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(54) Silver halide photgraphic light-sensitive material.

(57) A silver halide photographic light-sensitive material comprising a support and at least one silver halide emulsion layer thereon, said silver halide emulsion layer containing a monodisperse silver halide emulsion manufactured in the presence of at least one type of thiosulfonic acid compounds represented by formulas [I], [II], and [III]:

[I] $R\text{-}SO_2S\text{-}M$

[II] $R\text{-}SO_2S\text{-}R^1$

[III] $RSO_2S\text{-}Lm\text{-}SSO_2\text{-}R^2$ wherein R, R^1, and R^2 may be the same or different and represent an aliphatic group, an aromatic group, or a heterocyclic group, M represents a cation, L represents a divalent bonding group, $\underline{m}$ represents 0 or 1, compounds represented by formulas [I] to [III] can be polymers containing, as a repeating unit, divalent groups derived from compounds represented by formulas [I] to [III], and if possible, R, R^1, R^2, and L can be bonded with each other to form a ring.

Silver halide photographic light-sensitive material

The present invention relates to a silver halide photographic light-sensitive material and, more particularly, to a silver halide photographic light-sensitive material having high sensitivity and producing low fog and a high maximum image density. The present invention also relates to a silver halide photographic light-sensitive material having a small variation over time in sensitivity and fog during its storage.

Basic properties required for a photographic silver halide emulsion are high sensitivity, low fog, and fine grains.

In order to increase the sensitivity of an emulsion, (1) to increase the number of photons absorbed by a single grain; (2) to increase an efficiency of converting photoelectrons generated by light absorption into a silver cluster (latent image); and (3) to increase development activity for effectively utilizing the formed latent image., are required. Increasing the size of grains increases the number of absorbed photons per grain but degrades image quality. Increasing the development activity is an effective means of increasing the sensitivity. In the case of parallel development as color development, however, the grain condition is generally degraded by increasing the development activity. In order to increase the sensitivity without grain condition degradation, it is most preferable to increase the efficiency of converting photoelectrons into a latent image, i.e., increase a quantum sensitivity. In order to increase the quantum sensitivity, low-efficiency processes such as recombination and latent image dispersion must be minimized. It is known that a reduction sensitization method of forming a small silver nucleus without development activity inside or the surface of a silver halide grain is effective to prevent recombination.

James et al. have found that the sensitivity can be increased with a lower fog level than that in normal reduction sensitization when a kind of reduction sensitization, in which a coating film of an emulsion subjected to gold-plus-sulfur sensitization is vacuum-deaerated and then heat-treated in a hydrogen atmosphere, is performed. This sensitization method is well known as hydrogen sensitization and is effective as a lab-scale high sensitization means. The hydrogen sensitization is actually used in the field of astrograph.

The method of reduction sensitization has been studied for a long time. Carroll, Lowe et al., and Fallens et al. disclose that a tin compound, a polyamine compound, and a thiourea dioxide-based compound are effective as a reduction sensitizer in U.S. Patents 2,487,850 and 2,512,925 and British Patent 789,823, respectively. Collier compares properties of silver nuclei formed by various reduction sensitization methods in "Photographic Science and Engineering", Vol. 23, P. 113 (1979). She used dimethylamineborane, stannous chloride, hydrazine, and methods of high-pH ripening and low-pAg ripening. Reduction sensitization methods are also disclosed in U.S. Patents 2,518,698, 3,201,254, 3,411,917, 3,779,777, and 3,930,867. Not only selection of a reduction sensitizer but also a method of using a reducing agent are disclosed in, e.g., JP-B-57-33572 ("JP-B-" means examined Japanese patent publication), JP-B-58-1410, and JP-A-57-179835 ("JP-A-" means unexamined published Japanese patent application). Techniques of improving storage stability of an emulsion subjected to reduction sensitization are disclosed in JP-A-57-82831 and JP-A-60-178445. Regardless of a number of studies as described above, an increase in sensitivity is insufficient as compared with that obtained in hydrogen sensitization in which a light-sensitive material is treated with hydrogen gas in a vacuum. This is reported by Moisar et al. in "Journal of Imaging Science", Vol. 29. P. 233 (1985).

As described above, the conventional techniques of reduction sensitization are insufficient to satisfy a recent demand for a photographic light-sensitive material with high sensitivity and high image quality.

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

It is another object of the present invention to provide a silver halide photographic light-sensitive material having the properties of the above object and producing a high maximum image density.

It is still another object of the present invention to provide a photographic light-sensitive material having a small variation over time in sensitivity and fog during its storage.

The above objects of the present invention are achieved by silver halide photographic light-sensitive materials described in following items (1) to (4).

(1) A silver halide photographic light-sensitive material comprising a support and at least one silver halide emulsion layer thereon, said silver halide emulsion layer containing a monodisperse silver halide emulsion manufactured in the presence of at least one type of compounds (to be referred as thiosulfonic acid compounds) represented by formulas [I], [II], and [III].

[I] $R\text{-}SO_2S\text{-}M$

[II] $R\text{-}SO_2S\text{-}R^1$

[III] $RSO_2S\text{-}L_m\text{-}SSO_2\text{-}R^2$
wherein R, R^1, and R^2 can be the same or different and represent an aliphatic group, an aromatic group, or a heterocyclic group, M represents a cation, L represents a divalent linking group, m represents 0 or 1. Compounds represented by formulas [I] to [III] can be polymers containing, as a repeating unit, divalent groups derived from compound represented by formulas [I] to [III], and, if possible, R, R^1, R^2 and L can be bonded with each other to form a ring.

(2) A material described in item (1), wherein the monidisperse silver halide emulsion is reduction-sensitized in the presence of at lest one type of thiosulfonic acid compounds represented by formulas [I], [II], and [III] during precipitation of silver halide grains.

(3) A silver halide photographic light-sensitive material comprising a support and at least one silver halide emulsion layer thereon, said silver halide emulsion layer containing a monodisperse silver halide emulsion reduction-sensitized by ascorbic acid or at least one of derivatives of ascorbic acid in a process of manufacturing a silver halide emulsion.

(4) A material described in item (3), wherein the silver halide emulsion is a moodisperse silver halide emulsion reduction-sensitized in the presence of at least one type of compounds represented by formulas [I], [II], and [III].

The present invention will be described in detail below.

Process of manufacturing silver halide emulsions are roughly classified into, e.g., grain formation, desalting, chemical sensitization, and coating steps. Grain formation is further classified into e.g. nuclation, ripening, and precipitation substeps. These steps are sometimes performed not in the above-mentioned order but in a reverse order or repeatedly.

At least one type of compounds represented by formulas [I], [II], and [III] can be added in any step from grain formation to coating processes of a monodisperse silver halide emulsion. The compound is preferably added in the grain formation process of silver halide grains, and more preferably, during precipitation of the grains. Most preferably, reduction sensitization is performed in the presence of the compound during precipitation of the monodisperse silver halide grains. The reduction sensitization can be performed during any of nucleation as the initial stage of grain formation, physical ripening, and precipitation. Although the reduction sensitization is normally performed prior to chemical sensitization (preferably gold-plus-sulfur sensitization), it can be performed after the chemical sensitization if necessary. In the case of performing chemical sensitization in addition to gold sensitization, the reduction sensitization is preferably performed before the chemical sensitization so as not to produce an undesired fog. The reduction sensitization is most preferably performed during precipitation of silver halide grains. In this case, "precipitation" means a state in which silver halide grains are being grown and precipitated by physical ripening or addition of water-soluble silver salt and water-soluble alkali halide. The method of performing the reduction sensitization during the precipitation includes a method in which the reduction sensitization is performed while addition of silver salt and alkali halide is temporarily stopped during precipitation and then precipitation is further continued.

The reduction sensitization employed in the present invention can be selected from a method of adding a known reducing agent in a silver halide emulsion, a method called silver ripening in which precipitating or ripening is performed in a low-pAg atmosphere of a pAg of 1 to 7, and a method called high-pH ripening in which precipitating or ripening is performed in a high-pH atmosphere of a pH of 8 to 11. These methods can be used in a combination of two or more thereof.

A method of adding a reduction sensitizer is preferable because the level of reduction sensitization can be precisely adjusted.

Known examples of the reduction sensitizer are stannous salt, amines and polyamines, a hydrazine derivative, formamidinesulfinic acid, a silane compound, and a borane compound. The reduction sensitizer for use in the present invention can be selected from these known compounds, and the compounds can be used singly or in a combination of two or more thereof. Preferable compounds of the reduction sensitizer are stannous chloride, thiourea dioxide, and dimethylamineborane. An addition amount of the reduction sensitizer depends on emulsion manufacturing conditions and therefore must be selected to satisfy the conditions. A preferable addition amount falls within the range of 10^{-7} to 10^{-3} per mol of a silver halide.

The reduction sensitizer is used as a solution dissolved in water or a solvent, e.g., glycols, ketones, esters, or amides, and the solution can be added during grain formation, or before or after chemical sensitization. Although the reduction sensitizer can be added in any step of emulsion manufacturing process, it is most preferably added during grain precipitation. The reduction sensitizer is preferably added at an arbitrary timing during grain formation though it can be added in a reaction vessel beforehand. In addition, the reduction sensitizer can be added in an aqueous solution of a water-soluble silver salt or water-soluble alkali halide to perform grain formation by using the aqueous solution. A method of adding a solution of the reduction sensitizer several times or continuously adding it over a long time period as grain formation progresses is also preferable.

Thiosulfonic acid compounds represented by formulas [I], [II], and [III] will be described in more detail below. When R, R^1, and R^2 each present an aliphatic group, it is a saturated or unsaturated, straight-chain, branched or cyclic aliphatic hydrocarbon group and is preferably alkyl having 1 to 22 carbon atoms or alkenyl or alkinyl having 2 to 22 carbon atoms. These groups can have a substituent group. Examples of the alkyl are methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, 2-ethylhexyl, decyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, isopropyl, and t-butyl.

Examples of the alkenyl are allyl and butenyl.

Examples of the alkinyl are propargyl and butynyl.

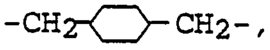
An aromatic group of R, R^1, and R^2 includes aromatic group of single-ring or condensed-ring. The aromatic group preferably has 6 to 20 carbon atoms. Examples of such an aromatic group are phenyl and naphthyl. These groups can have substituent group.

A heterocyclic group of R, R^1, and R^2 includes a 3- to 15-membered ring having at least one element of nitrogen, oxygen, sulfur, selenium, and tellurium and at least one carbon atom. Examples of the heterocyclic group are rings of pyrrolidine, piperidine, pyridine, tetrahydrofurane, thiophene, oxazole, thiazole, imidazole, benzothiazole, benzoxazole, benzimidazole, selenazole, benzoselenazole, tellurazole, triazole, benzotriazole, tetrazole, oxadiazole, and thiadiazole. 3- to 6-membered ring is preferred.

Examples of the substituent group on R, R^1, and R^2 are an alkyl group (e.g., methyl, ethyl, and hexyl), an alkoxy group (e.g., methoxy, ethoxy, and octyloxy), an aryl group (e.g., phenyl, naphthyl, and tolyl), a hydroxyl group, a halogen atom (e.g., fluorine, chlorine, bromine, and iodine), an aryloxy group (e.g. phenoxy), an alkylthio group (e.g., methylthio and butylthio), an arylthio group (e.g. phenylthio), an acyl group (e.g. acetyl, propionyl, butyryl, and valeryl), a sulfonyl group (e.g. methyl sulfonyl and phenylsulfonyl), an acylamino group (e.g., acetylamino and benzaoylmino), a sulfonylamino group (e.g., methanesulfonylamino and benzenesulfonylamino), an acyloxy group (e.g., acetoxy and benzoxy), carboxyl, cyano, sulfo, amino, $-SO_2SM$ (M represent a monovalent cation), and $-SO_2R^1$.

A divalent linking group represented by L includes an atom or an atom group containing at least one of C, N, S, and O. Examples of L are alkylene, alkenylene, alkynylene, arylene, -O-, -S-, -NH-, -CO-, and $-SO_2-$. These divalent group can be used singly or in a combination of two or more thereof.

Preferably L represent divalent aliphatic group or a divalent aromatic group. Examples of the divalent aliphatic group of L are $-(CH_2)_n-$ (n = 1 to 12), $-CH_2-CH=CH-CH_2-$, $-CH_2C{\equiv}CCH_2-$,

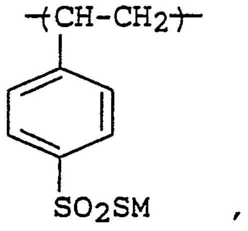


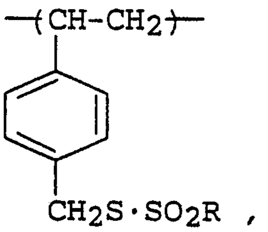
and xylylene. Examples of the divalent aromatic group of L are phenylene and naphthylene.

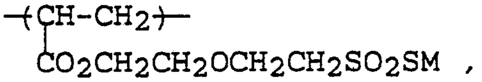
These linking groups can have further substituent group above-mentioned.

M is preferably a metal ion, an ammonium ion, or an organic cation. Examples of the metal ion are a lithium ion, a sodium ion, and a potassium ion. Examples of the organic cation are an organic ammonium ion (e.g., tetramethylammonium, and tetrabutylammonium), an organic phosphonium ion (e.g. tetraphenylphosphonium), and a guanidinium ion.

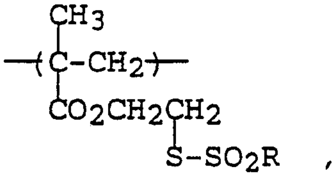
When a compound represented by each of formulas [I] to [III] is a polymer, examples of its repeating unit are as follows:



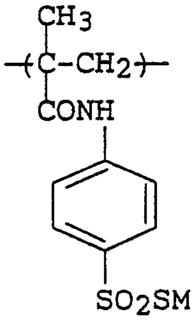




$$-\!\!\left(\underset{\displaystyle CO_2CH_2CH_2OCH_2CH_2SO_2SM}{CH}-CH_2\right)\!\!-\ ,$$



$$-\!\!\left(\overset{\displaystyle CH_3}{\underset{\displaystyle CO_2CH_2\underset{\displaystyle S-SO_2R}{CH_2}}{C}}-CH_2\right)\!\!-\ ,$$



Each of the above polymers can be a homopolymer or a copolymer with another copolymerizable monomer.

Examples of a compound represented by formula [I], [II], or [III] are listed in Table A to be presented later. However, compounds are not limited to those in Table A.

Thiosulfonic acid compounds represented by formulas [I], [II], and [III] can be easily synthesized by methods described or cited in JP-A-54-1019; British Patent 972,211; "Journal of Organic Chemistry", Vol. 53, PP. 396 (1988); and "Chemical Abstracts", Vol. 59, 9776e.

A preferable addition amount of a compound represented by formula [I], [II], or [III] is 10^{-7} to 10^{-1} mol per mol of a silver halide. The addition amount is more preferably 10^{-6} to 10^{-2} and most preferably 10^{-5} to 10^{-3} mol per mol of a silver halide.

A conventional method of adding an additive in a photographic emulsion can be adopted to add thiosulfonic acid compounds represented by formulas [I] to [III] in manufacturing process. For example, a water-soluble compound can be added in the form of an aqueous solution having an arbitrary concentration. A water-insoluble or hardly water-soluble compound is dissolved in an arbitrary organic solvent (such as alcohols, glycols, ketones, esters, and amides) which is miscible with water and does not adversely affect photographic properties, and then added as a solution.

As described above, a compound represented by formula [I], [II], or [III] can be added at any timing during manufacturing process such as during grain formation of a silver halide emulsion, or before or after chemical sensitization. The compound is preferably added before or during reduction sensitization. The compound is most preferably added while water-soluble silver salt and alkali halide are added.

Although the compound can be added in a reaction vessel beforehand, it is preferably added at an arbitrary timing during grain formation. In addition, a compound represented by formula [I], [II], or [III] can be added in an aqueous solution of a water-soluble silver salt or water-soluble alkali halide to perform grain formation by using the aqueous solution. A method of adding a solution of a compound represented by formula [I], [II], or [III] several times or continuously adding it over a long time period as grain formation progresses is also preferable.

A thiosulfonic acid compound most preferable in the present invention is represented by formula [I].

Examples of ascorbic acid and its derivative (to be referred to as an "ascorbic acid compound" hereinafter) are as follows.

(A-1) L-ascorbic Acid
(A-2) Sodium L-ascorbate
(A-3) Potassium L-ascorbate
(A-4) DL-ascorbic Acid
(A-5) Sodium D-ascorbate
(A-6) L-ascorbyl-6-acetate
(A-7) L-ascorbyl-6-palmitate
(A-8) L-ascorbyl-6-benzoate
(A-9) L-ascorbyl-5,6-diacetate
(A-10) L-ascorbyl-5,6-O-isopropylidene

In order to add the above ascorbic acid compounds in a process of manufacturing a silver halide emulsion of the present invention, they may be dispersed directly in an emulsion. Alternatively, the ascorbic acid compound may be dissolved in a single solvent or solvent mixture of, e.g., water, methanol, and ethanol and then added during the manufacturing process.

It is desired that the ascorbic acid compound of the present invention is used in an amount much larger than a preferable addition amount of a conventional reduction sensitizer. For example, JP-B-57-33572 describes "an amount of a reducing agent normally does not exceed 0.75×10^{-2} milli equivalent (8×10^{-4} mol/AgX mol) per gram of silver ions. An amount of 0.1 to 10 mg (10^{-7} to 10^{-5} mol/AgX mol for ascorbic acid) per kg of silver nitrate is effective in many cases" (reduced values are calculated by the present inventors). U.S. Patent 2,487,850 describes that "a tin compound can be used as a reduction sensitizer in an addition amount of 1×10^{-7} to 44×10^{-6} mol". JP-A-57-179835 describes that it is suitable to add about 0.01 mg to about 2 mg of thiourea dioxide or about 0.01 mg to about 3 mg of stannous chloride per mol of a silver halide. A preferable addition amount of the ascorbic acid compound used in the present invention depends on factors such as a grain size and a halogen composition of an emulsion, an emulsion preparation temperature, a pH, and a pAg. The addition amount, however, is selected within the range of, preferably, 5×10^{-5} mol to 1×10^{-1} mol, more preferably, 5×10^{-4} mol to 1×10^{-2} mol, and most preferably, 1×10^{-3} mol to 1×10^{-2} mol per mol of a silver halide.

Although the ascorbic acid compound of the present invention can be added at any timing in an emulsion manufacturing process, it is most preferably added during grain precipitation. The ascorbic acid compound is preferably added at an arbitrary timing in grain formation though it can be added in a reaction vessel beforehand. In addition, the ascorbic acid compound can be added in an aqueous solution of a water-soluble silver salt or water-soluble alkali halide to perform grain formation by using this aqueous solution. A method of adding a solution of the ascorbic acid compound several times or continuously adding it over a long time period as grain precipitation progresses is also preferable.

A method of performing reduction sensitization by using the ascorbic acid compound of the present invention is superior to a conventional reduction sensitization method in sensitivity, fog, and storage stability. In accordance with other conditions, however, it is sometimes more preferable to use the ascorbic acid compound with another reduction sensitization method. In this case, however, it is preferred that the other reduction sensitization method is used as merely an auxiliary means of reduction sensitization and the ascorbic acid compound is used as a main reduction sensitization. The other sensitization method combined with the method using the ascorbic acid compound can be selected from a method of adding another known reduction sensitizer to a silver halide emulsion, a method called silver ripening of precipitating or ripening in a low-pAg atmosphere of a pAg of 1 to 7, and a method called high-pH ripening of precipitating or ripening in a high-pH atmosphere of a pH of 8 to 11.

Of these other reduction sensitization method to be combined with the method using the ascorbic acid compound, a method of adding another reduction sensitizer is generally preferable because the level of reduction sensitization can be precisely adjusted.

As the another known reduction sensitizer, stannous salt, amines and polyamines, a hydrazine derivative, formamidinesulfinic acid, a silane compound, and a borane compound are known. The ascorbic acid compound, however, can provide superior results to those obtained by the above known reduction sensitizers.

In the present invention, it is preferred that reduction sensitization is performed by using the ascorbic acid compound in a process of manufacturing a silver halide emulsion. Also, the reduction sensitization is preferably performed in the presence of at least one compound selected from compounds represented by formulas [I], [III], and [III].

In the present invention, a monodisperse silver halide emulsion means an emulsion in which silver halide grains falling within the grain size region ranging from -20% to +20% of a maximum grain size $\bar{r}$ occupies 60% or more, preferably, 70% or more, and most preferably, 80% or more of a total silver halide grain weight.

It should be noted that the maximum grain size $\bar{r}$ is defined as a grain size r^1 which maximizes a product value of $[n^1 \times (r^1)^3]$, wherein n^1 denotes a frequency of a grain having a grain size r^1. The value of $\bar{r}$ (the number of significant digits are 3, and the least significant digit is rounded) is equal to a grain size for giving a maximum value of a volume frequency curve.

The grain size is a diameter in the case of a spherical silver halide grain and is a sphere-equivalent diameter in the case of a grain having a shape other than a sphere.

A silver halide which can be used in combination with a light-sensitive material of the present invention can have any composition containing a component selected from the group consisting of silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide, and silver chloride. A preferable silver halide is silver iodobromide containing 30 mol% or less of silver iodide, silver bromide, or silver chlorobromide.

A silver halide grain which can be used in the monodisperse silver halide emulsion of the present invention can be selected from a regular crystal not including a twined crystal plane and grain including a twined crystal plane described in Japan Photographic Society ed., "Silver Salt Photographs, Basis of Photographic Industries", (Corona Co., P. 163) such as a single twined crystal including one twined crystal face, a parallel multiple twined crystal including two or more parallel twined crystal faces, and a non-parallel multiple twined crystal including two or more non-parallel twined crystal faces, in accordance with its application. In the case of a regular crystal, a cubic grain comprising (100) faces, an octahedral grain comprising (111) faces, and a dodecahedral grain comprising (110) faces disclosed in JP-B-55-42737 and JP-A-60-222842 can be used. In addition, a grain comprising (h11), e.g., (211) faces, a grain comprising (hh1), e.g., (331) faces, a grain comprising (hk0), e.g., (210) faces, and a grain comprising (hk1), e.g., (321) faces as reported in "Journal of Imaging Science", Vol. 30, P. 247, 1986 can be selectively used in accordance with an application although a preparation method must be improved. A grain including two or more types of faces, e.g., a tetradecahedral grain comprising both (100) and (111) faces, a grain comprising both (100) and (110) faces, and a grain comprising both (111) and (110) faces can be selectively used in accordance with an application.

