	6.5 mℓ	2.5 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.0	5.5

Fixing Solution:		
	Mother Solution (g)	Replenisher (g)
Disodium Ethylenediaminetetraacetate	0.5	1.0
Sodium Sulfite	7.0	12.0
Sodium Bisulfite	5.0	9.5
Ammonium Thiosulfate Aqueous Solution (70%)	170.0 mℓ	240.0 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.7	6.6

Washing Solution: Common for mother solution and replenisher

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange regin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type strongly basic anion exchange resin (Amberlite IRA-400) to set concentrations of calcium and magnesium ion to be 3 mg/ℓ or less. Subsequently, 20 mg/ℓ of sodium isocyanuric acid dichloride and 150 mg/ℓ of sodium sulfate were added. The pH of the solution fell within the range of 6.5 to 7.5.

Stabilizing Solution:	Mother Solution (g)	Replenisher (g)
Formalin (37%)	2.0 mℓ	3.0 mℓ
Polyoxyehtylene-p-monononylphenylether (avearage polymerization degree = 10)	0.3	0.45
Disodium Ethylenediaminetetraacetate	0.05	0.08
Water to make	1.0 ℓ	1.0 ℓ
pH	5.0 - 8.0	5.0 - 8.0

Prior to the treatments of the samples of Example, 500 m of a Super HR100 negative film (width = 35 mm) available from Fuji Photo Film Co., Ltd. were treated to obtain steady running solutions.

Table 6 shows results of measuring densities of the treated samples.

Table 6

Sample	Fine Grain Emulsion of Layer 18	DIR Compound			Red-Sensitive Layer		Blue-Sensitive Layer		Graininess*	
		Layer 3	Layer 7	Layer 13	Fogging Density	Sensitivity	Fogging Density	Sensitivity	Red-Sensitive Layer	Blue-Sensitive Layer
501 (Comparative Example)	Silver Bromide	ExC-2	ExM-2	ExY-2	Control	100	Control	100	0.032	0.043
502 (Comparative Example)	Silver Chloride	ExC-2	ExM-2	ExY-2	± 0	108	+0.01	110	0.029	0.042
503 (Comparative Example)	Silver Bromide	D-30	D-29	D-12	-0.01	98	-0.01	98	0.028	0.041
504 (Present Invention)	Silver Chloride	D-30	D-29	D-12	± 0	105	+0.01	105	0.024	0.035

* Graininess was measured at a portion having a cyan image density of 0.5 and an yellow image density of 1.0 with an aperture of 48 µm.

An amount of the fine grain emulsion in the layer 18 of the sample 501 was adjusted such that the sensitivities of the red- and blue-sensitive layers were set to be 105, thereby preparing a sample 501′. The grainineses of red- and blue-sensitive layers of the obtained sample were 0.028 and 0.040, respectively.

As a result, the combination of the present invention was most effective in sensitivity and graininess.

Example 6

In the samples 501 and 502 of Example 5, equimolar amounts of D-18, D-5, and D-41 were used in place of ExC-2, ExM-2, and ExY-2, respectively, thereby preparing samples 505 (comparative example) and 506 (present invention). 1,000 m of these samples were exposed and treated in accordance with the processes of Example 5 to obtain running processing solutions (A) and (B). A color negative film SHR-100 available from Fuji Photo Film Co., Ltd. was exposed and processed by the solutions (A) and (B). As a result, the sensitivity of a sample processed by the solution (A) was much more reduced than that of a sample processed by the solution (B). That is, a development inhibiting component flows little out from the sample of the present invention.

Example 7

The mother solution and replenisher of the color developing solutions of Example 5 were adjusted such that the consentrations of potassium bromide and potassium iodide were set as shown in Table 7 below, thereby preparing processing solutions (C), (D), and (E).

Table 7

	Potassium Bromide	Potassium Iodide
Processing Solution C	1.2 g/ℓ	1.0 mg/ℓ
D	1.8 g/ℓ	1.0 mg/ℓ
E	1.5 g/ℓ	2.0 mg/ℓ

When the samples 503 and 504 of Example 5 were exposed and processed by the above three types of solutions, the results as shown in Table 8 were obtained. The sensitivities are represented by relative values assuming that the sensitivity obtained by the solution (C) is 100.

Table 8

Sample		Solution C	Solution D	Solution E
503 (Comparative Example)	Red-Sensitive Layer	100	90	85
	Blue-Sensitive Layer	100	68	59
504 (Comparative Example)	Red-Sensitive Layer	100	88	85
	Blue-Sensitive Layer	100	85	82

As shown in Table 8, the sample of the present invention is stable to a variation in the processing solutions.

Example 8

A silver iodobromide tabular emulsion A was prepared by a method described in Japanese Patent Application No. 61-209445.

30 g of inactive gelatin and 6 g of potassium bromide were dissolved in 1 ℓ of distilled water and the resultant solution was stirred at 60° C. 35 cc of an aqueous solution in which 5.0 g of silver nitrate were dissolved and 35 cc of an aqueous solution in which 3.2 g of potassium bromide and 0.98 g of potassium iodide were dissolved were added to the above stirred solution at a flow rate of 70 cc/min. for 30 seconds. Thereafter, the pAg of the resultant solution mixture was increased up to 10, and ripening was performed for 30 minutes, thereby preparing a seed emulsion.

Subsequently, a predetermined amount of 1 ℓ of an aqueous solution in which 145 g of silver nitrate was dissolved and equimolar amount of a solution mixture of potassium bromide and potassium iodide were added at a predetermined temperature, a predetermined pAg, and an addition rate close to a critical growth rate, thereby preparing a tabular core emulsion. Thereafter, the remaining silver nitrate solution and equimolar amount of a solution mixture of potassium bromide and potassium iodide having a different composition were added to cover cores at an addition rate close to a critical growth rate, thereby preparing a core/shell type silver iodobromide tabular emulsion A.

The emulsion A had an aspect ratio of 6.7, a grain size (sphere-equivalent diameter) of 0.76 μm, a core/shell ratio (volume ratio) of 1/1, an iodide content core/shell ratio of 12/3, an average iodide content of 7.5 mol%, and a surface iodide content (XPS) of 5.2%.

Measurement of XPS was performed by using ESCA-750 available from Shimadzu Corp. Mg-Kα - (acceleration voltage = 8 kV, current = 30 mA) was used as excitation X rays to obtain peak areas corresponding to I-3d5/2 and Ag-3d5/2, thereby obtaining an average silver iodide content on the surface of a silver halide grain on the basis of the obtained intensity ratio.

The silver iodobromide tabular emulsion A was chemically sensitized such that an optimal sensitivity was obtained by 1/100-sec. exposure.

A sample 801 having the following multilayered structure was manufactured.

The coating amounts of a silver halide and colloidal silver are represented in units of g/m^2 of silver, those of couplers, additives, and gelatin are represented in units of g/m^2, and that of sensitizing dyes is represented by the number of mols per mol of the silver halide in the same layer.

Formulas of compounds presented in the following compositions are listed in Table 18 to be presented later.

Layer 1: Antihalation Layer	
Black Colloidal Silver	0.2
Gelatin	1.3
ExM-9	0.2
UV-1	0.03
UV-2	0.06
UV-3	0.06
Solv-1	0.15
Solv-2	0.15
Solv-3	0.05

Layer 2: Interlayer	
Gelatin	0.5

Layer 3: Low-Speed Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 4 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.5 μm, variation coefficient of sphere-equivalent diameter = 20%, tabular grain, diameter/thickness ratio = 3.0) coating silver amount	1.2
Silver Iodobromide Emulsion (AgI = 3 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.3 μm, variation coefficient of sphere-equivalent diameter = 15%, spherical grain, diameter/thickness ratio = 1.0) coating silver amount	0.6
Gelatin	1.0
ExS-1	4×10^{-4}
ExS-2	5×10^{-5}
ExS-3	1×10^{-6}
ExC-1	0.05
ExC-2	0.50
ExC-3	0.03
ExC-4	0.12
ExC-5	0.01

Layer 4: High-Speed Red-Sensitive Emulsion Layer	
Silver Iodobromide Emulsion (A) coating silver amount	0.7
Gelatin	1.0
ExS-1	3×10^{-4}
ExS-2	2.3×10^{-5}
ExS-3	0.5×10^{-6}
ExS-11	3.0×10^{-5}
ExC-6	0.11
ExC-7	0.05
ExC-4	0.05
Solv-1	0.05
Solv-3	0.05

Layer 5: Interlayer	
Gelatin	0.5
Cpd-1	0.1
Solv-1	0.05

Silver Iodobromide Emulsion (AgI = 4 mol%, surface high AgI type, sphere-equivalent diameter = 0.5 µm, variation coefficient of sphere-equivalent diameter = 15%, tabular grain, diameter/thickness ratio = 4.0) coating silver amount	0.35
Silver Iodobromide Emulsion (AgI = 3 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.3 µm, variation coefficient of sphere-equivalent diameter = 25%, spherical grain, diameter/thickness ratio = 1.0) coating silver amount	0.20
Gelatin	1.0
ExS-4	2×10^{-4}
ExS-5	5×10^{-4}
ExS-6	1×10^{-4}
ExS-7	3×10^{-5}
ExS-8	3×10^{-5}
ExS-9	4×10^{-5}
ExM-8	0.4
ExM-9	0.07
ExM-10	0.02
ExY-11	0.03
Solv-1	0.3
Solv-4	0.05

Layer 7: High-Speed Green-Sensitive Emulsion Layer	
Silver Iodobromide Emulsion (A) coating silver amount	0.8
ExS-4	2×10^{-4}
ExS-5	5×10^{-4}
ExS-6	1×10^{-4}
ExS-7	3×10^{-5}
ExS-8	3×10^{-5}
ExS-9	4×10^{-5}
ExM-8	0.1
ExM-34	0.01
ExM-9	0.02
ExY-11	0.03
ExC-2	0.03
ExM-14	0.01
Solv-1	0.2
Solv-4	0.01

Layer 8: Interlayer	
Gelatin	0.5
Cpd-1	0.05
Solv-1	0.02

Layer 9: Doner Layer Having Interlayer Effect

Silver Iodobromide Emulsion (AgI = 2 mol%, internally high AgI type, sphere-equivalent diameter = 1.0 μm, variation coefficient of sphere-equivalent diameter = 15%, tabular grain, diameter/thickness ratio = 6.0) coating silver amount	0.35
Silver Iodobromide Emulsion (AgI = 2 mol%, internally high AgI type, sphere-equivalent diameter = 0.4 μm, variation coefficient of sphere-equivalent diameter = 20%, tabular grain, diameter/thickness ratio = 6.0) coating silver amount	0.20
Gelatin	0.5
ExS-3	8×10^{-4}
ExY-13	0.11
ExM-12	0.03
ExM-14	0.10
Solv-1	0.20

Layer 10: Yellow Filter Layer	
Yellow Colloidal Silver	0.05
Gelatin	0.5
Cpd-2	0.13
Cpd-1	0.10

Layer 11: Low-Speed Blue-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 4.5 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.7 µm, variation coefficient of sphere-equivalent diameter = 15%, tabular grain, diameter/thickness ratio = 7.0) coating silver amount	0.3
Silver Iodobromide Emulsion (AgI = 3 mol%, homogeneous AgI type, sphere-equivalent diameter = 0.3 µm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 7.0) coating silver amount	0.15
Gelatin	1.6
ExS-10	2×10^{-4}
ExC-16	0.05
ExC-2	0.10
ExC-3	0.02
ExY-13	0.07
ExY-17	1.0
Solv-1	0.20

Layer 12: High-Speed Blue-Sensitive Emulsion Layer	
Silver Iodobromide Emulsion (A) coating silver amount	0.5
Gelatin	0.5
ExS-10	1×10^{-4}
ExY-15	0.20
ExY-13	0.01
Solv-1	0.10

Layer 13: 1st Protective Layer	
Gelatin	0.8
UV-4	0.1
UV-5	0.15
Solv-1	0.2
Cpd-5	0.2
Cpd-6	0.2

Layer 14: 2nd Protective Layer	
Fine Grain Silver Bromide Emulsion (I = 2 mol, s/r = 0.2, 0.07 µm)	0.5
Gelatin	0.45
Polymethylmethacrylate Grain (diameter = 1.5 µm)	0.2
H-1	0.4
Cpd-3	0.5
Cpd-4	0.5

A sample 802 was prepared following the same procedures as for the sample 801 except that the coupler ExC-5 of the layer 3 was replaced with ExC-18 in an amount 0.5 times (number of mols) that of ExC-5, the coupler ExY-11 of the layers 6 and 7 was replaced with ExY-19 in an amount 3 times (number of mols) that of ExY-11, and the coupler ExY-13 of the layers 9, 11, and 12 was replaced with ExY-19 in an amount 3 times (number of mols) that of ExY-13.

Samples 803 and 804 were prepared following the same procedures as for the samples 801 and 802 except that the fine grain silver bromide emulsion in the layer 14 was replaced with the same silver amount of the silver chloride emulsion of Example 5.

These samples were left to stand at a temperature of 40° C and a relative humidity of 70% for 14 hours and subjected to exposure for sensitometry, and the following color development was performed. Densities of the treated samples were measured with red-, green-, and blue-filter.

Processing Method III

The color development process was performed at 38° C in accordance with the following process steps.

Color Development	3 min. 15 sec.
Bleaching	6 min. 30 sec.
Washing	2 min. 10 sec.
Fixing	4 min. 20 sec.
Washing	3 min. 15 sec.
Stabilization	1 min. 05 sec.

Compositions of the processing solutions used in the respective steps were as follows.

Color Developing Solution	
Diethylenetriaminepentaacetic Acid	1.0 g
1-hydroxyethylidene-1,1-diphosphonic Acid	2.0 g
Sodium Sulfite	4.0 g
Potassium Carbonate	30.0 g
Potassium Bromide	1.4 g
Potassium Iodide	1.3 mg
Hydroxyamine Sulfate	2.4 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g
Water to make	1.0 ℓ
pH	10.0

Bleaching Solution	
Ferric Ammonium Ethylenediaminetetraacetate	100.0 g
Disodium Ethylenediamineteraacetate	10.0 g
Ammonium Bromide	150.0 g
Ammonium Nitrate	10.0 g
Water to make	1.0 ℓ
pH	6.0

Fixing Solution	
Disodium Ethylenediaminetetraacetate	1.0 g
Sodium Sulfite	4.0 g
Ammonium Thiosulfate Aqueous Solution (70%)	175.0 g
Sodium Bisulfite	4.6 g
Water to make	1.0 ℓ
pH	6.6

Stabilizing Solution	
Formalin (40%)	2.0 mℓ
Polyoxyehtylene-p-monononylphenylether (average polymerization degree = 10)	0.3 g
Water to make	1.0 ℓ

These samples were left to stand at a temperature of 40 °C and a relative humidity of 70% for 14 hours and used to photograph a Macbeth chart under daylight tungsten light, and the above color development was performed.

The negative film photographing the Macbeth chart was manually printed on color paper (Fuji Color Paper AGL #653 to 258) on the basis of gray. 18 colors of the obtained print were represented by a U*V*W* color specification system. This will be described later. In order to represent how these points differ from original chromaticity points of the Macbeth chart, an average color difference $\Delta\overline{Euv}$ defined by the following equation was calculated:

$$\Delta\overline{Euv} = \frac{\sum_{i=1}^{n}}{n}[U^*_{pi}-U^*_{oi})^2 + (V^*_{pi}-V^*_{oi})^2 + (W^*_{pi}-W^*_{oi})^2]^{1/2}$$

where U^*_{pi}, V^*_{pi}, and W^*_{pi} are values of ith U*, V*, and W* of the Macbeth chart on the color print, respectively, and U^*_{pi}, V^*_{pi}, and W^*_{pi} are values of ith U*, V*, and W* of the original Macbeth chart, respectively.

In order to evaluate color reproduction of a silver halide light-sensitive material, a method of comparing colors of a color sample with those on color print paper obtained by photographing and printing the color sample is often adopted. A typical example of the color sample is a color checker available from Macbeth Co. of the U.S.A. An organoleptic test or instrumental measurement is performed to quantitatively evaluate, when white, gray, and black of the color checker are reproduced on color print paper, how correctly the remaining 18 color patches are reproduced on the color print paper. Various methods of quantitatively testing a color difference have been proposed by many researchers. For example, colors of a photographed sample in Yoshinobu Naya, "Industrial Chromatics", Asakura Shoten and a reproduced print are instrumentally measured under the same illumination condition, and values of color specification and color difference equations are calculated on the basis of an obtained tristimulus values.

In the present invention, the color reproduction was quantitatively tested on the basis of a color difference equation proposed in an article inserted by David Eastwood in the magazine "Farbe", Vol. 24, No. 1, from page 97.

Note that a gray gradation on the paper was almost r = 1.25.

The obtained photographic properties and the values of $\Delta\overline{Euv}$ are shown in Table 9 below. The photographic properties are represented by relative sensitivities of red-, green-, and blue-sensitive layers assuming that the sensitivity of the sample 801 is 100.

Table 9

Sample No.	Red-Sensitive Layer	Green-Sensitive Layer	Blue-Sensitive Layer	$\Delta\overline{Euv}$
801 (Comparative Example)	100	100	100	8.2
802 (Comparative Example)	89	90	92	15.2
803 (Preset Invention)	106	98	106	7.9
804 (Comparative Example)	92	90	95	15.5

Example 9

An amount of the compound V-12 used in the silver chloride fine grain emulsion of Example 5 was adjusted to 0 mol, 0.8 × 10^{-3} mol, 1.0 × 10^{-2} mol, and 1.5 × 10^{-2} mol per mol of $AgNO_3$, thereby preparing fine grain emulsions EM-1 to EM-4, respectively.

Samples 901 to 904 were prepared following the same procedures as for the sample 504 of Example 5 except that the above emulsions EM-1 to EM-4 were used in place of the fine grain emulsion of the sample 504.

The samples 503 and 901 to 904 were stored at a temperature of 40°C and a humidity of 70% for one day and then stored at a temperature of 45°C and a humidity of 80% for three days. The samples were exposed and processed following the same procedures as in Example 5 to obtain images, and the densities of the images were measured. Table 10 shows the fogging densities and the sensitivities based on a value obtained by processing a sample stored at a temperature of 40°C and a humidity of 70%. The measurement values are represented by those obtained from the blue-sensitive layer.

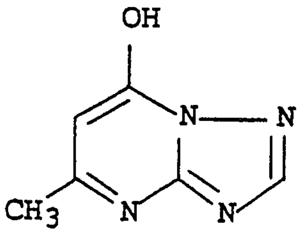
Table 10

Sample	Fogging Density	Sensitivity
503 (Comparative Example)	+0.03	-0.12
901 (Comparative Example)	+0.38	-0.15
902 (Present Invention)	+0.03	-0.02
903 (Present Invention)	+0.01	-0.03
904 (Present Invention)	-0.02	-0.08

As is apparent from Table 10, while the silver chloride fine grain emulsion not adsorbing a compound represented by general formula V easily causes an increase in fogging density or a decrease in sensitivity during its storage, the storage stability of the emulsion adsorbing a compound represented by formula V is significantly improved.

Table 11

II-1



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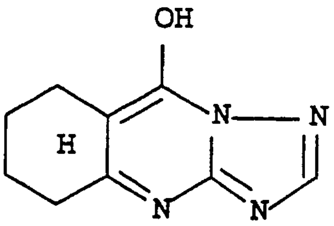

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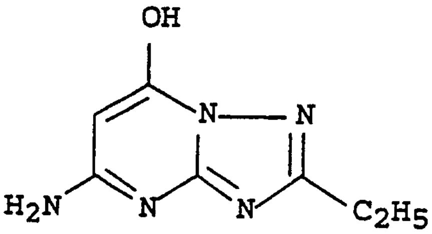

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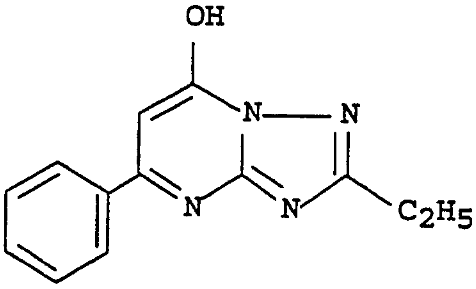

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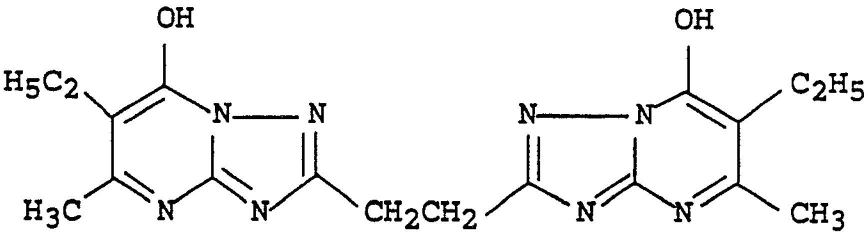

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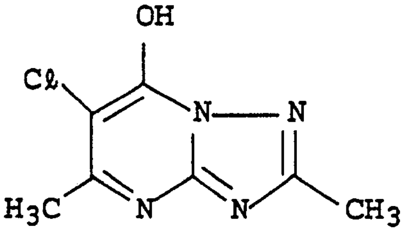

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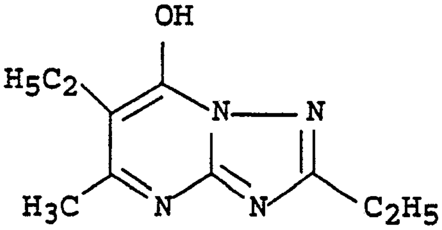

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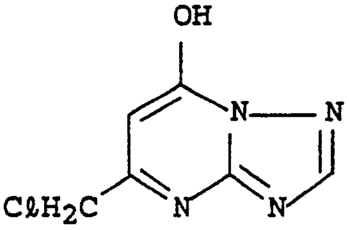

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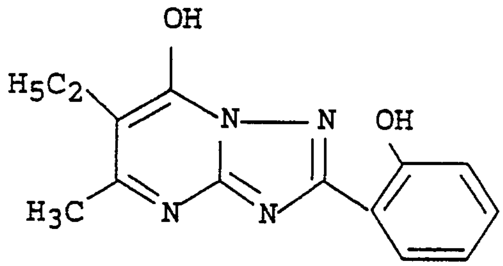

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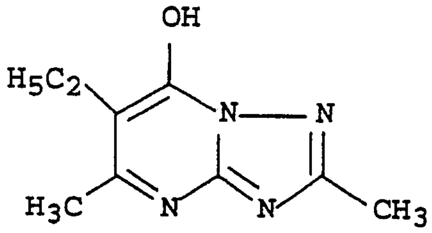

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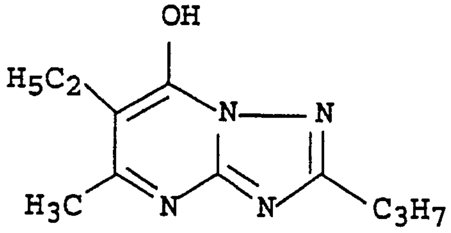

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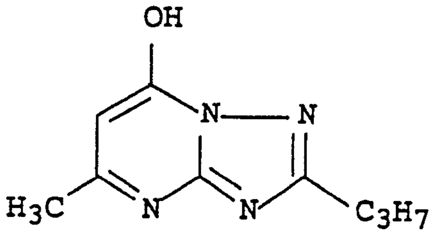

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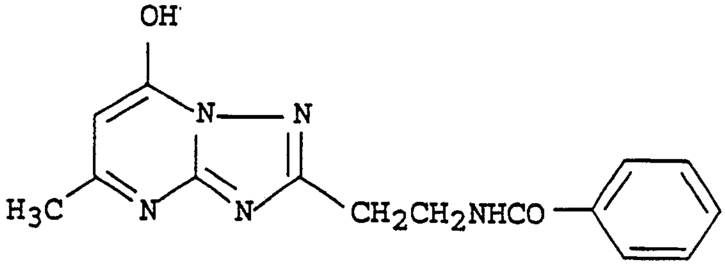

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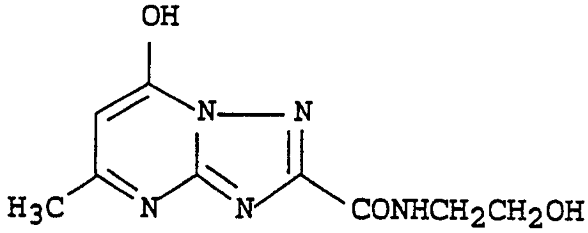

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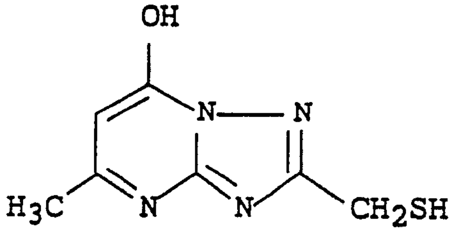

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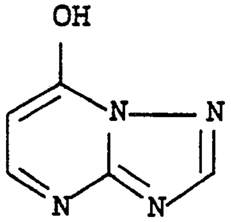
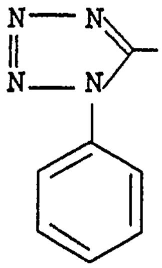


Table 12

III-1



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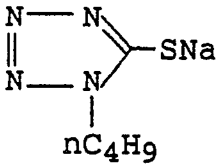

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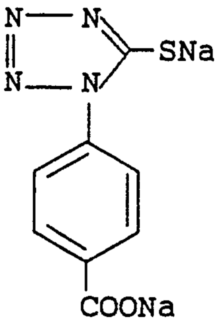

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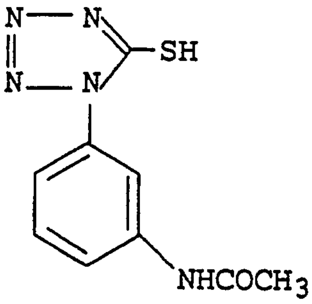

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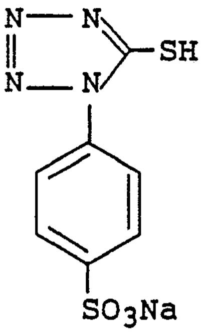

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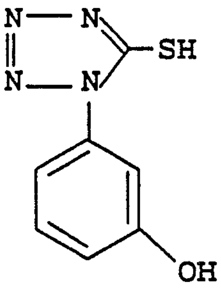

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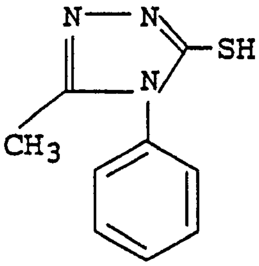

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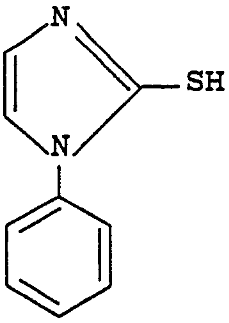

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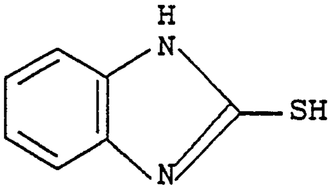

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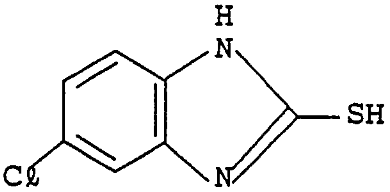

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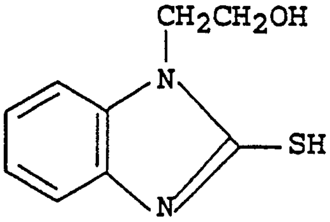

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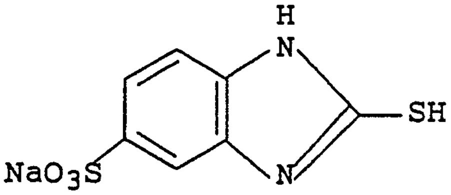

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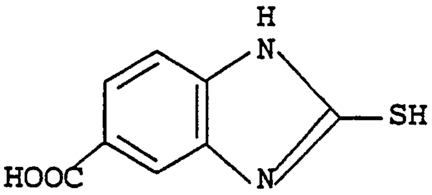

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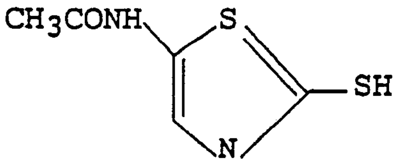

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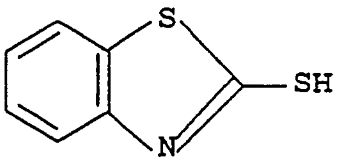

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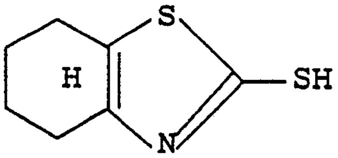

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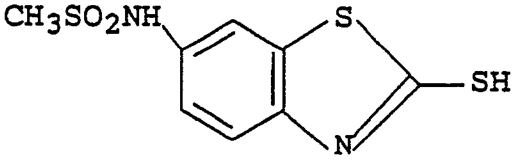

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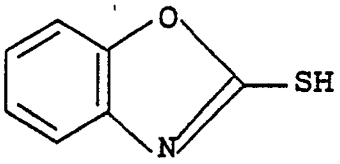

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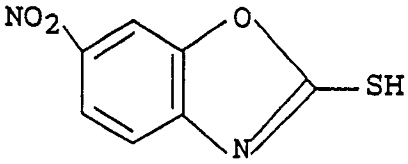

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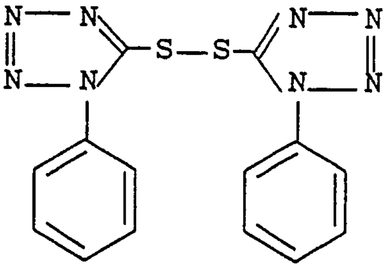

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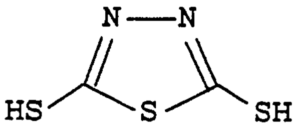

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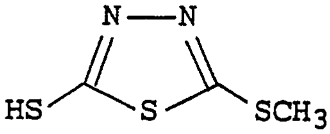

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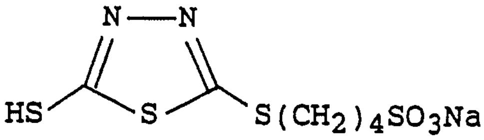

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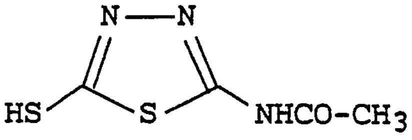