In the emulsion of the present invention, octahedral grains having a (111) face and tetradecahedral grains having both of a (100) face and a (111) face in one grain are particularly preferable.

The silver halide grains may be fine grains having a grain size of 0.1 µm or less or large grains having a projected surface area diameter of 10 µm.

In the present invention, two or more types of monodisperse silver halide emulsions manufactured in the presence of a thiosulfonic acid compound represented by formula [I], [II], or [III] and having different maximum-frequency grain sizes can be mixed in the same layer or independently coated on different layers. In addition, two or more types of polydisperse silver halide emulsions or monodisperse emulsions other than that of the present invention can be mixed in an amount of half or less, and preferably, 30 wt% or less with respect to a total weight of silver halide grains.

The photographic emulsions for use in the present invention can be prepared using the methods described in, for example, P. Glafkides, "Chimie et Physique Photographique", Paul Montel, 1967; Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966; and V.L. Zelikman et al., "Making and Coating the photographic emulsion", Focal Press, 1964. The described method is, for example, an acid method, a neutralization method, and an ammonia method. Also, as a system for reacting a soluble silver salt and a soluble halide, a single mixing method, a double mixing method, or a combination thereof can be used. Also, a so-called back mixing method for forming silver halide grains in the presence of excessive silver ions can be used. As one system of the double mixing method, a so-called controlled double jet method, wherein the pAg in the liquid phase in which the silver halide is generated is kept at a constant value can be used. According to this method, a silver halide emulsion having a regular crystal form and almost uniform grain sizes is obtained.

In preparing a silver halide emulsion consisting of regular grains, grains having a desired grain size can be obtained by performing nucleation and precipitation by a double jet method while a pAg is maintained constant and a supersaturation degree is held so as not to cause re-nucleation.

In addition, a method described in JP-A-54-48521 can be applied. In a preferred embodiment of this method, an aqueous potassium iodobromide-gelatin solution and an aqueous ammonium silver nitrate solution are preferably added to an aqueous gelatin solution containing silver halide grains while an addition speed is changed as a function of a time. In this embodiment, by arbitrarily selecting, e.g., a time function of the addition speed, a pH, a pAg, and a temperature, a high monodisperse silver halide emulsion can be prepared. This method is described in detail in, e.g., "Photographic Science and Engineering", Vol. 6, PP. 159 to 165 (1962); "Journal of Photographic Science", Vol. 12, PP. 242 to 251 (1964), U.S. Patent 3,655,394; and British Patent 1,413,748.

A tabular grain having an aspect ratio of 3 or more can also be used in the present invention. The tabular grain can be easily prepared by methods described in, for example, Cleve, "Photography Theory and Practice", P. 131, (1930); Gutoff, "Photographic Theory Science and Engineering", Vol. 14, PP. 248 to 257, (1970); and U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520 and British Patent 2,112,157. When the tabular grain is used, covering power and a color sensitizing efficiency of a sensitizing dye can be advantageously improved. These advantages are described in detail in the U.S. Patent 4,434,226.

Tabular grains are preferable as an emulsion of the present invention. In particular, tabular grains in which grains having an aspect ratio of 3 to 8 occupy 50% or more of a total projected surface area are preferred.

Monodisperse tabular grains can be manufactured by, e.g., the following method. That is, a fine grain tabular silver iodobromide emulsion can be prepared by a double jet method in which equimolar amounts of an aqueous silver nitrate solution and an aqueous solution mixture of potassium bromide and potassium iodide are added.

Subsequently, equimolar amounts of an aqueous silver nitrate solution and an aqueous solution mixture of potassium bromide and potassium iodide are added while a total addition amount and an addition speed are increased, thereby performing precipitation several times or continuously. During addition, a pAg is so controlled as to maintain a tabular shape and not to cause re-necleation. More specifically, the pAg is preferably 9 to 7.

A crystal structure may be uniform, may have different halogen compositions in its interior and on its surface, or may be a layered structure. These emulsion grains are dislosed in, e.g., British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877, and Japanese Patent Application 58-248469. In addition, a silver halide layers having a different composition each other may be epitaxially bonded, or a compound other than a silver halide such as a silver rhodanide or a lead oxide may be bonded.

The silver halide emulsion of the present invention preferably has a distribution or structure of a halogen composition in its grain. A typical example is a coreshell type or double structured grain having different halogen compositions in the interior and surface layer of the grain as disclosed in, e.g., JP-B-43-13162, JP-A-61 215540, JP-A-60-222845, and JP-A-61-75337. In such a grain, the shape of a core portion is sometimes identical to or sometimes different from that of the entire grain with a shell. More specifically, while the core portion is cubic, the grain with a shell is sometimes cubic or sometimes octahedral. On the contrary, while the core portion is octahedral, the grain with a shell is sometimes cubic or sometimes octahedral. In addition, while the core portion is a clear regular grain, the grain with a shell is sometimes slightly deformed or sometimes does not have any definite shape. Furthermore, not a simple double structure but a triple structure as disclosed in JP-A-60-222844 or a multilayered structure of more layers can be formed, or a thin film of a silver halide having a different composition can be formed on the surface of a core-shell double structure grain.

A structured grain can be obtained not only by giving the above surrounding structure on the core but also by giving a so-called junction structure. Examples of such a grain of junction structure are disclosed in, e.g., JP-A-59-133540, JP-A-58-108526, EP 199290A2, JP-B-58-24772, and JP-A-59-16254. A junction crystal having a composition different from that of a host crystal can be produced and bonded to an edge, corner, or face portion of the host crystal. Such a junction crystal can be formed on the host crystal regardless of whether the host crystal has a homogeneous halogen composition or a core-shell structure.

The junction structure can be naturally made by a combination of silver halides. In addition, the junction structure can be made by combining a silver salt compound not having a rocksalt structure, e.g., silver rhodanate or silver carbonate with a silver halide. A non-silver salt compound such as PbO can also be used as long as the junction structure can be made with a silver halide.

In a silver iodobromide grain having the above structure, a silver iodide concentration may have any distribution. For example, in a core-shell type grain, the silver iodide content may be high at a core portion and low at a shell portion or vice versa. Similarly, in a grain having the junction structure, the silver iodide content may be high in a host crystal and relatively low in a junction crystal or vice versa.

In a grain having the above structure, a boundary portion between different halogen compositions may be clear or unclear due to forming a mixed crystal. Alternatively, a continuous structural change may be positively made in the boundary portion.

The silver halide emulsion for use in the present invention can be subjected to a treatment for rounding a grain as disclosed in, e.g., EP-0096727BI and EP-0064412BI or a treatment of modifying the surface of a grain as disclosed in DE-2306447C2 and JP-A-60-221320.

The silver halide emulsion according to the present invention is preferably used as a surface latent image type. It can be also used, however, as an internal latent image type emulsion by selecting a developing solution or development conditions as disclosed in JP-A-59-133542. In addition, a shallow internal latent image type emulsion covered with a thin shell can be effective in accordance with an application.

A solvent for silver halide can be effectively used to promote ripening. On the other hand, in a known conventional method, an excessive amount of halogen ions are supplied in a reaction vessel in order to promote ripening. Therefore, it is apparent that ripening can be promoted by only supplying a halide solution into a reaction vessel. In additon, other ripening agents can be used. In this case, a total amount of these other ripening agents can be mixed in a dispersion medium in the reaction vessel before a silver salt and a halide are added therein, or they can be added in the reaction vessel together with one or more halides, a silver salt or a deflocculant. Alternatively, the ripening agents can be added independently in the step of adding a halide and a silver salt.

Examples of the ripening agent other than the halogen ion are ammonium, an amine compound and a thiocyanate such as an alkali metal thiocyanate (especially sodium thiocyanate or potassium thiocyanate), and ammonium thiocyanate.

In the present invention, it is very important to perform chemical sensitization, typically sulfur sensitization or gold sensitization. Photographic properties of grains doped with 1×10^{-4} mol/mol Ag of multivalent metal ions are significantly improved when chemical sensitization is performed. A portion at which the chemical sensitization is performed differs depending on the composition, structure, or shape of an emulsion grain or an application of the emulsion. A chemical sensitized nucleus is embedded either in a deep portion inside a grain or in a shallow portion from the grain surface or formed on the surface of a grain. Although the present invention is effective in any case, the chemical sensitized nucleus is most preferably formed in a portion near the surface. That is, the present invention is more effective in the surface latent image type emulsion than in the internal latent image type emulsion.

Chemical sensitization can be performed by using active gelatin as described in T.H. James, "The Theory of the Photographic Process", 4th ed., Macmillan, 1977, PP. 67 to 76. Alternatively, chemical sensitization can be performed at a pAg of 5 to 10, a pH of 5 to 8 and a temperature of 30 to 80°C by using sulfur, selenium, tellurium, gold, platinum, palladium or irridium, or a combination of a plurality of these sensitizers as described in Research Disclosure Vol. 120, No. 12,008 (April, 1974), Research Disclosure Vol. 34, No. 13,452 (June, 1975), U.S. Patents 2,642,361, 3,297,446, 3,772,031, 3,857,711, 3,901,714, 4,266,018, and 3,904,415, and British Patent 1,315,755. Chemical sensitization is optimally performed in the presence of a gold compound and a thiocyanate compound, a sulfur-containing compound described in U.S. Patents 3,857,711, 4,266,018 and 4,054,457 or a sulfur-containing compound such as a hypo, thiourea compound and a rhodanine compound. Chemical sensitization can also be performed in the presence of a chemical sensitization assistant. An example of the chemical sensitization assistant is a compound known to suppress fogging and increase sensitivity in the chemical sensitization process such as azaindene, azapyridazine, and azapyrimidine. Examples of a chemical sensitization assistant modifier are described in U.S. Patents 2,131,038, 3,411,914, 3,554,757, JP-A-58-126526 and G.F. Duffin, "Photographic Emulsion Chemistry", PP. 138 to 143.

The photographic emulsion of the present invention can contain various compounds in order to prevent fogging during manufacture, storage, or a photographic process of the light-sensitive material or to stabilize photographic properties. Examples of the compound known as an antifoggant or stabilizer are azoles, e.g., benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, and mercaptotetrazoles (especially, 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriadines; a thioketo compound such as oxadrinthione; azaindenes, e.g., triazaindenes, tetraazaindenes (especially, 4-hydroxy)-substituted(1,3,3a,7)tetraazaindenes), and pentaazaindenes. Examples are described in U.S. Patents 3,954,474 and 3,982,947 and JP-B-52-28660.

The photographic emulsion used in the present invention can be spectrally sensitized by, e.g., methine dyes. Examples of the dye used for this purpose are a cyanine dye, merocyanine dye, a composite cyanine dye, a composite merocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye, and a hemioxonol dye. Most effective dyes are those belonging to a cyanine dye, a merocyanine dye, and a composite merocyanine dye. In these dyes, any nucleus normally used as a basic heterocyclic nucleus in cyanine dyes can be contained. Examples of the nucleus are a pyrroline nucleus, an oxazoline nucleus, a thiozoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, and a pyridine nucleus; a nucleus obtained by condensation of an alicyclic hydrocarbon ring to each of the above nuclei; and a nucleus obtained by condensation of an aromatic hydrocarbon ring to each of the above nuclei, e.g., an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxadole nucleus, a naphthooxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, and a quinoline nucleus. These nuclei can have a substituent group on a carbon atom.

For a merocyanine dye or composite merocyanine dye, a 5- or 6-membered heterocyclic nucleus having a ketomethylene structure, e.g., a pyrazoline-5-one nucleus, a thiohydantoin nucleus, a 2-thiooxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus, and a thiobarbituric acid nucleus can be contained.

These sensitizing dyes can be used singly or in a combination of two or more thereof. A combination of the sensitizing dyes is often used especially in order to perform supersensitization. Typical examples of the combination are described in U.S. Patents 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, 4,026,707, British

Patents 1,344,281 and 1,507,803, JP-B-43-4936 and JP-B-53-12375, and JP-A-52-110618 and JP-A-52-109925.

The emulsion can contain, in addition to the sensitizing dye, a dye not having a spectral sensitizing effect or a substance substantially not absorbing visible light and having supersensitization.

The dye can be added in the emulsion at any timing conventionally known to be effective in emulsion preparation. Most ordinarily, the dye is added after completion of chemical sensitization and before coating. However, the dye can be added at the same time as a chemical sensitizer to simultaneously perform spectral sensitization and chemical sensitization as described in U.S. Patents 3,628,969 and 4,225,666. The dye can also be added before chemical sensitization as described in JP-A-58-113928, or added before completion of silver halide grain precipitation to start spectral sensitization. In addition, as described in U.S. Patent 4,225,666, a part of the above compound can be added before chemical sensitization and the remaining portion is added thereafter. Further, as described in U.S. Patent 4,183,756, the compound can be added at any timing during silver halide grain formation.

An addition amount of the above dye can be 4×10^{-6} to 8×10^{-3} mol per mol of a silver halide. When a silver halide grains has a preferable size of 0.2 to 1.2 μm, an addition amount of about 5×10^{-5} to 2×10^{-3} mol is more effective.

The above various additives are used in the light-sensitive material of the present invention. In addition to the above additives, however, various additives can be used in accordance with applications.

These additives are described in Research Disclosures, Item 17643 (Dec. 1978) and Item 18716 (Nov. 1979) and they are summarized in the following table.

Additives	RD No.17643	RD No.18716
1. Chemical sensitizers	page 23	page 648, right column
2. Sensitivity increasing agents		do
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, ultra-violet 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	page 26	page 651, left column
10. Binder	page 26	do
11. Plasticizers, lubricants	page 27	page 650, right column
12. Coating assistant, surface active agents	pages 26-27	do
13. Antistatic agents	page 27	do

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 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, and 4,401,752, JP-B-58-10739, and British Patents 1,425,020 and 1,476,760.

Preferred examples of a magenta coupler are 5-pyrazolone and pyrazoloazole compounds. Most preferable examples of the compound are described in, e.g., U.S. Patents 4,310,619 and 4,351,897, EP 73,636, U.S. Patents 3,061,432 and 3,752,067, Research Disclosure No. 24220 (June 1984), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-43659, and U.S. Patents 4,500,630 and 4,540,654.

Examples of a cyan coupler are phenol and naphthol couplers. Preferable examples of the coupler are 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, EP 121,365A, U.S. Patents 3,446,622, 4,333,999, 4,451,559, and 4,427,767, and EP 161,626A.

Preferable examples of a colored coupler for correcting additional, undesirable absorption of 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, and 4,367,282, and British Patent 2,102,173.

Couplers releasing a photographically useful residue upon coupling are also preferably used in the present invention. Preferable 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-60-184243, 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 Patent 2,097,140, 2,131,188, and JP-A-59-157638 and JP-A-59-170840.

Other 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; DIR redox compound, a DIR coupler, a DIR coupler releasing coupler, and a DIR coupler 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 European Patent No. 173,302A; bleaching accelerator releasing couplers described in, e.g., R.D. Nos. 11449 and 24241 and JP-A-61-201247; and a ligand releasing coupler described in, e.g., U.S. Patent 4,553,477.

Although examples of the color coupler which can be used in the present invention will be presented in Table B, the color coupler is not limited to these examples.

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)isophthlate, and bis(1,1-diethylpropyl)phthalate; esters of phosphoric acid or phosphonic acid, e.g., triphenylphosphate, tricresylphosphate, 2-ethylhexyldiphenylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, tributoxyethylphosphate, trichloropropylphosphate, di-2-ethylhexylphenylphosphonate; esters of benzoic acid, 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; esters of aliphatic carboxylic acid, 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 an auxiliary solvent. Typical examples of the auxili 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 loadable latex are described in U.S. Patent 4,199,363, West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230, and the like.

Although the present invention can be applied to any light-sensitive material, it is preferably applied to various color light-sensitive materials. Typical examples of the color light-sensitive 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.

When the light-sensitive material according to the present invention is used as a material for color photographing, the present invention can be applied to light-sensitive materials having various structures and to light-sensitive materials having combinations of various layer structures and special color materials.

Typical examples are: light-sensitive materials, in which a coupling speed and diffusibility of a color coupler is combined with a layer structure, as disclosed in, e.g., JP-B-47-49031, JP-B-49-3843, JP-B-50-21248, JP-A-59-58147, JP-A-59-60437, JP-A-60-227256, JP-A-61-4043, JP-A-61-43743, and JP-A-61-42657; light sensitive materials, in which a same-color-sensitive layer is divided into two or more layers, as disclosed in JP-B-49-15495 and U.S. Patent 3843469; and light-sensitive materials, in which an arrangement of high-and low-sensitivity layers or an arrangement of layers having different color sensitivities is defined, as disclosed in JP-B-53-37017, JP-B-53-37018, JP-A-51-49027, JP-A-52-143016, JP-A-53-97424, JP-A-53-97831, JP-A-62-200350, and JP-A-59-177551.

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 processed for development by the ordinary processes as described, for example, in above-described Research Disclosure, No. 17643, pages 28 to 29 and ibid., No. 18716, page 651, left column to right column.

A color developer used in developing of the light-sensitive material of the present invention is, preferably, an aqueous alkaline solution containing, as a main component, color developing agent of an aromatic primary amine-series. As the color developing agent, an aminophenol-series compound is effective. In addition, a p-phenylenediamine-series compound is preferably used. Typical examples of the p-phenylenediamine-series 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-N-β-methoxyethylaniline, 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 solution 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 solution can also contain a preservative such as hydroxylamine, diethylhydroxylamine, 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, generally, black-and-white development is performed and then color development is performed. For a black-and-white developer solution, 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 developer solution and the black-and-white developer solution is generally 9 to 12. Although a replenishment amount of the developer solution depends on a color photographic light-sensitive material to be processed for development, it is generally 3 liters or less per m^2 of the light-sensitive material. The replenishment amount can be decreased to be 500 mℓ or less by decreasing a bromide ion concentration in a replenishing solution. In the case of decreasing the replenishment amount, a contact area of the developer solution in a processing tank with air is preferably decreased in order to prevent evaporation and oxidation of the solution. The replenishment amount can be also decreased by using a means capable of suppressing an accumulation amount of bromide ions in the developer solution.

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 of the developer solution and using the color developing agent at a high concentration.

The photographic emulsion layer is generally subjected to bleaching after color development. The bleaching can be performed either simultaneously with fixing (bleach-fixing) or independently thereof. In addition, in order to increase a processing speed, bleach-fixing can be performed after bleaching. Also, the processing can be performed in a bleach-fixing bath having two continuous tanks, wherein fixing can be performed before bleach-fixing, or bleaching can 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; 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 iron (III) or cobalt (II) with an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, and glycoletherdiaminetetraacetic acid, or a complex salt with citric acid, tartaric acid or malic acid; a persulfate; a bromate; a permanganate; and a nitrobenzene. Of these compounds, an iron (III) complex salt with aminopolycarboxylic acid such as an iron (III) complex salt with ethylenediaminetetraacetic acid, and a persulfate are preferred because they can increase a processing speed and prevent an environmental contamination. Especially, the iron (III) complex salt with aminopolycarboxylic acid is effective in both the bleaching solution and bleach-fixing solution. The pH of the bleaching solution or the bleach-fixing solution using the iron (III) complex salt with 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 prebath, if necessary. Examples of the effective bleaching accelerator are described in the following patent specifications: compounds having a mercapto group or a disulfide group described in, e.g., U.S. Patent 3,893,858, West German Patent Nos. 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 Research Disclosure No. 17,129 (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; iodides described in West German Patent No. 1,127,715 and JP-A-58-16235; polyoxyethylene compounds described in West German Patent Nos. 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. Of the above compounds, a compound having a mercapto group or a disulfide group is preferable because it has a good accelerating effect. In particular, the compounds described in U.S. Patent 3,893,858, West German Patent No. 1,290,812, and JP-A-53-95630 are preferable. The compound described in U.S. Patent 4,552,834 is also preferable. These bleaching accelerators can be added in the light-sensitive material. These bleaching accelerators are effective especially in bleach-fixing of a color light-sensitive material for photographing.

Examples of the fixing agent are a thiosulfate, a thiocyanate, a thioether-series 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 silver halide color photographic light-sensitive material of the present invention is normally subjected to washing with water and/or stabilizing steps after desilvering. An amount of water used in the washing step can be arbitrarily determined over a broad range depending on the properties of the light-sensitive material (e.g., a property determined by used substance such as 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 proliferate and floating substances produced by the bacteria can 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 very effectively utilized, as described in Japanese Patent Application No. 61-131632. In addition, a germicide such as an isothiazolone compound and thiabendazole described in JP-A-57-8542, a germicide of chlorine-series 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 Bokabi Gakkai ed., "Cyclopedia 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 to 45° C, and preferably, 30 seconds to 5 minutes at 25 to 40° C. The light-sensitive material of the present invention can be processed directly by a stabilizing solution 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.

Further, stabilizing is sometimes performed subsequently to washing. An example thereof is the case in which a stabilizing bath containing formalin and a surface-active agent is used as a final bath of the color light-sensitive material for photographing. various chelating agents and antifungal agents can be added also in the stabilizing bath.

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

The silver halide color light-sensitive material of the present invention can contain a color developing agent in order to simplify processing for development and increase the processing speed. In the case of adding the color developing agent in the color light-sensitive material, it is preferred to use various precursors of the color developing agent. Examples of the precursor are an indoaniline-series 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 Research Disclosure No. 13,924; a metal complex salt described in U.S. Patent 3,719,492; and a urethane-series compound described in JP-A-53-135628.

The silver halide color light-sensitive material of the present invention can 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 to 50° C. Although a normal solution temperature is 33 to 38° C, processing can be accelerated at a higher temperature to shorten a processing time, or quality of image and/or stability of a processing solution can 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 can be performed.

The silver halide light-sensitive material of the present invention can also be applied to heat 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.

The present invention will be described in more detail below by way of its examples.

Example 1

60 g of gelatin and 900 mℓ of water were added to a stainless reaction vessel having a volume of 4 ℓ, and equal volume of an aqueous silver nitrate solution and an aqueous solution mixture of potassium bromide and potassium iodide were added to the vessel maintained at 60° C, thereby preparing a silver iodobromide emulsion to serve as a core. Subsequently, equal volume of an aqueous silver nitrate solution and an aqueous potassium bromide solution were added to cover the core with silver bromide, thereby preparing a core/shell type silver iodobromide emulsion.

Addition times and concentrations of addition solutions are listed in Table 1-1.

During addition, a pAg was kept at 8.6 for first 10 minutes, at 8.3 for following 80 minutes, and at 7.3 for last 20 minutes.

After grain formation, the emulsion was subjected to a normal desalting/washing process and then redispersed at a temperature of 40° C, a pAg of 8.9, and a pH of 6.3, thereby preparing an emulsion Em-101. The prepared emulsion comprises octahedral grains having a (111) face with a maximum grain size of 0.6 µm and an average AgI content (prescription value) of 5 mol%. In the emulsion, a weight of a silver halide falling within the grain size region ranging from -20% to +20% of a maximum grain size was 75% of a total silver halide grain weight.

Table 1-1

Time (min)	Aqueous Silver Nitrate Solution		Aqueous Pottasium Halide Solution			Stirring Speed [rpm]
	$AgNO_3$	Amount	KBr	KI	Amount	
0 ~ 10	0.32 g	120 mℓ	0.20 g	0.031 g	120 mℓ	750
10 ~ 30	2.55 g	240 mℓ	1.61 g	0.25 g	240 mℓ	
30 ~ 50	20.4 g	240 mℓ	12.9 g	1.99 g	240 mℓ	
50 ~ 70	81.6 g	240 mℓ	51.4 g	7.97 g	240 mℓ	1000
70 ~ 90	122.3 g	240 mℓ	77.1 g	12.0 g	240 mℓ	
90 ~ 110	227.2 g	240 mℓ	159.1 g	0	240 mℓ	

When grain formation was performed following the same procedures as for Em-101, thiosulfonic acid compounds 1-6, 1-2, 1-16, and 1-21 were added one minute before shell formation was started, and optimal amounts of the following reduction sensitizers 2-A, 2-B, and 2-C were added one minute after shell formation was started, thereby preparing emulsions Em-102 to Em-113 of the present invention listed in Table 1-2 below.

Table 1-2

Emulsion No.	Thiosulfonic Acid		Reduction Sensitizer	
	Compound	Addition Amount (per mol of Ag)	Compound	Addition Amount (per mol of Ag)
Em-102	1-6	3×10^{-5}	2-A	1×10^{-4}
Em-103	do	do	2-B	1×10^{-5}
Em-104	do	do	2-C	1×10^{-5}
Em-105	1-2	do	2-A	1×10^{-4}
Em-106	do	do	2-B	1×10^{-5}
Em-107	do	do	2-C	3×10^{-5}
Em-108	1-16	do	2-A	3×10^{-5}
Em-109	do	do	2-B	3×10^{-6}
Em-110	do	do	2-C	3×10^{-5}
Em-111	1-21	do	2-A	1×10^{-4}
Em-112	do	do	2-B	1×10^{-5}
Em-113	do	do	2-C	1×10^{-5}
(Reduction Sensitizers)				
2-A Thiourea Dioxide 2-B Dimethylamineborane 2-C Tin Chloride				

Em-114 was prepared following the same procedures as for Em-101 except that a stirring speed was reduced to be 500 rpm after 50 minutes in Table 1-1. The prepared emulsion comprised grains with a maximum grain size of 0.6 µm and had an average AgI content (prescription value) of 5 mol%. In the emulsion, a weight of a silver halide falling within the grain size region ranging from -20% to +20% of a maximum grain size was 65% of a total silver halide grain weight.

When grain formation was performed following the same procedures as for Em-114, optimal amounts of thiosulfonic acid compounds and reduction sensitizers were added following the same procedures as for Em-105 to Em-107 and Em-111 to Em-113, thereby preparing emulsions Em-115 to Em-120 of the present invention listed in Table 1-3.

Table 1-3

Emulsion No.	Thiosulfonic Acid		Reduction Sensitizer	
	Compound	Addition Amount (per mol of Ag)	Compound	Addition Amount (per mol of Ag)
Em-115	1-2	3×10^{-5}	2-A	1×10^{-4}
Em-116	do	do	2-B	1×10^{-5}
Em-117	do	do	2-C	3×10^{-5}
Em-118	1-21	do	2-A	1×10^{-4}
Em-119	do	do	2-B	1×10^{-5}
Em-120	do	do	2-C	1×10^{-5}

Emulsions as comparative examples were prepared as follows. Em-121 was prepared following the same procedures as for Em-101 except that during core formation, aqueous solutions of silver nitrate and potassium halide were added such that addition amounts were maintained constant per unit time and a maximum grain size was adjusted to equal to that of Em-101. The prepared emulsion had a maximum grain size of 0.6 µm and an average AgI content (prescription value) of 5 mol%. In the emulsion, a weight of a silver halide falling within the grain size region ranging from -20% to +20% of the maximum grain size was 55% of a total silver halide grain weight.

When grain formation was performed following the same procedures as for Em-121, optimal amounts of thisulfonic acid compounds and reduction sensitizers were added following the same procedures as for Em-102 to Em-113, thereby preparing emulsions Em-122 to Em-133 listed in Table 1-4 as comparative examples.

Table 1-4

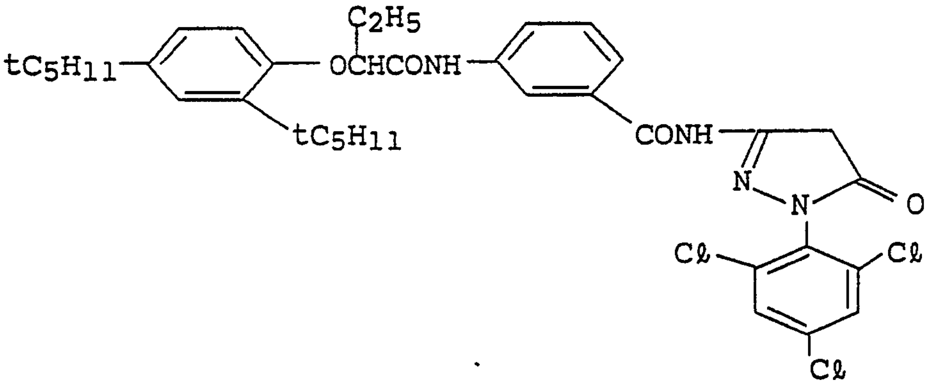
Emulsion No.	Thiosulfonic Acid		Reduction Sensitizer	
	Compound	Addition Amount (per mol of Ag)	Compound	Addition Amount (per mol of Ag)
Em-122	1-6	3×10^{-5}	2-A	1×10^{-4}
Em-123	do	do	2-B	1×10^{-5}
Em-124	do	do	2-C	1×10^{-5}
Em-125	1-2	do	2-A	1×10^{-4}
Em-126	do	do	2-B	1×10^{-5}
Em-127	do	do	2-C	3×10^{-5}
Em-128	1-16	do	2-A	3×10^{-5}
Em-129	do	do	2-B	3×10^{-6}
Em-130	do	do	2-C	3×10^{-5}
Em-131	1-21	do	2-A	1×10^{-4}
Em-132	do	do	2-B	1×10^{-5}
Em-133	do	do	2-C	1×10^{-5}

The emulsion Em-102 to Em-113 of the present invention and the emulsions Em-101, Em-114, and Em-121 to Em-133 prepared as described above were optimally subjected to gold-plus-sulfur sensitization by using sodium thiosulfate and chloroauric acid to prepare emulsions.

Emulsion and protective layers in amounts as listed in Table 1-5 were coated on triacetylcellulose film supports having undercoating layers.

Table 1-5

(1)	Emulsion Layer	
	Emulsion...chemically sensitized emulsions 101 to 133	
		(silver 1.7 × 10^{-2} mol/m^2)
	Coupler	(1.5 × 10^{-3} mol/m^2)



	Tricresylphosphate	(1.10 g/m^2)
	Gelatin	(2.30 g/m^2)
(2)	Protective Layer	
	2,4-dichlorotriazine-6-hydroxy-s-triazine sodium salt	(0.08 g/m^2)
	Gelatin	(1.80 g/m^2)

These samples were subjected to sensitometry exposure, then performing the following color development.

The processed samples were subjected to density measurement by using a green filter. The obtained photographic performance results are listed in Table 1-6.

Development was performed under the following conditions at a temperature of 38° C.

1. Color Development ...2 min. 45 sec.
2. Bleaching ...6 min. 30 sec.
3. Washing ...3 min. 15 sec.
4. Fixing ...6 min. 30 sec.
5. Washing ...3 min. 15 sec.
6. Stabilizing ...3 min. 15 sec.

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

Color Developer solution:	
Sodium Nitrilotriacetic Acid	1.4 g
Sodium Sulfite	4.0 g
Sodium Carbonate	30.0 g
Potassium Bromide	1.4 g
Hydroxylamine Sulfate	2.4 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methyl-aniline Sulfate	4.5 g
Water to make	1 ℓ

Bleaching Solution:	
Ammonium Bromide	160.0 g
Ammonia Water (28% w/w)	25.0 mℓ
Iron (III) Sodium Ethylenediaminetetraacetate trihydrate	130 g
Glacial Acetic Acid	14 mℓ
Water to make	1 ℓ

Fixing Solution:	
Sodium Tetrapolyphosphate	2.0 g
Sodium Sulfite	4.0 g
Ammonium Thiosulfate (700 g/ℓ)	175.0 mℓ
Sodium Bisulfite	4.6 g
Water to make	1 ℓ

Stabilizing Solution:	
Formalin	8.0 mℓ
Water to make	1 ℓ

In this case, normal wedge exposure was performed both for 1 sec. and for 1/100 sec.

A light source was adjusted at a color temperature of 4,800° K by using a filter, and blue light was extracted by using a blue filter (BPN42: available from Fuji Photo Film Co. Ltd.). Sensitivities were compared using density at a point from a fog by an optical density of 0.2. The sensitivities are listed as relative sensitivities assuming that the sensitivity of a sample using the emulsion Em-101 is 100 (100 for both 1/100" and 1"). In addition, the maximum density Dmax is represented as a relative density assuming that Dmax of the sample using Em-101 is 100.

As is apparent from Table 1-6, in the emulsions of the present invention, low fog, high sensitivity, and a high Dmax are shown.

Table 1-6

Emulsion No.	1-sec Exposure Sensitivity	1/100-sec Exposure Sensitivity	Fog	Maximum Density (Dmax)	
Em-101	100	100	0.18	100	Comparative Example
Em-102	136	131	0.20	127	Present Invention
Em-103	142	137	0.23	123	do
Em-104	132	129	0.21	124	do
Em-105	146	136	0.21	125	do
Em-106	149	141	0.23	120	do
Em-107	137	131	0.21	125	do
Em-108	131	121	0.21	125	do
Em-109	131	124	0.23	120	do
Em-110	132	121	0.22	121	do
Em-111	132	124	0.22	123	do
Em-112	128	122	0.23	121	do
Em-113	128	121	0.22	124	do
Em-114	98	99	0.17	94	Comparative Example
Em-115	143	133	0.21	122	Present Invention
Em-116	146	139	0.23	177	do
Em-117	133	127	0.21	123	do
Em-118	130	122	0.20	119	do
Em-119	125	118	0.23	118	do
Em-120	124	119	0.21	120	do
Em-121	97	99	0.17	89	Comparative Example
Em-122	116	110	0.25	82	do
Em-123	110	104	0.25	83	do
Em-124	113	107	0.24	84	do
Em-125	120	110	0.24	89	do
Em-126	120	109	0.26	90	do

Emulsion No.	1-sec Exposure Sensitivity	1/100-sec Exposure Sensitivity	Fog	Maximum Density (Dmax)	
Em-127	115	110	0.25	92	do
Em-128	109	104	0.24	96	do
Em-129	108	102	0.28	92	do
Em-130	109	103	0.26	90	do
Em-131	109	102	0.24	91	do
Em-132	107	102	0.26	93	do
Em-133	108	103	0.24	92	do

Example 2

Em-201 which is perfectly identical to Em-101 was prepared following the same procedures as in Example 1.

When grain formation was performed following the same procedures as for Em-201, a reduction sensitizer A-1 (L-ascorbic acid) and tin chloride were added in amounts listed in Table 2-1 one minute after shell formation was started, thereby preparing emulsions Em-202 and Em-203.

Table 2-1

Emulsion	Reduction Sensitizer	Addition Amount Per Mol of Ag
Em-202	L-ascorbic Acid	2×10^{-3} mol
Em-203	Tin Chloride (II)	1×10^{-5} mol

When grain formation was performed following the same procedures as for Em-201, thiosulfonic compounds 1-2, 1-6, and 1-16 were added one minute before shell formation was started, and optimal amounts of reduction sensitizers L-ascorbic acid and tin chloride were added one minute after shell formation was started, thereby preparing emulsions Em-204 to Em-209 of the present invention and comparative examples.

Table 2-2

Emulsion	Reduction Sensitizer		Thiosulfonic Acid Compound	
	Compound	Addition Amount (per mol of Ag)	Compound	Addition Amount (per mol of Ag)
Em-204	L-ascorbic Acid	2×10^{-3} mol	1-2	3×10^{-5} mol
Em-205	"	"	1-6	"
Em-206	"	"	1-16	"
Em-207	Tin Chloride	1×10^{-5} mol	1-2	"
Em-208	"	"	1-6	"
Em-209	"	"	1-16	"

Em-210 was prepared following the same procedures as for Em-201 except that a stirring speed was reduced to be 500 rpm after 50 minutes in Table 1-1. The prepared emulsion had a maximum grain size of 0.6 µm and an average AgI content (prescription value) of 5 mol%. In the emulsion, a weight of a silver halide falling within the grain size region ranging from -20% to +20% of a maximum grain size was 65% of a total silver halide grain weight.

When grain formation was performed following the same procedures as for Em-210, optimal amounts of thiosulfonic acid compounds and reduction sensitizers were added following the same procedures as for Em-202 to Em-209, thereby preparing emulsions Em-211 to Em-216 of the present invention listed in Table 2-3.

Table 2-3

Emulsion	Reduction Sensitizer		Thiosulfonic Acid Compound	
	Compound	Addition Amount	Compound	Addition Amount
		(per mol of Ag)		(per mol of Ag)
Em-211	L-ascorbic Acid	2 x 10^{-3} mol	--	--
Em-212	"	"	1-2	3 x 10^{-5} mol
Em-213	"	"	1-16	"
Em-214	Tin Chloride	1 x 10^{-5} mol	--	--
Em-215	"	"	1-2	3 x 10^{-5} mol
Em-216	"	"	1-16	"

Emulsions as comparative examples were prepared as follows. Em-217 was prepared following the same procedures as for Em-201 except that during core formation, aqueous solutions of silver nitrate and potassium halide were added such that addition amounts thereof were maintained constant per unit time and a maximum grain size was adjusted to equal to that of Em-201. The prepared emulsion had a maximum grain size of 0.6 µm and an average AgI content (prescription value) of 5 mol%. In the emulsion, a weight of a silver halide falling within the grain size region ranging from -20% to +20% of the maximum grain size was 55% of a total silver halide grain weight.

When grain formation was performed following the same procedures as for Em-217, optimal amounts of thisulfonic acid compounds and reduction sensitizers were added following the same procedures as for Em-202 to Em-209, thereby preparing emulsions Em-218 to Em-223 of the present invention listed in Table 2-4.

Table 2-4

Emulsion	Reduction Sensitizer		Thiosulfonic Acid Compound	
	Compound	Addition Amount	Compound	Addition Amount
		(per mol of Ag)		(per mol of Ag)
Em-218	L-ascorbic Acid	2 x 10^{-3} mol	--	--
Em-219	"	"	1-2	3 x 10^{-5} mol
Em-220	"	"	1-16	"
Em-221	Tin Chloride	1 x 10^{-5} mol	--	--
Em-222	"	"	1-2	3 x 10^{-5} mol
Em-223	"	"	1-16	"

The emulsions Em-201 to Em-223 of the present invention and the comparative examples were optimally subjected to gold-plus-sulfur sensitization by using sodium thiosulfate and chloroauric acid to prepare emulsions.

Samples 201 to 223 of this example were prepared following the same procedures as in Example 1 except that the emulsions Em-201 to Em-223 were used instead of the emulsion Em-101. Subsequently, sensitometry was performed following the same procedures as in Example 1 except that an exposure time was changed from "1 sec. and 1/100 sec." to "10 sec. and 1/100 sec." The obtained results are summarized in Table 2-5.

Table 2-5

Sample	1/100-sec Sensitivity	10-sec Sensitivity	Fog	Maximum Density	Remarks
201	100	100	0.18	100	Comparative Example
202	122	130	0.19	121	Present Invention
203	100	104	0.29	105	Comparative Example
204	130	140	0.17	127	Present Invention
205	128	135	0.18	125	"
206	126	133	0.18	124	"
207	121	128	0.21	119	Comparative Example
208	121	127	0.20	118	"
209	118	124	0.23	115	"
210	99	98	0.21	92	"
211	121	128	0.22	120	Present Invention
212	129	137	0.20	124	"
213	125	131	0.22	122	"
214	98	100	0.33	100	Comparative Example
215	119	125	0.25	110	"
216	112	119	0.27	107	"
217	99	97	0.17	84	"
218	116	120	0.19	94	"
219	119	125	0.18	97	Comparative Example
220	118	123	0.18	96	"
221	95	99	0.31	89	"
222	112	118	0.20	94	"
223	108	114	0.21	92	"

As is apparent from Table 2-5, in the emulsions of the present invention, low fog, high sensitivity (especially in case of low intensity), and a high Dmax are shown.

The samples 201 to 223 coated with the emulsions Em-201 to Em-223, respectively, were stored at a temperture of 25° C and a humidity of 60% for 12 months, and the sensitometry test was similarly performed. Table 2-6 shows the results represented by relative sensitivities assuming that the sensitivity of the sample 201 obtained before storage is 100.

Table 2-6

Sample	1/100-sec Sensitivity	10-sec Sensitivity	Fog	Remarks
201	98	95	0.19	Comparative Example
202	120	128	0.20	Present Invention
203	88	92	0.45	Comparative Example
204	129	139	0.18	Present Invention
205	126	133	0.18	"
206	125	132	0.19	"
207	97	101	0.33	Comparative Example
208	96	100	0.33	"
209	93	98	0.38	"
210	96	94	0.22	"
211	120	127	0.23	Present Invention
212	128	136	0.20	"
213	125	131	0.22	"
214	81	85	0.51	Comparative Example
215	84	90	0.37	"
216	83	89	0.42	"
217	95	92	0.19	"
218	113	118	0.21	"
219	117	120	0.19	"
220	115	119	0.20	Comparative Example
221	78	83	0.43	"
222	82	87	0.31	"
223	81	86	0.35	"

As is apparent from Table 2-6, a decrease in sensitivity and an increase in fog of each sample coated with the emulsion of the present invention are small after storage. That is, good storage stability is shown in each sample.

When the experiment was made following the same procedures as described above for the ascorbic acid compounds A-2 to A-10, the same effects were obtained.

Example 3

A plurality of layers having the following ccmpositions were coated on an undercoated triacetylcellulose film support to prepare a multilayered color light-sensitive material 301.

(Light-Sensitive Layer Composition)

Numerals corresponding to the respective components indicate coating amounts in units of g/m^2. Coating amounts of a silver halide and colloid silver are represented by a silver amount. A coating amount of a sensitizing dye is represented in units of mols per mol of a silver halide in the same layer.

Layer 1: Antihalation Layer	
Black Colloid Silver	0.2
Gelatin	2.6
Cpd-3	0.2
Solv-1	0.02

Layer 2: Interlayer	
Fine Grain Silver Bromide (average grain size = 0.07 μm)	0.15
Gelatin	1.0

Layer 3: Low-Sensitivity Red-Sensitive Emulsion Layer

Monodisperse Silver Iodobromide Emulsion (silver iodide = 5.5 mol%, maximum grain size = 0.3 μm, variation coefficient of grain size (to be referred to as simply "variation coefficient" hereinafter) = 19%)	1.5
Gelatin	3.0
ExS-1	2.0×10^{-4}
Exs-2	1.0×10^{-4}
Exs-3	0.3×10^{-4}
ExC-1	0.7
ExC-2	0.1
ExC-3	0.02
Cpd-1	0.01
Solv-1	0.8
Solv-2	0.2
Solv-4	0.1

Layer 4: High-Sensitivity Red-Sensitive Emulsion Layer	
Monodisperse Silver Iodobromide Emulsion I	1.2
Gelatin	2.5
ExS-1	3.0×10^{-4}
EXS-2	1.5×10^{-4}
ExS-3	0.45×10^{-4}
ExC-4	0.15
ExC-5	0.05
ExC-2	0.03
ExC-3	0.01
Solv-1	0.05
Solv-2	0.3

Layer 5: Interlayer	
Gelatin	0.8
Cpd-2	0.05
Solv-3	0.01

Layer 6: Low-Sensitivity Green-Sensitive Emulsion Layer	
Monodisperse Silver Iodobromide Emulsion (silver iodide = 5 mol%, maximum grain size = 0.3 μm, variation coefficient = 19%)	0.4
Monodisperse Silver Iodobromide Emulsion (silver iodide = 7 mol%, maximum grain size = 0.5 μm, variation coefficient = 20%)	0.8
Gelatin	3.0
ExS-4	1×10^{-4}
ExS-5	4×10^{-4}
ExS-6	1×10^{-4}
ExM-6	0.2
ExM-7	0.4
ExM-8	0.16
ExC-9	0.05
Solv-2	1.2
Solv-4	0.05
Solv-5	0.01

Layer 7: High-Sensitivity Green-Sensitive Emulsion Layer	
Monodisperse Silver Iodobromide Emulsion II	0.9
Gelatin	1.6
ExS-4	0.7×10^{-4}
ExS-5	2.8×10^{-4}
ExS-6	0.7×10^{-4}
ExM-7	0.05
ExM-8	0.04
ExC-9	0.01
Solv-1	0.08
Solv-2	0.3
Solv-4	0.03

Layer 8: Yellow Filter Layer	
Yellow Colloid Silver	0.2
Gelatin	0.9
Cpd-2	0.2
Solv-2	0.1

Layer 9: Low-Sensitivity Blue-Sensitive Emulsion Layer	
Monodisperse Silver Iodobromide Emulsion (silver iodide = 6 mol%, maximum grain size = 0.3 µm, variation coefficient = 20%)	0.4
Monodisperse Silver Iodobromide Emulsion (silver iodide = 5 mol%, maximum grain size = 0.6 µm, variation coefficient = 17%)	0.4
Gelatin	2.9
ExS-7	1×10^{-4}
ExS-8	1×10^{-4}
ExY-10	1.2
ExC-3	0.05
Solv-2	0.4
Solv-4	0.1

Layer 10: High-Sensitivity Blue-Sensitive Emulsion Layer	
Monodisperse Silver Iodobromide Emulsion III	0.5
Gelatin	2.2
ExS-7	5×10^{-5}
ExS-8	5×10^{-5}
ExY-10	0.4
ExC-3	0.02
Solv-2	0.1

Layer 11: 1st Protective Layer	
Gelatin	1.0
Cpd-3	0.1
Cpd-4	0.1
Cpd-5	0.1
Cpd-6	0.1
Solv-1	0.1
Solv-4	0.1

Layer 12: 2nd Protective Layer	
Fine Grain Silver Bromide Emulsion (average grain size = 0.07 µm)	0.25
Gelatin	1.0
Polymethylmethacrylate Grain (diameter = 1.5 µm)	0.2
Cpd-8	0.5

In addition to the above components, a surfactant Cpd-7 and a hardener H-1 were added. Formulas of the used compounds are listed in Table C.