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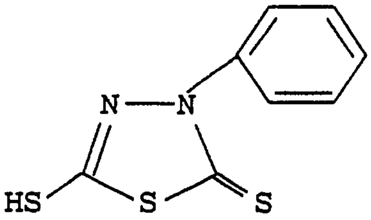

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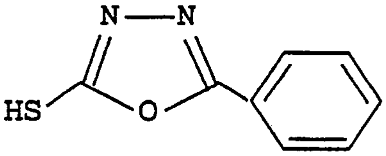

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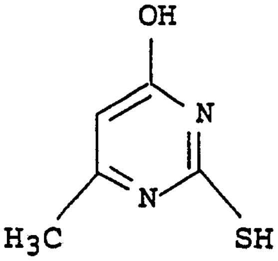

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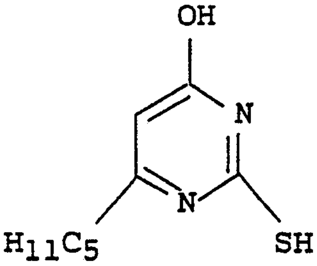

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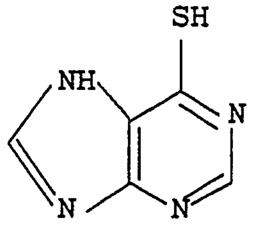

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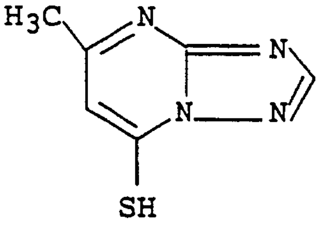

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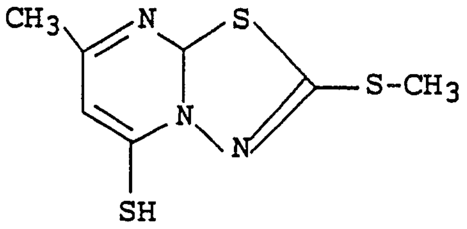

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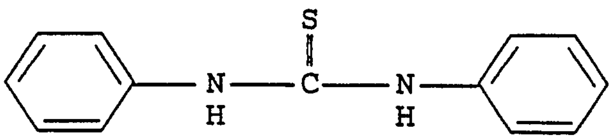

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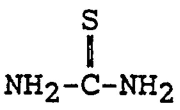
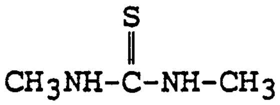


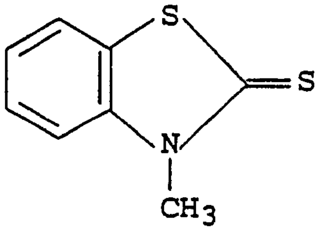
$$NH_2-\overset{S}{\overset{\|}{C}}-NH_2$$

III-34



$CH_3NH-\overset{\overset{S}{\|}}{C}-NH-CH_3$

IV-1



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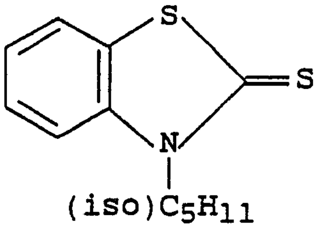

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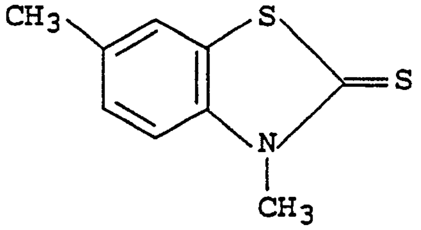

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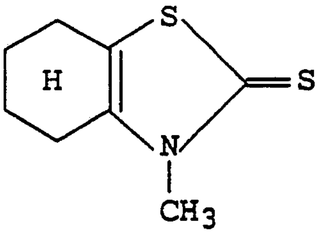

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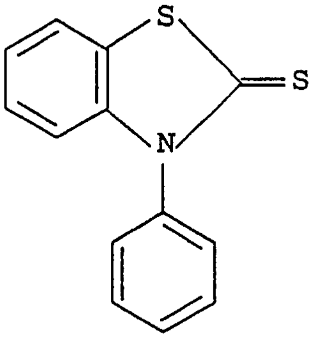

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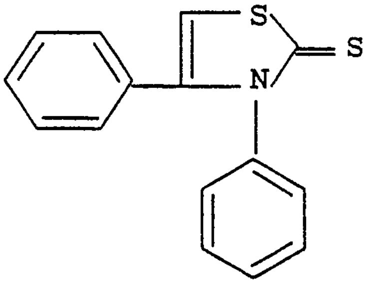

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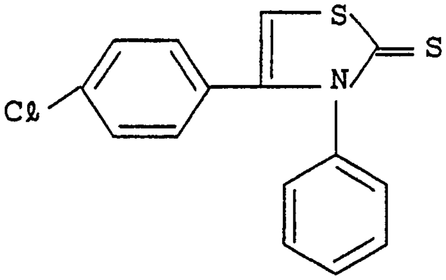

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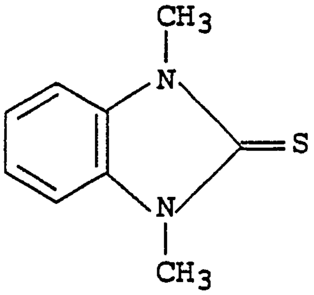

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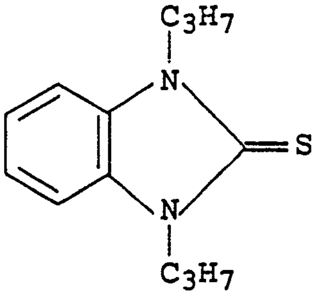
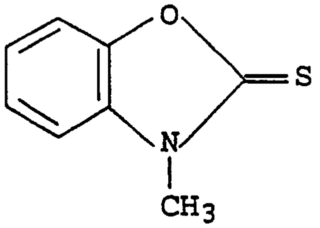


IV-10



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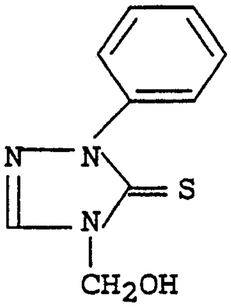

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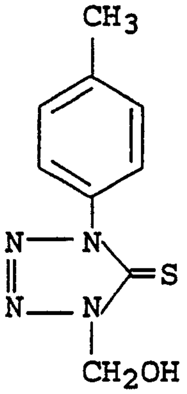

Table 13

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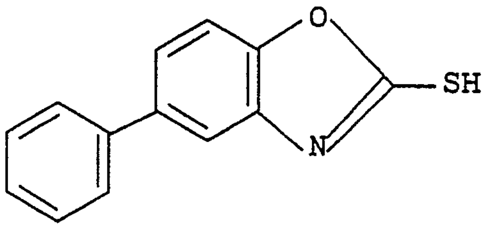

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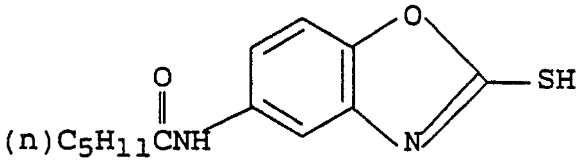

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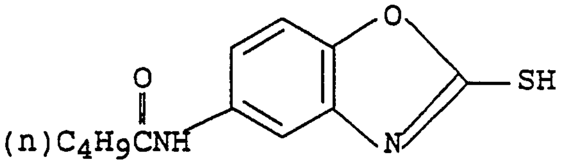

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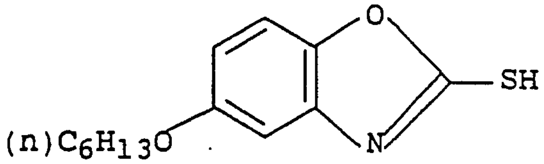

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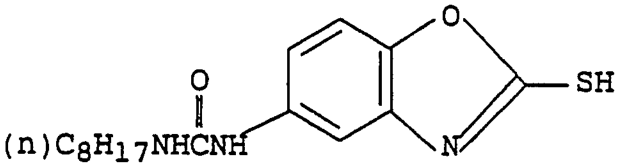

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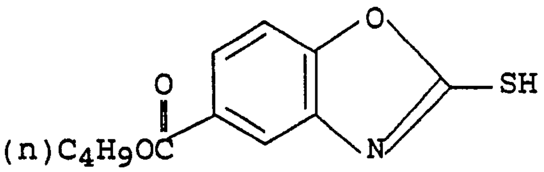

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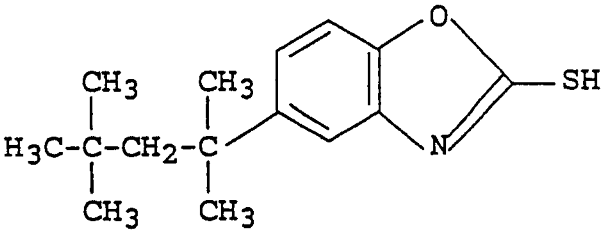

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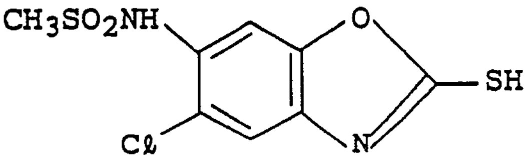

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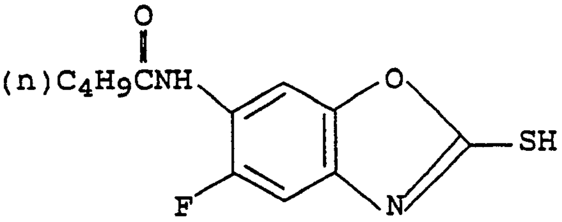

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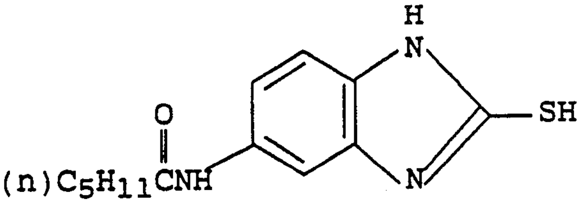

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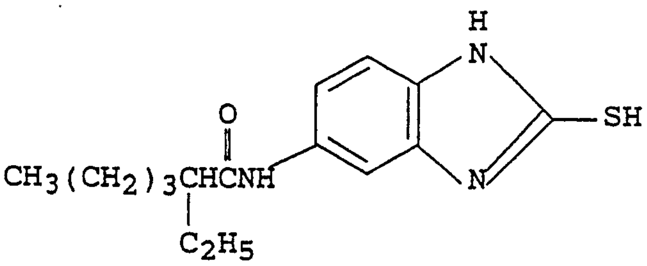

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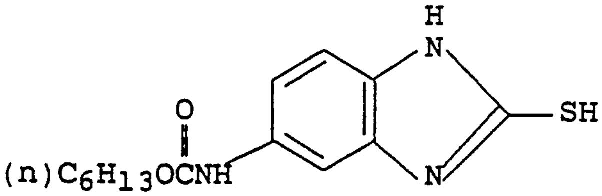

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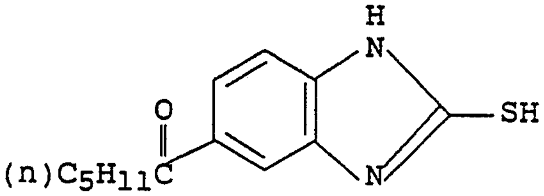

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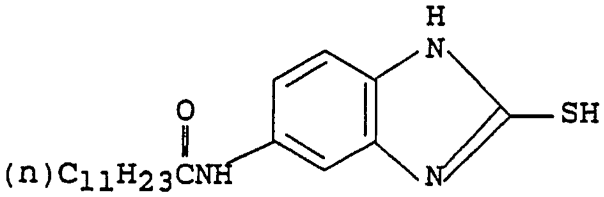

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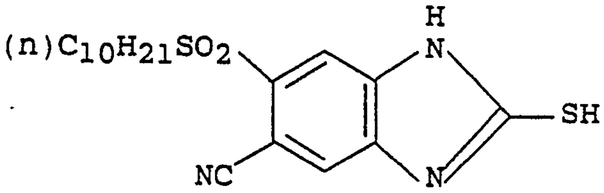

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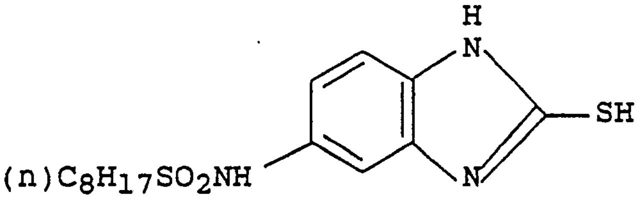

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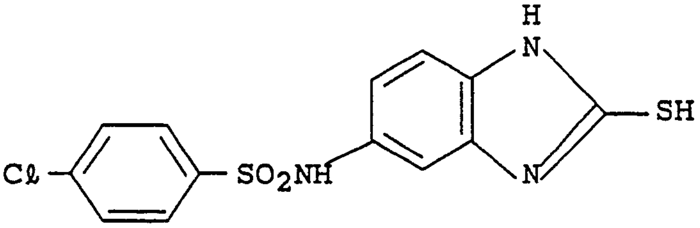

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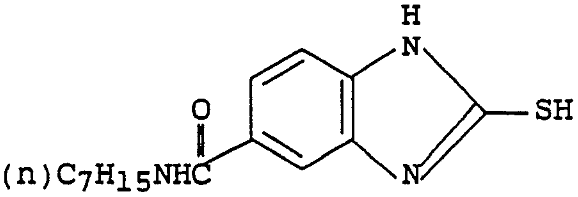

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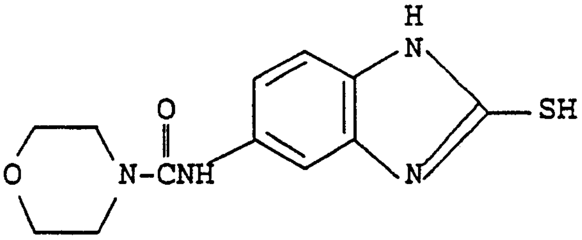

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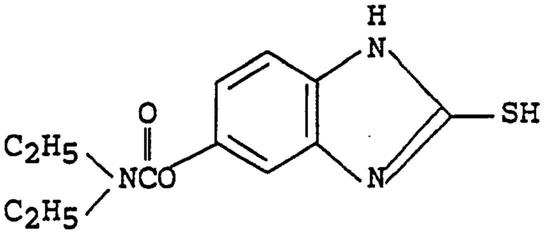

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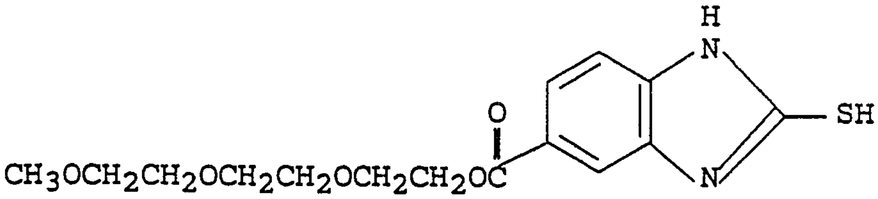

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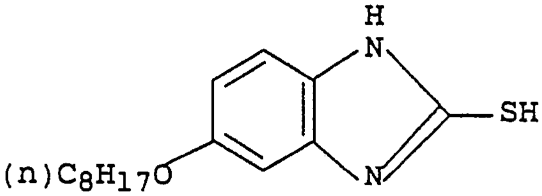

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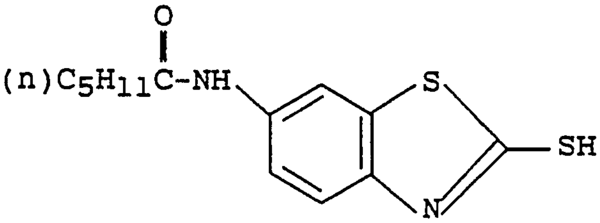

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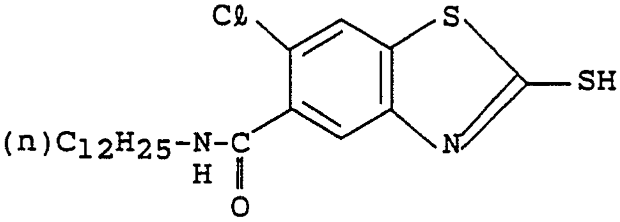

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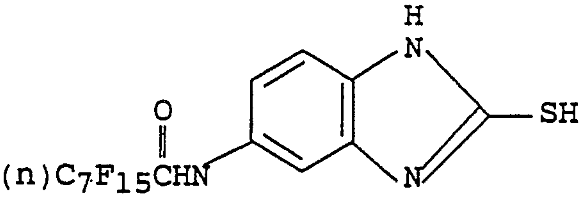

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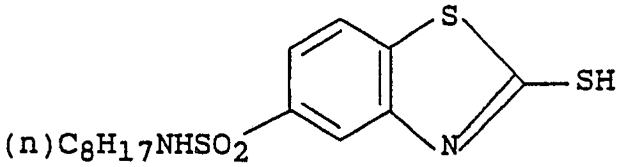

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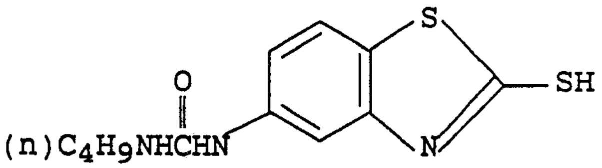

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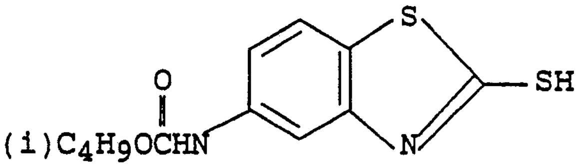

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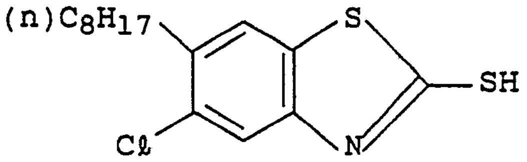

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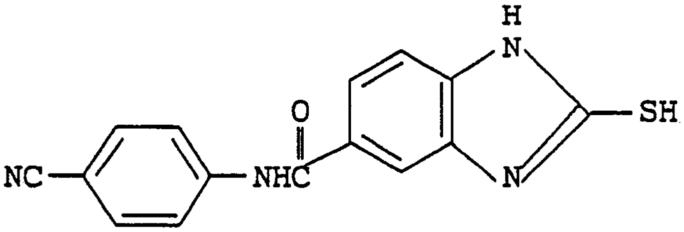

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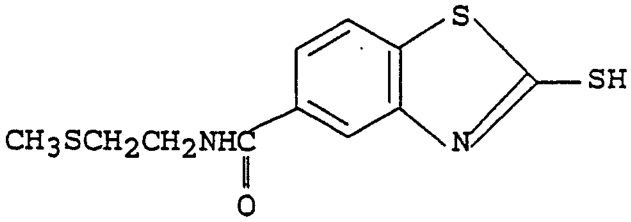

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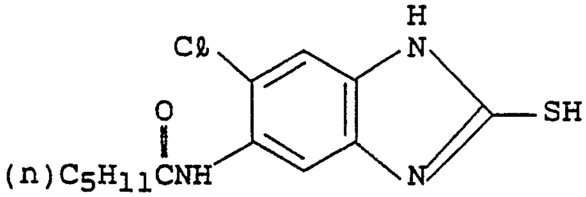

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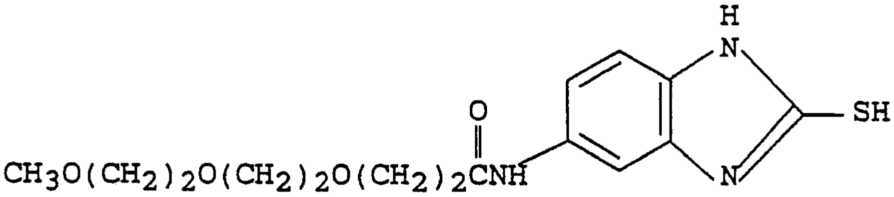

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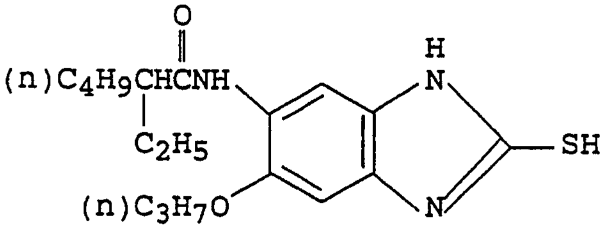

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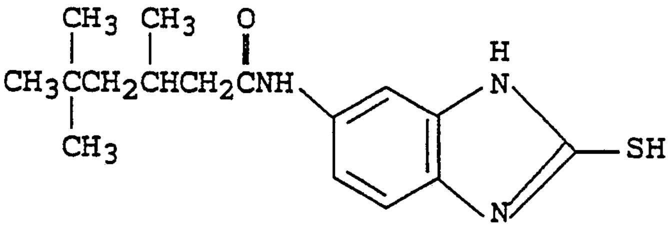

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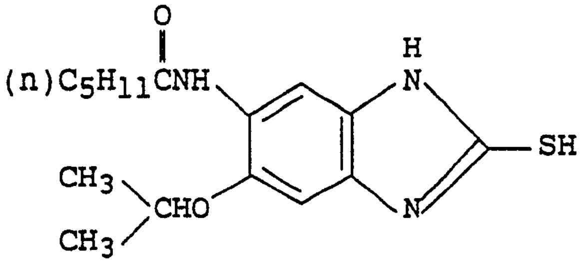

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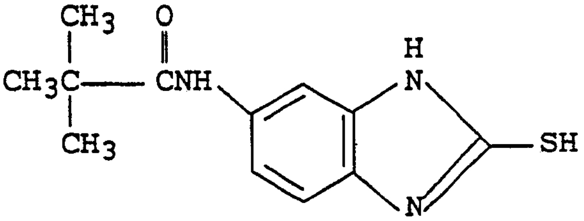

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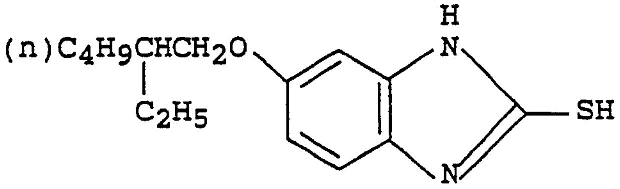

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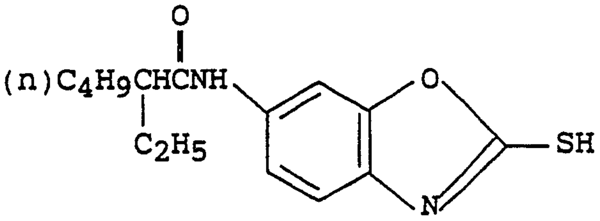

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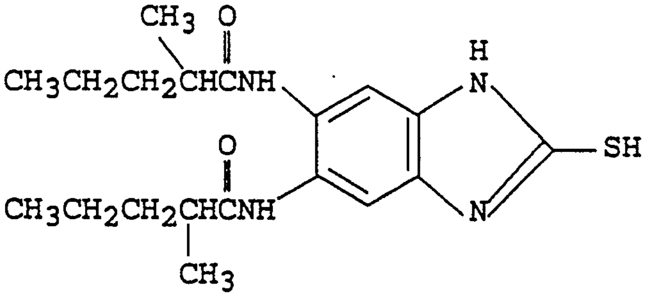

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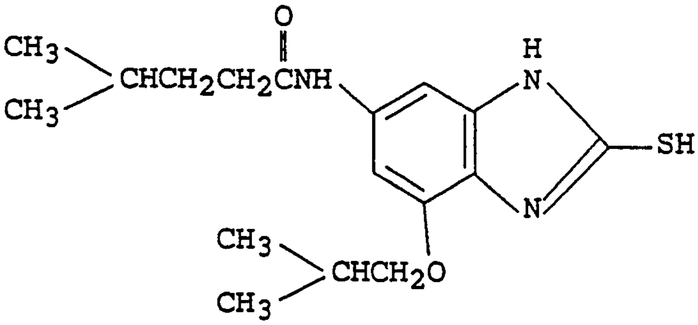

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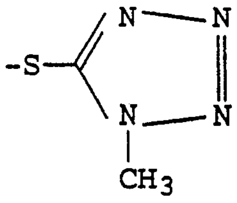

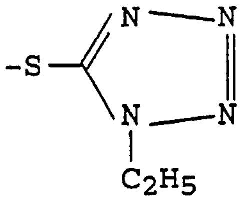

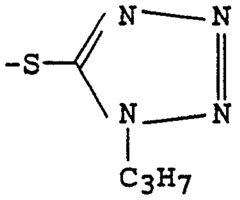

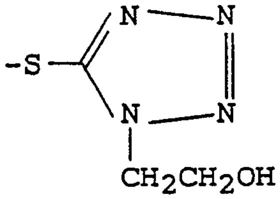

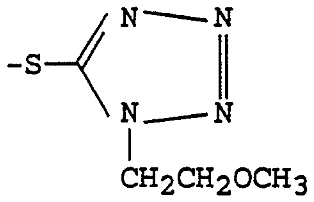

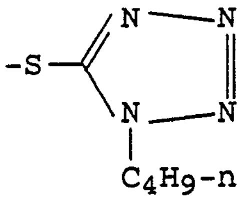

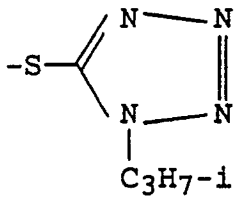

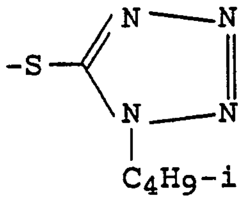

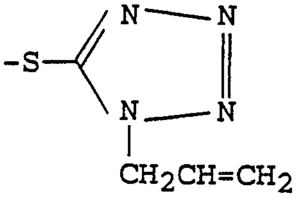
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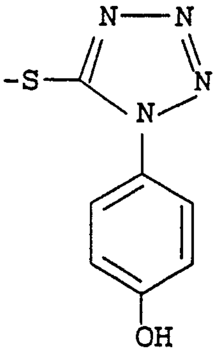
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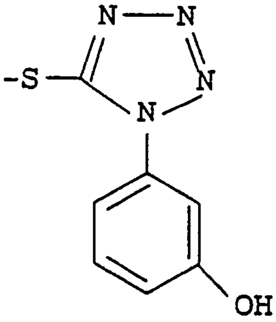
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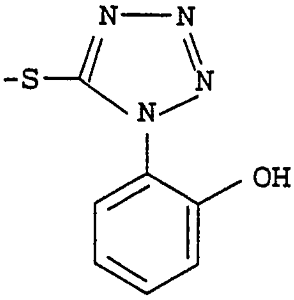
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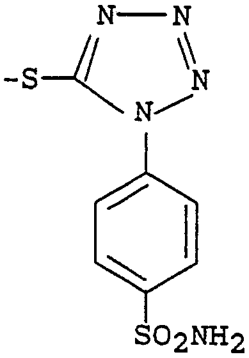
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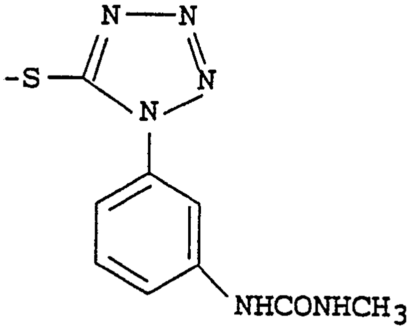
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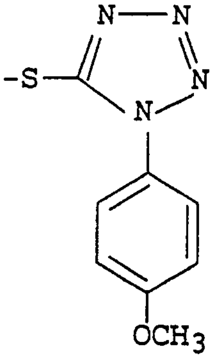
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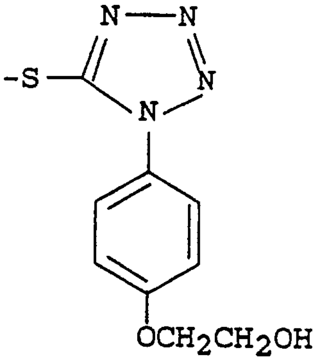
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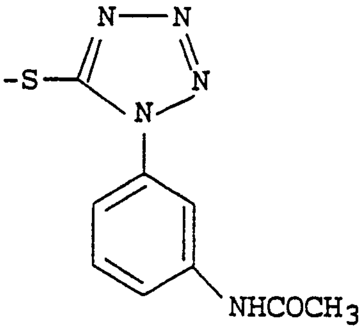
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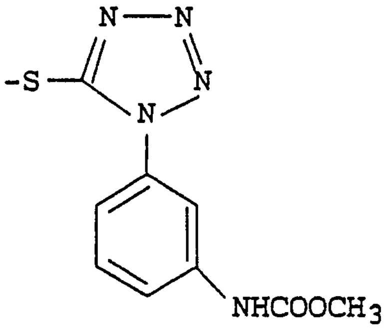
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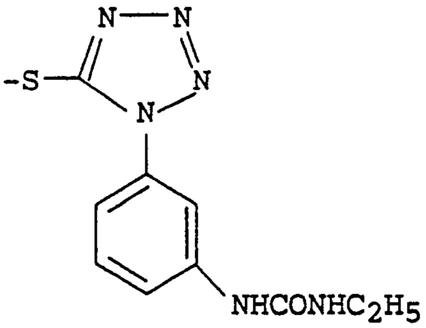
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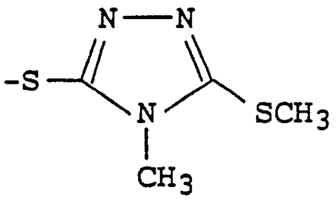
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SCH3
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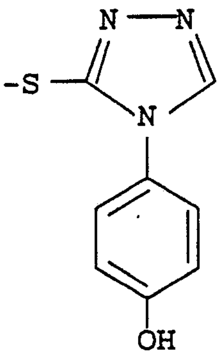
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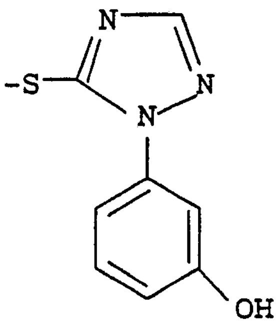
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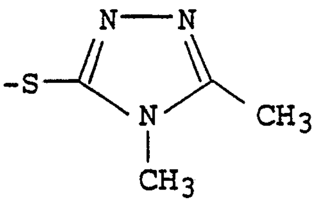
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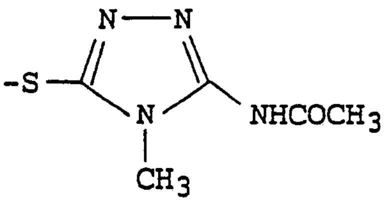
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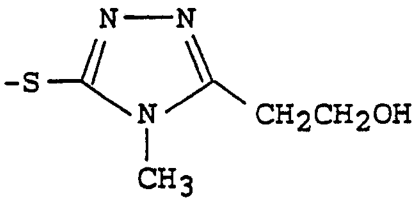
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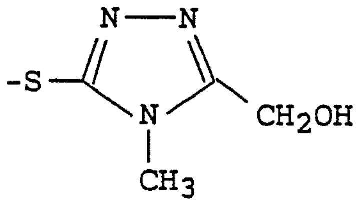
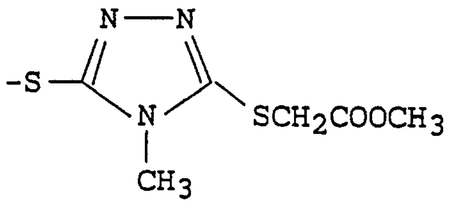
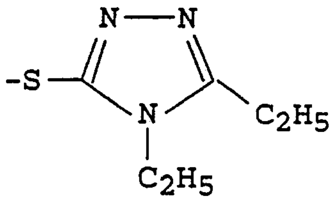
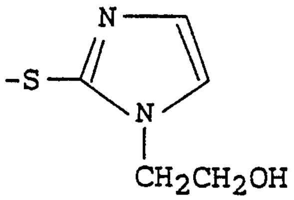
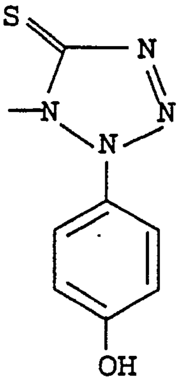
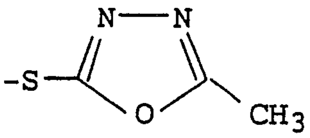


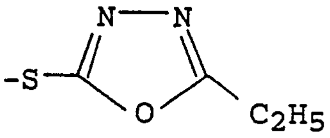


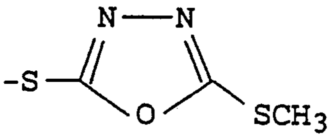


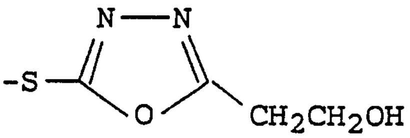


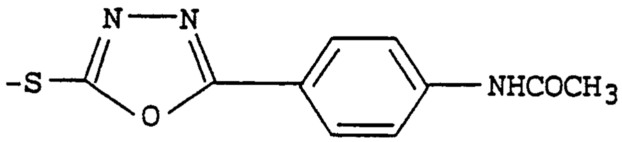


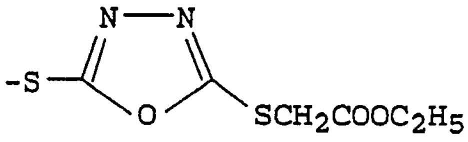


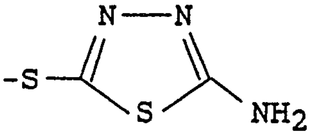


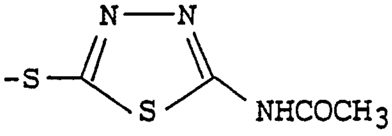


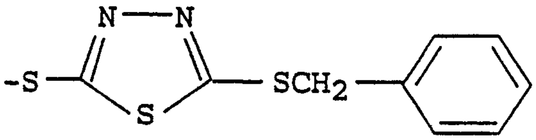


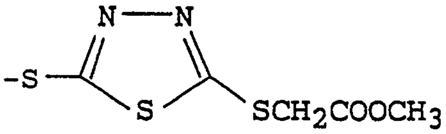


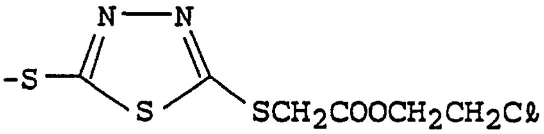


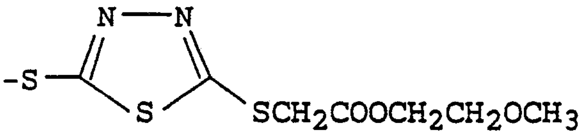


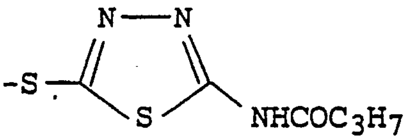


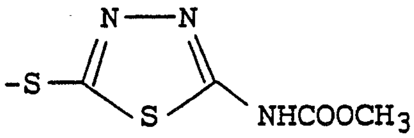


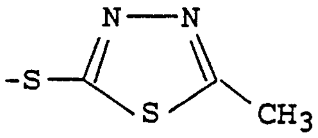


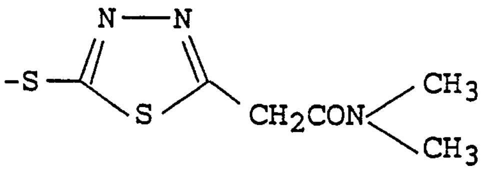


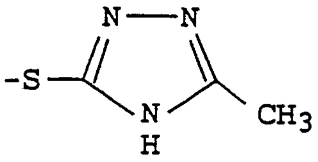


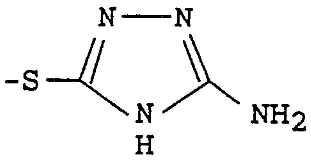


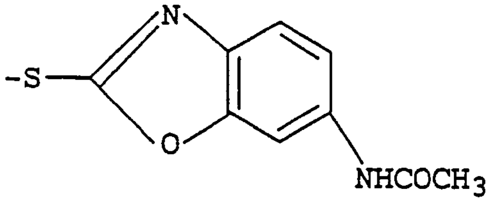


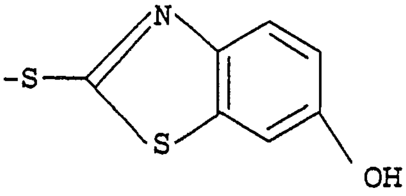

N
N
-S
S
CH3

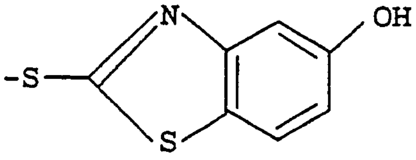

N
N
-S
S
CH2CON
CH3
CH3

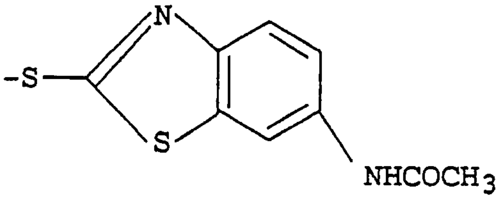

N
N
-S
N
H
CH3

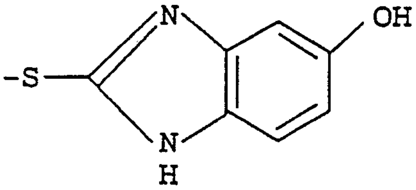

N
N
-S
N
H
NH2

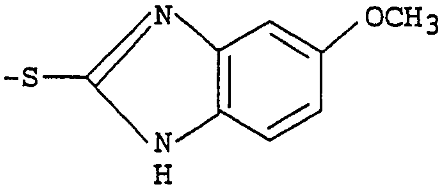

N
-S
O
NHCOCH3

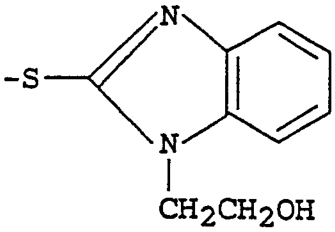

N
-S
S
OH

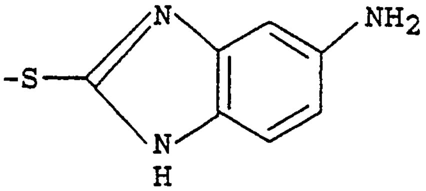

N
OH
-S
S

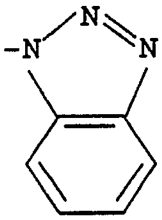

N
-S
S
NHCOCH3

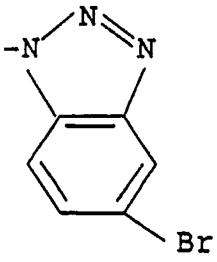

N
OH
-S
N
H

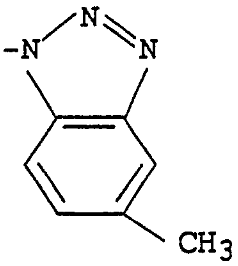

N
OCH3
-S
N
H

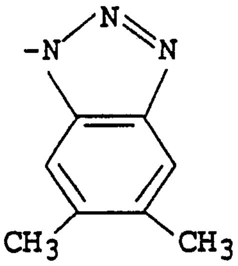

N
-S
N
CH2CH2OH

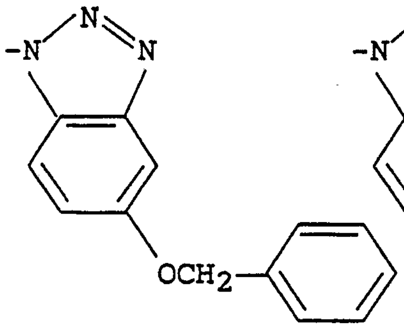

N
NH2
-S
N
H

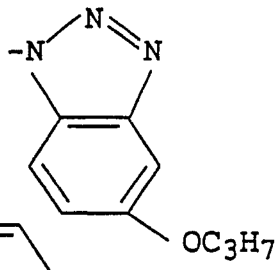


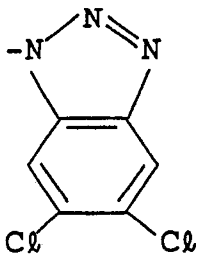


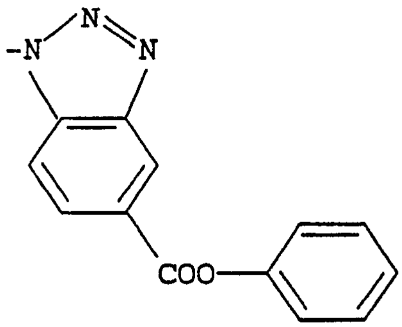


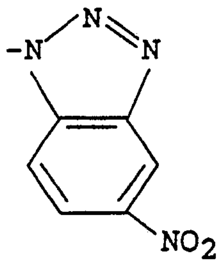


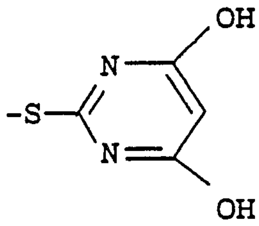


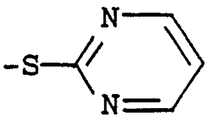


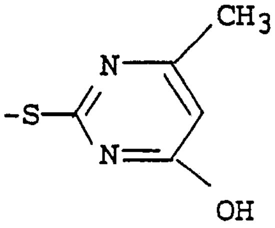


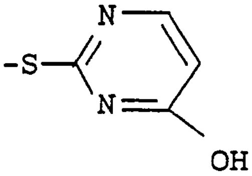


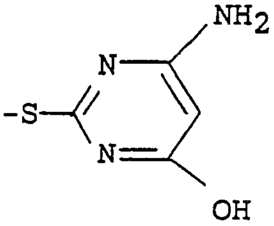


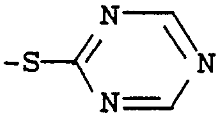


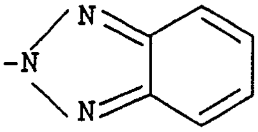












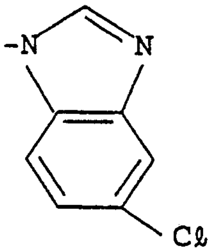
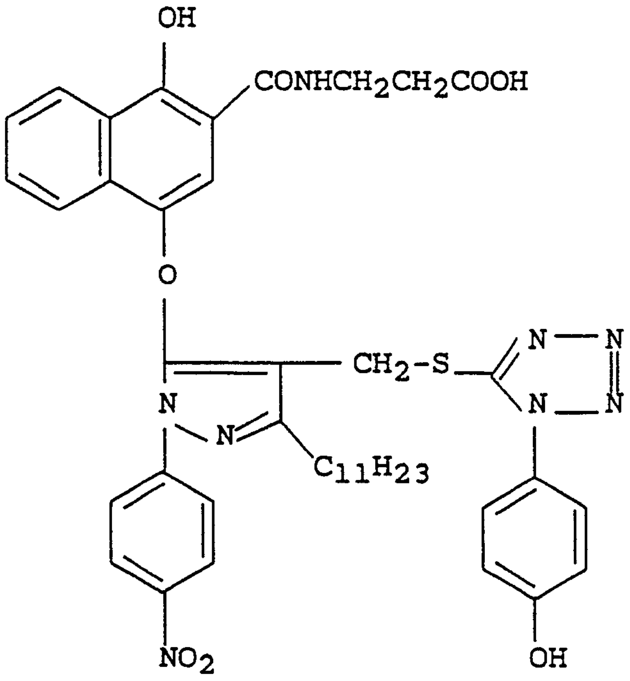
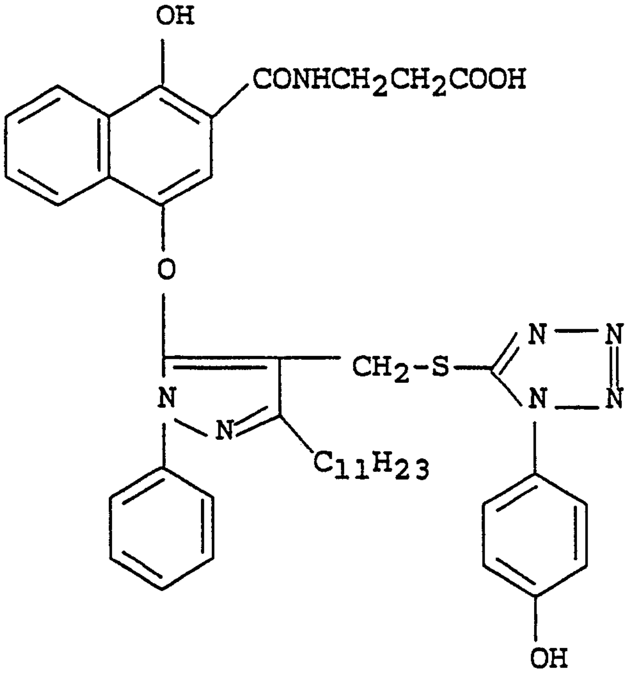


Table 15

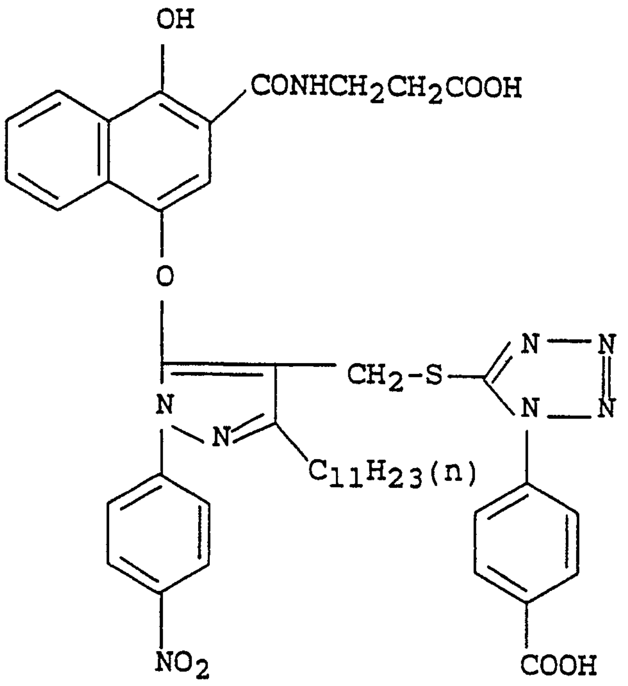
(D-1)



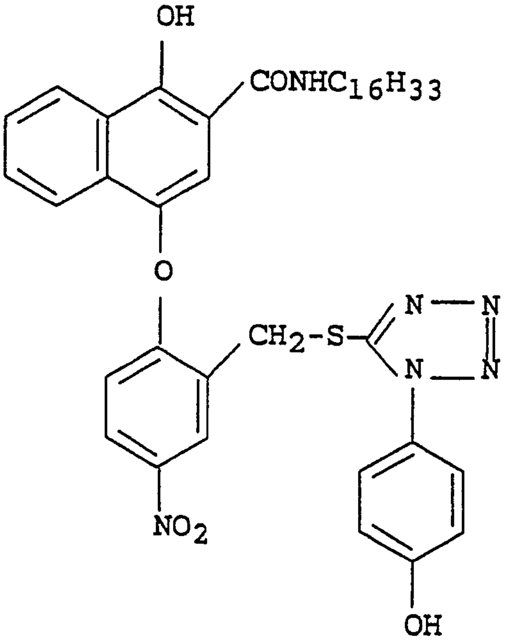
(D-2)



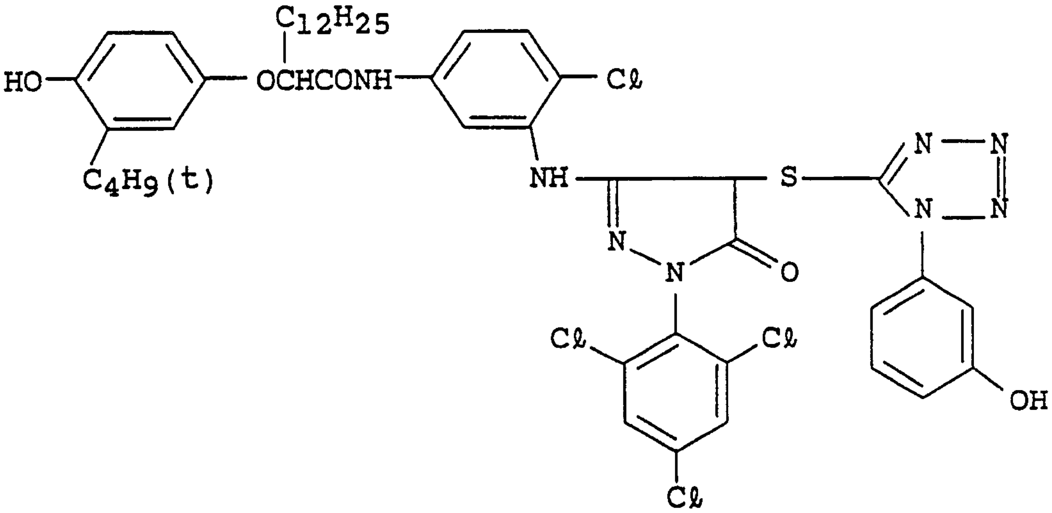
(D-3)


OH
CONHCH2CH2COOH
O
N
N
CH2-S
N
N
N
N
C11H23(n)
NO2
COOH

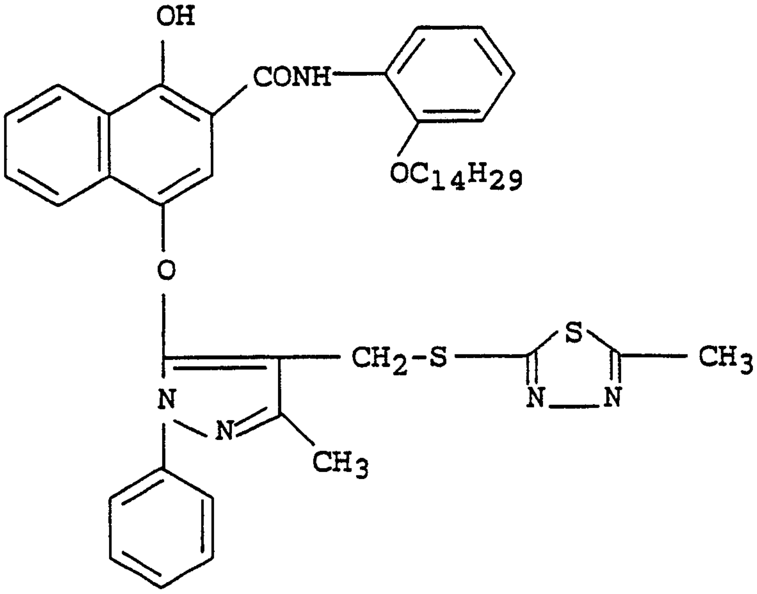
(D-4)


OH
CONHC16H33
O
CH2-S
N
N
N
N
NO2
OH

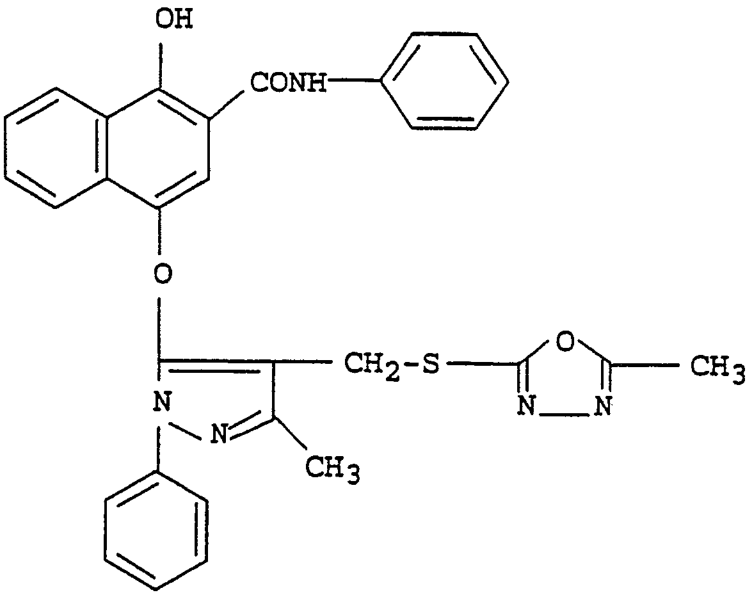
(D-5)



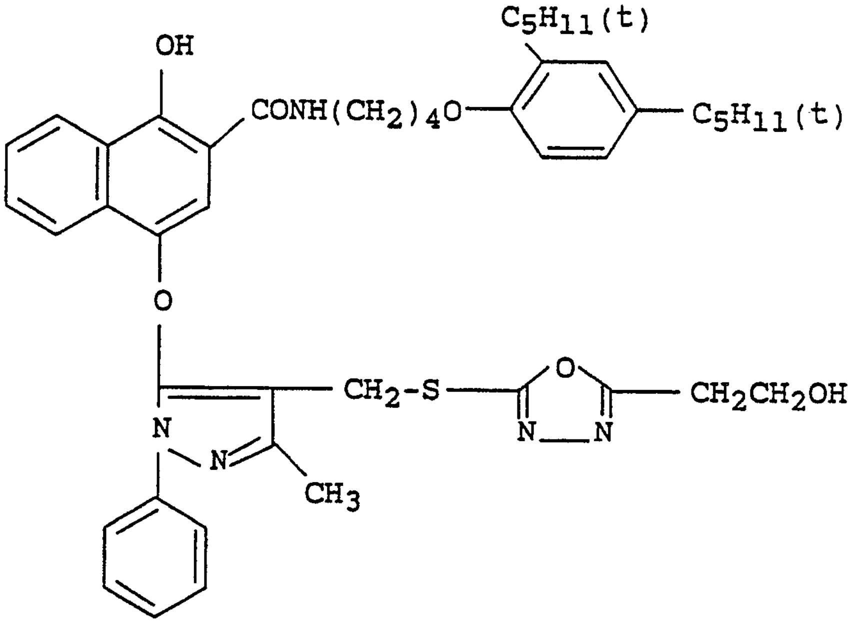
(D-6)



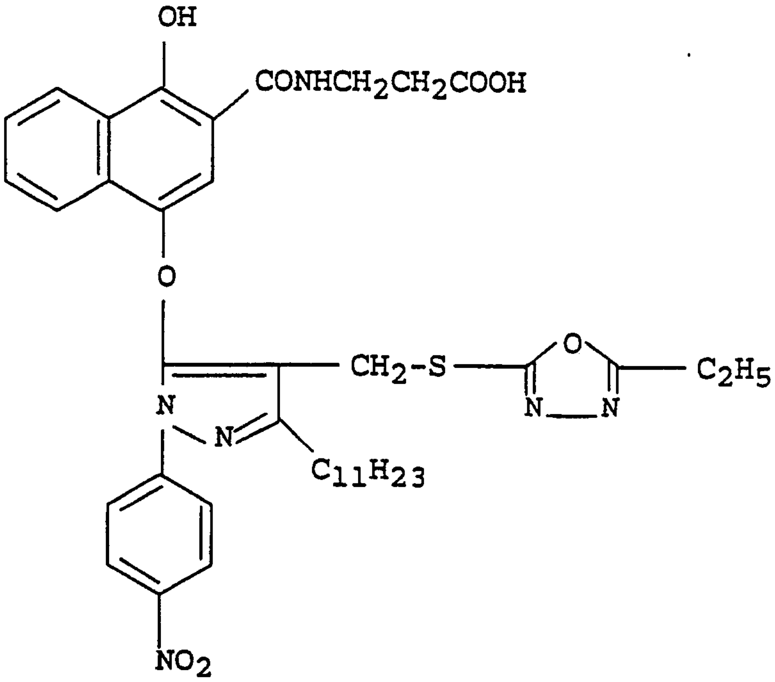
(D-7)



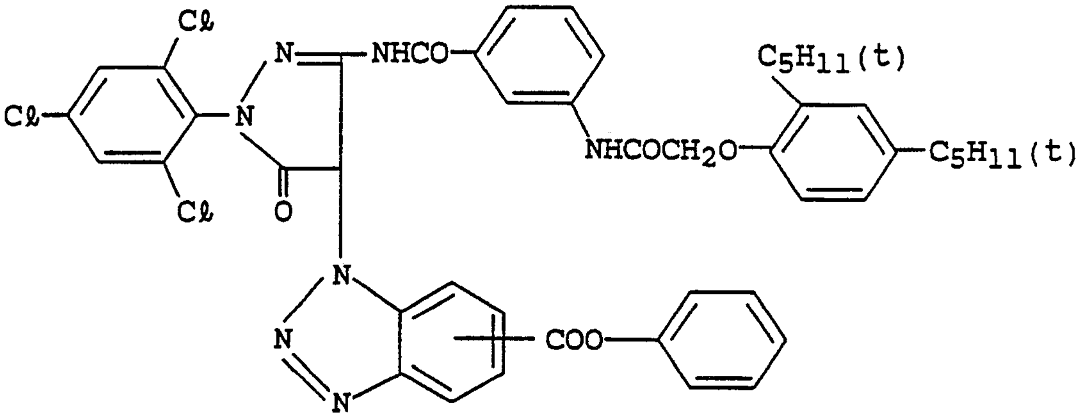
(D-8)



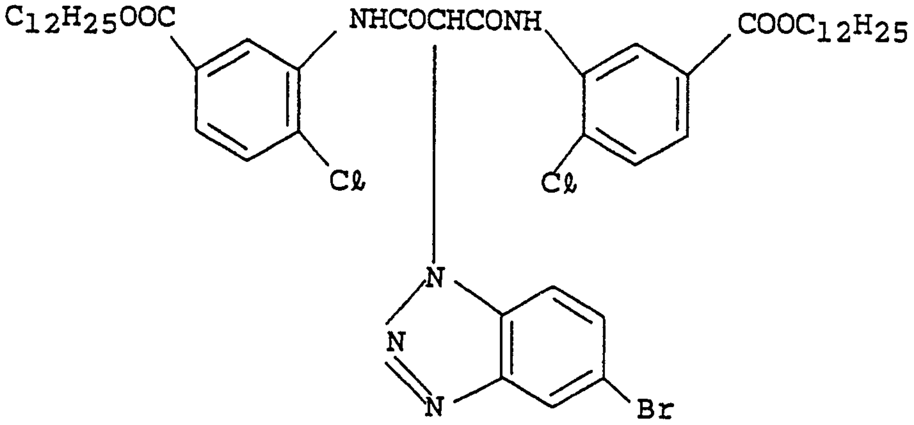
(D-9)


OH
CONHCH2CH2COOH
O
CH2-S
O
N
N
C2H5
N
N
C11H23
NO2

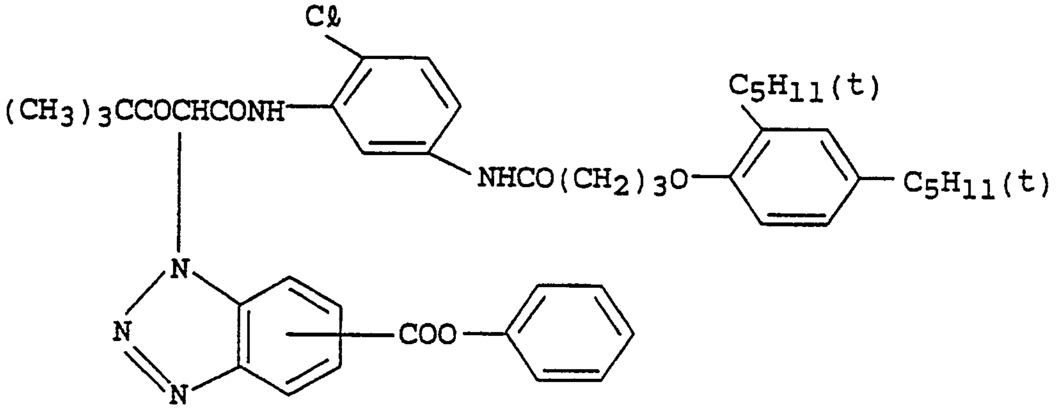
(D-10)