The iodide content and the shell portion silver amount of Em-101 during core grain formation were arbitrarily changed to prepare the monodisperse silver iodobromide emulsion I (silver iodide = 3.5 mol%, maximum grain size = 0.7 µm) of the layer 4, the monodisperse silver iodobromide emulsion II (silver iodide = 3.5 mol%, maximum grain size = 0.8 µm) of the layer 7, and the monodisperse silver iodobromide emulsion III (silver iodide = 6 mol%, maximum grain size = 1.2 µm) of the layer 10, thereby preparing a sample 301. Percentages of gains falling within the grain size region ranging from -20% to +20% of the maximum grain size were 73% in the emulsion I; 70% in the emulsion II; and 66% in the emulsion III. The emulsions I to III were optimally subjected to gold-plus-sulfur sensitization by using sodium thiosulfate and chloroauric acid.

Samples 302 to 305 were prepared following the same procedures as for the sample 301 except that the above emulsions were replaced with emulsions produced by adding thiosulfonic acid compounds and reduction sensitizers as shown in Table 3-1(A) during grain formation as in the case of Em-102 to Em-113.

These samples were subjected to sensitometry exposure, then to the following color development.

The processed samples were subjected to density measurement by using red, green, and blue filters. The obtained results are shown in Table 3-1.

The results of photographic performance are represented by relative sensitivities of the red-, green-, and blue-sensitive layers assuming that the sensitivities of the sample 301 are each 100.

Processing Method:

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.

The processing solution compositions 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
Hydroxylamine Sulfate	2.4 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylanilinesulfate	4.5 g
Water to make	1.0 ℓ
pH	10.0

Bleaching Solution:	
Ferric Ammonium Ethylenediaminetetraacetate	100.0 g
Disodium Ethylenediaminetetraacetate	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 mℓ
Sodium Bisulfite	4.6 g
Water to make	1.0 ℓ
pH	6.6

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

Table 3-1(A)

Sample No.	Layer 4			
	Monodisperse Silver Iodobromide Emulsion I			
	Thiosulfonic Acid		Reduction Sensitizer	
	Compound	Addition Amount (per mol of Ag)	Compound	Addition Amount (per mol of Ag)
301 (Comparative Example)	--	--	--	--
302 (Present Invention)	1-6	3×10^{-5}	2-B	1×10^{-5}
303 (Present Invention)	1-2	"	2-A	1×10^{-4}
304 (Present Invention)	1-16	"	2-C	3×10^{-5}
305 (Present Invention)	1-21	"	2-A	1×10^{-4}

Sample No.	Layer 7			
	Monodisperse Silver Iodobromide Emulsion II			
	Thiosulfonic Acid		Reduction Sensitizer	
	Compound	Addition Amount (per mol of Ag)	Compound	Addition Amount (per mol of Ag)
301 (Comparative Example)	--	--	--	--
302 (Present Invention)	1-6	3×10^{-5}	2-B	1×10^{-5}
303 (Present Invention)	1-2	"	2-A	1×10^{-4}
304 (Present Invention)	1-16	"	2-C	3×10^{-5}
305 (Present Invention)	1-21	"	2-A	1×10^{-4}

(Continued)

Sample No.	Layer 10			
	Monodisperse Silver Iodobromide Emulsion III			
	Thiosulfonic Acid		Reduction Sensitizer	
	Compound	Addition Amount (per mol of Ag)	Compound	Addition Amount (per mol of Ag)
301 (Comparative Example)	--	--	--	--
302 (Present Invention)	1-6	3×10^{-5}	2-B	1×10^{-5}
303 (Present Invention)	1-2	"	2-A	1×10^{-4}
304 (Present Invention)	1-16	"	2-C	3×10^{-5}
305 (Present Invention)	1-21	"	2-A	1×10^{-4}

Table 3-1(B)

Sample No.	Red-Sensitive Layer		Green-Sensitive Layer		Blue-Sensitive Layer	
	Fog	Sensitivity	Fog	Sensitivity	Fog	Sensitivity
301 (Comparative Example)	0.07	100	0.08	100	0.08	100
302 (Present Invention)	0.08	130	0.09	133	0.10	136
303 (Present Invention)	0.09	129	0.09	130	0.10	135
304 (Present Invention)	0.09	129	0.10	120	0.11	122
305 (Present Invention)	0.09	121	0.10	123	0.11	125

As is apparent from Table 3-1, in the emulsions of the present invention, an effect of increasing sensitivity with almost no increase in fog is shown.

Example 4

Samples 401 to 404 were prepared following the same procedures as for the sample 301 in Example 3. Note that in the samples 402 to 404, Em-204 to Em-206 were used to prepare the monodisperse silver iodobromide emulsions I to III for use in the layers 4, 7, and 10, respectively, and thiosulfonic acid compounds and a reduction sensitizer L-ascorbic acid were added to the emulsions as shown in Table 4-1-(A). The samples 402 to 404 are the same as the sample 401 except for this point.

The samples 401 to 404 were subjected to sensitometry exposure following the same procedures as in Example 3. Subsequently, color development and then measurement were performed following the same procedures as in Example 3. The results are summarized in Table 4-1 (B).

Table 4-1(A)

Sample No.	Layer 4 Monodisperse Silver Iodobromide Emulsion I		
	Thiosulfonic Acid Compound		L-ascorbic Acid
	Compound	Addition Amount (per mol of Ag)	Addition Amount (per mol of Ag)
401 (Comparative Example)	---	---	---
402 (Present Invention)	1-2	3×10^{-5} mol	2×10^{-3} mol
403 (Present Invention)	1-6	"	"
404 (Present Invention)	1-16	"	"

(Continued)

Sample No.	Layer 7 Monodisperse Silver Iodobromide Emulsion II		
	Thiosulfonic Acid Compound		L-ascorbic Acid
	Compound	Addition Amount (per mol of Ag)	Addition Amount (per mol of Ag)
401 (Comparative Example)	---	---	---
402 (Present Invention)	1-2	3 × 10^{-5} mol	2 × 10^{-3} mol
403 (Present Invention)	1-6	"	"
404 (Present Invention)	1-16	"	"

Sample No.	Layer 10 Monodisperse Silver Iodobromide Emulsion III		
	Thiosulfonic Acid Compound		L-ascorbic Acid
	Compound	Addition Amount (per mol of Ag)	Addition Amount (per mol of Ag)
401 (Comparative Example)	---	---	---
402 (Present Invention)	1-2	3 × 10^{-5} mol	2 × 10^{-3} mol
403 (Present Invention)	1-6	"	"
404 (Present Invention)	1-16	"	"

Table 4-1(B)

Sample No.	Red-Sensitive Layer		Green-Sensitive Layer		Blue-Sensitive Layer	
	Fog	Sensitivity	Fog	Sensitivity	Fog	Sensitivity
401 (Comparative Example)	0.07	100	0.08	100	0.08	100
402 (Present Invention)	0.08	132	0.09	135	0.10	138
403 (Present Invention)	0.09	131	0.09	132	0.10	137
404 (Present Invention)	0.09	130	0.10	125	0.11	128

As is apparent from Table 4-1, in the emulsions of the present invention, an effect of increasing the sensitivity with almost no increase in fog is shown.

When photographic properties were checked after storage following the same procedures as in Example 2, each sample using the emulsion of the present invention had good storage stability.

Example 5

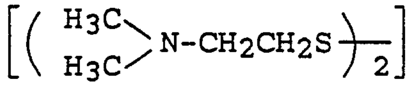
The samples 301 to 305 were exposed following the same procedures as in Example 3 and processed as follows by using an automatic developing machine.

Processing Method		
Step	Time	Temperature
Color Development	3 min. 15 sec.	38° C
Bleaching	1 min. 00 sec.	38° C
Bleach-Fixing	3 min. 15 sec.	38° C
Washing (1)	40 sec.	35° C
Washing (2)	1 min. 00 sec.	35° C
Stabilizing	40 sec.	38° C
Dry	1 min. 15 sec.	55° C

The processing solution compositions will be described below.

Color Developing Solution:	g
Diethylenetriaminepentaacetic Acid	1.0
1-hydroxyethylidene-1,1 diphosphonic acid	3.0
Sodium Sulfite	4.0
Potassium Carbonate	30.0
Potassium Bromide	1.4
Potassium Iodide	1.5 mg
Hydroxyamine Sulfate	2.4
4-[N-ethyl-N-(β-hydroxyethyl)amino]-2-methylanilinesulfate	4.5
Water to make	1.0 L
pH	10.05

Bleaching Solution: g

Ferric Ammonium Ethylenediaminetetraacetate (Dihydrate)	120.0
Disodium Ethylenediaminetetraacetate	10.0
Ammonium Bromide	100.0
Ammonium Nitrate	10.0
Bleaching Accelerator	0.005 mol
 $\left[\left(\begin{matrix}H_3C\\H_3C\end{matrix}\!>\!N\text{-}CH_2CH_2S\right)_{\!2}\right]$	
Ammonia Aqueous Solution (27%)	15.0 mℓ
Water to make	1.0 L
pH	6.3

Bleach-Fixing Solution:	g
Ferric Ammonium Ethylenediaminetetraacetate (Dihydrate)	50.0
Disodium Ethylenediaminetetraacetate	5.0
Sodium Sulfite	12.0
Ammonium Thiosulfate Aqueous Solution (70%)	240.0 mℓ
Ammonia Aqueous Solution (27%)	6.0 mℓ
Water to make	1.0 L
pH	7.2

Washing Solution:

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type strongly basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/L or less. Subsequently, 20 mg/L of of sodium isocyanuric acid dichloride and 1.5 g/L of sodium sulfate were added. The pH of the solution fell within the range of 6.5 to 7.5.

Stabilizing Solution:	g
Formalin (37%)	2.0 mℓ
Polyoxyethylene-p-monononylphenylether (average polymerization degree = 10)	0.3
Disodium Ethylenediaminetetraacetate	0.05
Water to make	1.0 L
pH	5.0 to 8.0

The samples 302 to 305 of the present invention provided the good results as in Example 3 after they were subjected to the above processing.

Example 6

The sample 401 of the comparative example and the sample 402 to 404 of the present invention obtained in Example 4 were exposed following the same procedures as in Example 4 and then processed by using an automatic developing machine.

A processing method and compositions of the processing solutions were the same as those in Example 5.

The samples 402 to 404 of the present invention provided the good results as in Example 4 after they were subjected to the above processing.

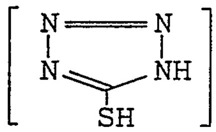
Example 7

The samples 301 to 305 of Example 3 were exposed following the same procedures as in Example 3 and processed as follows by using an automatic developing machine.

Processing Method		
Step	Time	Temperature
Color Development	2 min. 30 sec.	40° C
Bleach-Fixing	3 min. 00 sec.	40° C
Washing (1)	20 sec.	35° C
Washing (2)	20 sec.	35° C
Stabilizing	20 sec.	35° C
Drying	50 sec.	65° C

The processing solution compositions will be described below.

Color Developing Solution:	g
Diethylenetriaminepentaacetic Acid	2.0
1-hydroxyethylidene-1,1-diphosphonic acid	3.0
Sodium Sulfite	4.0
Potassium Carbonate	30.0
Potassium Bromide	1.4
Potassium Iodide	1.5 mg
Hydroxylamine Sulfate	2.4
4-[N-ethyl-N-(β-hydroxyethyl)amino]-2-methylaniline Sulfate	4.5
Water to make	1.0 L
pH	10.05

Bleach-Fixing Solution:	g
Ferric Ammonium Ethylenediaminetetraacetate (Dihydrate)	50.0
Disodium Ethylenediaminetetraacetate	5.0
Sodium Sulfite	12.0
Ammonium Thiosulfate Aqueous Solution (70%)	260.0 mℓ
Acetic Acid (98%)	5.0 mℓ
Bleaching Accelerator	0.01 mol
	
Water to make	1.0 L
pH	6.0

Washing Solution:

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type strongly basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/L or less. Subsequently, 20 mg/L of of sodium isocyanuric acid dichloride and 1.5 g/L of sodium sulfate were added. The pH of the solution fell within the range of 6.5 to 7.5.

Stabilizing Solution:	g
Formalin (37%)	2.0 mℓ
Polyoxyethylen-p-monononylphenylether (average polymerization degree = 10)	0.3
Disodium Ethylenediaminetetraacetate	0.05
Water to make	1.0 L
pH	5.0 to 8.0

The samples 302 to 305 of the present invention provided the good results as in Example 3 after they were subjected to the above processing.

Example 8

The sample 401 of the comparative example and the samples 402 to 404 of the present invention obtained in Example 4 were exposed following the same procedures as in Example 4 and then processed by using an automatic developing machine.

A processing method and compositions of processing solutions are the same as those in Example 7.

The samples 402 to 404 of the present invention provided the good results as in Example 4 after they were subjected to the above processing.

Example 9

A plurality of layers having the following compositions were coated on an undercoated triacetylcellulose film support to prepare a sample 901 as a multilayer color light-sensitive material.

Light-Sensitive Layer Composition:

Numerals corresponding to the respective components indicate coating amounts in units of g/m^2 except that the silver halide and colloid silver are represented in a silver-converted coating amount, and that a coating amount of the sensitizing dye is represented in units of mols per mol of the silver halide in the same layer.

Sample 901:

Layer 1: Antihalation Layer		
Black Colloid Silver	silver	0.18
Gelatin		1.40

Layer 2: Interlayer	
2,5-di-t-pentadecylhydroquinone	0.18
EX-1	0.07
EX-3	0.02
EX-12	0.002
U-1	0.06
U-2	0.08
U-3	0.10
HBS-1	0.10
HBS-2	0.02
Gelatin	1.04

Layer 3: 1st Red-Sensitive Emulsion Layer

Emulsion A	silver	0.25
Emulsion B	silver	0.25
Sensitizing Dye I		6.9×10^{-5}
Sensitizing Dye II		1.8×10^{-5}
Sensitizing Dye III		3.1×10^{-4}
EX-2		0.335
EX-10		0.020
Gelatin		0.87

Layer 4: 2nd Red-Sensitive Emulsion Layer		
Emulsion C	silver	1.0
Sensitizing Dye I		5.1×10^{-5}
Sensitizing Dye II		1.4×10^{-5}
Sensitizing Dye III		2.3×10^{-4}
EX-2		0.400
EX-3		0.050
EX-10		0.015
Gelatin		1.30

Layer 5: 3rd Red-Sensitive Emulsion Layer		
Emulsion D	silver	1.60
Sensitizing Dye I		5.4×10^{-5}
Sensitizing Dye II		1.4×10^{-5}
Sensitizing Dye III		2.4×10^{-4}
EX-3		0.010
EX-4		0.080
EX-2		0.097
HBS-1		0.22
HBS-2		0.10
Gelatin		1.63

Layer 6: Interlayer	
EX-5	0.040
HBS-1	0.020
Gelatin	0.80

Layer 7: 1st Green-Sensitive Emulsion Layer		
Emulsion A	silver	0.15
Emulsion B	silver	0.15
Sensitizing Dye V		3.0×10^{-5}
Sensitizing Dye VI		1.0×10^{-4}
Sensitizing Dye VII		3.8×10^{-4}
EX-6		0.260
EX-1		0.021
EX-7		0.030
EX-8		0.025
HBS-1		0.100
HBS-3		0.010
Gelatin		0.63

Layer 8: 2nd Green-Sensitive Emulsion Layer		
Emulsion C	silver	0.45
Sensitizing Dye V		2.1×10^{-5}
Sensitizing Dye VI		7.0×10^{-5}
Sensitizing Dye VII		2.6×10^{-4}
EX-6		0.094
EX-8		0.018
EX-7		0.026
HBS-1		0.160
HBS-3		0.008
Gelatin		0.50

Layer 9: 3rd Green-Sensitive Emulsion Layer		
Emulsion (Monodisperse Silver Iodobromide Emulsion III in Example 2)	silver	1.2
Sensitizing Dye V		3.5×10^{-5}
Sensitizing Dye VI		8.0×10^{-5}
Sensitizing Dye VII		3.0×10^{-4}
EX-13		0.015
EX-11		0.100
EX-1		0.025
HBS-1		0.25
HBS-2		0.10
Gelatin		1.54

Layer 10: Yellow Filter Layer		
Yellow Colloid Silver	silver	0.05
EX-5		0.08
HBS-1		0.03
Gelatin		0.95

Layer 11: 1st Blue-Sensitive Emulsion Layer

Emulsion A	silver	0.08
Emulsion B	silver	0.07
Emulsion E	silver	0.07

Sensitizing Dye VIII	3.5×10^{-4}
EX-9	0.721
EX-8	0.042
HBS-1	0.28
Gelatin	1.10

Layer 12: 2nd Blue-Sensitive Emulsion Layer		
Emulsion F	silver	0.45
Sensitizing Dye VIII		2.1×10^{-4}
EX-9		0.154
EX-10		0.007
HBS-1		0.05
Gelatin		0.78

Layer 13: 3rd Blue-Sensitive Emulsion Layer		
Emulsion G	silver	0.77
Sensitizing Dye VIII		2.2×10^{-4}
EX-9		0.20
HBS-1		0.07
Gelatin		0.69

Layer 14: 1st Protective Layer		
Emulsion H	silver	0.5
U-4		0.11
U-5		0.17
HBS-1		0.05
Gelatin		1.00

Layer 15: 2nd Protective Layer	
Polymethylacrylate Grains (grain size = about 1.5 μm)	0.54
S-1	0.20
Gelatin	1.20

In addition to the above components, a gelatin hardener H-1 and/or a surfactant were added to each layer. Structures of the used compounds are listed in Table D to be presented later.

The emulsions A to H are silver iodobromide emulsions. An average AgI content and the like of these emulsions are listed in Table below.

Table

(Emulsions A - H)

	Average AgI Content	Average Grain Size	Diameter/Thickness Ratio	Silver Amount Ratio
	(%)	(µm)		(AgI content (%))
Emulsion A	4.3	0.45	1	Core/Middle/Shell = 8/16/76 (0/27/0), Triple Structure Grain
" B	8.7	0.70	1	ditto
" C	10	0.75	2	Core/Shell = 1/2 (24/3), Double Structure Grain
" D	16	1.05	2	Core/Shell = 1/2 (40/0), Double Structure Grain
" E	4.3	0.25	1	Core/Middle/Shell = 8/16/76 (0/27/0), Triple Structure Grain
" F	14	0.75	2	Core/Shell = 1/2 (40/0), Double Structure Grain
" G	14	1.30	3	Core/Shell = 1/2 (24/3), Double Structure Grain
" H	1	0.07	1	

Samples 902 to 905 were prepared following the same procedures as for the sample 901 except that the emulsion of the layer 9 was replaced with an emulsion obtained by adding thiosulfonic acid compounds and reduction sensitizers during grain formation as in the case of Em-102 to Em-113.

These samples were subjected to sensitometry exposure and color development following the same procedures as in Example 3.

Densities of the processed samples were measured by using a green filter. The measurement results are summarized in Table 9-1.

Photographic properties are represented by the sensitivity of a green-sensitive layer as a relative sensitivity assuming that the sensitivity of the sample 901 is 100.

Table 9-1

Sample No.	Layer 9				Green-Sensitive Layer	
	Monodisperse Silver Iodobromide Emulsion III					
	Thiosulfonic Acid		Reduction Sensitizer			
	Compound	Addition Amount (per mol of Ag)	Compound	Addition Amount (per mol of Ag)	Fog	Sensitivity
901 (Comparative Example)	--	--	--	--	0.05	100
902 (Present Invention)	1-6	3×10^{-5}	2-A	1×10^{-4}	0.06	128
903 (Present Invention)	1-2	"	2-B	1×10^{-5}	0.06	135
904 (Present Invention)	1-16	"	2-B	3×10^{-6}	0.07	123
905 (Present Invention)	1-21	"	2-C	1×10^{-5}	0.07	120

As is apparent from Table 9-1, in the emulsions of the present invention, an effect of increasing the sensitivity with almost no increase in fog is shown.

Example 10

A plurality of layers having the following compositions were coated on an undercoated cellulose triacetate film support to prepare sample 1001 as a multilayer color light-sensitive material.

Compositions of Light-Sensitive Layers:

The coating amounts of a silver halide and colloid 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.

Layer 1: Antihalation Layer

Black Colloid 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 Silver Bromide Grain (sphere-equivalent diameter = 0.07 μm) coating silver amount	0.15
Gelatin	1.0
ExC-4	0.03
Cpd-2	0.2

Layer 3: 1st Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 8.5 mol%, internally high AgI type, sphere-equivalent diameter = 1.0 μm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 3.0) coating silver amount	0.42

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	0.33
Gelatin	1.0
ExS-1	4.5×10^{-4}
ExS-2	1.5×10^{-4}
ExS-3	0.4×10^{-4}
ExC-1	0.40
ExC-2	0.11
ExC-3	0.009
ExC-4	0.023
Solv-1	0.24

Layer 4: 2nd Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 8.5 mol%, internally high AgI type, sphere-equivalent diameter = 1.0 µm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 3.0) coating silver amount	0.55
Gelatin	0.7
ExS-1	3×10^{-4}
ExS-2	1×10^{-4}
ExS-3	0.3×10^{-4}
ExC-1	0.10
ExC-2	0.05
ExC-4	0.25
Solv-1	0.20

Layer 5: 3rd Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 11.3 mol%, internally high AgI type, sphere-equivalent diameter = 1.4 µm, variation coefficient of sphere-equivalent diameter = 28%, tabular grain, diameter/thickness ratio = 6.0) coating silver amount	1.29
Gelatin	0.6
ExS-1	2×10^{-4}
ExS-2	0.6×10^{-4}
ExS-3	0.2×10^{-4}
ExC-2	0.08
ExC-4	0.01
ExC-5	0.06
Solv-1	0.12
Solv-2	0.12

Layer 6: Interlayer

Gelatin	1.0
Cpd-4	0.1
Solv-1	0.1

Layer 7: 1st Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 8.5 mol%, internally high AgI type, sphere-equivalent diameter = 1.0 µm, variation coefficient of sphere-equivalent diameter = 25%, tabular grain, diameter/thickness ratio = 3.0) coating silver amount	0.28
Silver Iodobromide Emulsion (AgI = 4.0 mol%, internally high AgI type, sphere-equivalent diameter = 0.7 µm, variation coefficient of sphere-equivalent diameter = 38%, tabular grain, diameter/thickness ratio = 2.0) coating silver amount	1.0
Gelatin	1.2
ExS-5	5×10^{-4}
ExS-6	2×10^{-4}
ExS-7	1×10^{-4}
ExM-1	0.50
ExM-2	0.10
ExM-5	0.03
Solv-1	0.2
Solv-4	0.03

Layer 8: 2nd Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 8.5 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	0.47
Gelatin	0.35
ExS-5	3.5×10^{-4}
ExS-6	1.4×10^{-4}
ExS-7	0.7×10^{-4}
ExM-1	0.12
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

Monodisperse Silver Iodobromide Emulsion III in Example 2 coating silver amount	1.3
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
Cpd-5	0.01
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-9	3×10^{-4}
ExY-1	0.6
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-9	2×10^{-4}
ExY-1	0.22
Solv-1	0.07

Layer 15: Interlayer

Fine Silver Iodobromide Grain (AgI = 2 mol%, homogeneous, 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 = 1.7 μm, variation coefficient of sphere-equivalent diameter = 28%, tabular grain, diameter/thickness ratio = 5.0) coating silver amount	1.4
Gelatin	0.5
ExS-9	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 Silver Chloride Grain (sphere-equivalent diameter = 0.07 μm) coating silver amount	0.36
Gelatin	0.7
Polymethylmethacrylate Grain (diameter = 1.5 μm)	0.2
W-1	0.02
H-1	0.4
Cpd-6	1.0

In addition to the above compositions, B-1 (total amount = 0.20 g/m^2), 1,2-benzisothiazoline-3-one (average amount = about 200 ppm with respect to gelatin), n-butyl-p-hydroxybenzoate (ditto, about 1,000 ppm), and 2-phenoxyethanol (ditto, about 1,000 ppm) were added to each layer. Formulas of the used compounds are listed in Table E.

Samples 1002 to 1004 were prepared following the same procedures as for the sample 1001 except that the emulsion of the layer 10 was replaced with an emulsion prepared by adding thiosulfonic acid compounds and a reduction sensitizer L-ascorbic acid during grain formation as in the case of Em-204 to Em-206.

These samples were subjected to sensitometry exposure and then color development following the same procedures as in Example 4.

Densities of the processed samples were measured by using a green filter. The obtained results are summarized in Table 10-1.

Photographic properties are represented by the sensitivity of a green-sensitive layer as a relative sensitivity assuming that the sensitivity of the sample 1001 is 100.

Table 10-1

Sample No.	Layer 10 Monodisperse Silver Iodobromide Emulsion III			Green-Sensitive Layer	
	Thiosulfonic Acid Compound		L-ascorbic Acid		
	Compound	Addition Amount (per mol of Ag)	Addition Amount (per mol of Ag)	Fog	Sensitivity
1001 (Comparative Example)	---	---	---	0.15	100
1002 (Present Invention)	1-2	3 × 10^{-5} mol	2 × 10^{-3} mol	0.17	135
1003 (Present Invention)	1-6	"	"	0.17	130
1004 (Present Invention)	1-16	"	"	0.18	123

As is apparent from Table 10-1, in the emulsions of the present invention, an effect of increasing the sensitivity with almost no increase in fog is shown. When the samples were stored following the same procedures as in Example 2 and their photographic properties were checked, the fog of the sample 1001 was significantly increased while its sensitivity was decreased. On the contrary, in the samples 1002 to 1004, better photographic properties than those of the comparative example 1001 are shown.

Example 11

The samples 301 to 305 of Example 3 and Samples 901 to 905 of Example 9 were exposed following the same procedures as in Example 3, 9 and processed as follows by using an automatic developing machine. As a result, it was confirmed that the samples according to the present invention provided the good effects similar to the result obtained in Example 3 and Example 9.

Table 11

Step	Processing Time	Processing Temperature	Amount of Replenishing Solution *	Tank Capacity
Color Developing	3 min. 15 sec	38.0° C	570 mℓ	8 liter
Bleaching	45 sec	38.0° C	130 mℓ	4 liter
Fixing	1 min. 30 sec	38.0° C	800 mℓ	6 liter
Washing (1)	20 sec	38.0° C	Countercurrent Replenishment From (2) To (1)	4 liter
Washing (2)	20 sec	38.0° C	500 mℓ	4 liter
Stabilizing	20 sec	38.0° C	500 mℓ	4 liter
Drying	1 min.	55° C		

* Amount per 1 m of a sample.

The compositions of the processing solution are summarized below.

Color Developer:	Mother Solution	Replenishing Solution
	(g)	(g)
Diethylenetriaminepentaacetic Acid	1.0	1.5
1-hydroxyethylidene-1,1 diphosphonic acid	3.0	3.2
Sodium Sulfite	4.0	4.9
Potassium Carbonate	38.0	40.0
Potassium Bromide	1.4	0.4
Potassium Iodide	1.5 mg	--
Hydroxyamine Sulfate	2.4	3.6
4-[N-ethyl-N-(β-hydroxyethyl)amino]-2-methylanilinesulfate	4.5	6.1
Water to make	1.0 ℓ	1.0 ℓ
pH	10.05	10.15

Bleaching Solution:	Mother Solution	Replenishing Solution
	(g)	(g)
1,3-diaminopropanetetracetic Acid Ferric Ammonium Monohydrate	140.0	180.0
1,3-diaminopropanetetracetic Acid	10.0	11.0
Ammonium Bromide	140.0	180.0
Ammonium Nitrate (70%)	30.0	40.0
Acetic Acid (98%)	25.0 mℓ	30.0 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	4.5	3.5

Fixing Solution:	Mother Solution	Replenishing Solution
	(g)	(g)
1-hydroxyethylidene-1,1-diphosphonic acid	1.0	1.5
Ammonium Sulfite	12.0	20.0
Aqueous Ammonium Thiosulfate Solution (700 g/ℓ)	320 mℓ	360 mℓ
Water to make	1.0 ℓ	1.0 ℓ
pH	6.7	6.4

Washing Water: Common for Mother Solution and Replenishing Solution

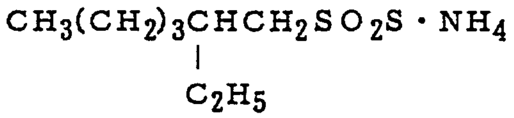
Tap water was supplied to a mixed-bed column filed with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type strongly basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/L or less. Subsequently, 20 mg/L of sodium isocyanuric acid dichloride and 1.5 g/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	Replenishing Solution
	(g)	(g)
Triethanolamine	2.0	3.0
Formalin (37%)	2.0 mℓ	3.0 mℓ
Polyoxyethylen-p-monononylphenylether (average 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

Table A

(1 - 1) CH_3SO_2SNa
(1 - 2) $C_2H_5SO_2SNa$
(1 - 3) $C_3H_7SO_2SK$
(1 - 4) $C_4H_9SO_2SLi$
(1 - 5) $C_6H_{13}SO_2SNa$
(1 - 6) $C_8H_{17}SO_2SNa$

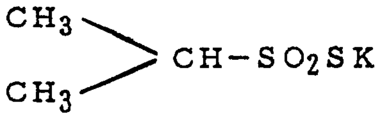
(1 − 7)



$$CH_3(CH_2)_3\underset{\displaystyle C_2H_5}{\underset{|}{C}}HCH_2SO_2S\cdot NH_4$$

(1 - 8) $C_{10}H_{21}SO_2SNa$
(1 - 9) $C_{12}H_{25}SO_2SNa$
(1 - 10) $C_{16}H_{33}SO_2SNa$

(1 -11)

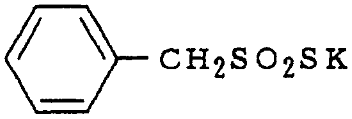


$$(CH_3)_2CH{-}SO_2SK$$

(1 - 12) t-$C_4H_9SO_2SNa$

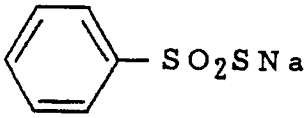
(1 - 13) $CH_3OCH_2CH_2SO_2S \cdot Na$

(1 -14)



(1 − 15) $CH_2{=}CHCH_2SO_2SNa$

(1 − 16)



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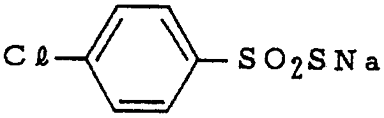

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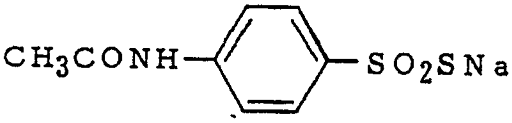
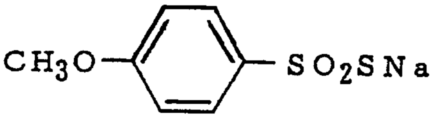


(1 − 19)



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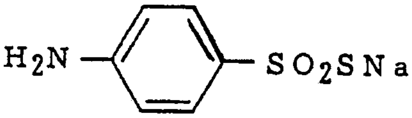
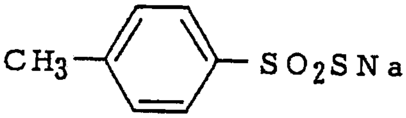
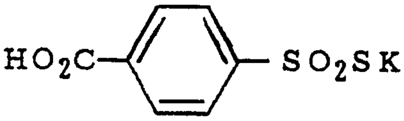


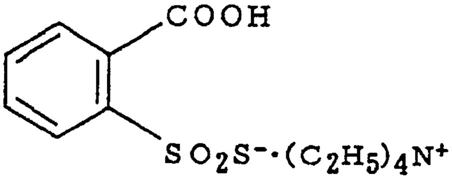
(1 − 21)



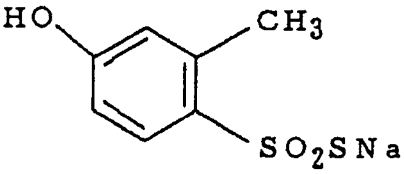
(1 − 22)



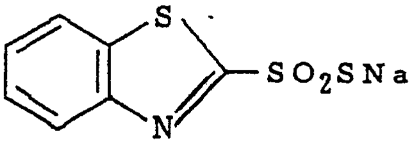
(1 − 23)



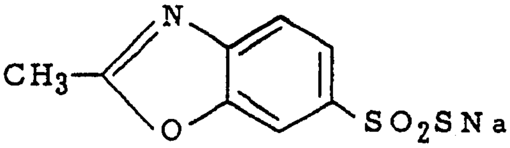
(1 − 24)



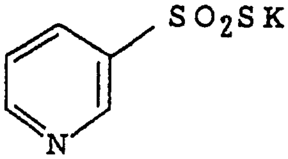
(1 − 25)



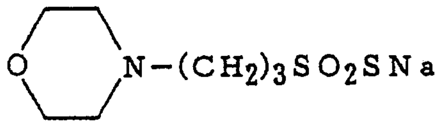
(1 − 26)



(1 − 27)



(1 − 28)

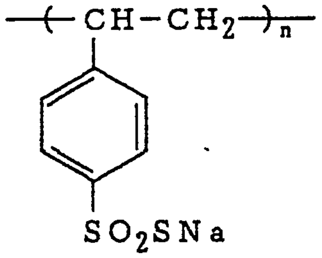


(1 − 29) $KSSO_2(CH_2)_2SO_2SK$

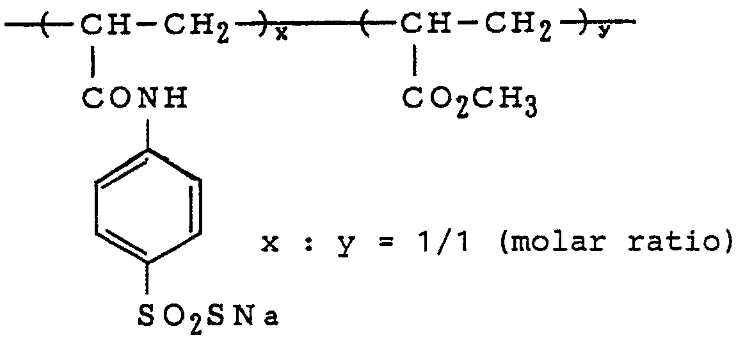
(1 − 30) $NaSSO_2(CH_2)_4SO_2SNa$

(1 − 31) $NaSSO_2(CH_2)_4S(CH_2)_4SO_2SNa$

(1 − 32)



(1 − 33)

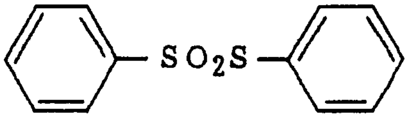


x : y = 1/1 (molar ratio)

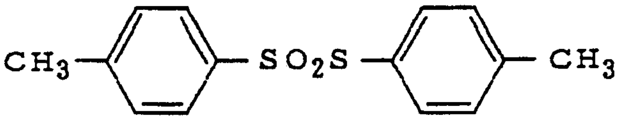
(2 − 1) $C_2H_5SO_2S-CH_3$

(2 − 2) $C_8H_{17}SO_2SCH_2CH_3$

(2 − 3)

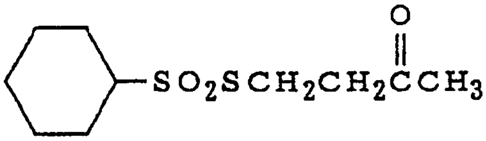


(2 − 4)

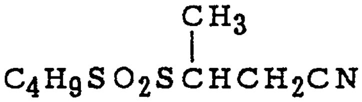


(2 − 5) $C_2H_5SO_2SCH_2CH_2CN$

(2 − 6)

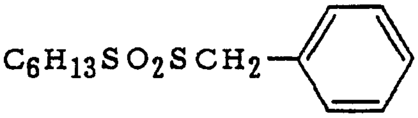


(2 − 7)

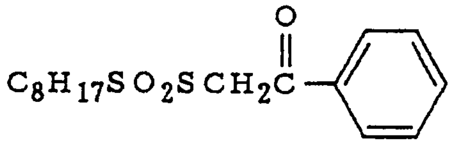


$$C_4H_9SO_2S\overset{CH_3}{\overset{|}{C}}HCH_2CN$$

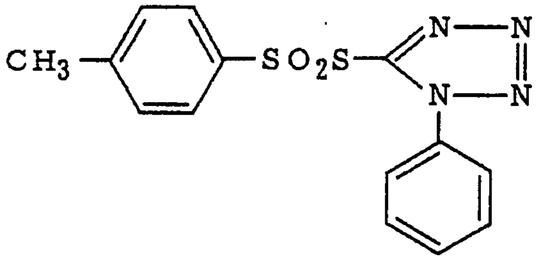
(2 − 8)



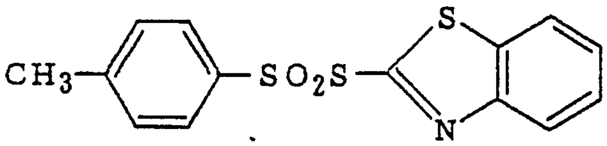
(2 - 9)



(2 - 10)



(2 - 11)



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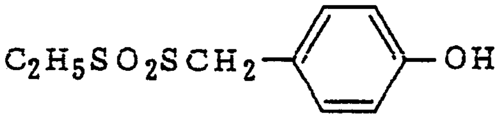
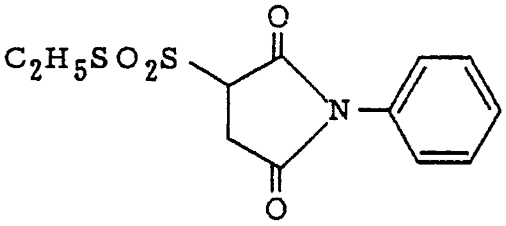
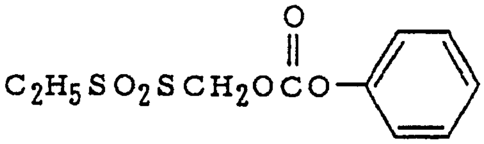


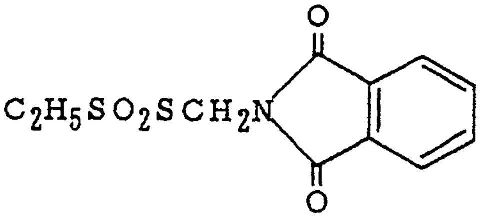
(2 - 13)



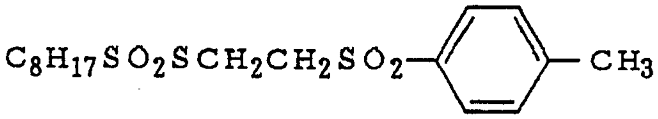
(2 −14)



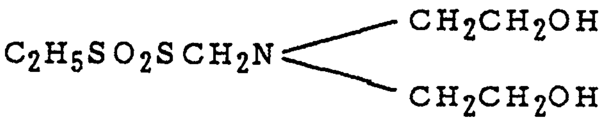
(2 −15)



(2 −16)



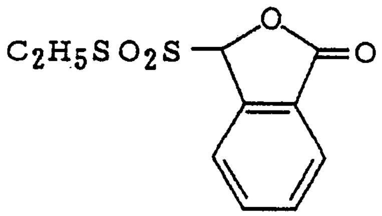
(2 −17)



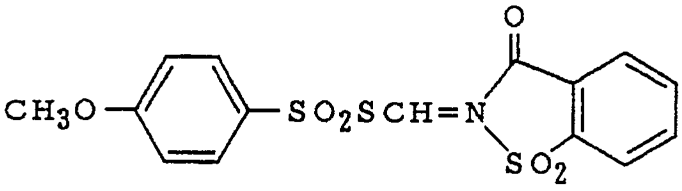
$$C_2H_5SO_2SCH_2N\begin{cases} CH_2CH_2OH \\ CH_2CH_2OH \end{cases}$$

(2 −18) $C_2H_5SO_2SCH_2CH_2CH_2CH_2OH$

(2 −19)



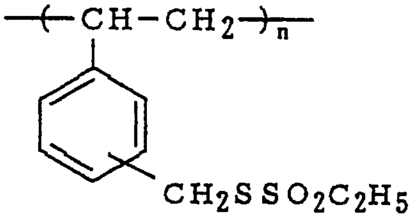
(2 −20)



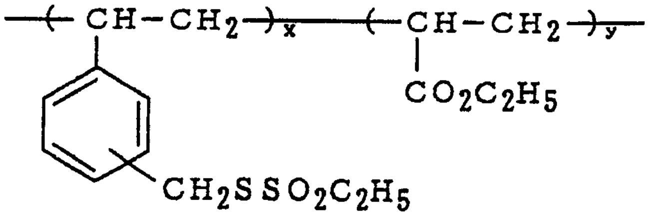
(2 −21) $CH_3SSO_2(CH_2)_4SO_2SCH_3$

(2 −22) $CH_3SSO_2(CH_2)_2SO_2SCH_3$

(2 −23)

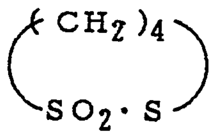


(2－24)

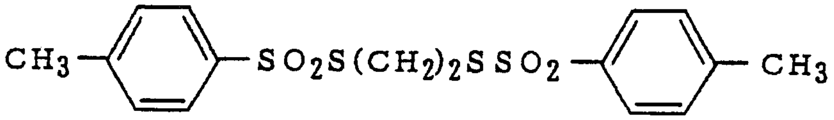


x : y = 2/1 (molar ratio)

(2－25)

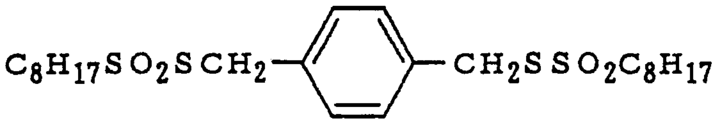


(3－1)

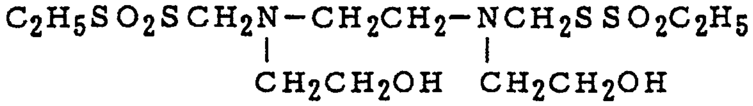


(3－2) $C_2H_5SO_2SCH_2CH_2SO_2CH_2CH_2SSO_2C_2H_5$

(3 – 3)

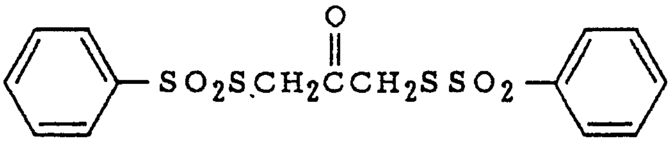


(3 – 4)

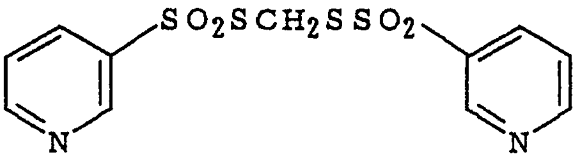


$$C_2H_5SO_2SCH_2\underset{\displaystyle CH_2CH_2OH}{\underset{|}{N}}-CH_2CH_2-\underset{\displaystyle CH_2CH_2OH}{\underset{|}{N}}CH_2SSO_2C_2H_5$$

(3 – 5)



(3 – 6)



(3 – 7) $C_2H_5SO_2SSSO_2C_2H_5$

(3 – 8) $(n)C_3H_7SO_2SSSO_2C_3H_7(n)$

(3 – 9)