Cℓ
Cℓ
Cℓ
N
N
NHCO
O
C5H11(t)
NHCOCH2O
C5H11(t)
N
N
N
COO

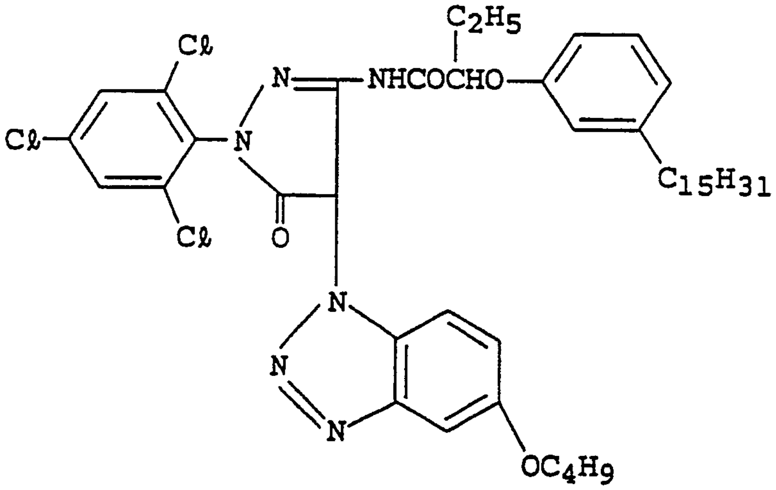
(D-11)


C12H25OOC
NHCOCHCONH
COOC12H25
Cl
Cl
N
N
N
Br

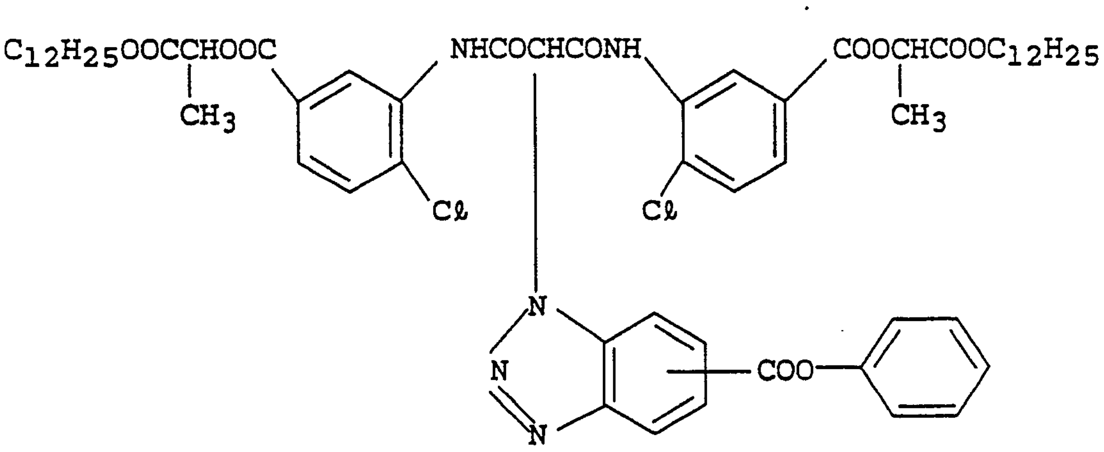
(D-12)


Cl
(CH3)3CCOCHCONH
C5H11(t)
NHCO(CH2)3O
C5H11(t)
N
N
N
COO

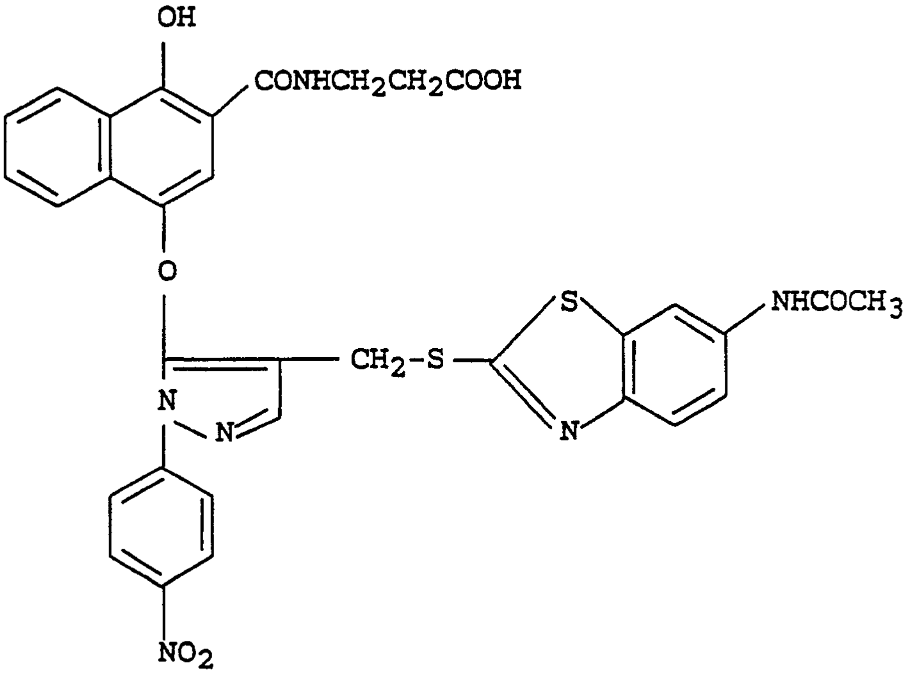
(D-13)


C2H5
Cl
N
NHCOCHO
Cl
N
C15H31
Cl
O
N
N
N
OC4H9

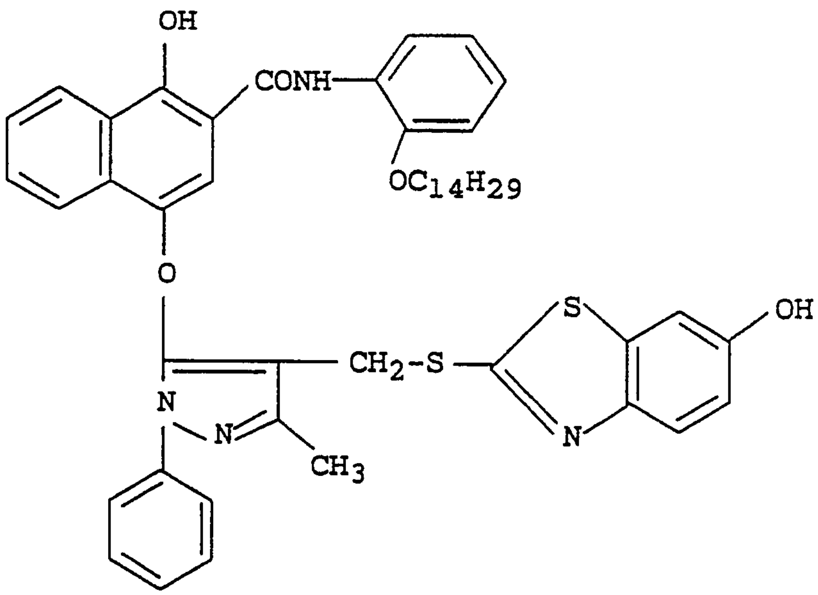
(D-14)


C12H25OOCCHOOC
CH3
NHCOCHCONH
COOCHCOOC12H25
CH3
Cℓ
Cℓ
N
N
N
COO

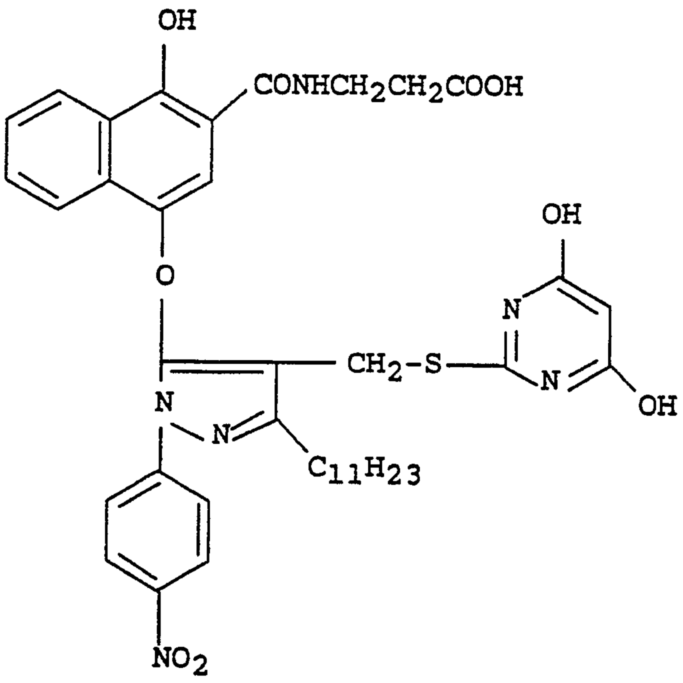
(D-15)


OH
CONHCH2CH2COOH
O
N
N
CH2-S
S
N
NHCOCH3
NO2

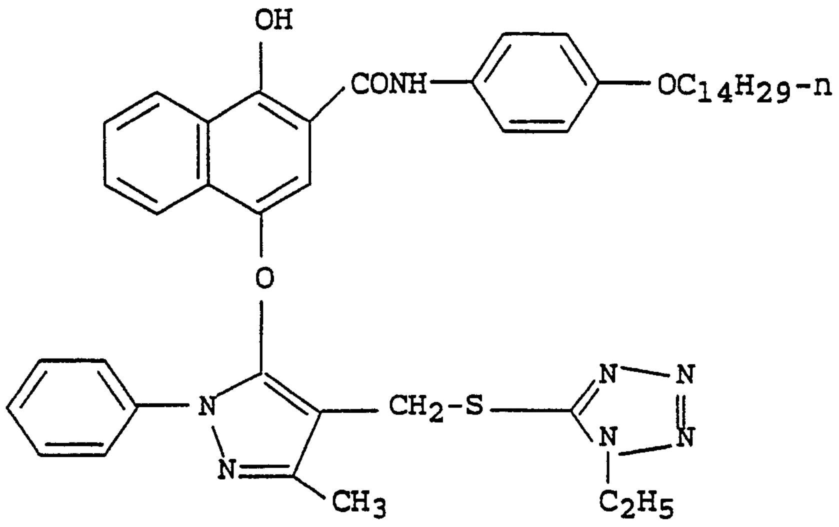
(D-16)


OH
CONH
$OC_{14}H_{29}$
O
S
OH
CH_2-S
N
N
N
CH_3

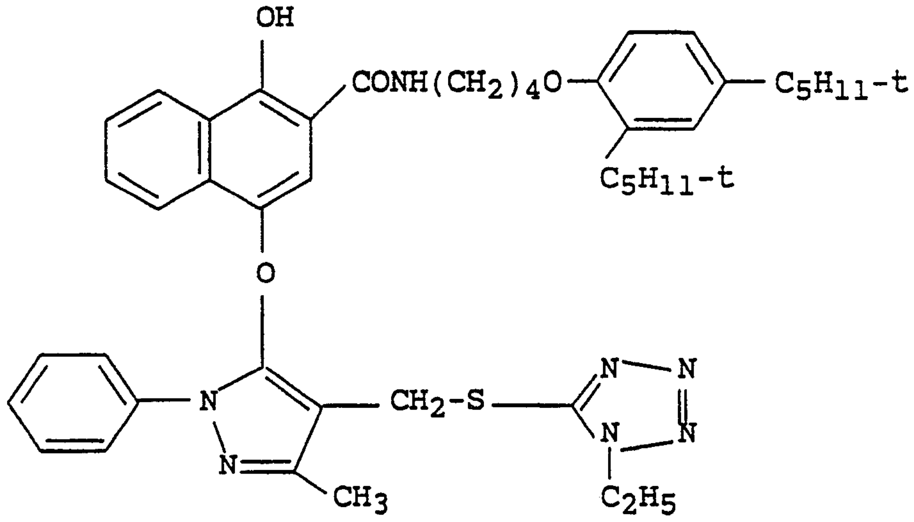
(D-17)


OH
$CONHCH_2CH_2COOH$
OH
O
N
CH_2-S
N
OH
N
N
$C_{11}H_{23}$
NO_2

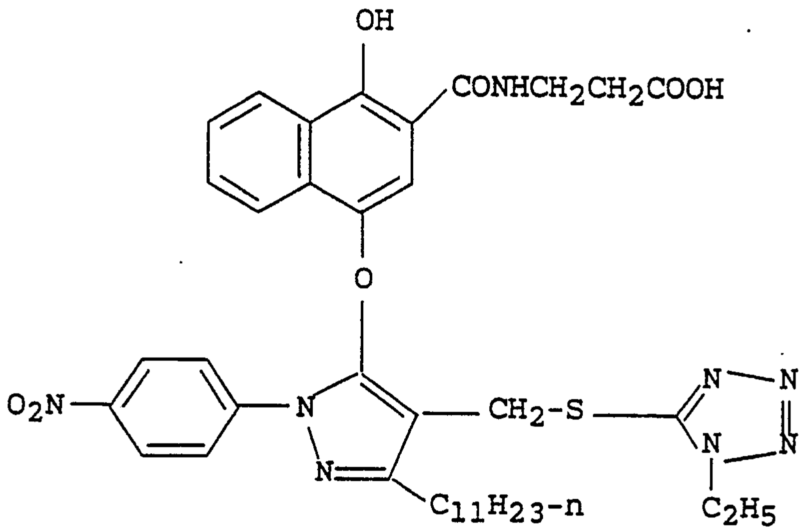
(D-18)


OH
CONH
OC14H29-n
O
N
N
CH3
CH2-S
N
N
N
N
C2H5

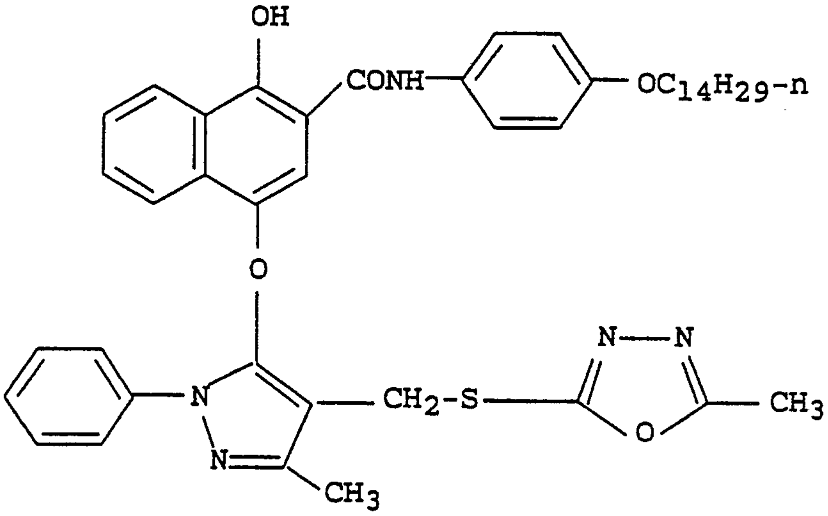
(D-19)


OH
CONH(CH2)4O
C5H11-t
C5H11-t
O
N
N
CH3
CH2-S
N
N
N
N
C2H5

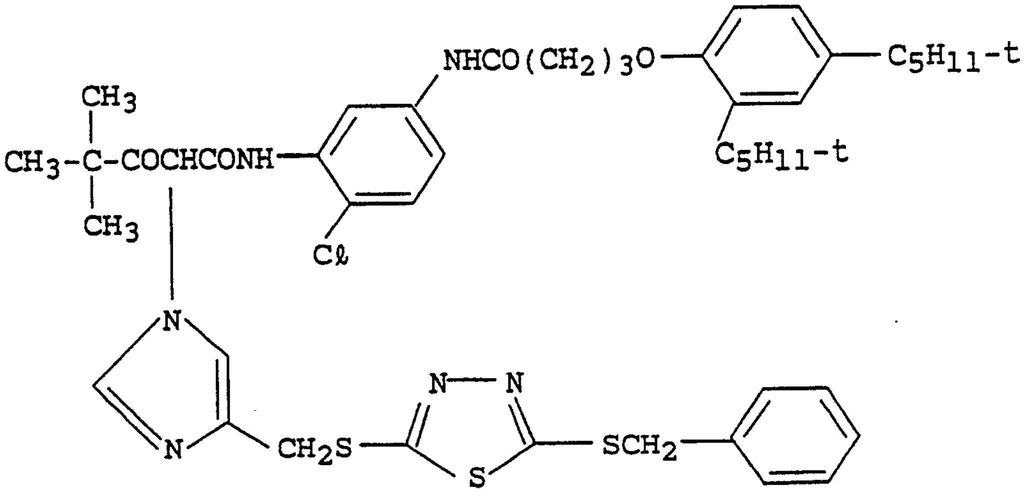
(D-20)


OH
CONHCH2CH2COOH
O
O2N
N
N
CH2-S
N
N
N
N
C11H23-n
C2H5

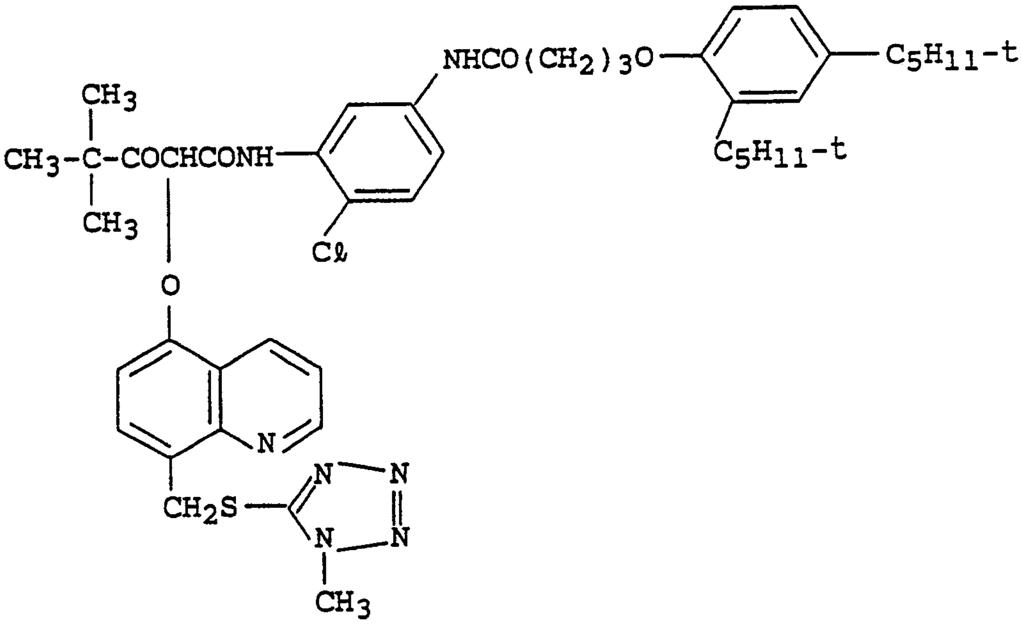
(D-21)


OH
CONH
OC14H29-n
O
N
N
CH2-S
N
N
O
CH3
CH3

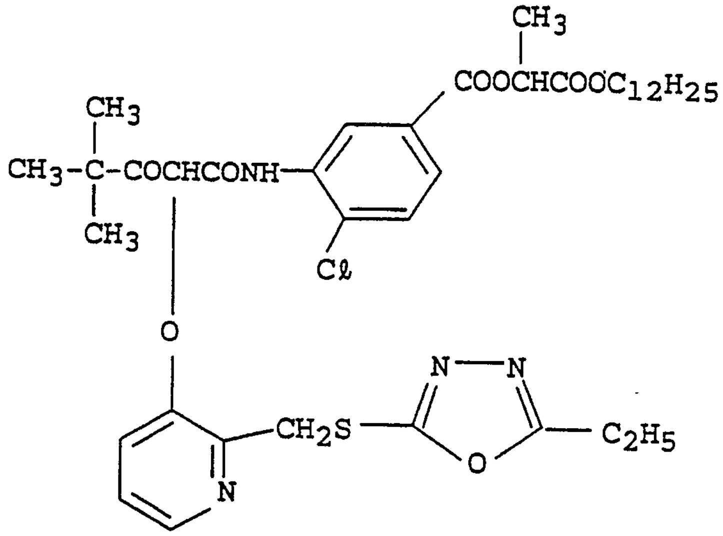
(D-22)



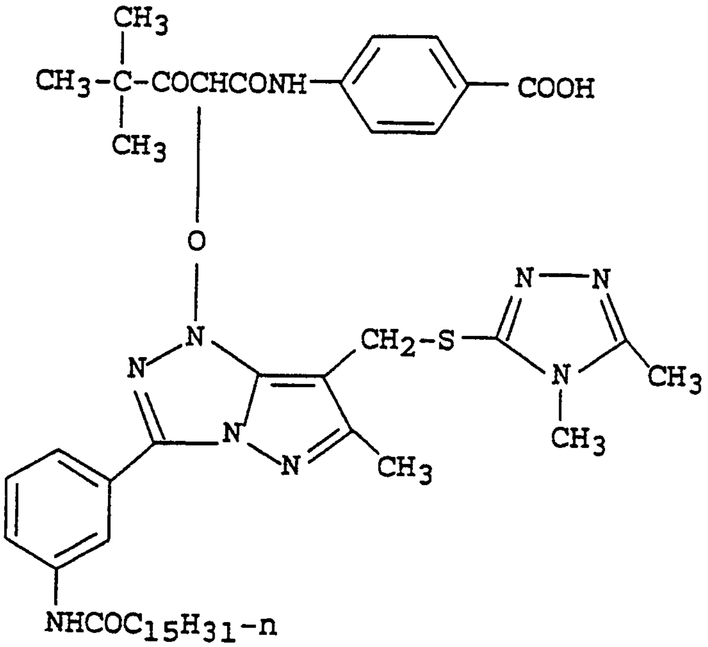
(D-23)



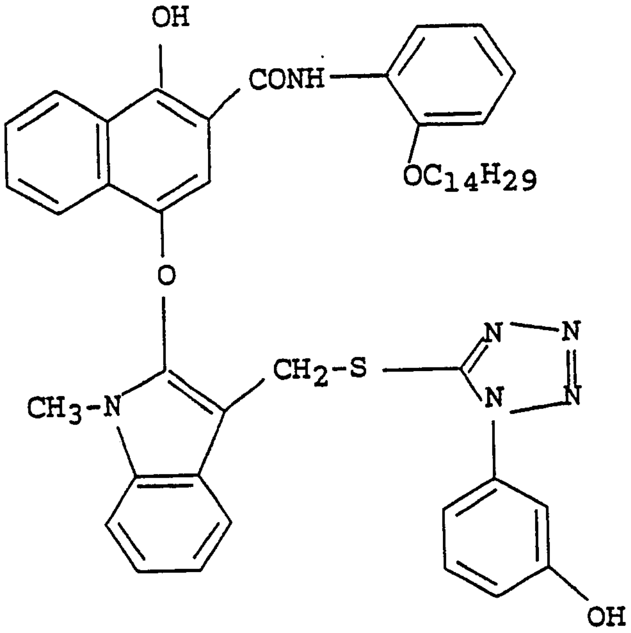
(D-24)



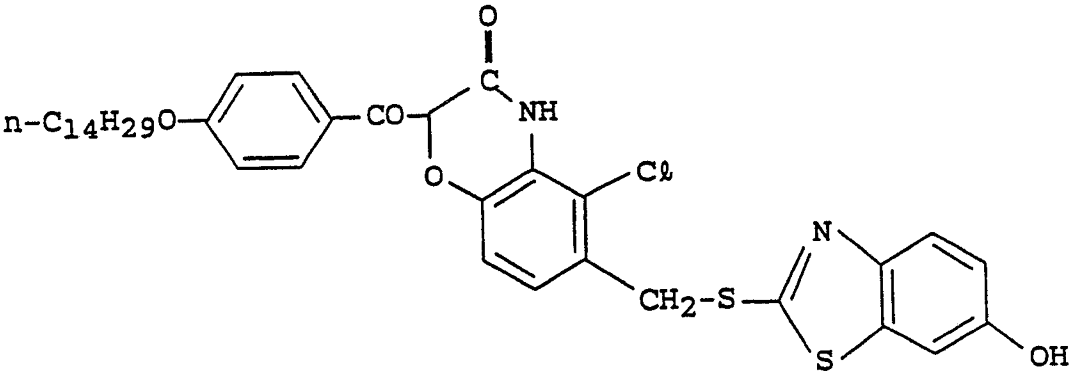
(D-25)



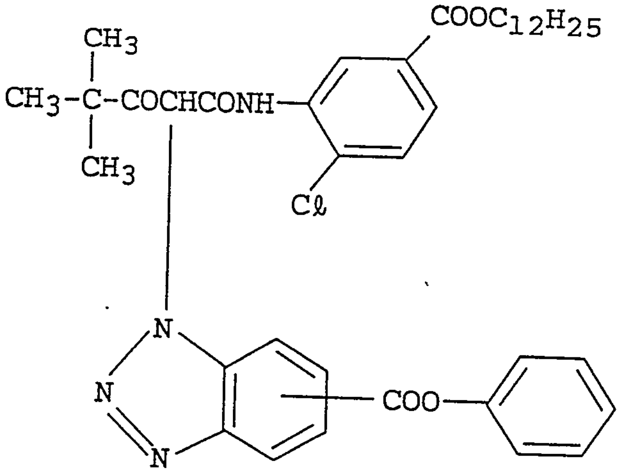
(D-26)


OH
CONH
$OC_{14}H_{29}$
O
CH_2-S
N
N
N
N
CH_3-N
OH

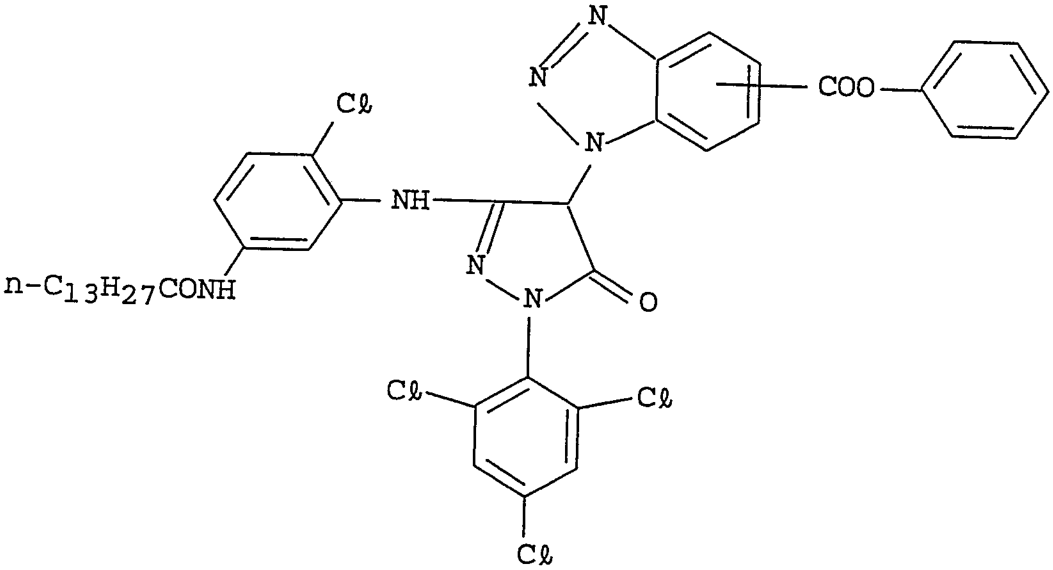
(D-27)


O
C
NH
n-$C_{14}H_{29}$O
CO
O
Cℓ
N
CH_2-S
S
OH

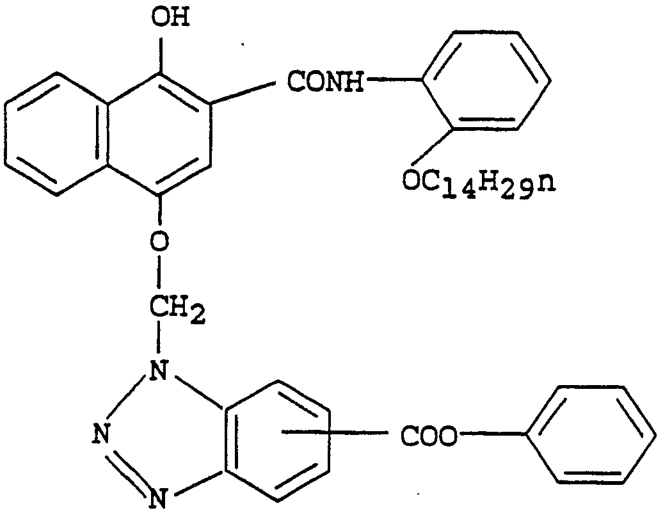
(D-28)


COOC12H25
CH3
CH3-C-COCHCONH
CH3
Cℓ
N
N
N
COO

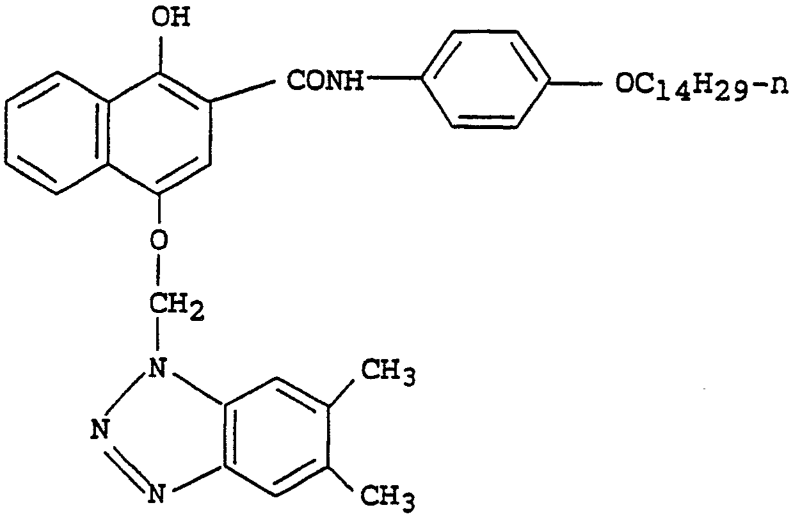
(D-29)


N
N
N
COO
Cℓ
NH
N
N
O
n-C13H27CONH
Cℓ
Cℓ
Cℓ

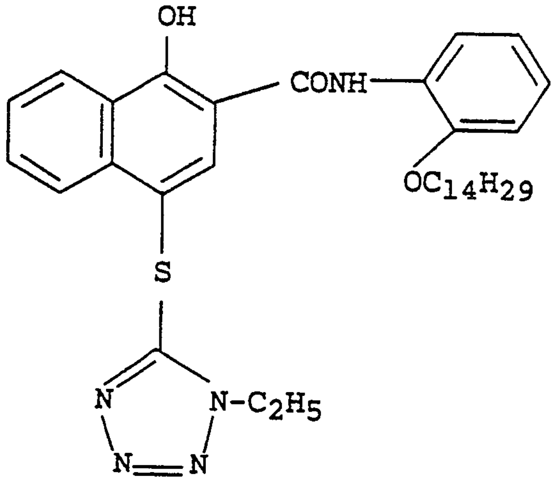
(D-30)