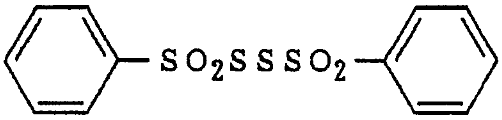
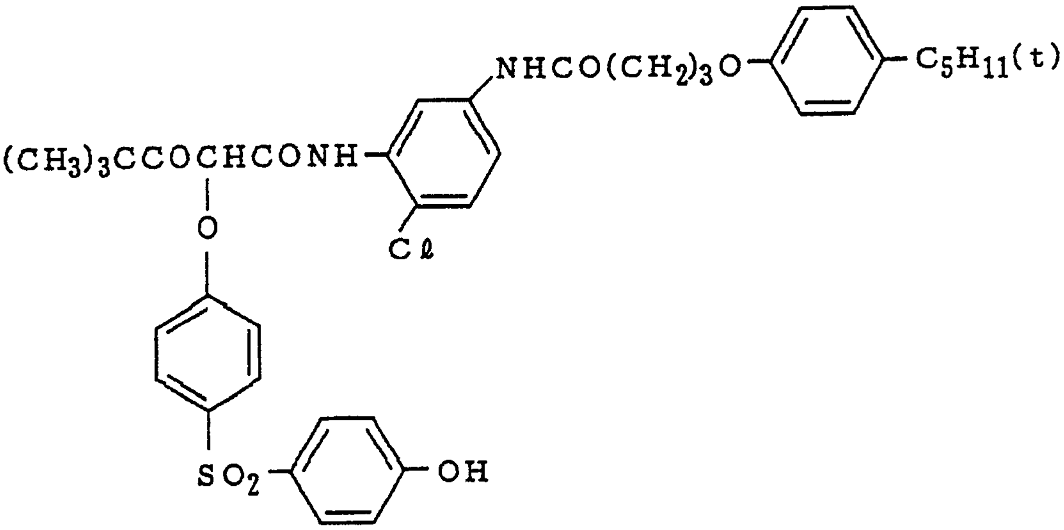
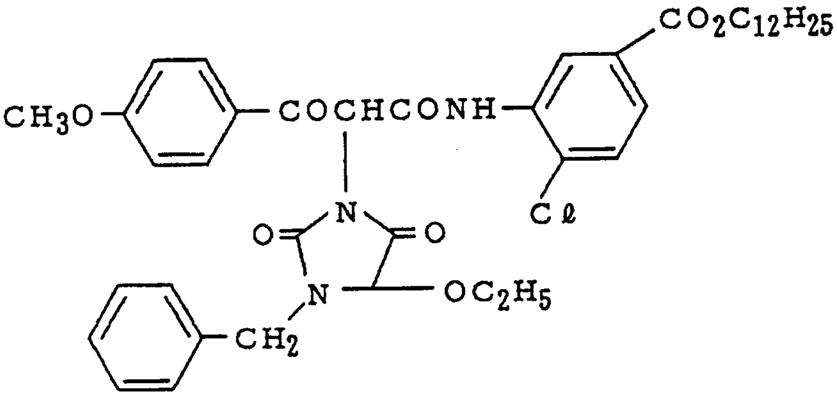


Table B

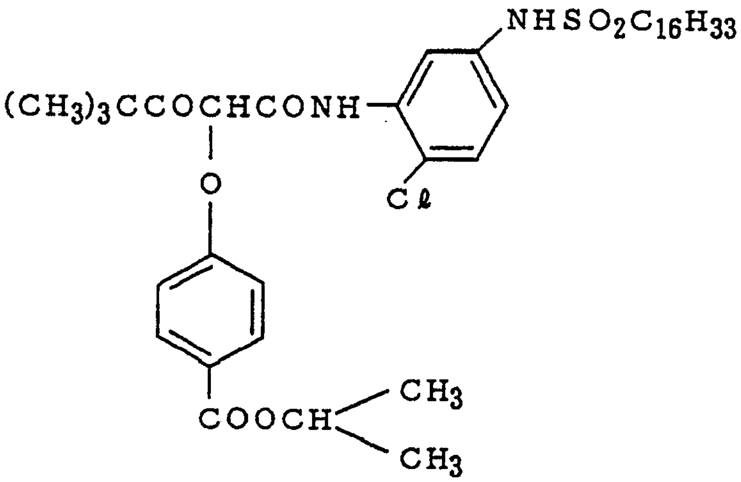
C – ①


NHCO(CH2)3O
C5H11(t)
(CH3)3CCOCHCONH
O
Cℓ
SO2
OH

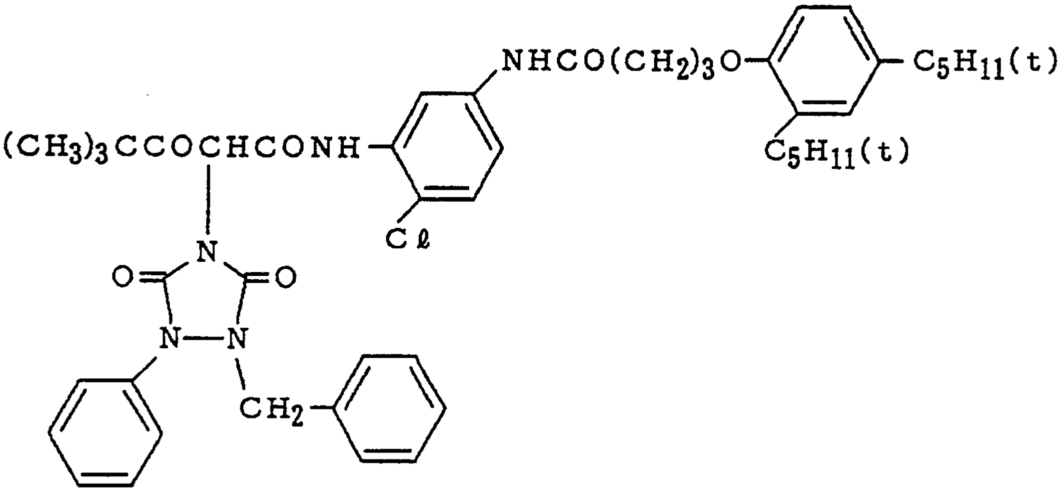
C – ②


CO2C12H25
CH3O
COCHCONH
N
O
O
Cℓ
N
OC2H5
CH2

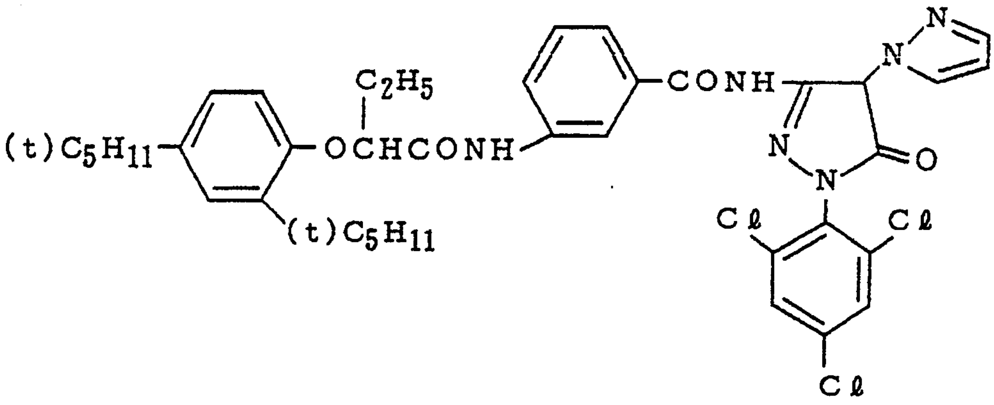
C – ③


NHSO2C16H33
(CH3)3CCOCHCONH
O
Cℓ
COOCH
CH3
CH3

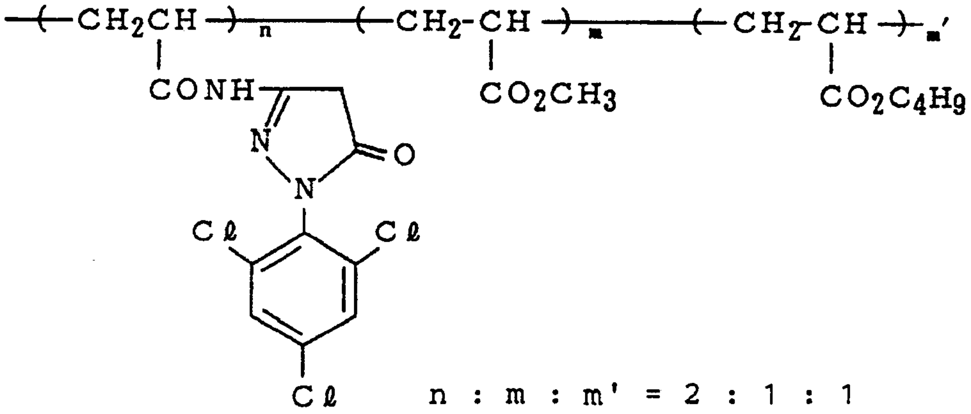
C – ④


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

C – ⑤



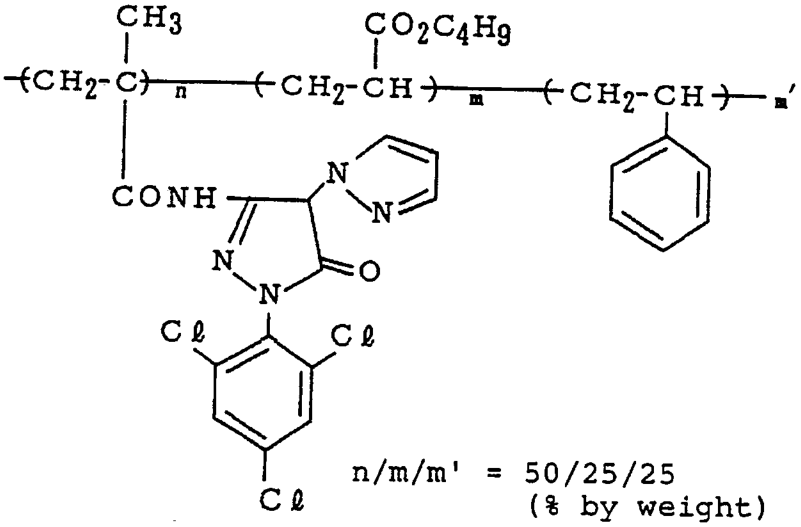
C – ⑥



n : m : m' = 2 : 1 : 1
(weight ratio)

molecular weight: about 40,000

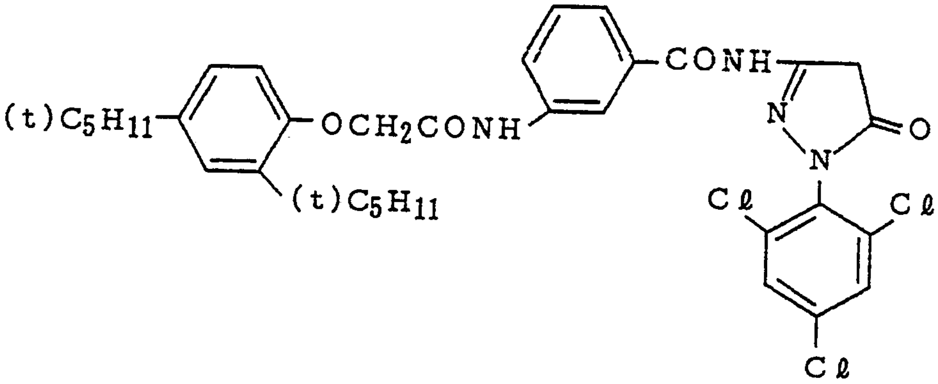
C-(7)



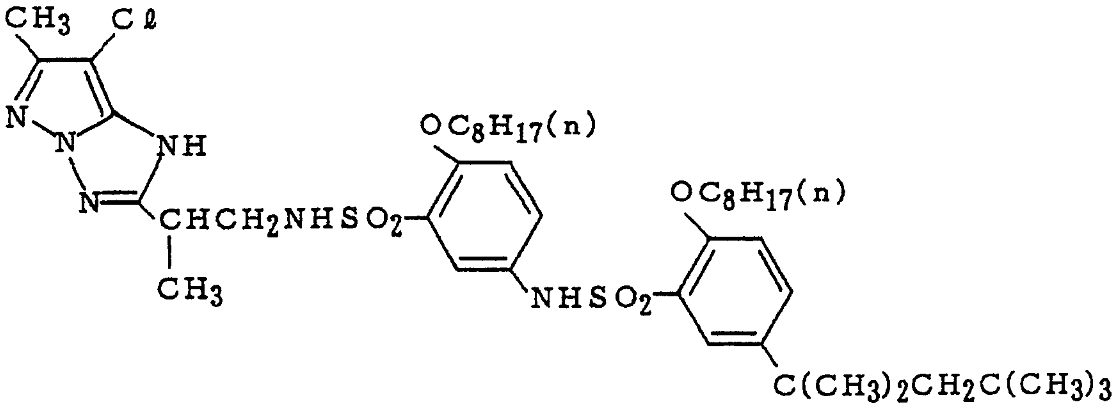
n/m/m' = 50/25/25
(% by weight)

average molecular weight:
about 30,000

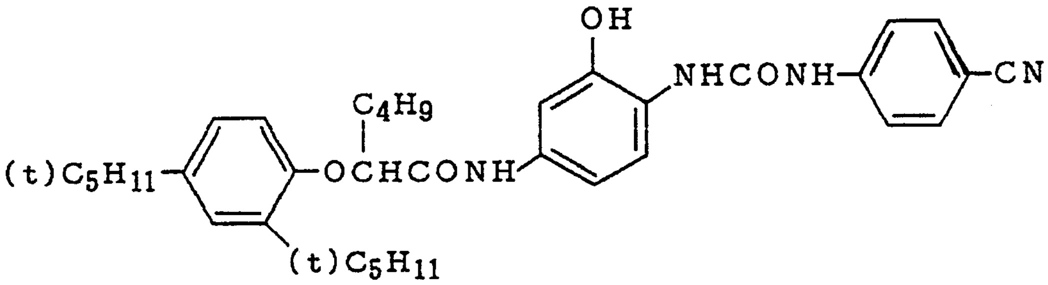
C-(8)



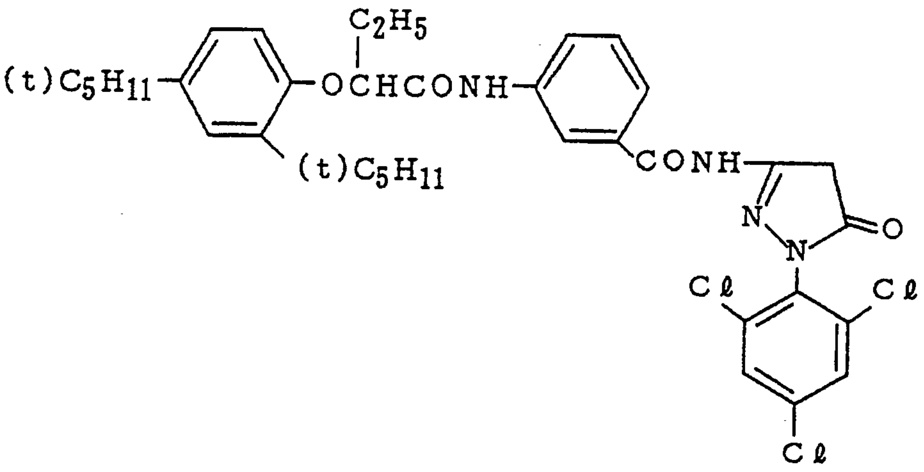
C – (9)



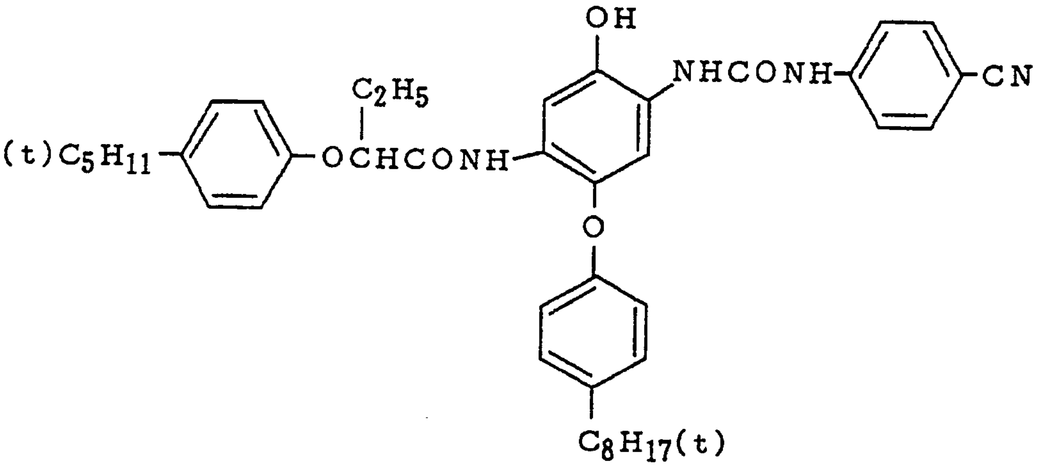
C – (10)



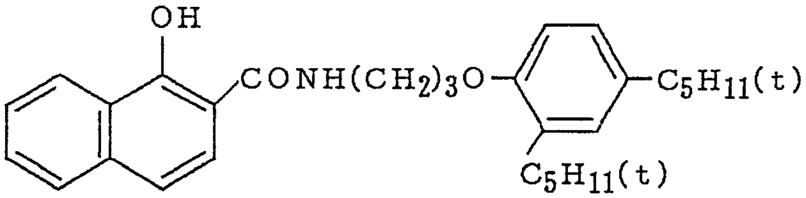
C－(11)


(t)C5H11
C2H5
OCHCONH
(t)C5H11
CONH
N
N
O
Cℓ
Cℓ
Cℓ

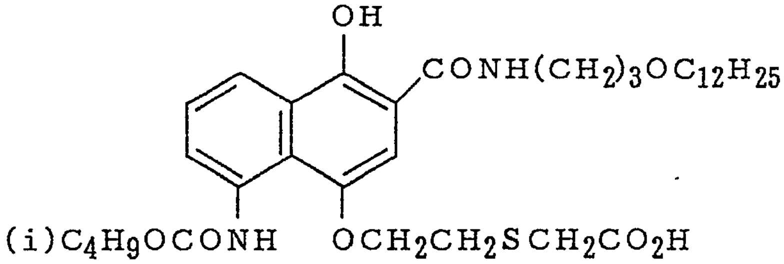
C－(12)


OH
NHCONH
CN
C2H5
(t)C5H11
OCHCONH
O
C8H17(t)

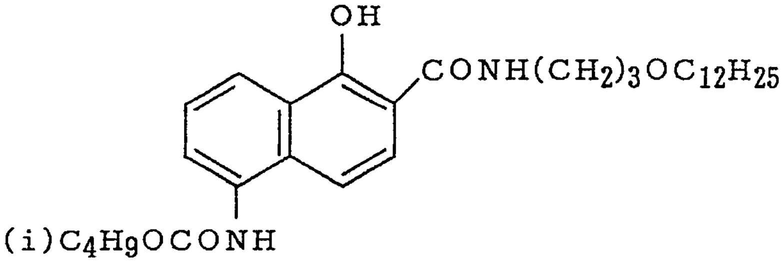
C－(13)


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)

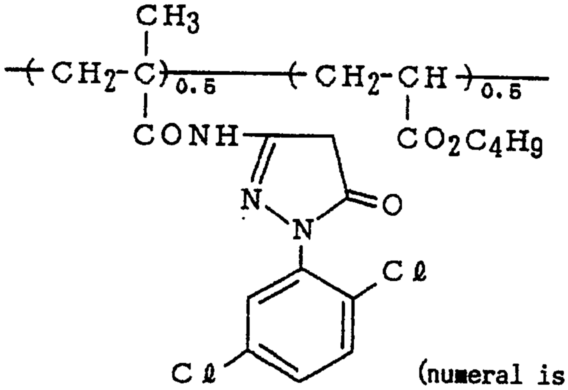
C－(14)


OH
CONH(CH2)3OC12H25
(i)C4H9OCONH
OCH2CH2SCH2CO2H

C－(15)

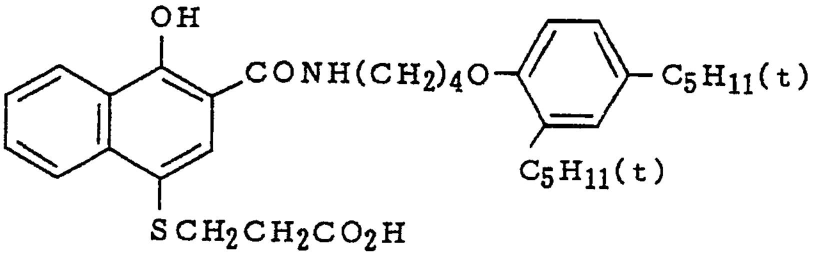

OH
CONH(CH2)3OC12H25
(i)C4H9OCONH

C－(16)

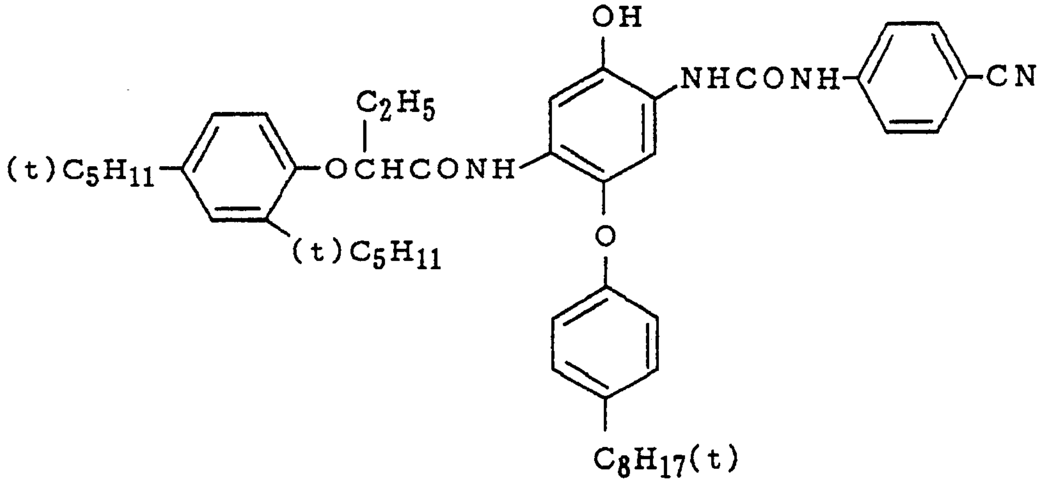


(numeral is weight ratio)