OH
CONH
OC14H29n
O
CH2
N
N
N
COO

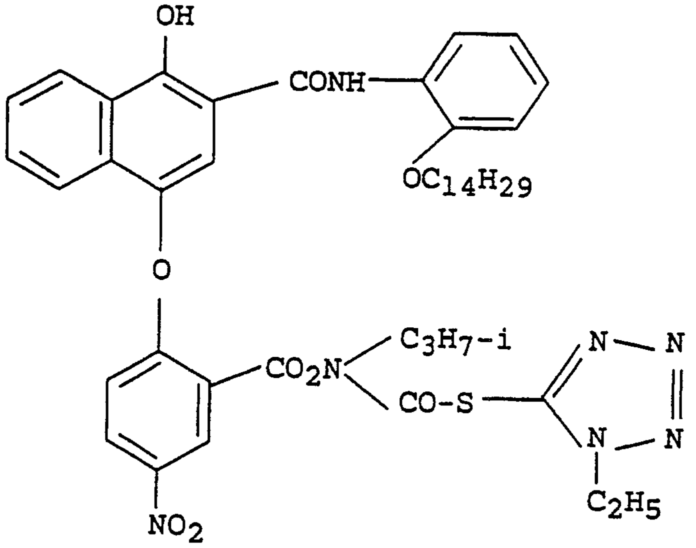
(D-31)


OH
CONH
OC14H29-n
O
CH2
N
N
N
CH3
CH3

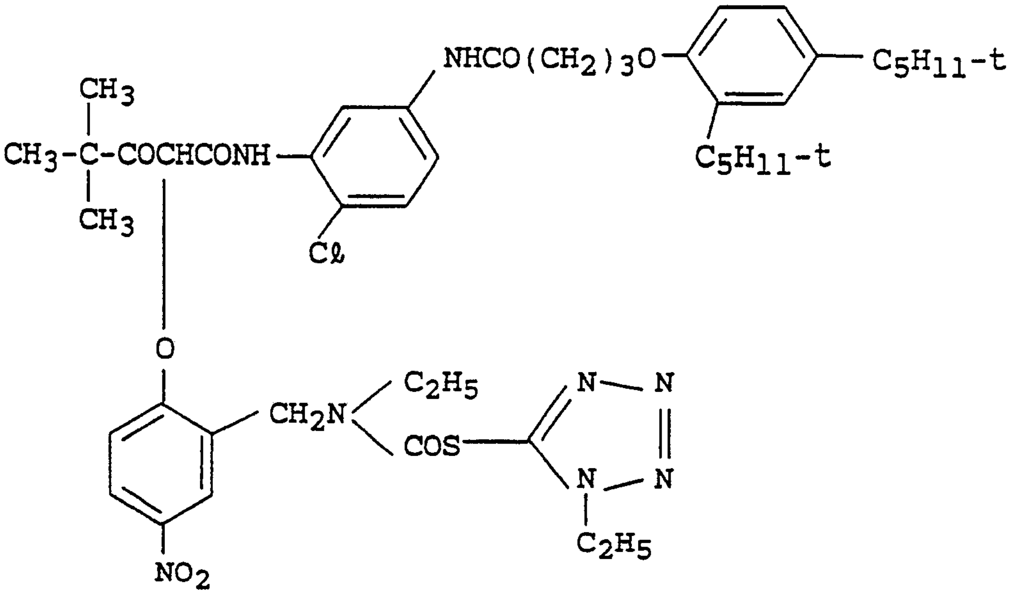
(D-32)


OH
CONH
OC14H29
S
N
N-C2H5
N
N

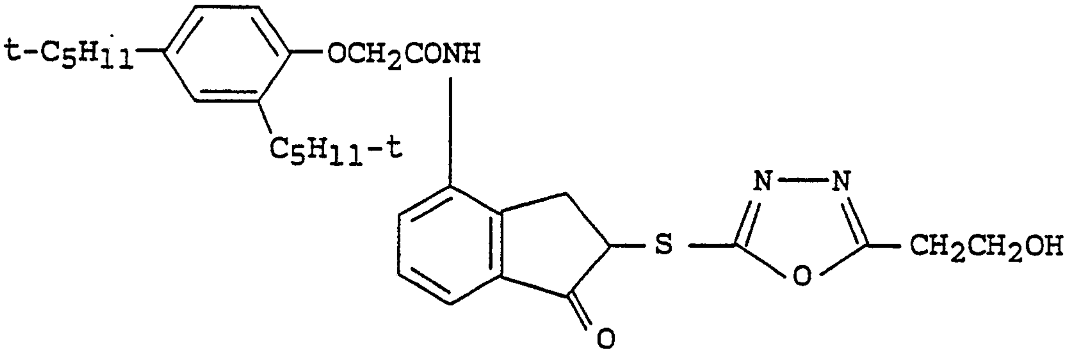
(D-33)


OH
CONH
OC14H29
O
CO2N
C3H7-i
CO-S
N
N
N
N
C2H5
NO2

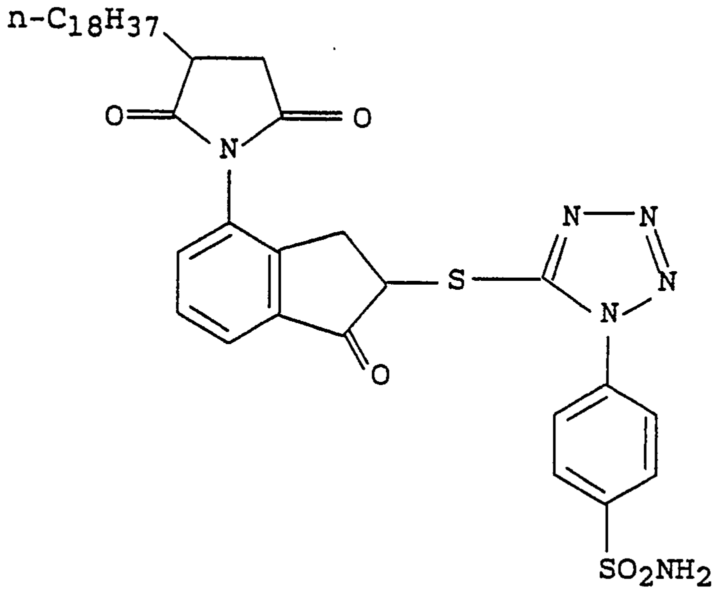
(D-34)



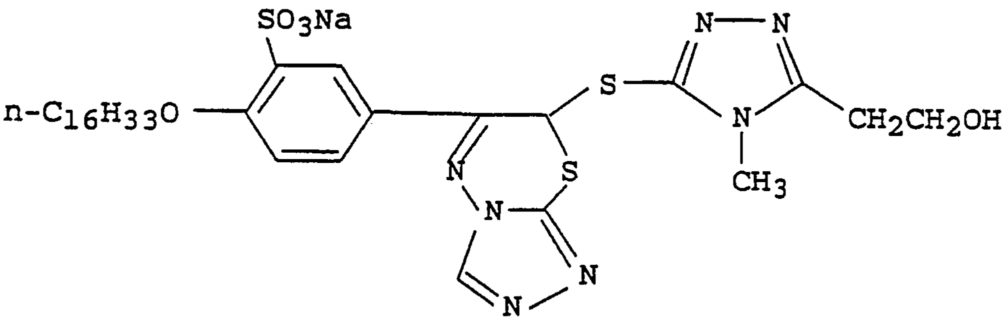
(D-35)



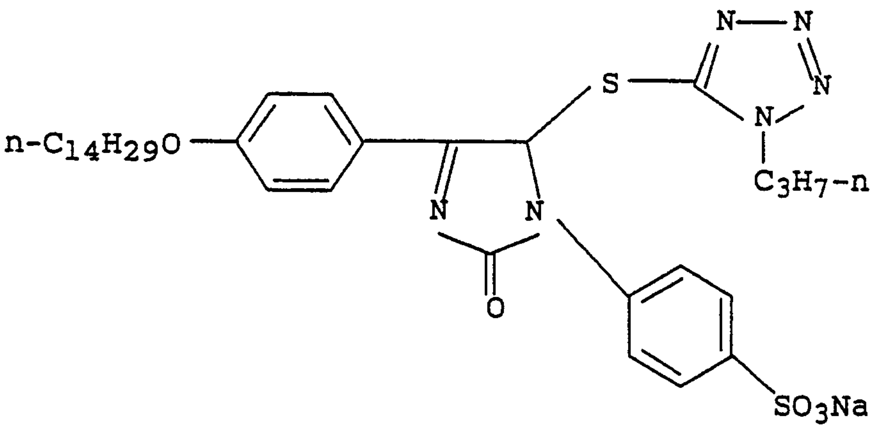
(D-36)



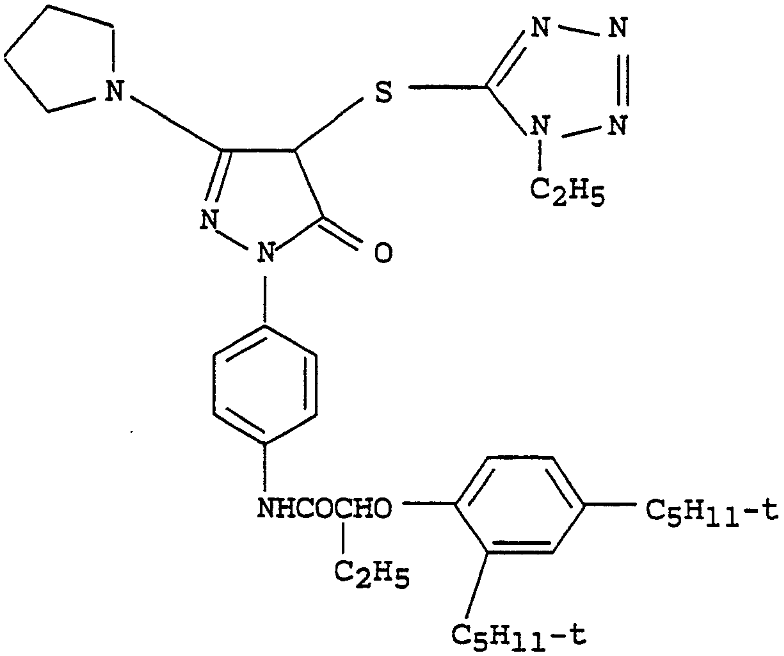
(D-37)



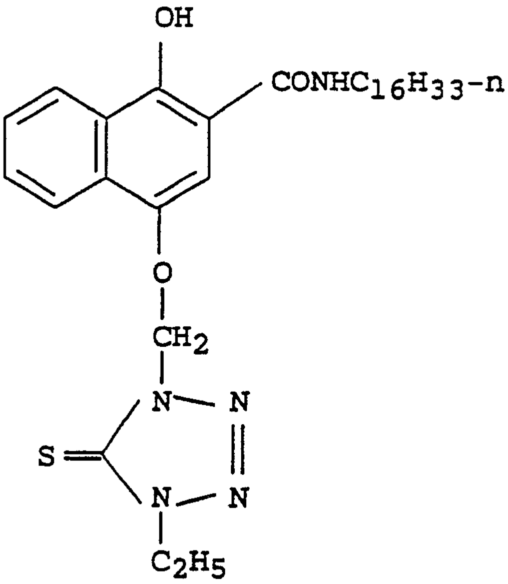
(D-38)



(D-39)


N
S
N
N
N
N
C2H5
N
N
O
NHCOCHO
C2H5
C5H11-t
C5H11-t

(D-40)


OH
CONHC16H33-n
O
CH2
N
N
S
N
N
C2H5

(D-41)

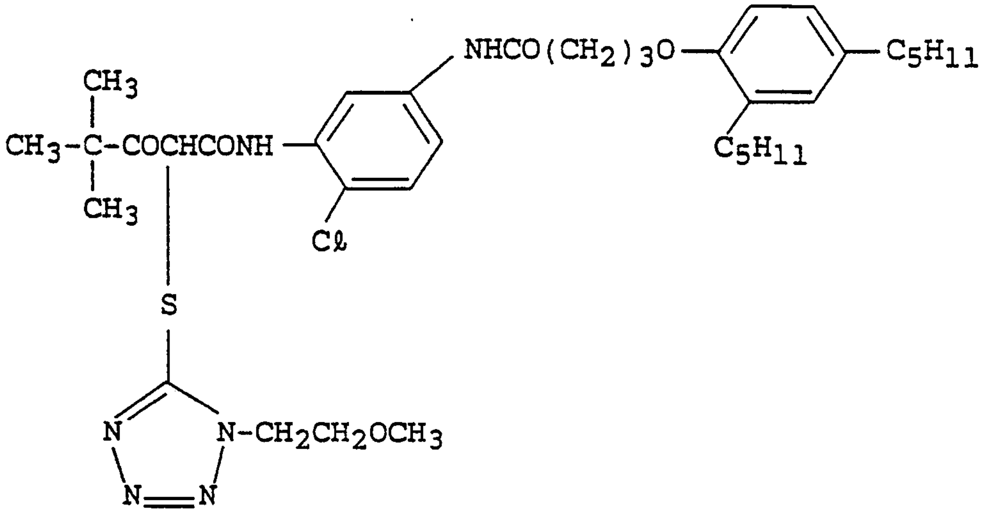
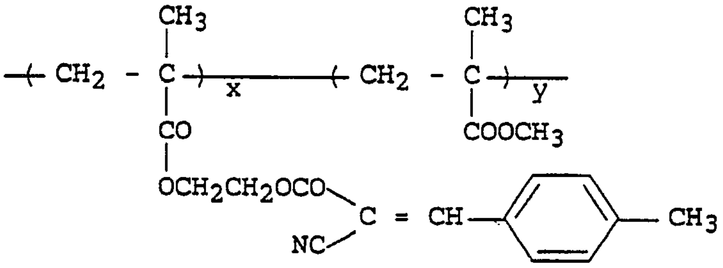

CH3
CH3-C-COCHCONH
CH3
Cℓ
NHCO(CH2)3O
C5H11
C5H11
S
N
N-CH2CH2OCH3
N
N

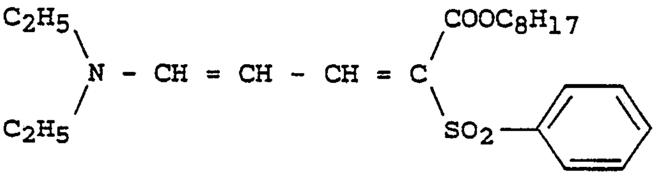
Table 16

UV-1

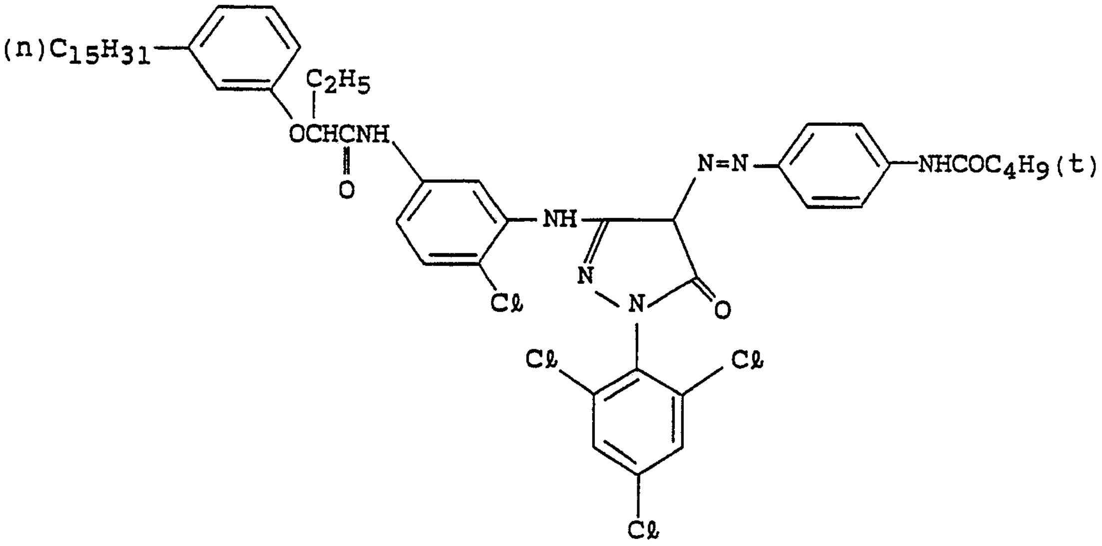


x/y = 7/3 (weight ratio)

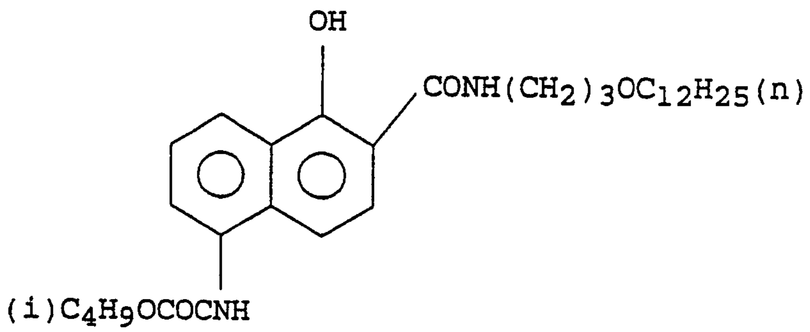
UV-2



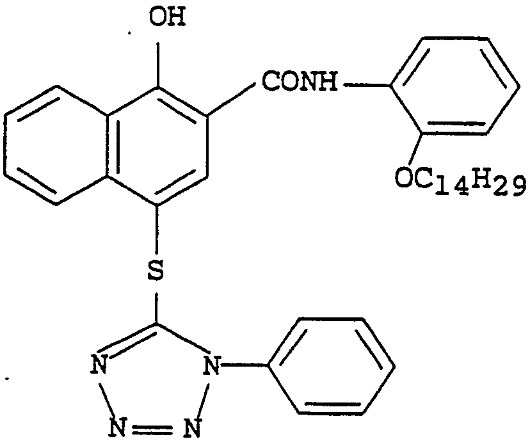
ExM-3



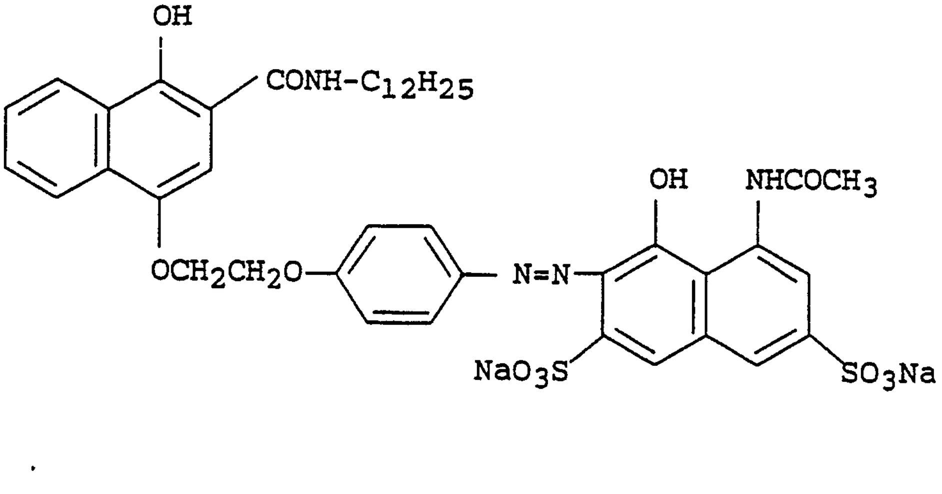
ExC-1



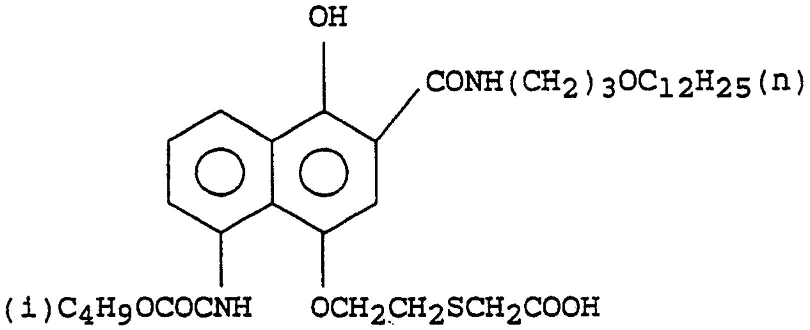
ExC-2



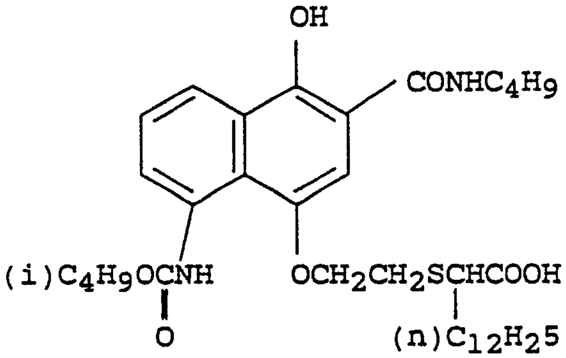
ExC-3



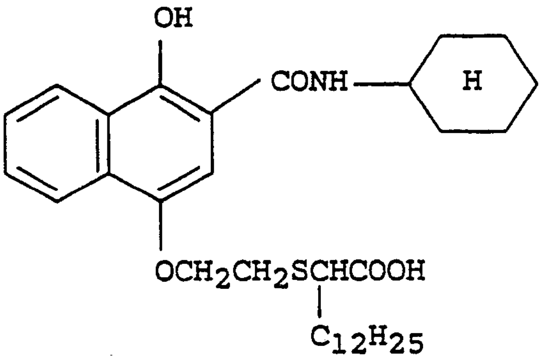
ExC-6



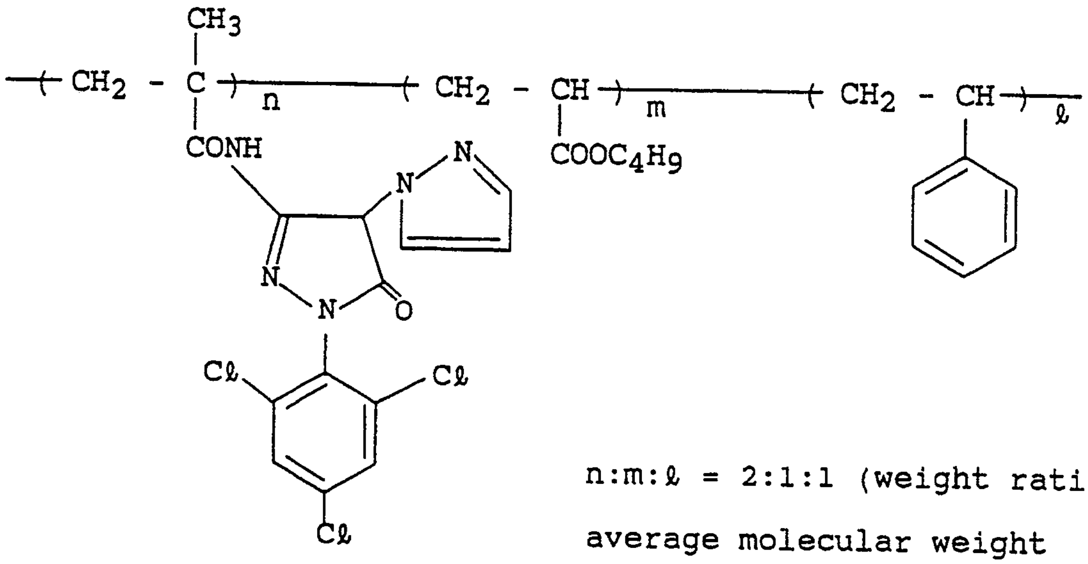
ExC-4



ExC-5



ExM-1

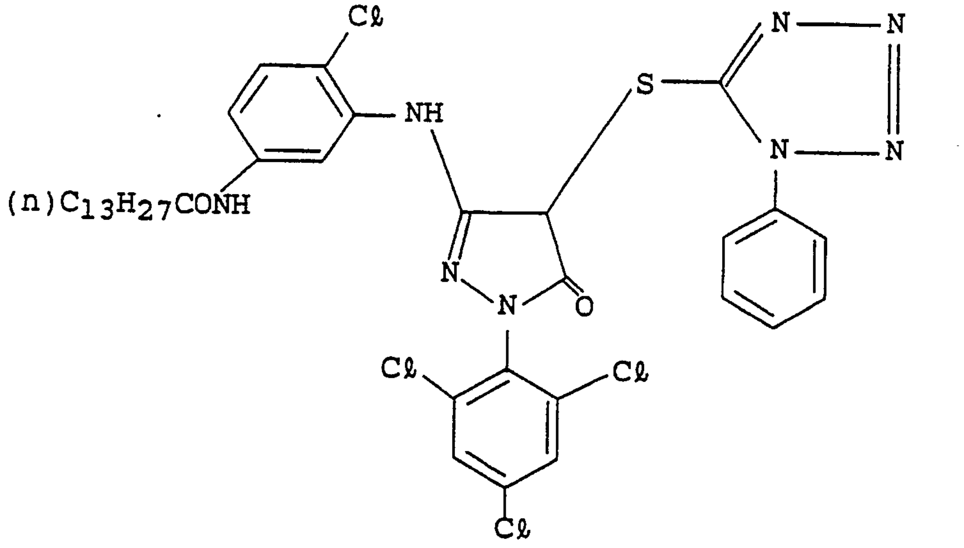


n:m:ℓ = 2:1:1 (weight ratio)

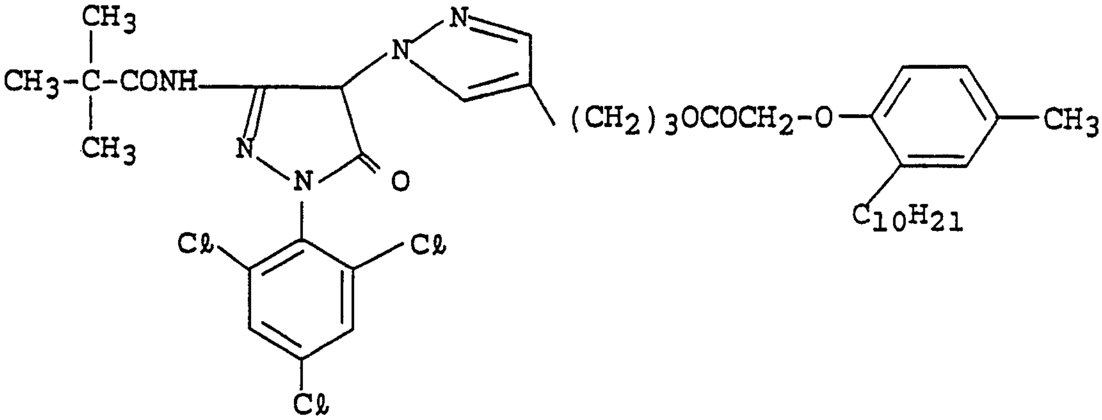
average molecular weight

40,000

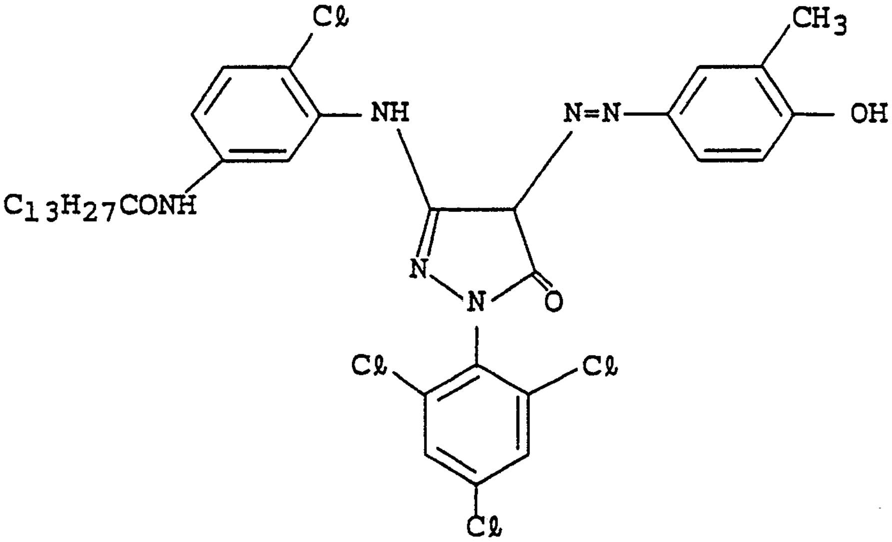
ExM-2



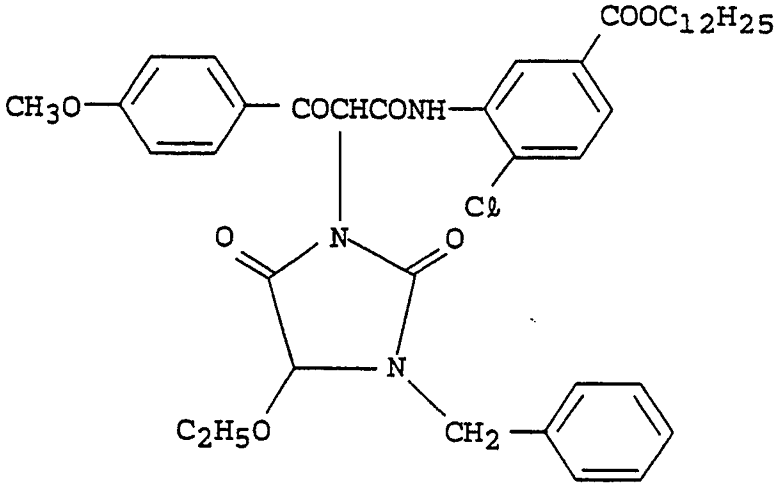
ExM-4



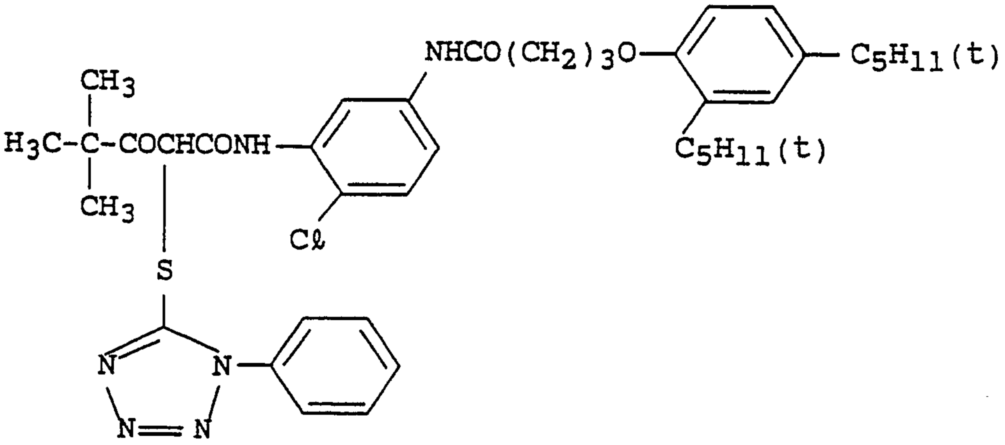
ExM-5



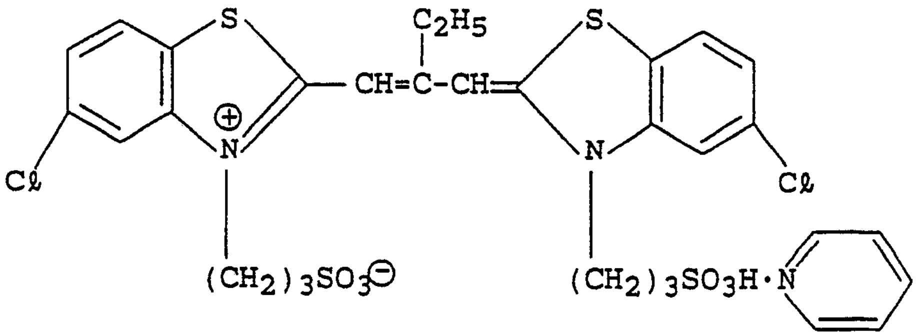
ExY-1


COOC12H25
CH3O
COCHCONH
Cl
O
N
O
N
C2H5O
CH2

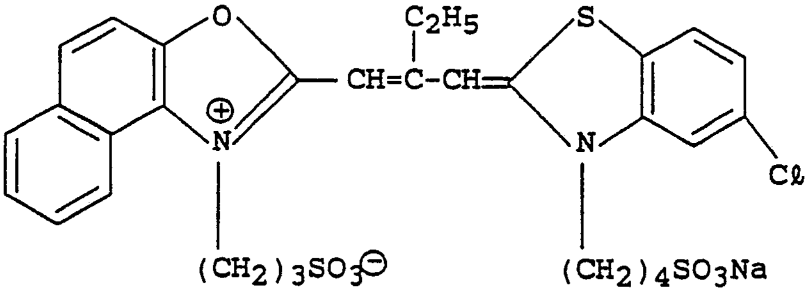
ExY-2


NHCO(CH2)3O
C5H11(t)
C5H11(t)
CH3
H3C-C-COCHCONH
CH3
Cl
S
N
N
N
N

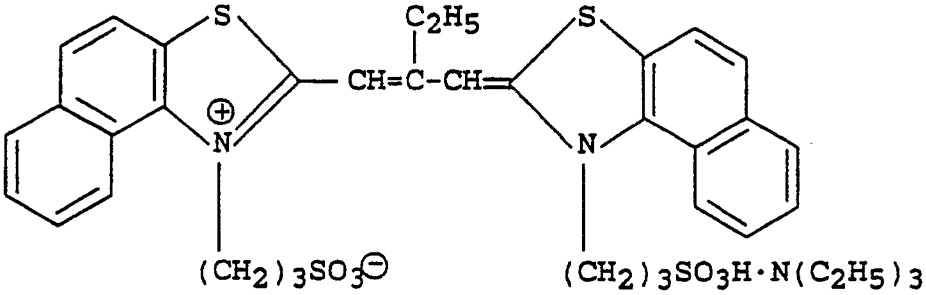
ExS-1



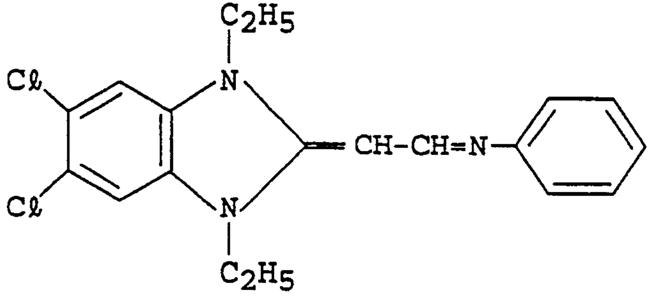
ExS-2



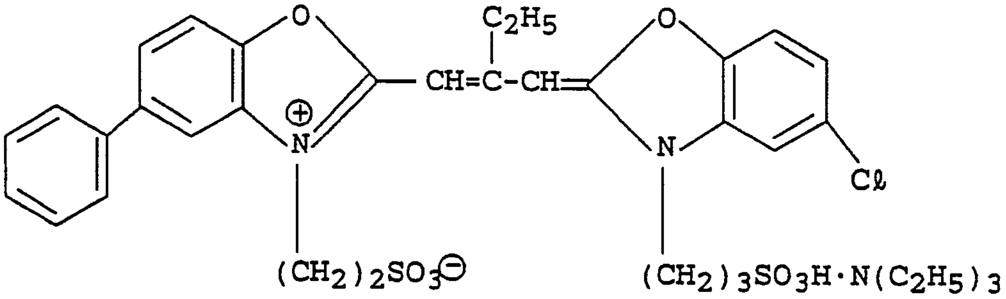
ExS-3



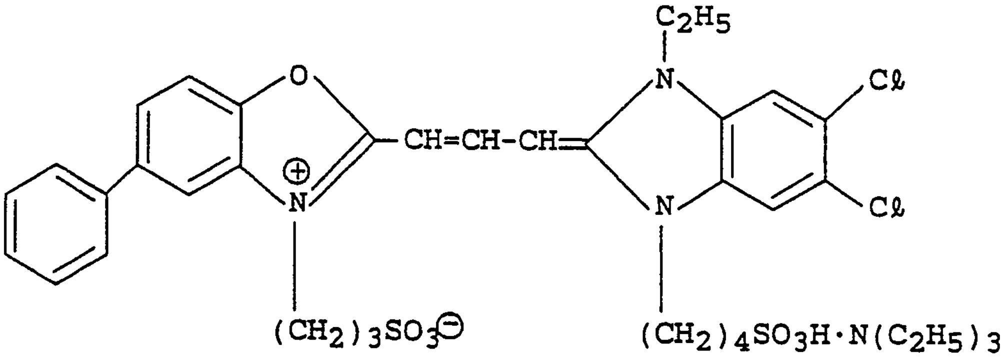
ExS-4



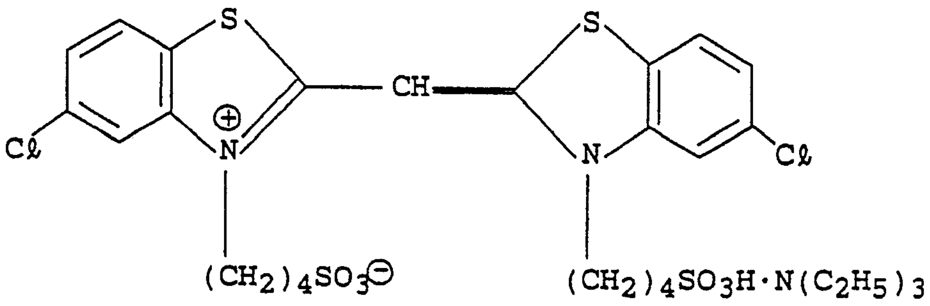
ExS-5



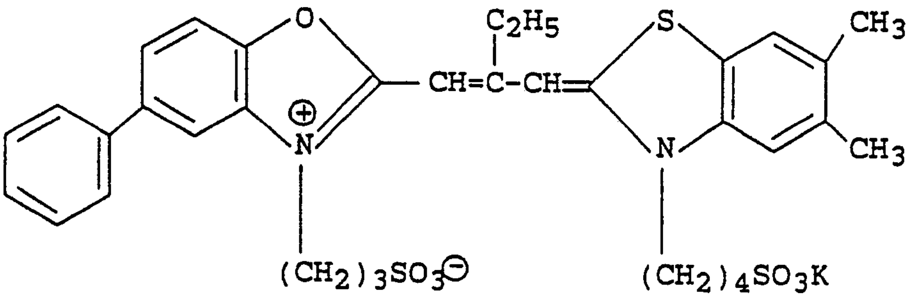
ExS-6



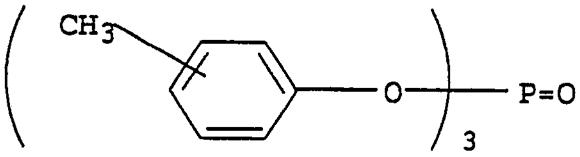
ExS-8



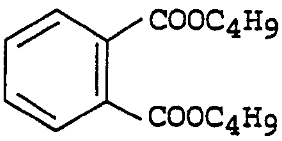
ExS-7



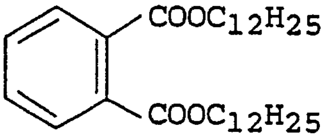
Solv-1



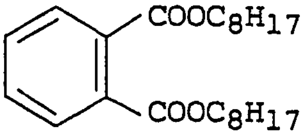
Solv-2



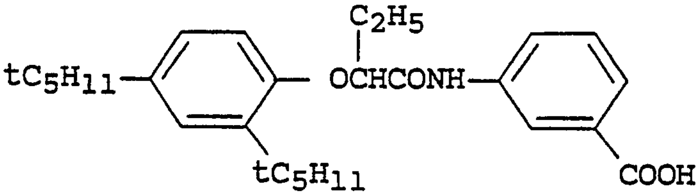
Solv-3



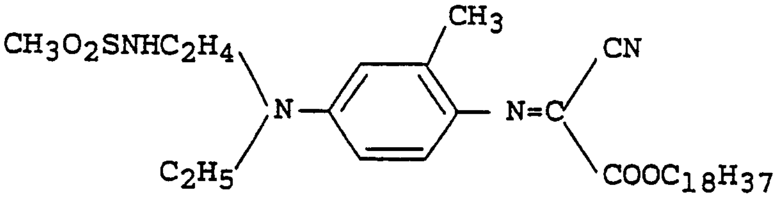
Solv-4



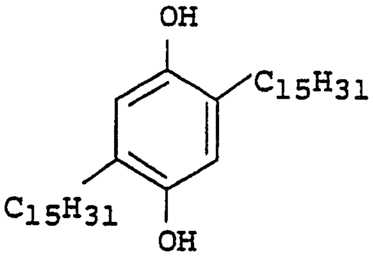
Solv-5



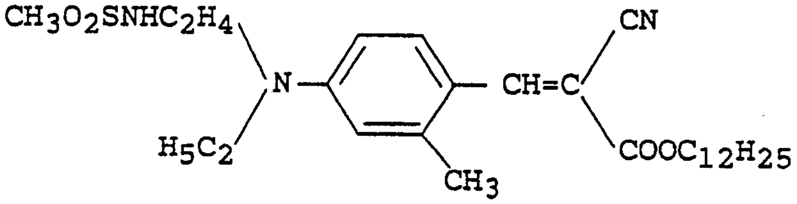
Cpd-1



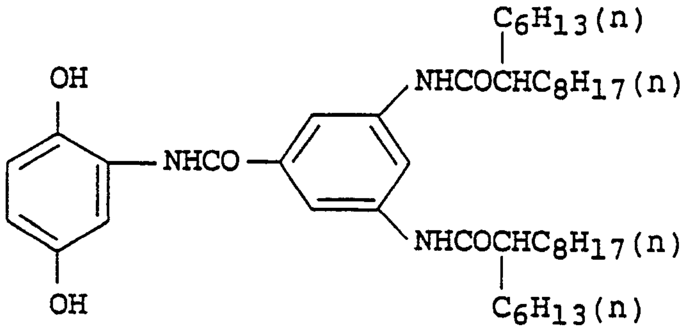
Cpd-2



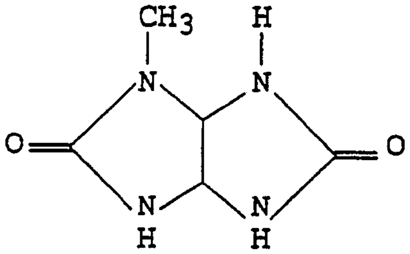
Cpd-3



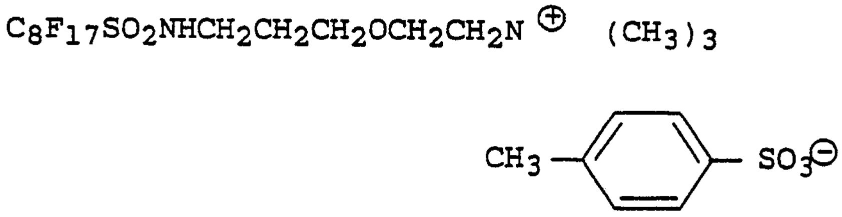
Cpd-4



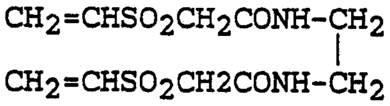
Cpd-5



W-1



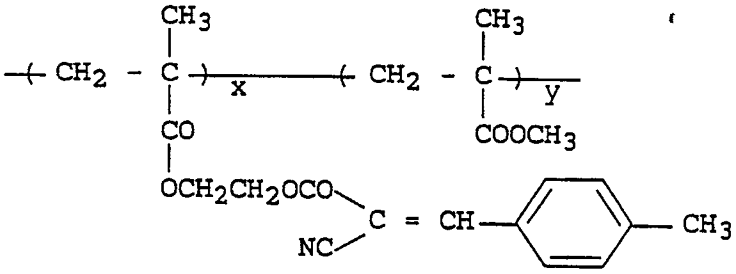
H-1



$$\begin{array}{l} CH_2{=}CHSO_2CH_2CONH{-}CH_2 \\ \qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CHSO_2CH2CONH{-}CH_2 \end{array}$$

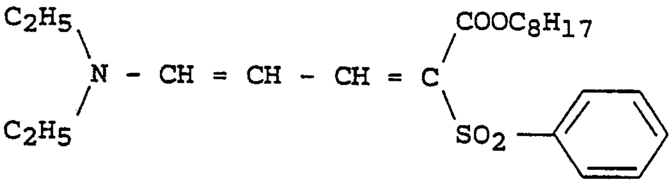
Table 17

UV-1

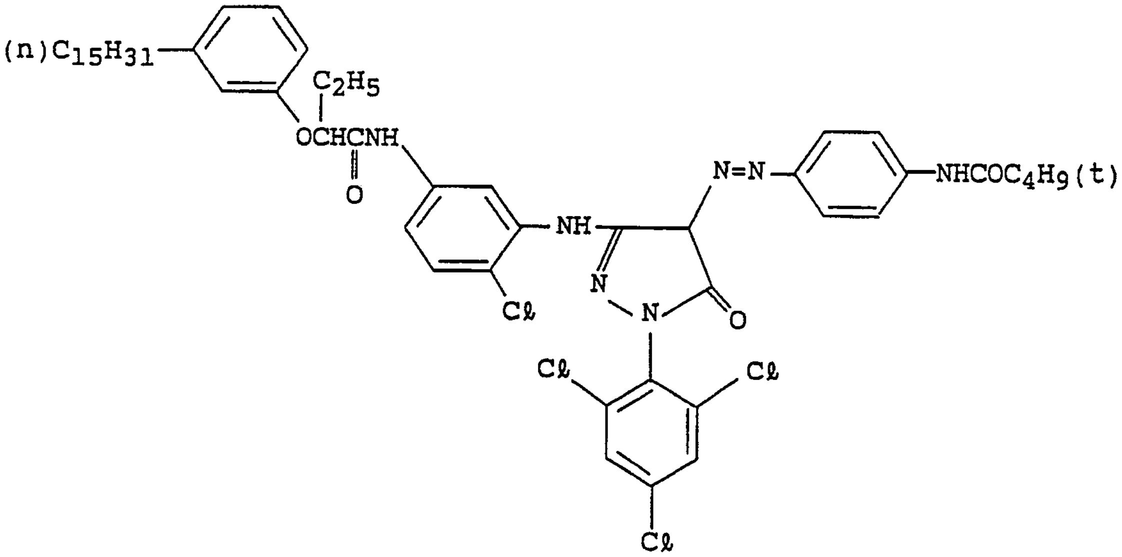


x/y = 7/3 (weight ratio)

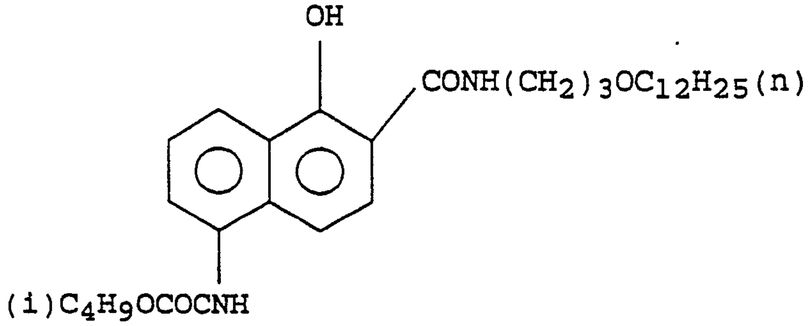
UV-2



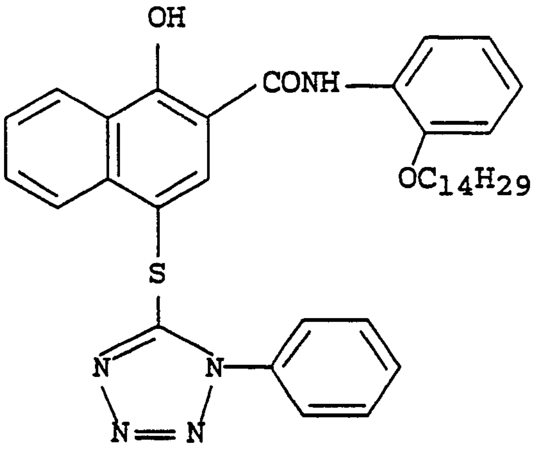
ExM-3



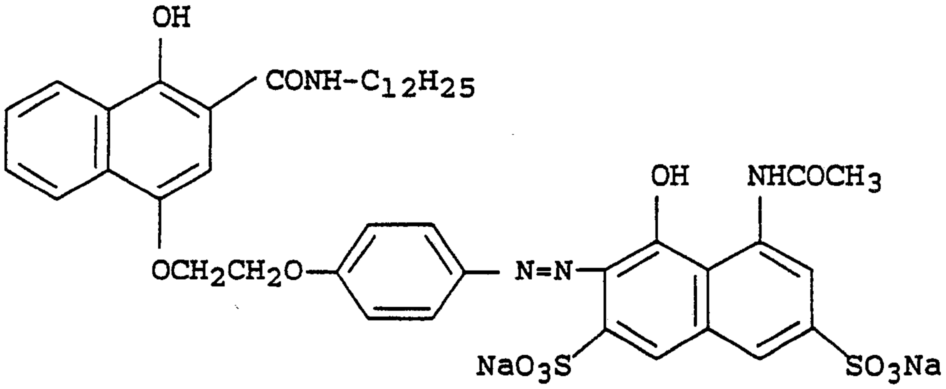
ExC-1



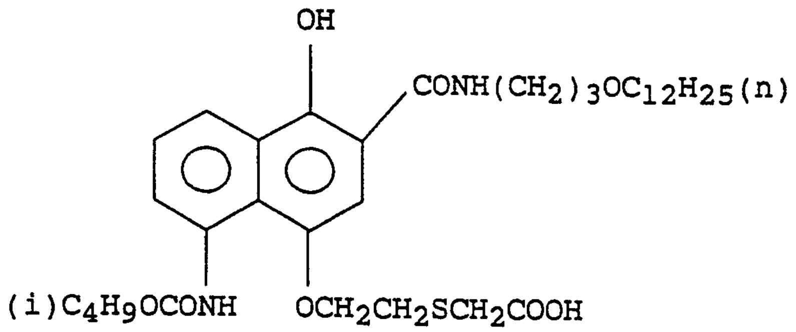
ExC-2



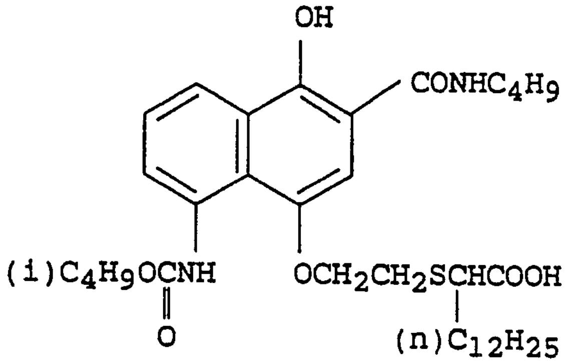
ExC-3



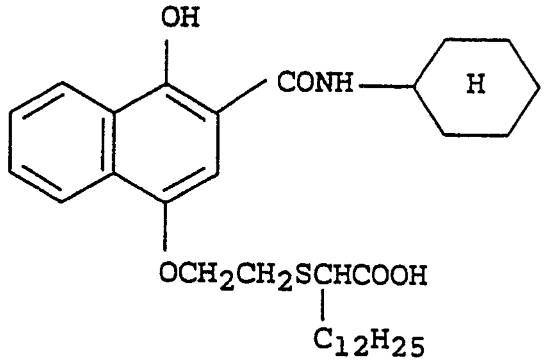
ExC-6



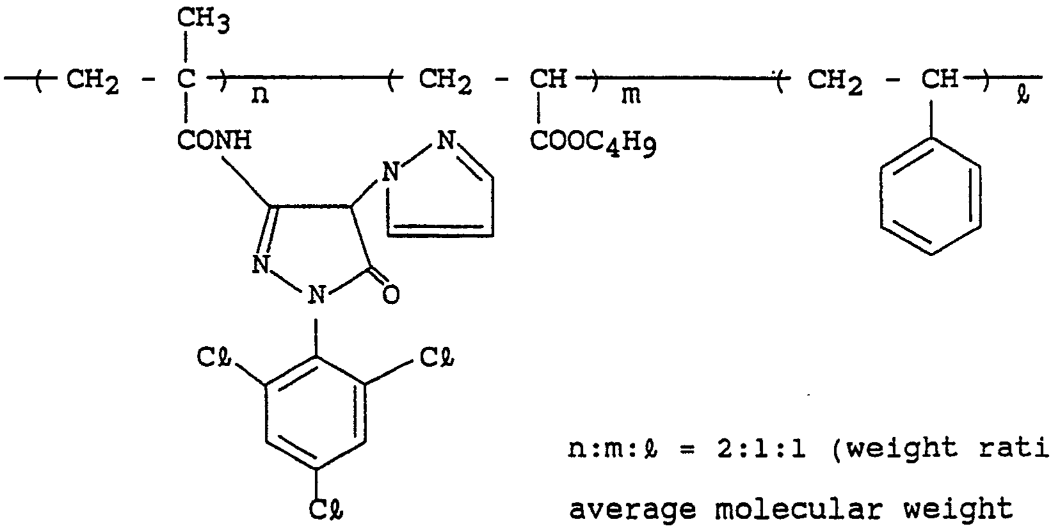
ExC-4



ExC-5



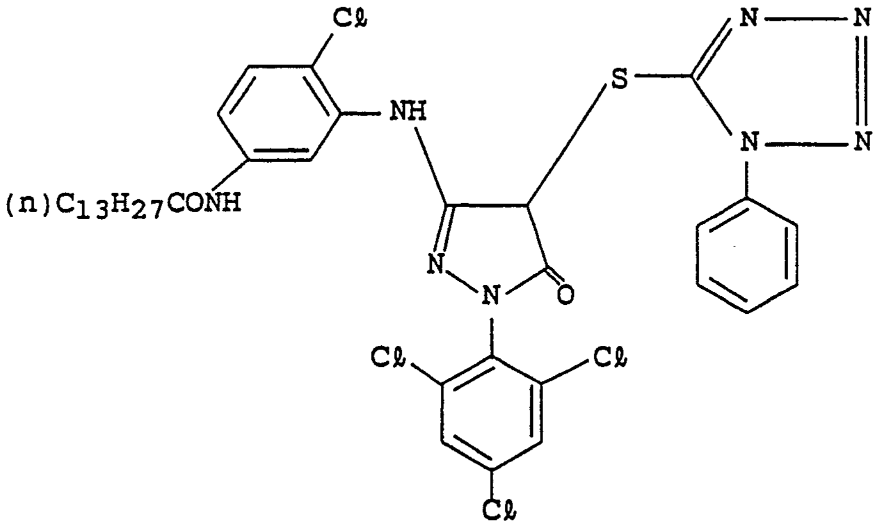
ExM-1



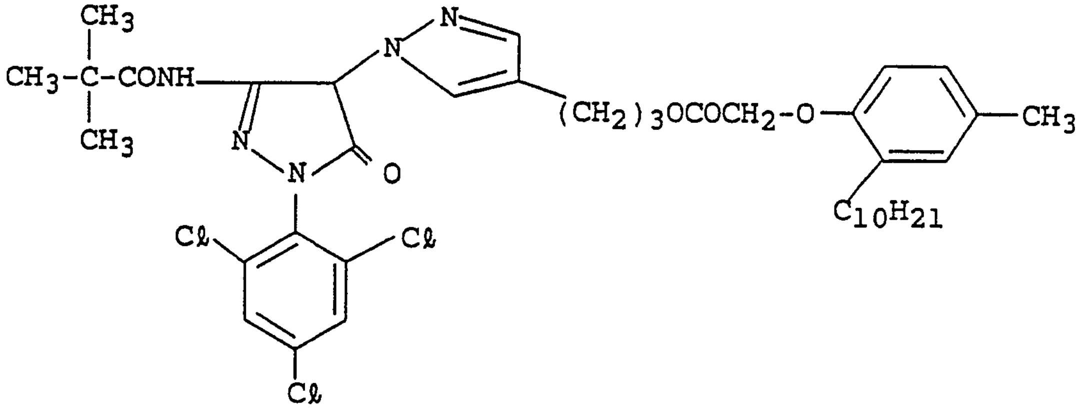
n:m:ℓ = 2:1:1 (weight ratio)