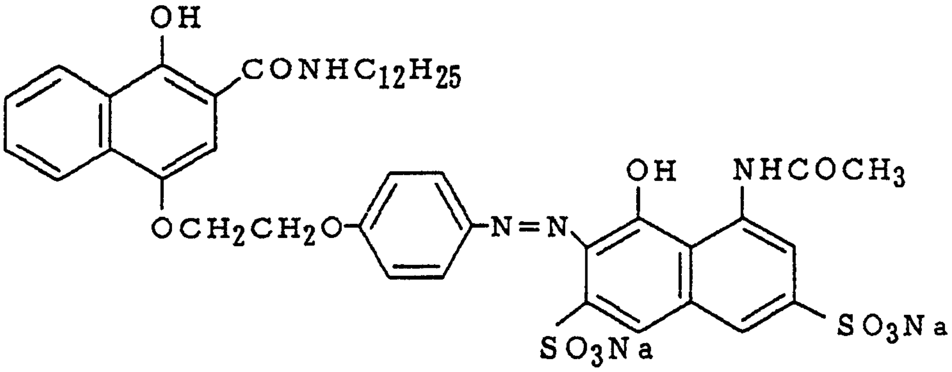
C－(17)



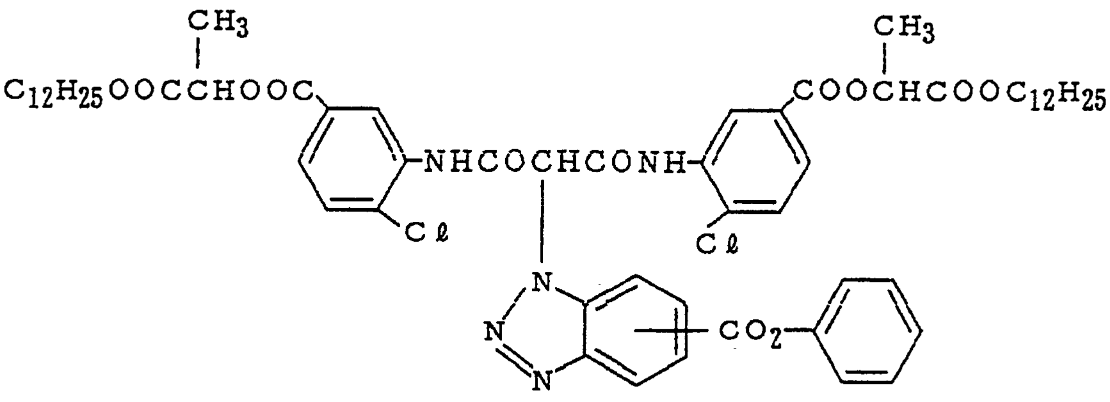
C－(18)


OH
NHCONH
CN
C_2H_5
(t)C_5H_{11}
OCHCONH
(t)C_5H_{11}
O
C_8H_{17}(t)

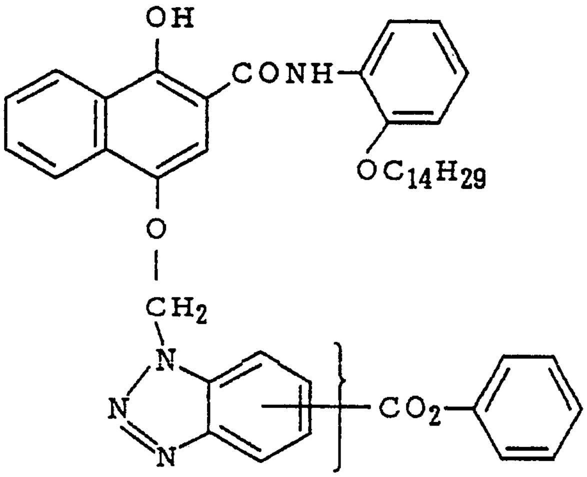
C－(19)


OH
$CONHC_{12}H_{25}$
OH
$NHCOCH_3$
OCH_2CH_2O
N=N
SO_3Na
SO_3Na

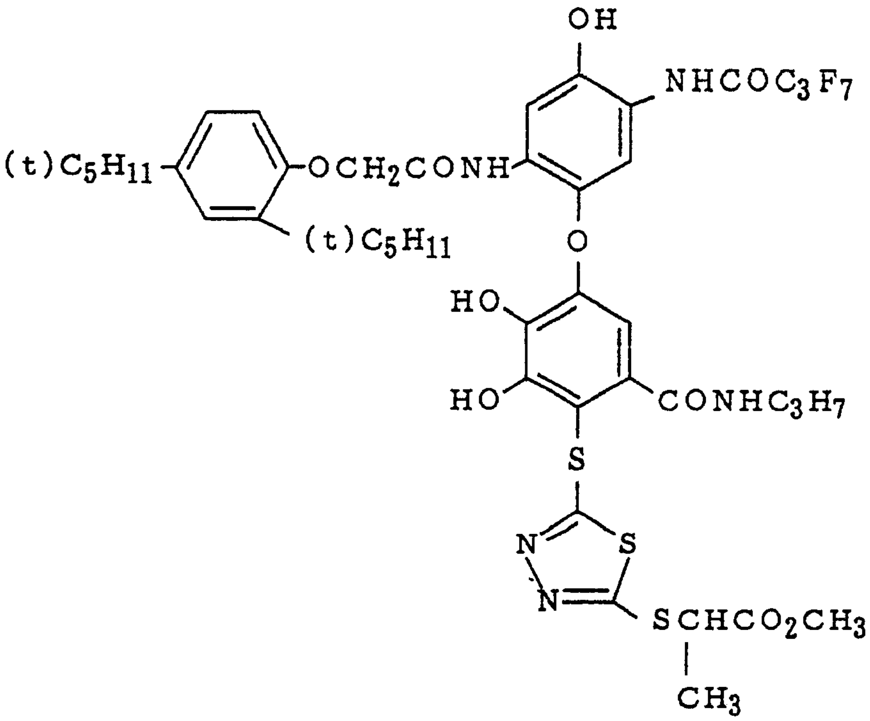
C－(20)



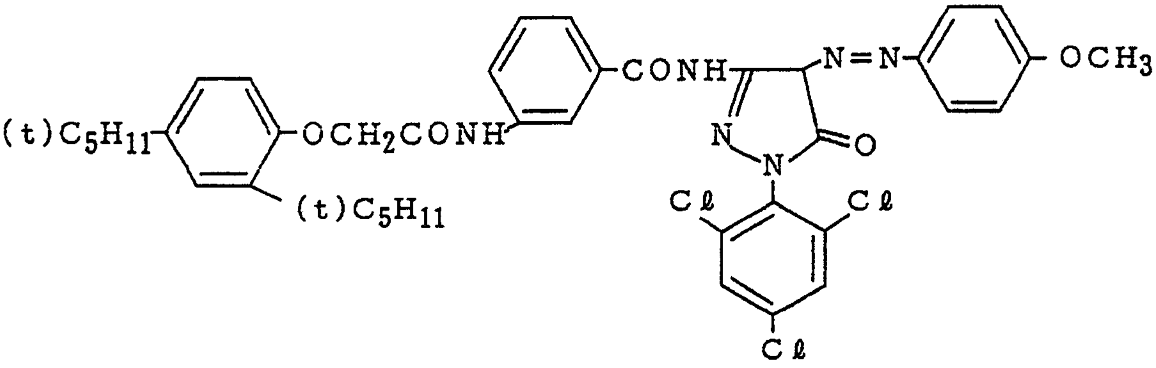
C－(21)



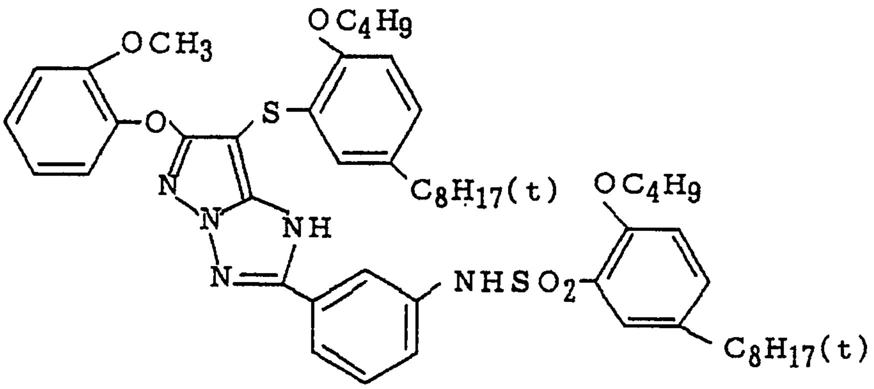
C－(22)


OH
NHCOC3F7
(t)C5H11
OCH2CONH
(t)C5H11
O
HO
HO
CONHC3H7
S
N
S
N
SCHCO2CH3
CH3

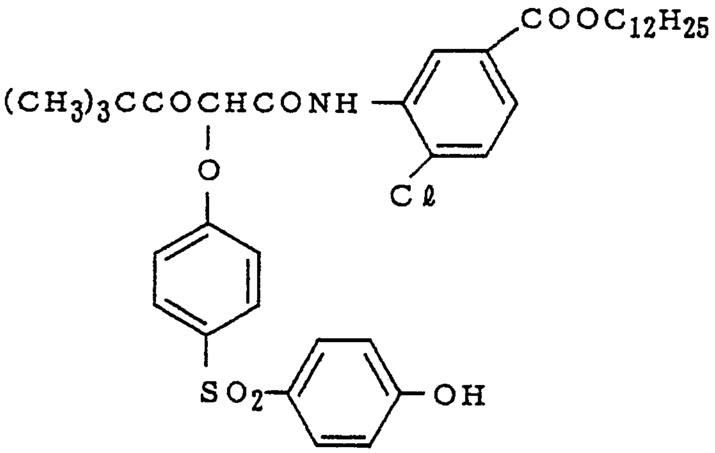
C－(23)


CONH
N=N
OCH3
(t)C5H11
OCH2CONH
N
N
O
(t)C5H11
Cℓ
Cℓ
Cℓ

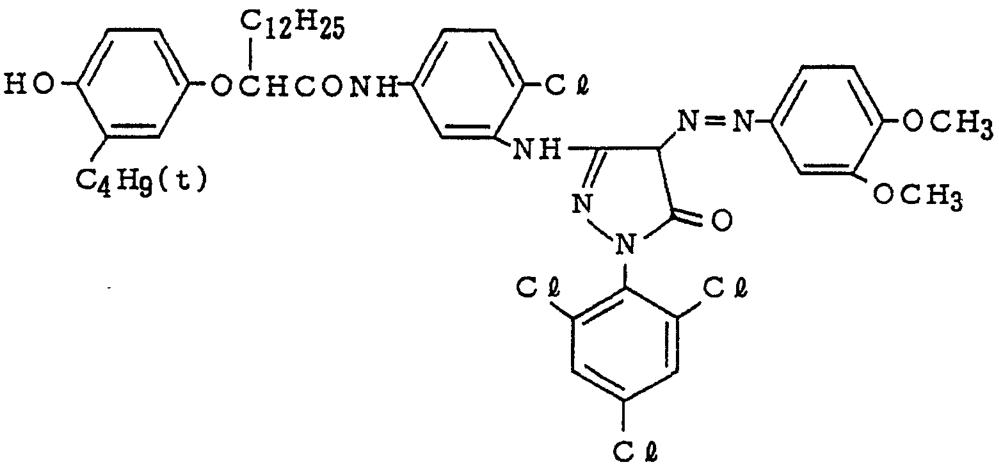
C－(24)


OCH3
OC4H9
O
S
N
N
NH
N
C8H17(t)
OC4H9
NHSO2
C8H17(t)

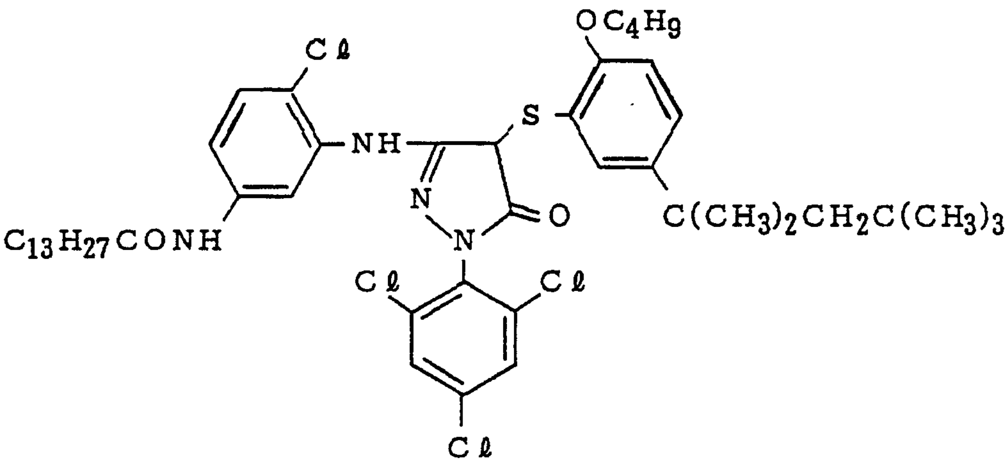
C－(25)


COOC12H25
(CH3)3CCOCHCONH
O
Cℓ
SO2
OH

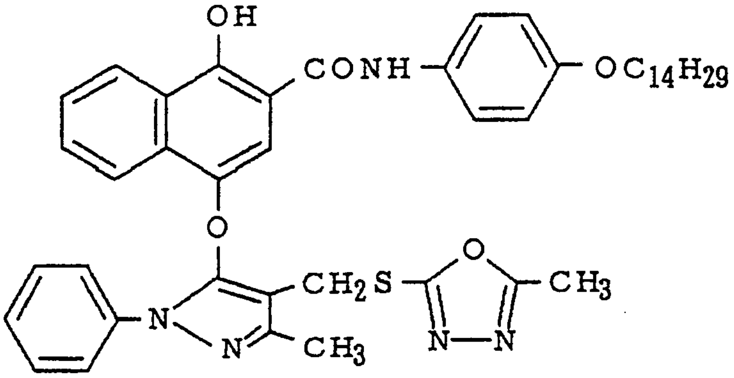
C − (26)


C12H25
HO
OCHCONH
Cℓ
NH
N=N
OCH3
OCH3
C4H9(t)
N
N
O
Cℓ
Cℓ
Cℓ

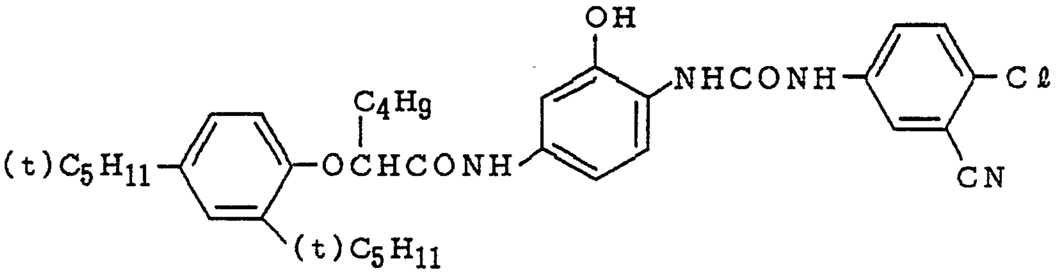
C − (27)


OC4H9
Cℓ
S
NH
N
N
O
C13H27CONH
C(CH3)2CH2C(CH3)3
Cℓ
Cℓ
Cℓ

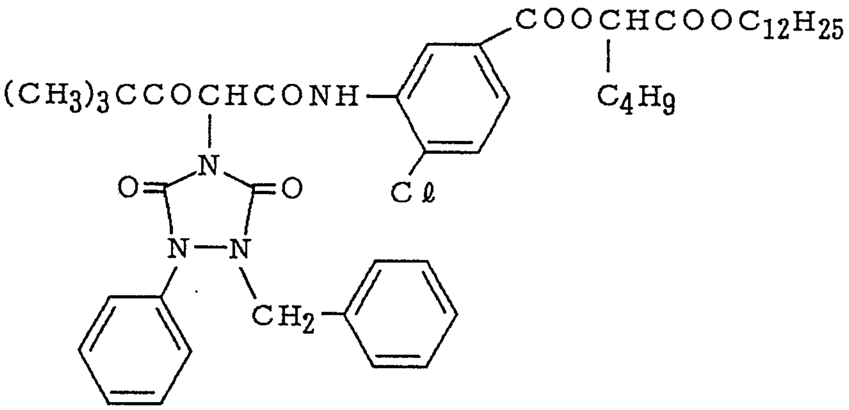
C－(28)


OH
CONH
OC14H29
O
CH2S
O
CH3
N
N
CH3
N—N

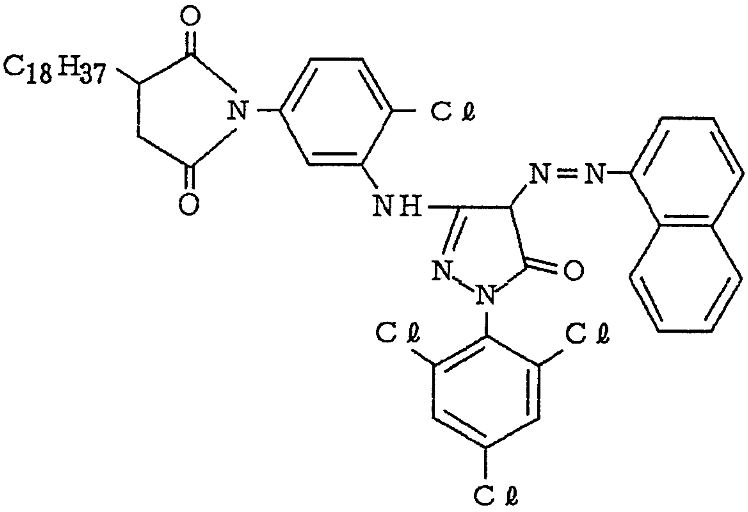
C－(29)


OH
NHCONH
Cℓ
C4H9
(t)C5H11
OCHCONH
CN
(t)C5H11

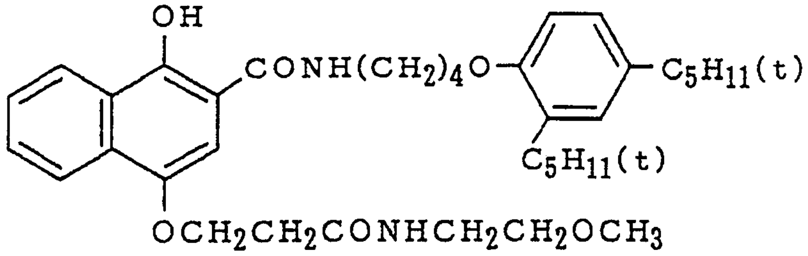
C－(30)


COOCHCOOC12H25
C4H9
(CH3)3CCOCHCONH
Cℓ
N
O
O
N
N
CH2

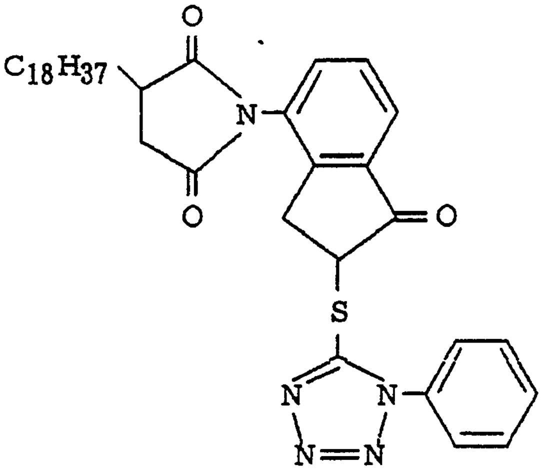
C－(31)


C18H37
O
O
N
Cℓ
NH
N=N
N
N
O
Cℓ
Cℓ
Cℓ

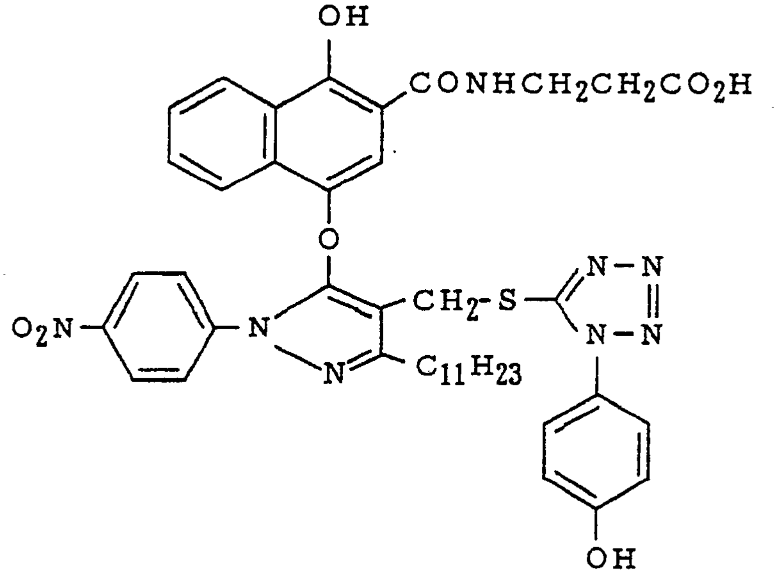
C − (32)


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)
OCH2CH2CONHCH2CH2OCH3

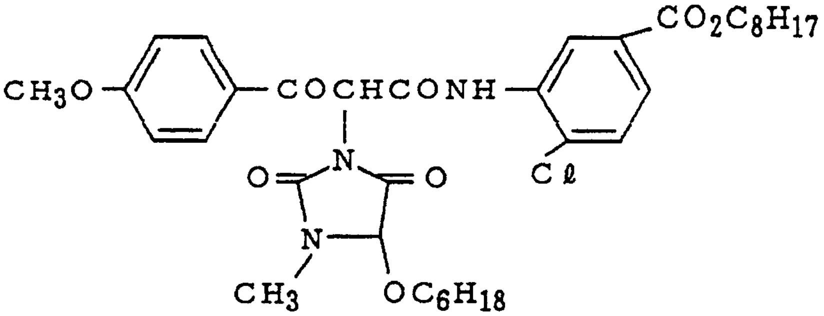
C − (33)