average molecular weight 40,000

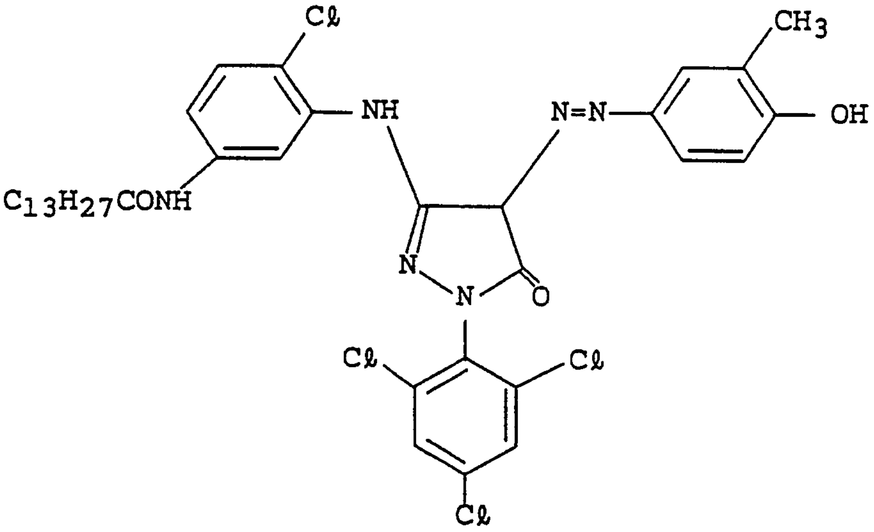
ExM-2



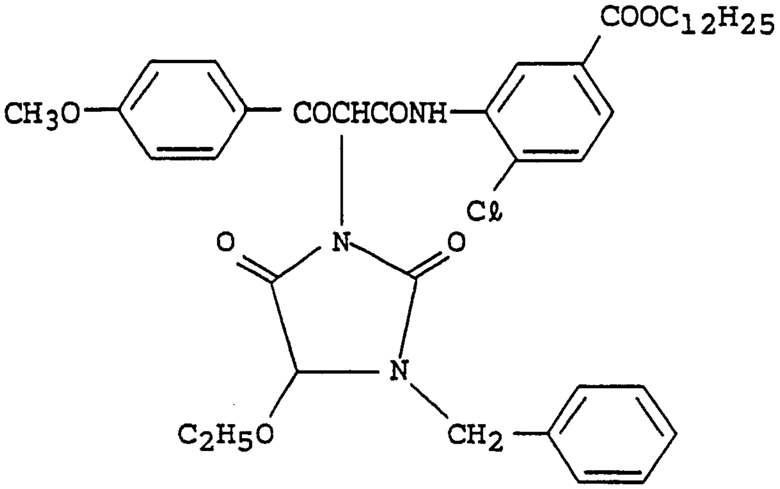
ExM-4


CH3
CH3-C-CONH
CH3
N
N
N
N
O
Cl
Cl
Cl
(CH2)3OCOCH2-O
CH3
C10H21

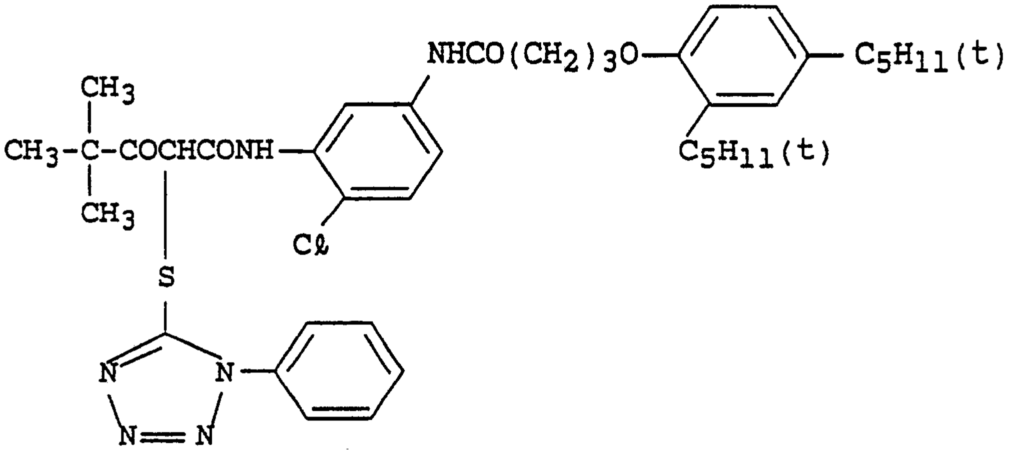
ExM-5


Cl
NH
N=N
CH3
OH
C13H27CONH
N
N
O
Cl
Cl
Cl

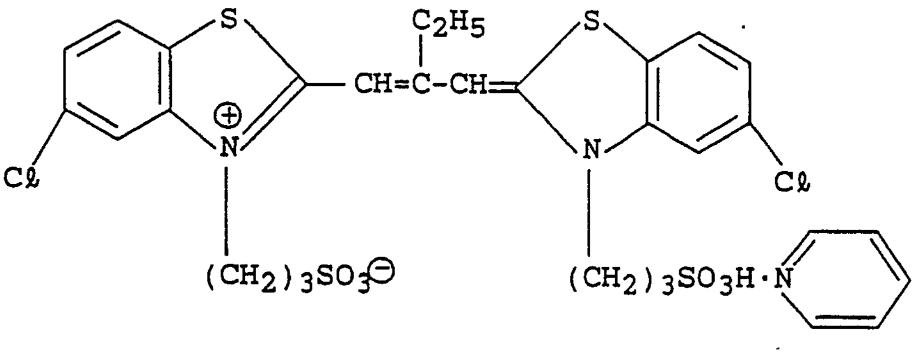
ExY-1


COOC12H25
CH3O
COCHCONH
Cℓ
O
N
O
N
C2H5O
CH2

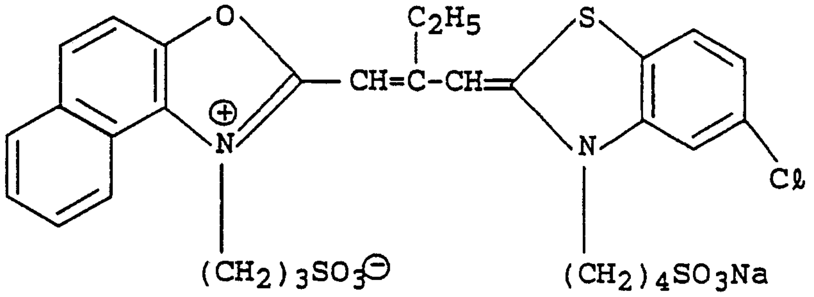
ExY-2


NHCO(CH2)3O
C5H11(t)
C5H11(t)
CH3
CH3-C-COCHCONH
CH3
Cℓ
S
N
N
N
N

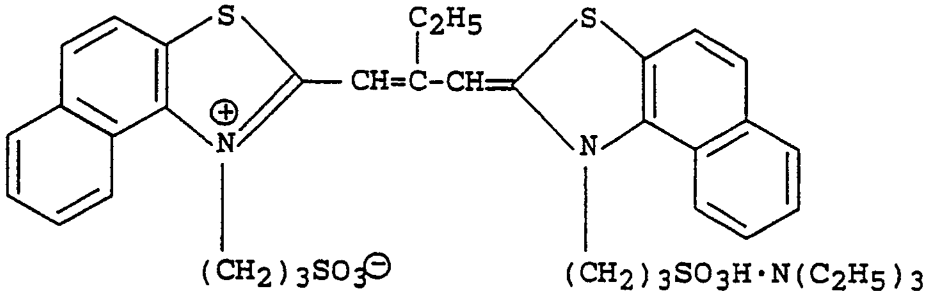
ExS-1



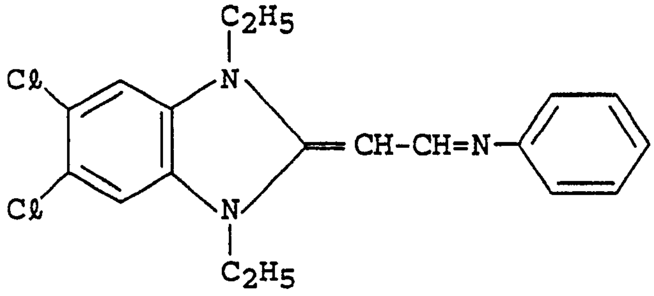
ExS-2



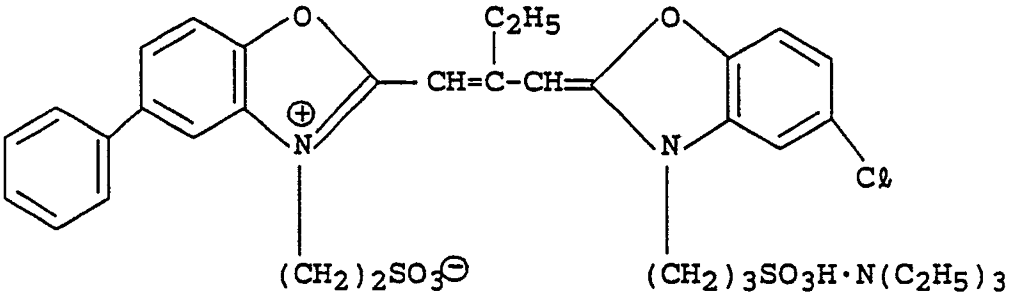
ExS-3



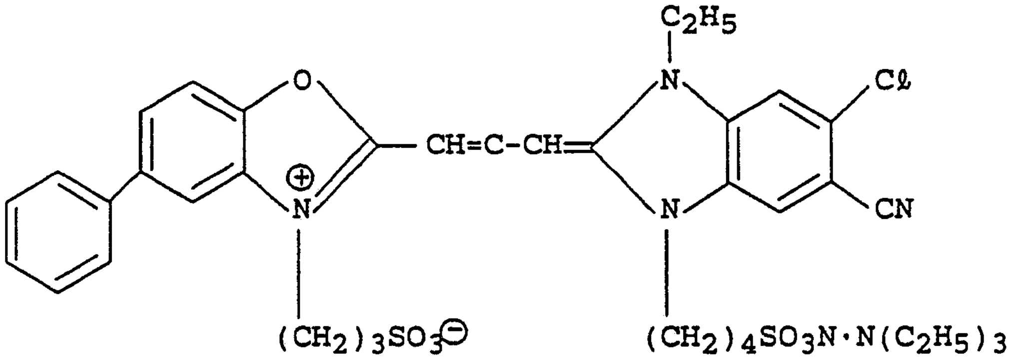
ExS-4



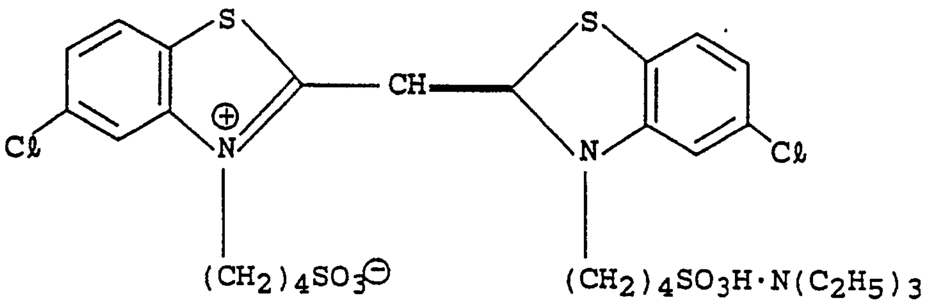
ExS-5



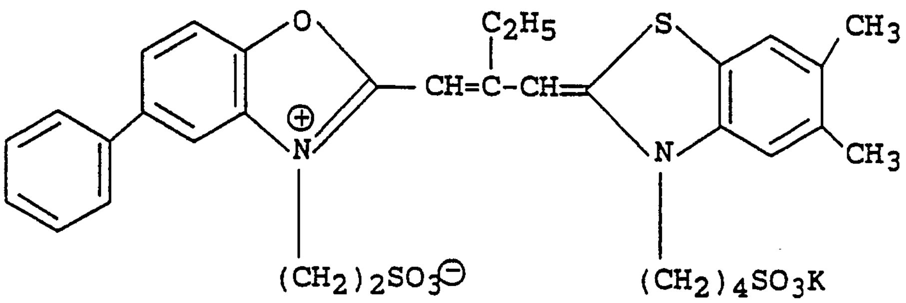
ExS-6



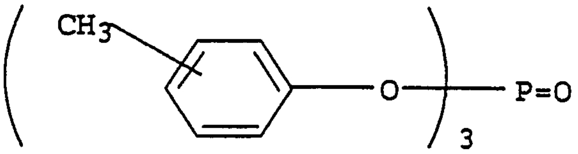
ExS-8



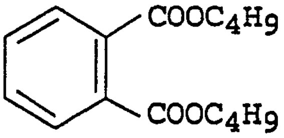
ExS-7



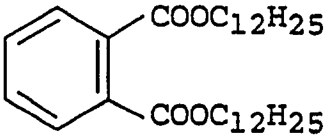
Solv-1



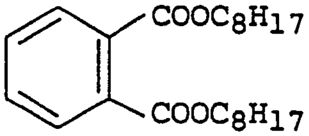
Solv-2



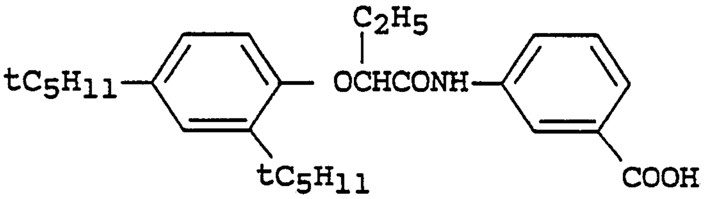
Solv-3



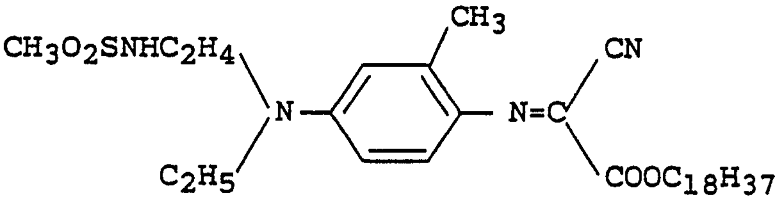
Solv-4



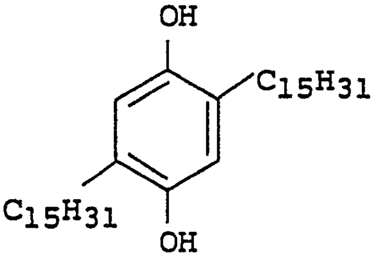
Solv-5



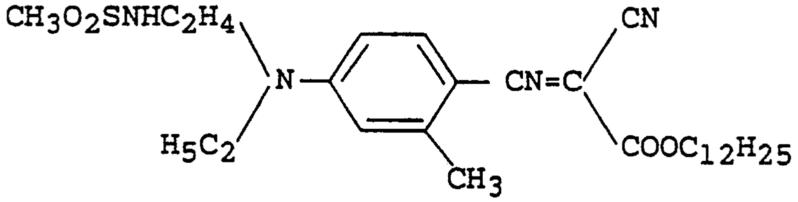
Cpd-1



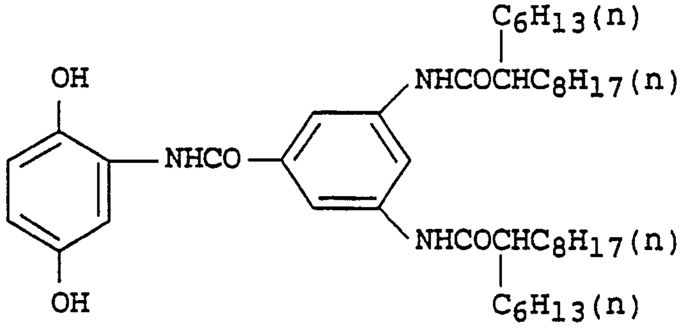
Cpd-2



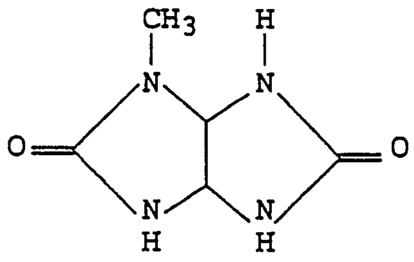
Cpd-3



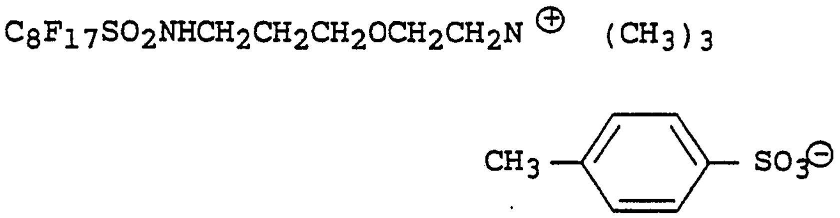
Cpd-4



Cpd-5

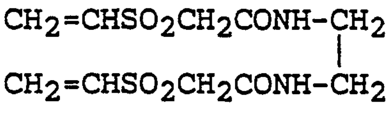


W-1



$C_8F_{17}SO_2NHCH_2CH_2CH_2OCH_2CH_2N^{\oplus}(CH_3)_3$

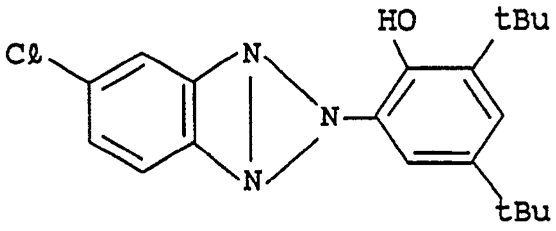
H-1



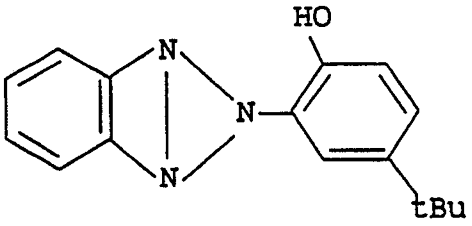
$$\begin{array}{l} CH_2{=}CHSO_2CH_2CONH{-}CH_2 \\ \qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CHSO_2CH_2CONH{-}CH_2 \end{array}$$

Table 18

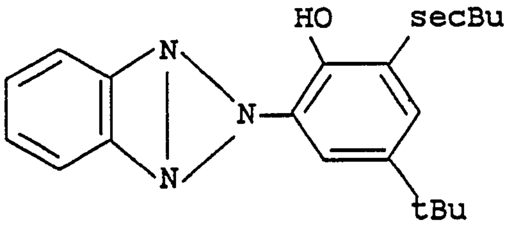
UV-1



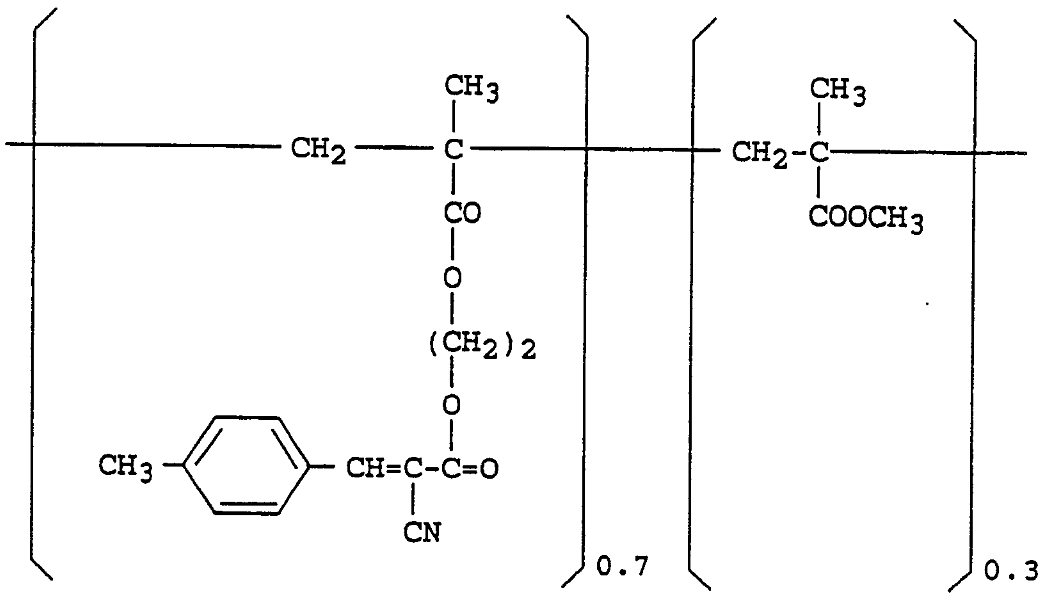
UV-2



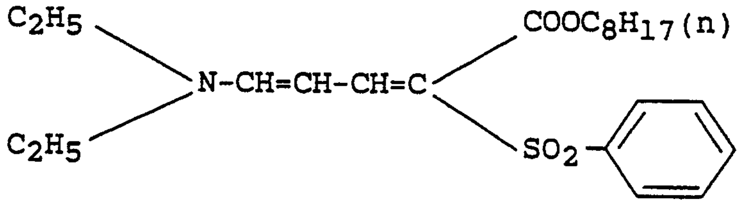
UV-3



UV-4



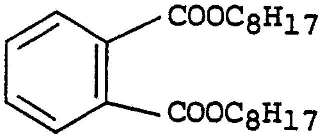
UV-5



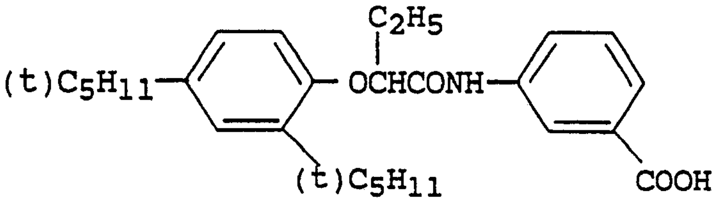
Solv-1 Tricresyl phosphate

Solv-2 Dibutyl phthalate

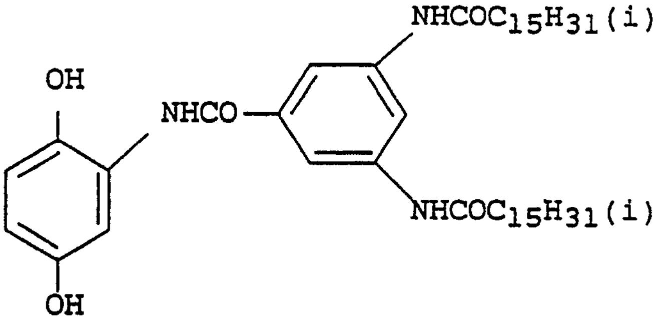
Solv-3



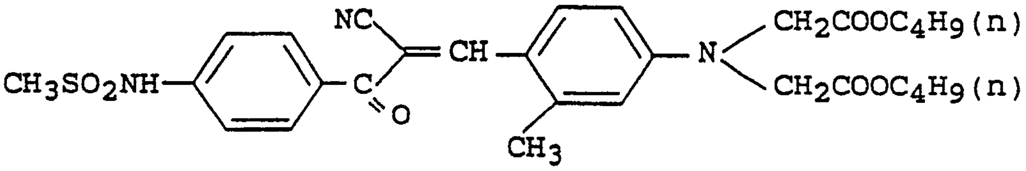
Solv-4



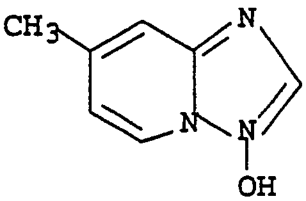
Cpd-1



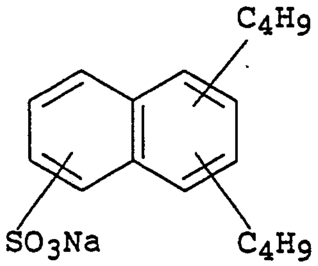
Cpd-2



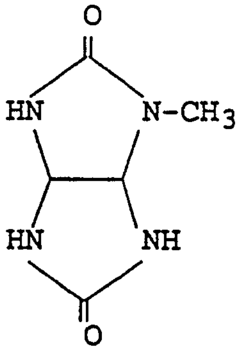
Cpd-3



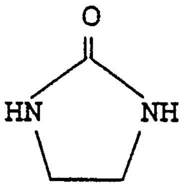
Cpd-4



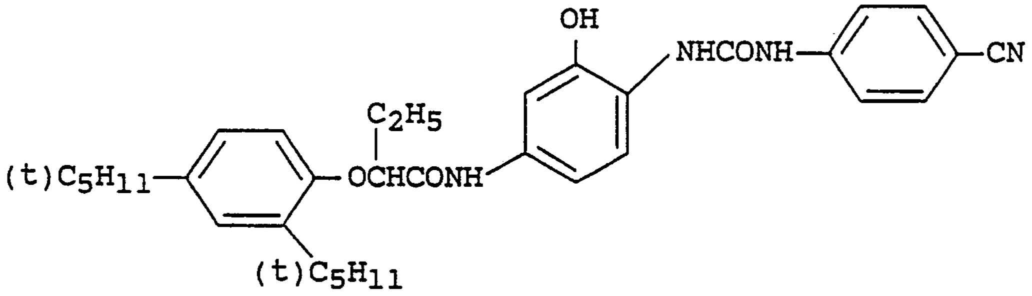
Cpd-5



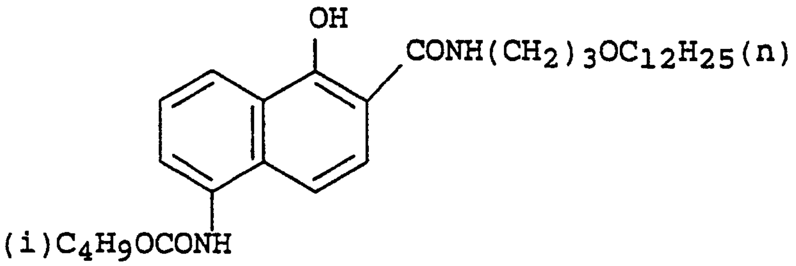
Cpd-6



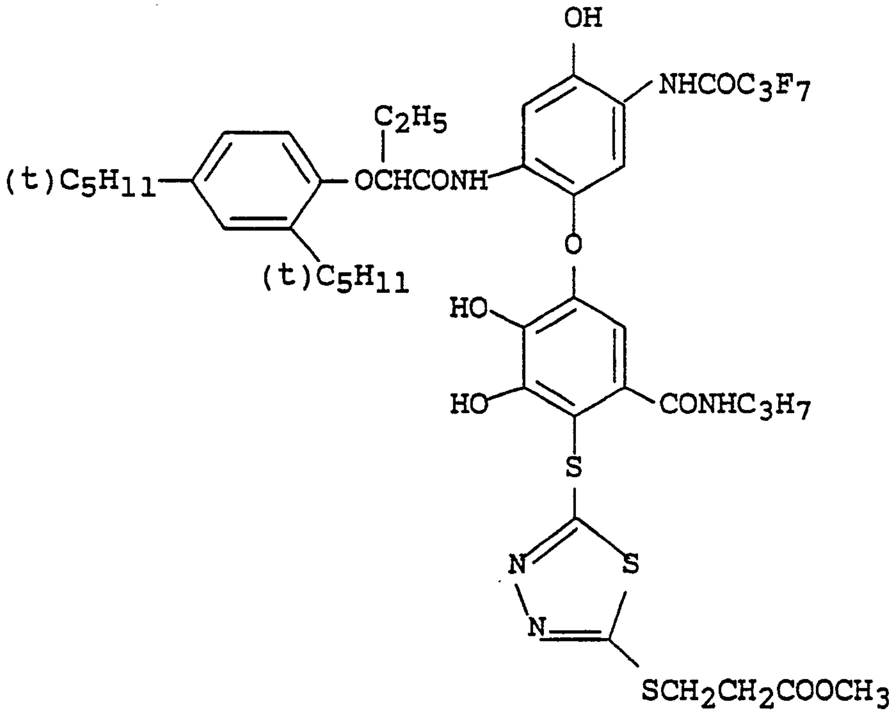
ExC-1



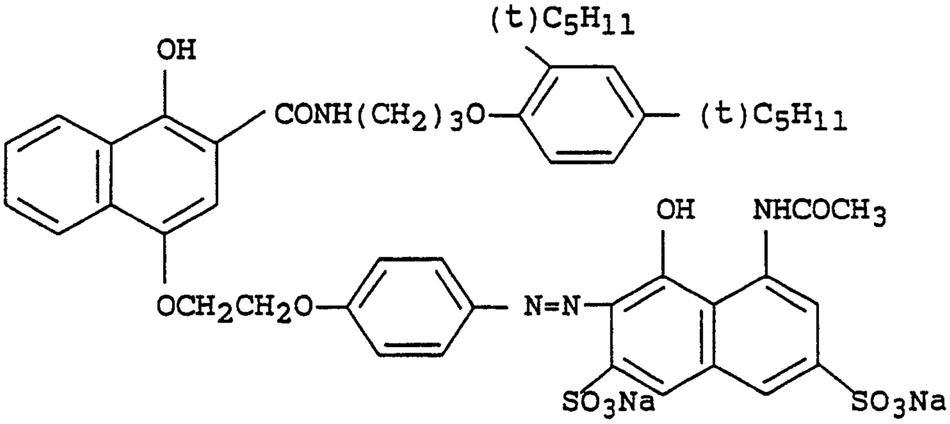
ExC-2



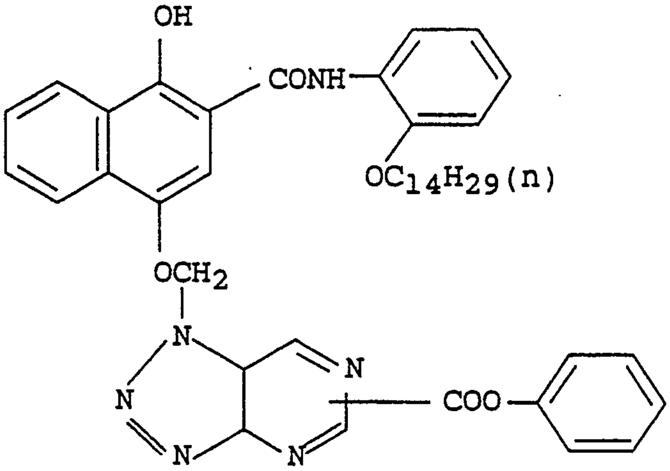
ExC-3


OH
$NHCOC_3F_7$
C_2H_5
$(t)C_5H_{11}$
OCHCONH
$(t)C_5H_{11}$
O
HO
HO
$CONHC_3H_7$
S
N
S
N
$SCH_2CH_2COOCH_3$

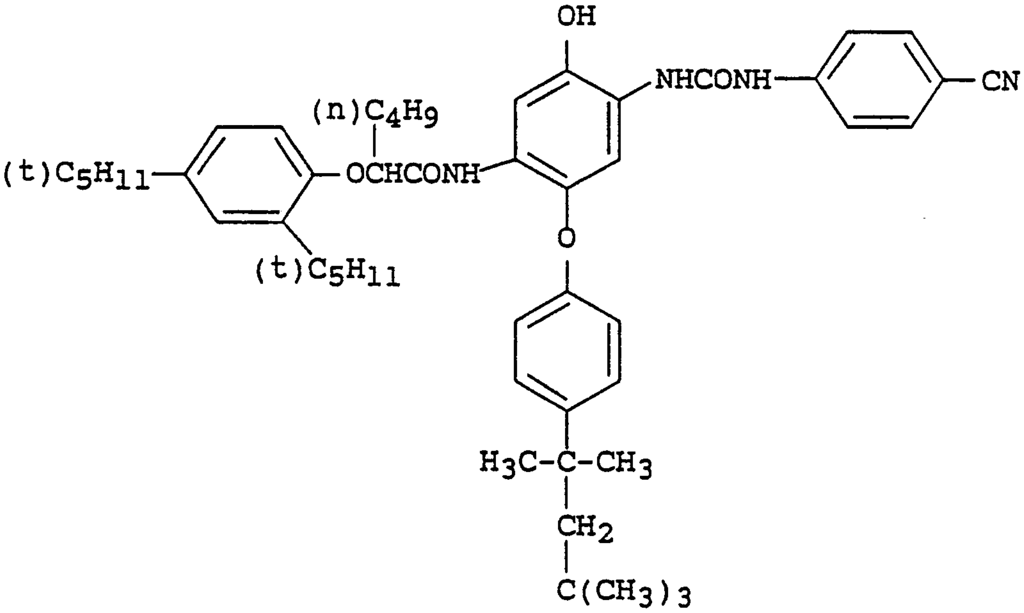
ExC-4


$(t)C_5H_{11}$
OH
$CONH(CH_2)_3O$
$(t)C_5H_{11}$
OH
$NHCOCH_3$
OCH_2CH_2O
N=N
SO_3Na
SO_3Na

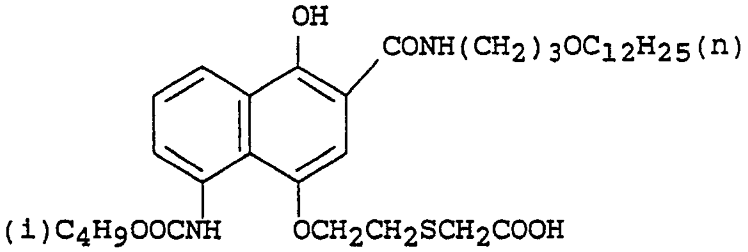
ExC-5


OH
CONH
$OC_{14}H_{29}(n)$
OCH_2
N
N
N
N
N
COO

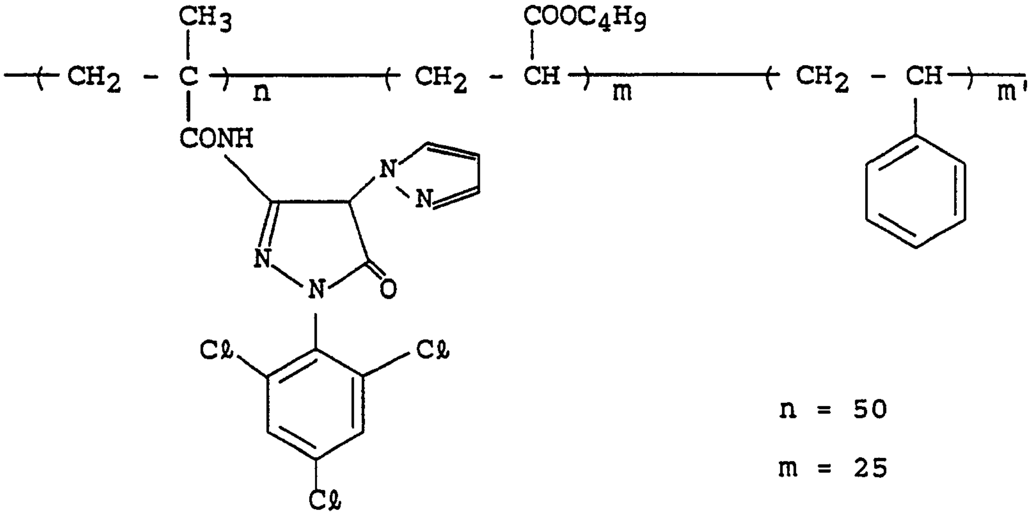
ExC-6


OH
NHCONH
CN
$(n)C_4H_9$
$(t)C_5H_{11}$
OCHCONH
$(t)C_5H_{11}$
O
$H_3C-C-CH_3$
CH_2
$C(CH_3)_3$

ExC-7



ExM-8



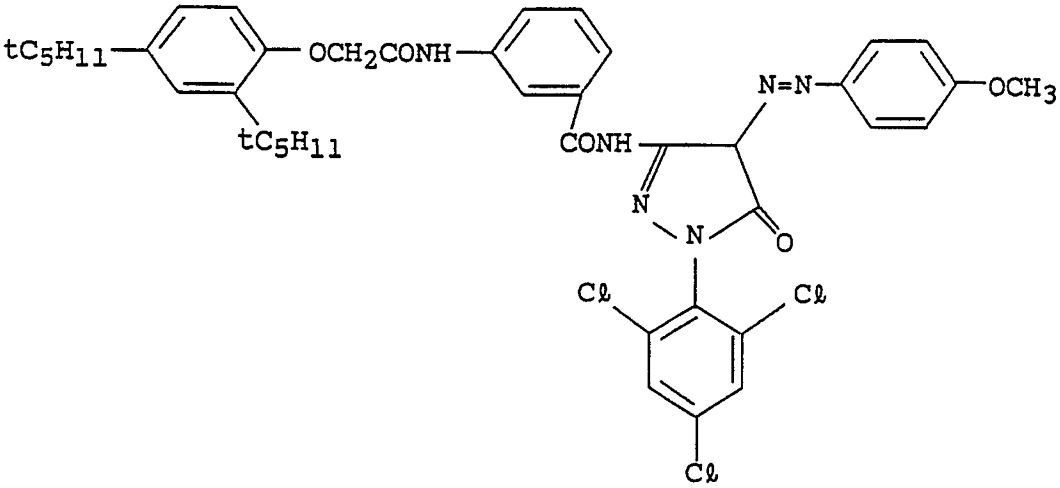
n = 50

m = 25

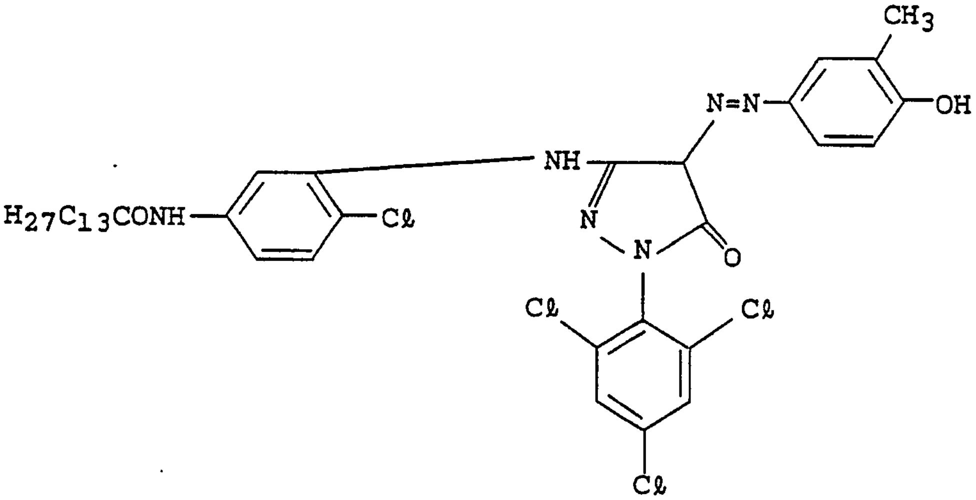
m' = 25

molecular weight = about 20000

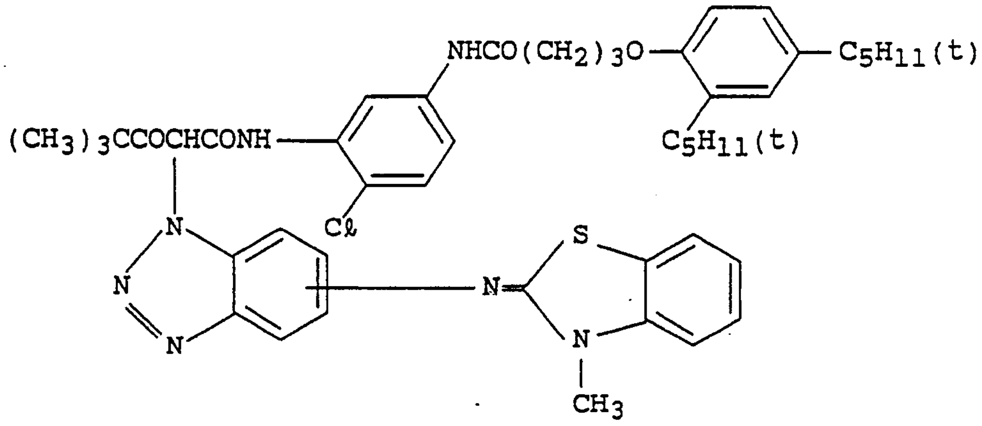
ExM-9


tC5H11
OCH2CONH
tC5H11
CONH
N=N
OCH3
N
N
O
Cl
Cl
Cl

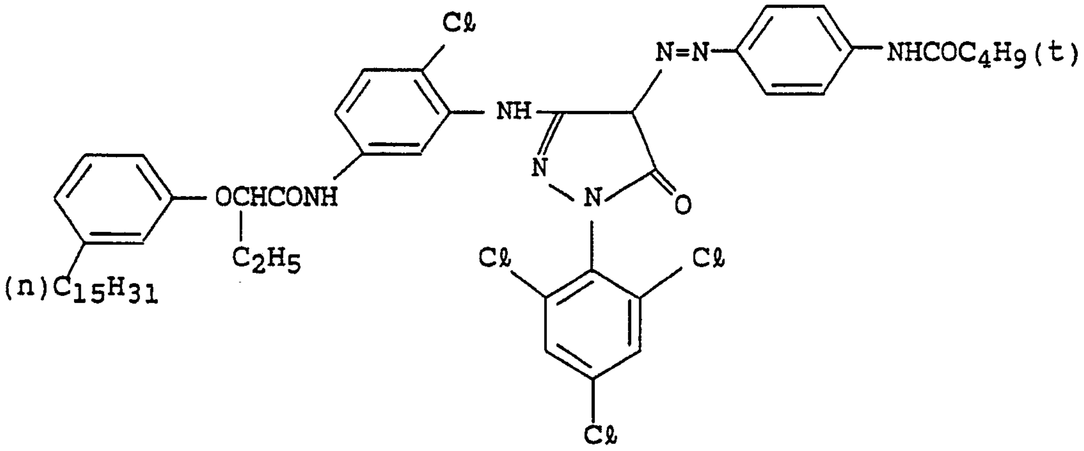
ExM-10


CH3
N=N
OH
NH
H27C13CONH
Cl
N
N
O
Cl
Cl
Cl

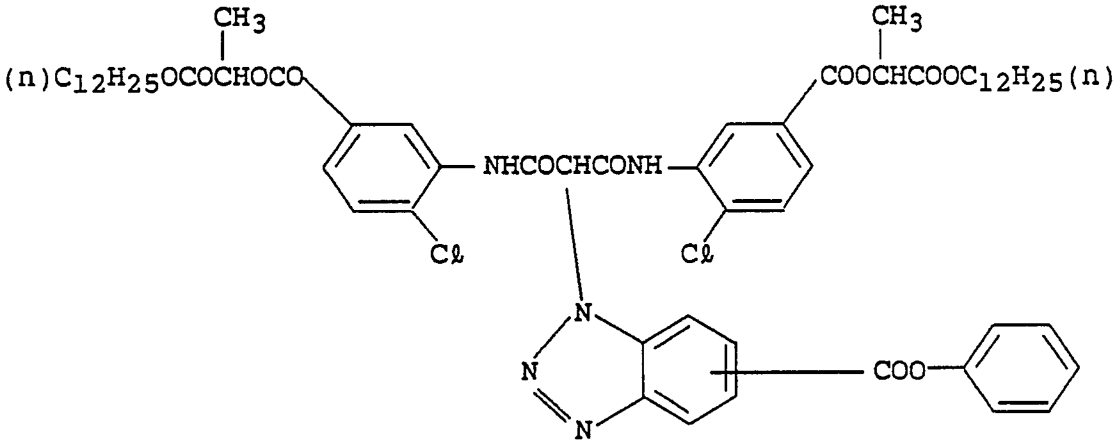
ExY-11


NHCO(CH2)3O
C5H11(t)
C5H11(t)
(CH3)3CCOCHCONH
Cl
N
N
N
N
S
N
CH3

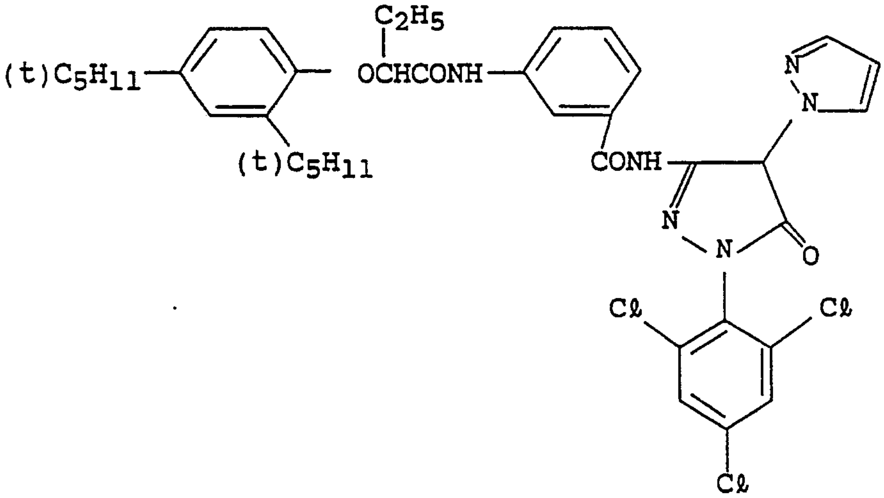
ExM-12


Cl
N=N
NHCOC4H9(t)
NH
OCHCONH
C2H5
(n)C15H31
N
N
O
Cl
Cl
Cl

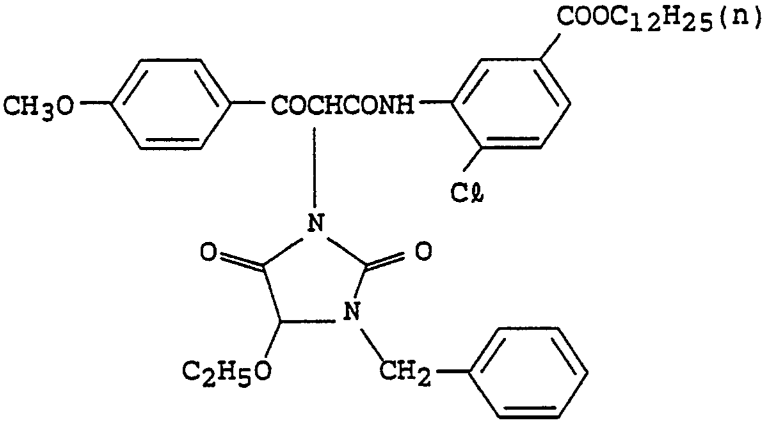
ExY-13



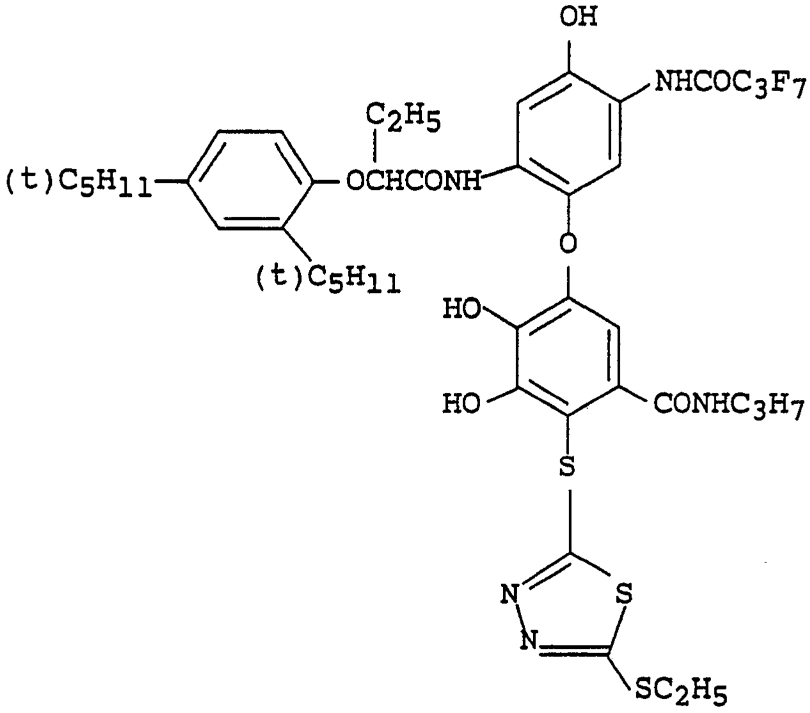
ExM-14



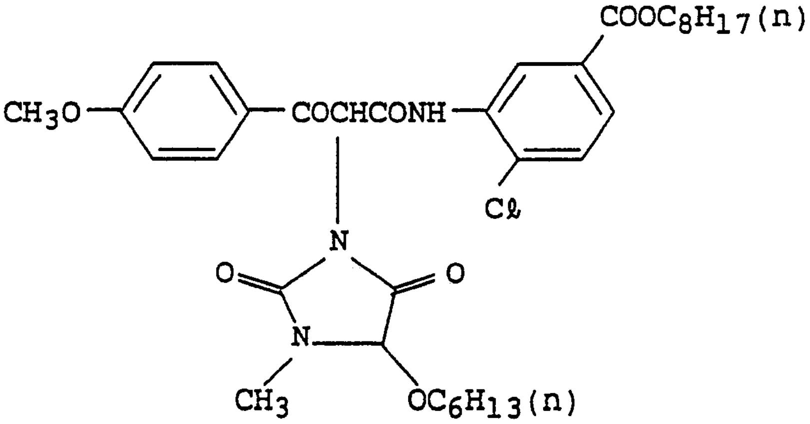
ExM-15



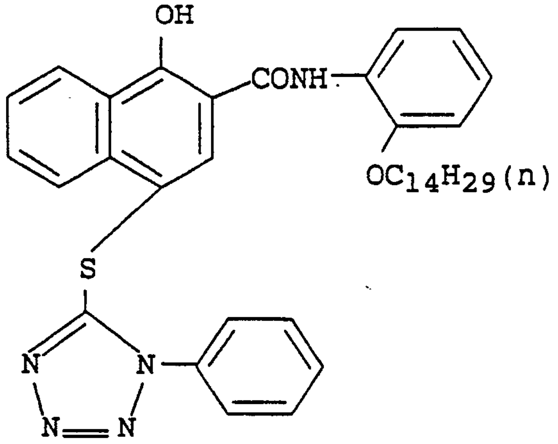
ExC-6


OH
NHCOC3F7
C2H5
(t)C5H11
OCHCONH
(t)C5H11
O
HO
HO
CONHC3H7
S
N
S
N
SC2H5

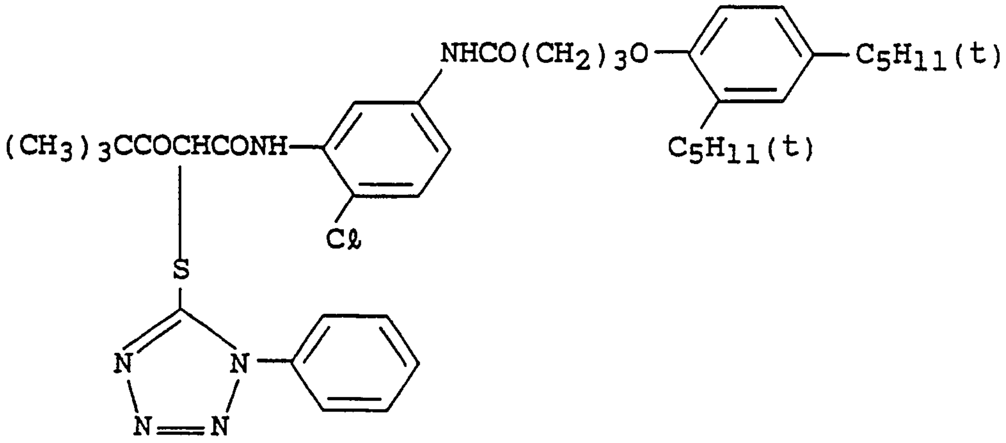
ExY-17


COOC8H17(n)
CH3O
COCHCONH
Cℓ
N
O
O
N
CH3
OC6H13(n)

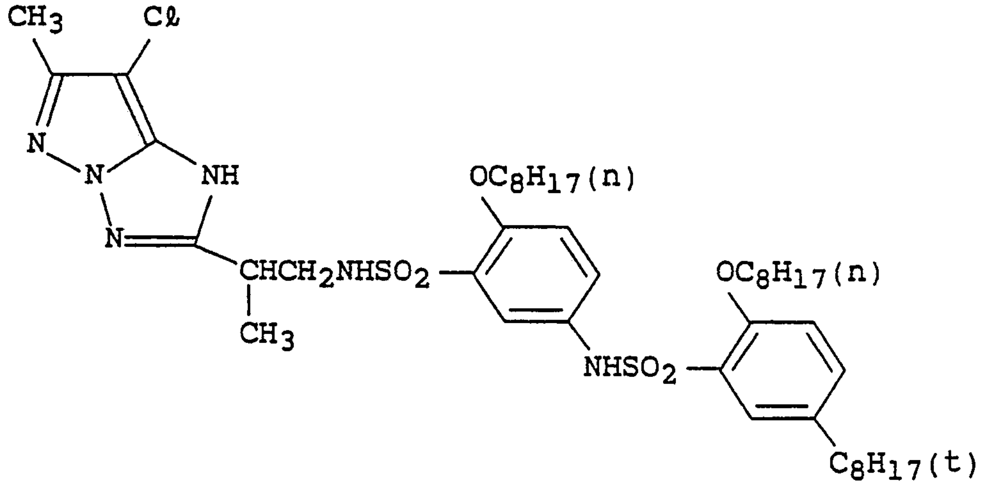
ExC-18



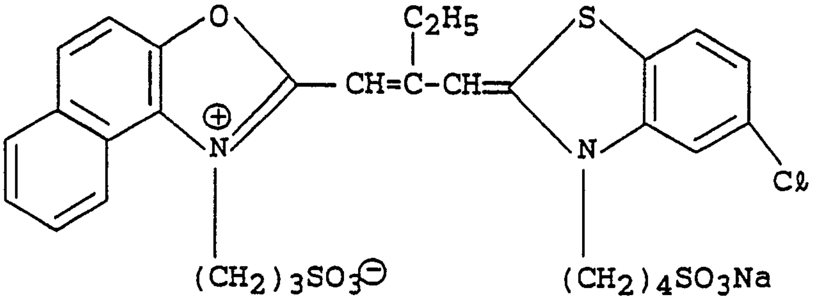
ExY-19



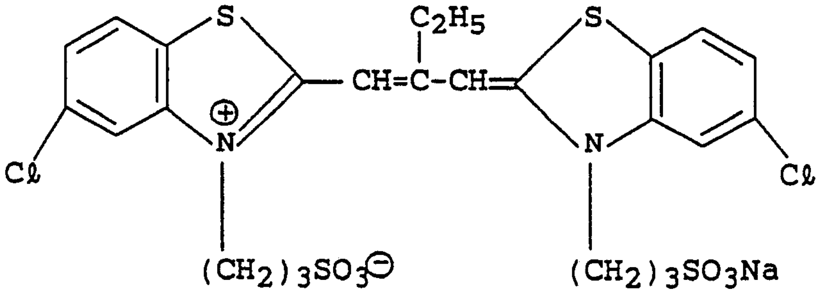
ExM-34



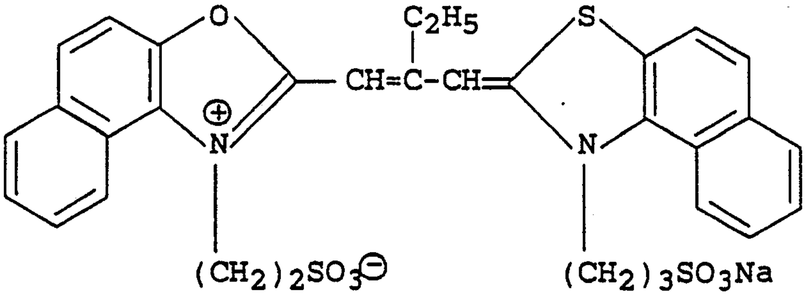
ExS-1



ExS-2



ExS-3



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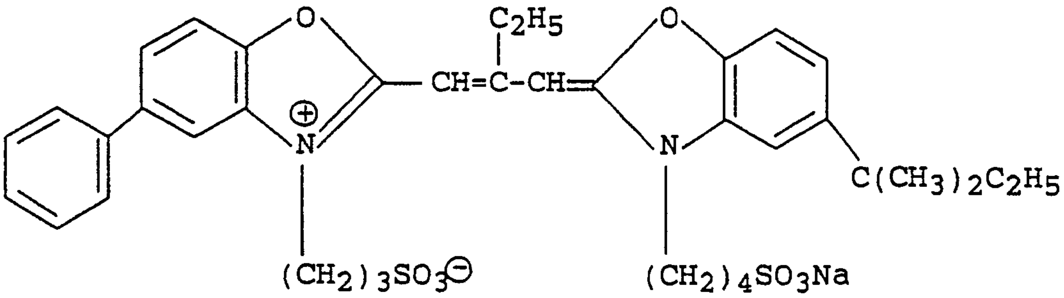

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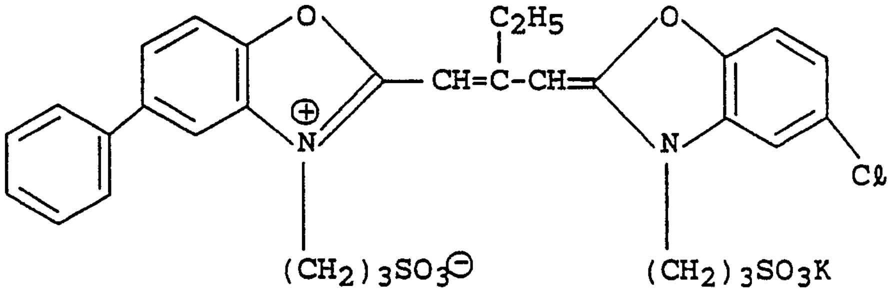

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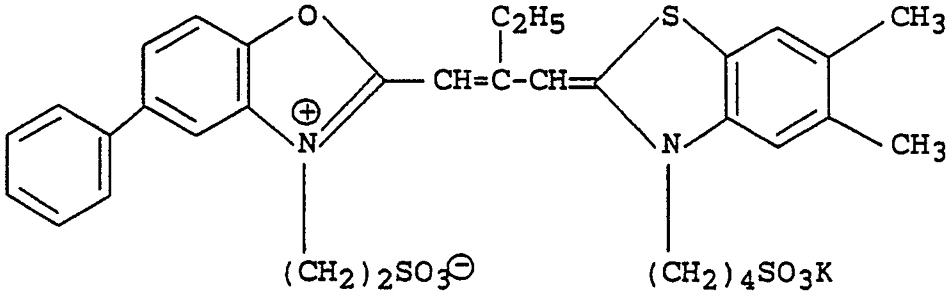

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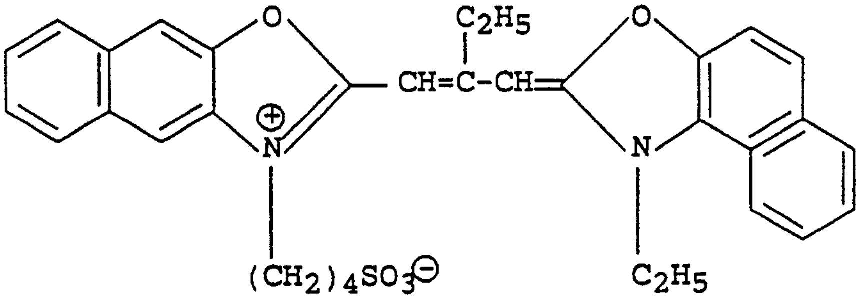
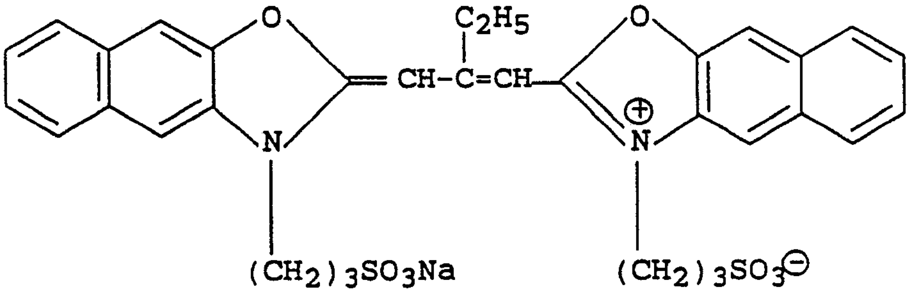
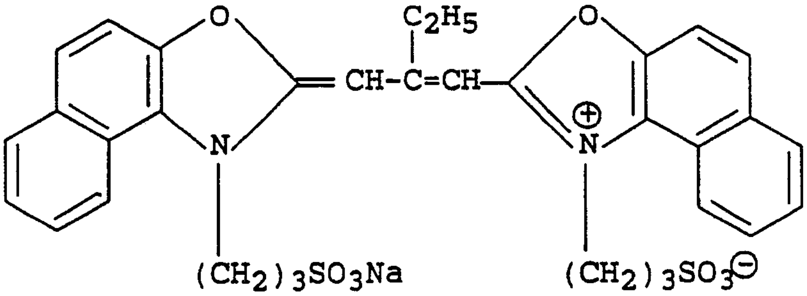


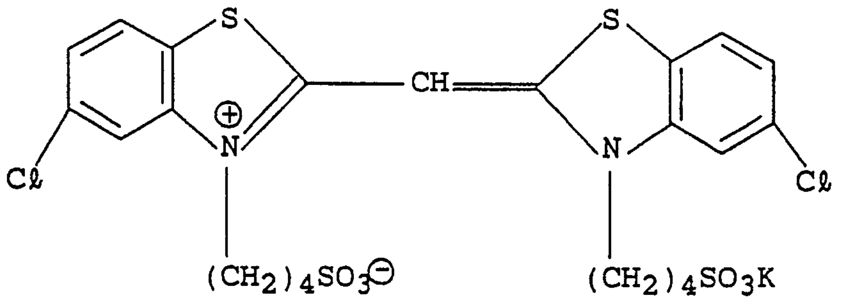
ExS-8



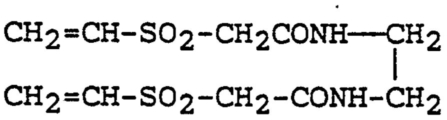
ExS-9



ExS-10

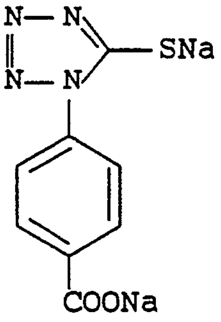


H-1



$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2CONH{-}CH_2 \\ CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \end{array}$$

ExS-11



Claims

1. A silver halide color photographic light-sensitive material which comprises a photographic light-sensitive layer having at least one silver halide emulsion layer on a support, wherein fine silver halide grains having an average grain size of less than 0.15 µm, adsorbing a compound for forming a silver salt having a solubility lower than that of silver bromide thereon, and having a silver chloride content of not less than 50 mol% are contained in said photographic light-sensitive layer.

2. A silver halide color photographic light-sensitive material which comprises at least one silver halide emulsion layer and at least one non-light-sensitive hydrophilic colloidal layer on a support, wherein fine silver halide grains having an average grain size of less than 0.15 µm, adsorbing a compound for forming a silver salt having a solubility lower than that of silver bromide thereon, and having a silver chloride content of not less than 50 mol% are contained in said at least one non-light-sensitive hydrophilic colloidal layer.

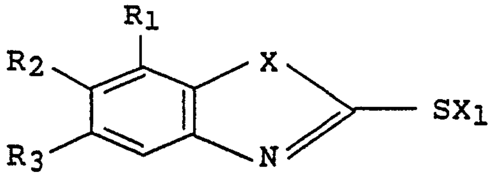
3. A silver halide color photographic light-sensitive material which comprises at least one silver halide emulsion layer on a support, wherein said silver halide color photographic light-sensitive material contains fine silver halide grains having an average grain size of less than 0.15 µm, adsorbing a compound for forming a silver salt having a lower solubility than that of silver bromide thereon, and having a silver chloride content of not less than 50 mol%, and contains a compound represented by following general formula (I):

A-(TIME)$_n$-B (I)

wherein A represents a coupler residue for releasing (TIME)$_n$-B upon a coupling reaction with an oxide of an aromatic primary amine developing agent, TIME represents a timing group which is bonded to a coupling active position of A and releases B after it is released from A upon the coupling reaction, and B represents an inhibiting group.

4. A material according to any one of claims 1 to 3, characterized in that the average size of said fine silver halide grains is less than 0.1 µm.

5. A material according to any one of claims 1 to 3, characterized in that said compound for forming a slightly soluble silver salt is represented by general formula (V):



... (V)

wherein X represents -O-, -NH-, or -S-, each of R_1, R_2, R_3, and R_4 independently represents a hydrogen atom or a group substitutable with a hydrogen atom, at least one of R_1, R_2, R_3, and R_4 being, directly or via a divalent connecting group, a substituted or unsubstituted alkyl or aryl group having not more than 13 carbon atoms, and X_1 represents a hydrogen atom or a cation for neutralizing a molecule.

6. A material according to any one of claims 1 to 3, characterized in that the silver chloride content of said fine silver halide grains is not less than 75 mol%.

7. A material according to any one of claims 1 to 3, characterized in that the silver chloride content of said fine silver halide grains is not less than 90 mol%.

8. A material according to any one of claims 1 to 3, characterized in that said material is a negative type color photographic light-sensitive material.