O
C18H37
N
O
O
S
N
N
N
N

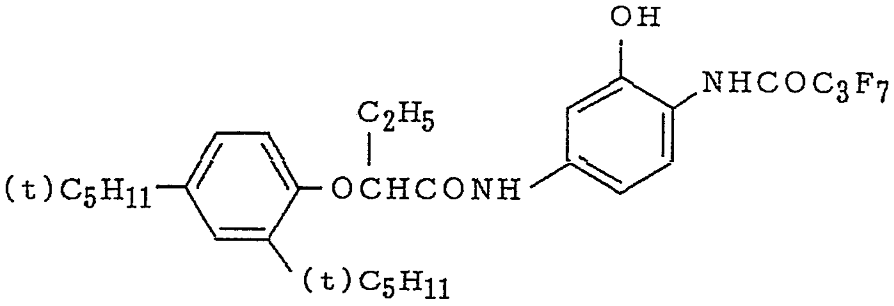
C − (34)


OH
CONHCH2CH2CO2H
O
O2N
N
N
CH2-S
N−N
N−N
C11H23
OH

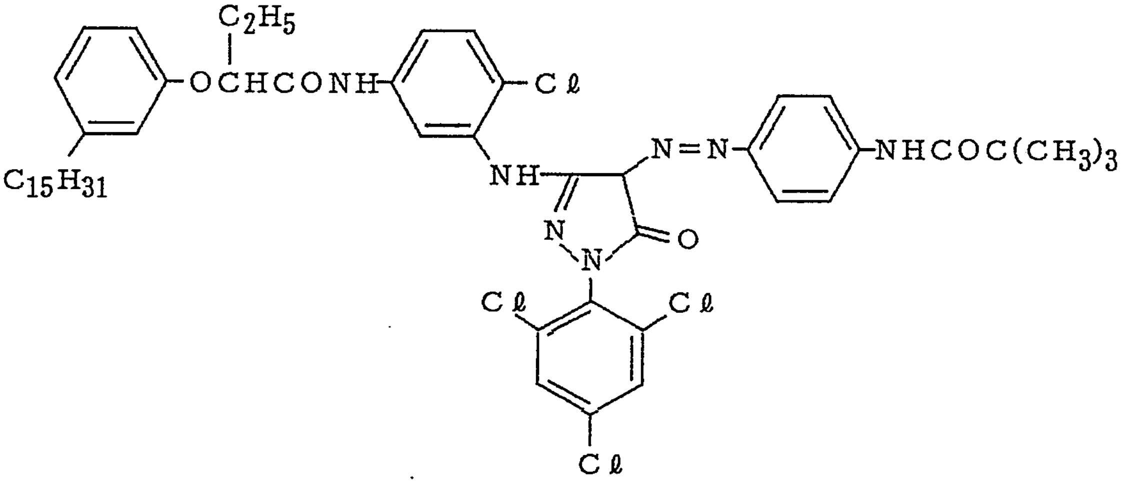
C − (35)


CO2C8H17
CH3O
COCHCONH
O
N
O
Cℓ
N
CH3
OC6H18

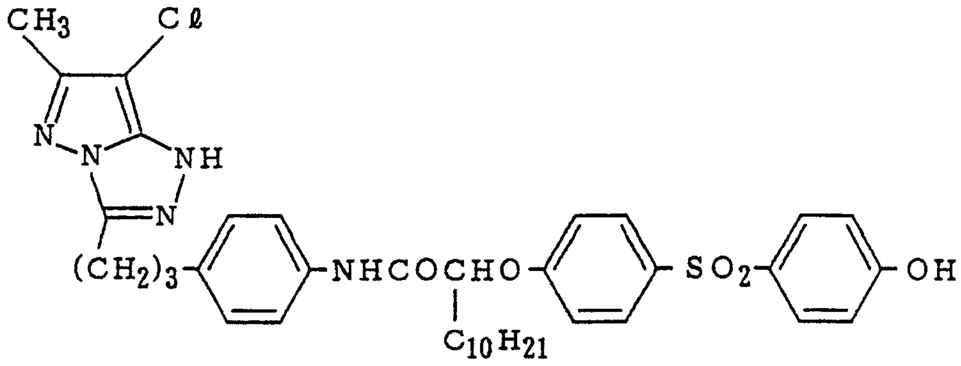
C – (36)


OH
NHCOC3F7
C2H5
(t)C5H11
OCHCONH
(t)C5H11

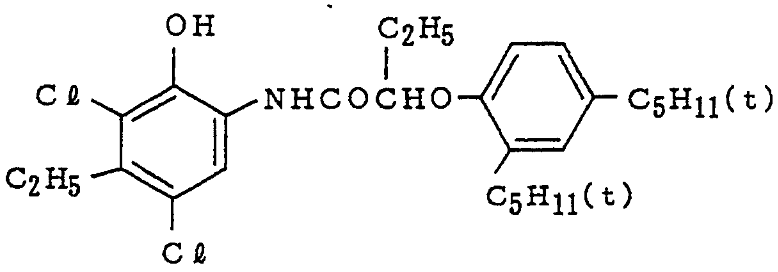
C – (37)


C2H5
OCHCONH
Cℓ
C15H31
NH
N=N
NHCOC(CH3)3
N
N
O
Cℓ
Cℓ
Cℓ

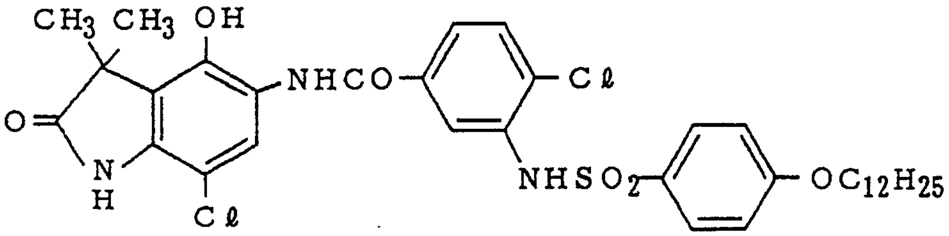
C − (38)



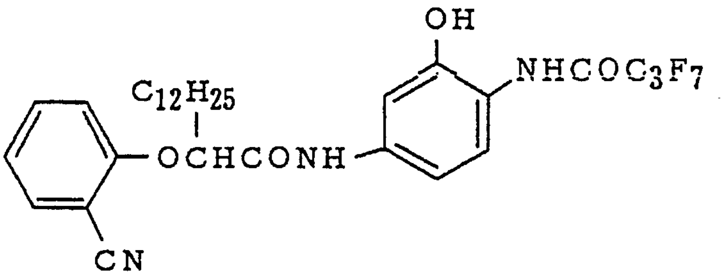
C − (39)



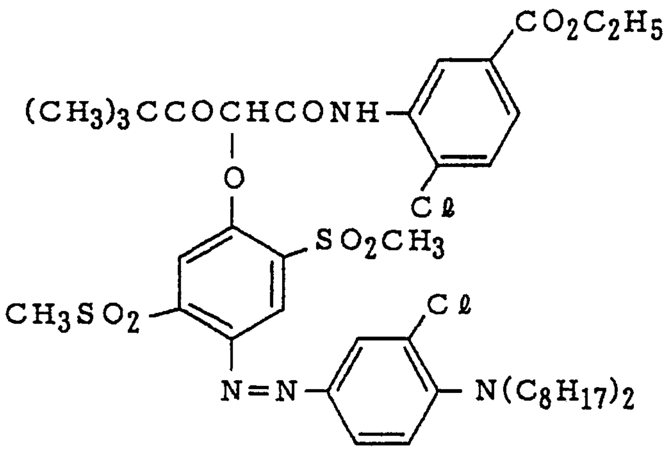
C − (40)



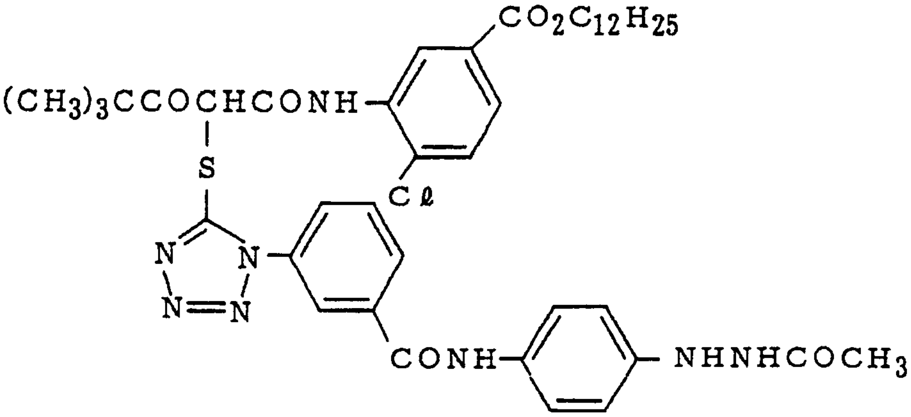
C－(41)



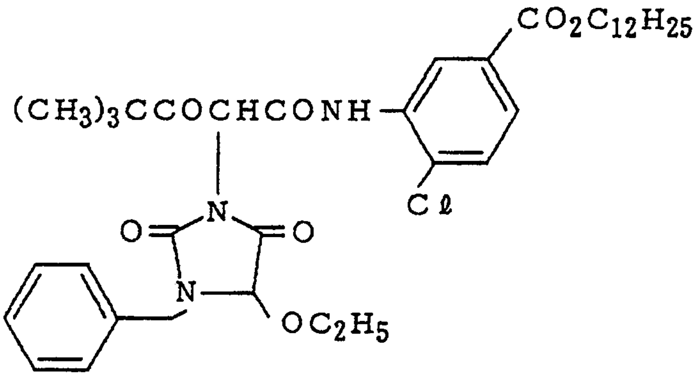
C－(42)



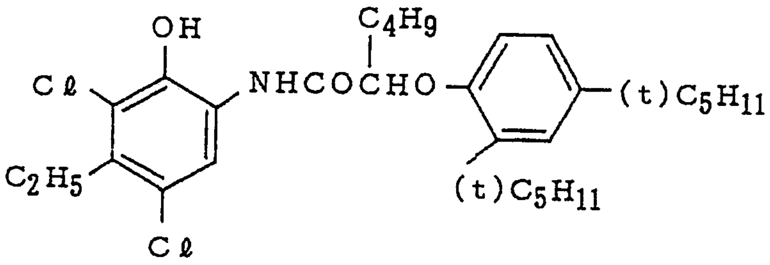
C – (43)


CO2C12H25
(CH3)3CCOCHCONH
S
Cℓ
N
N
N
N
CONH
NHNHCOCH3

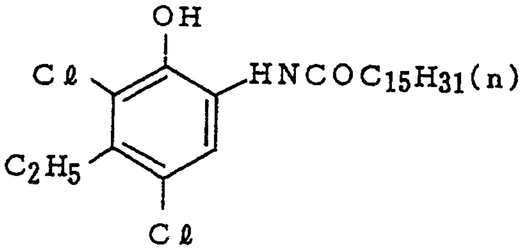
C – (44)


CO2C12H25
(CH3)3CCOCHCONH
Cℓ
O
N
O
N
OC2H5

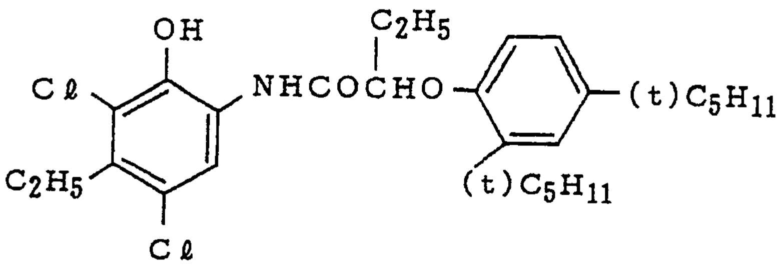
C－(45)


OH
Cℓ
C_4H_9
NHCOCHO
(t)C_5H_{11}
C_2H_5
(t)C_5H_{11}
Cℓ

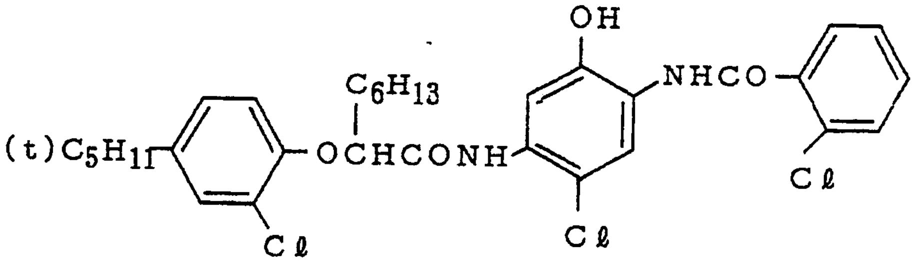
C－(46)


OH
Cℓ
HNCOC$_{15}$H$_{31}$(n)
C_2H_5
Cℓ

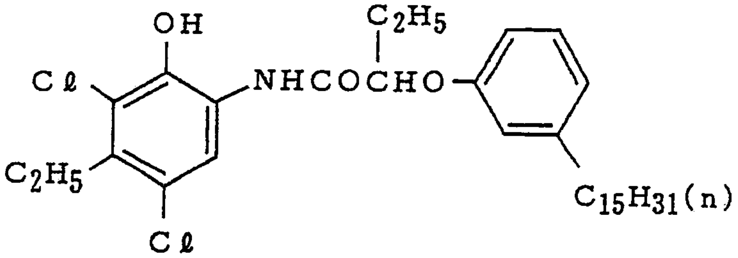
C－(47)


OH
C2H5
Cℓ
NHCOCHO
(t)C5H11
C2H5
(t)C5H11
Cℓ

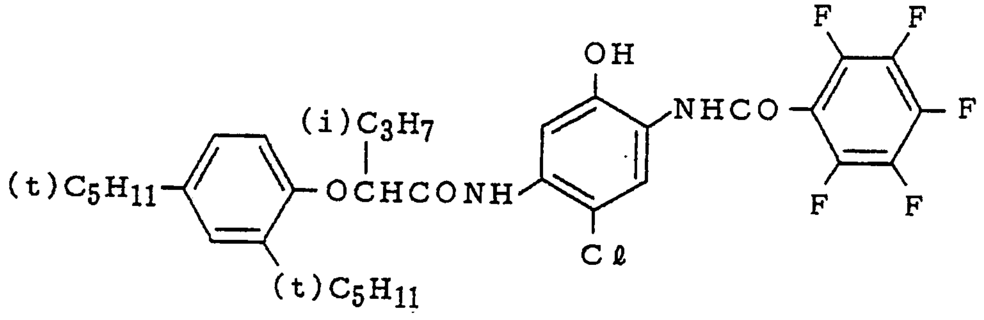
C－(48)


OH
C6H13
NHCO
(t)C5H11
OCHCONH
Cℓ
Cℓ
Cℓ

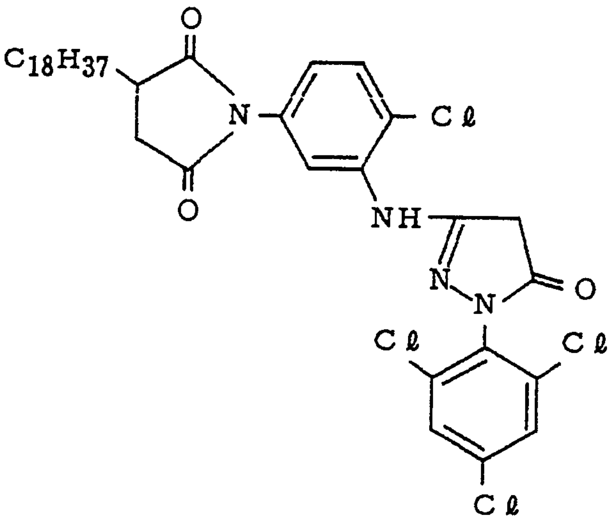
C－(49)


OH
C2H5
Cℓ
NHCOCHO
C2H5
C15H31(n)
Cℓ

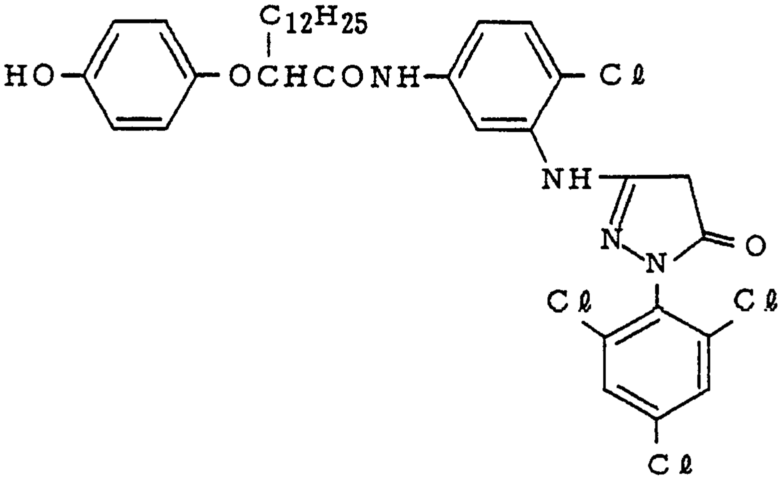
C－(50)


(t)C5H11
(i)C3H7
OCHCONH
(t)C5H11
OH
NHCO
Cℓ
F
F
F
F
F

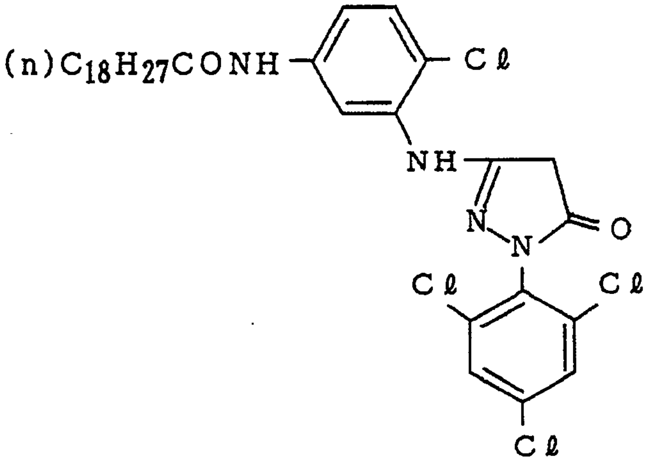
C－(51)


C18H37
O
N
O
Cℓ
NH
N
N
O
Cℓ
Cℓ
Cℓ

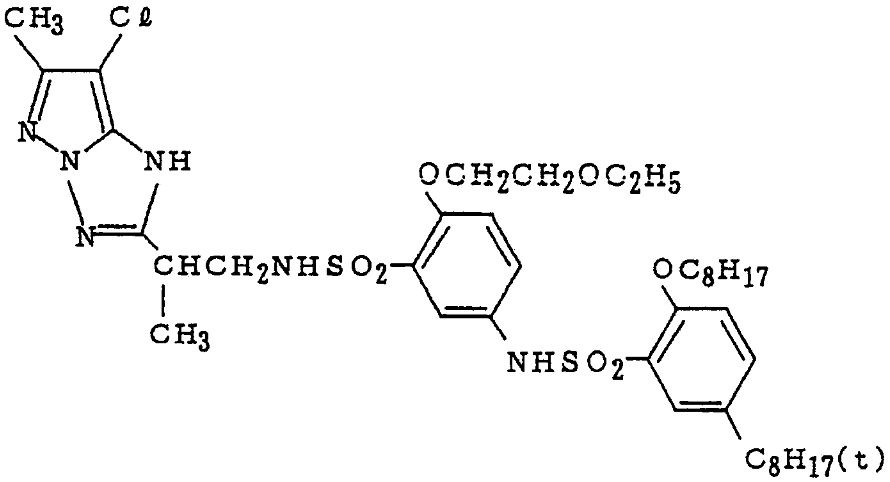
C－(52)


HO
OCHCONH
$C_{12}H_{25}$
Cl
NH
N
N
O
Cl
Cl
Cl

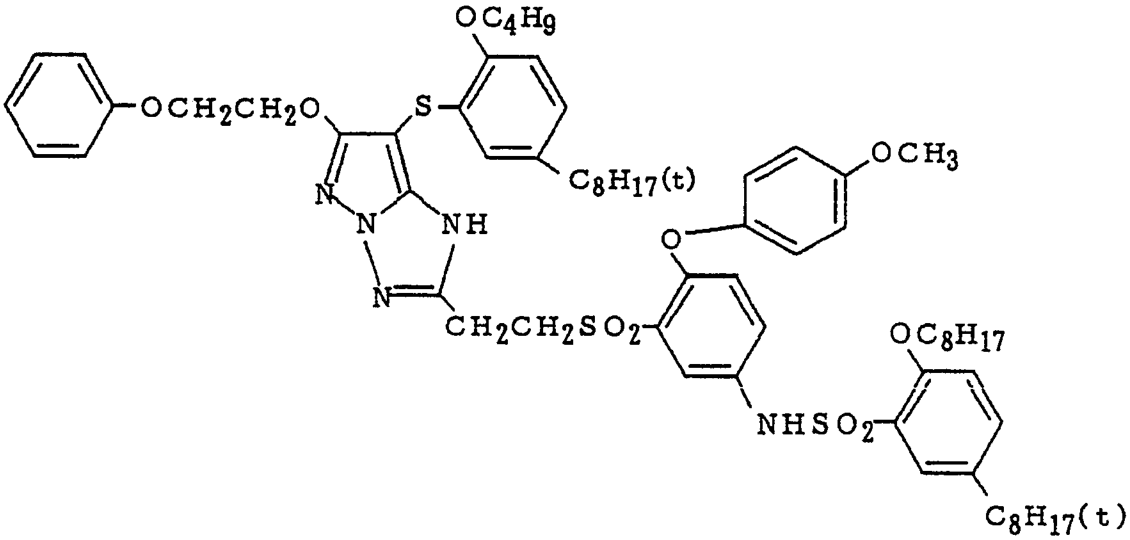
C－(53)


(n)$C_{18}H_{27}$CONH
Cl
NH
N
N
O
Cl
Cl
Cl

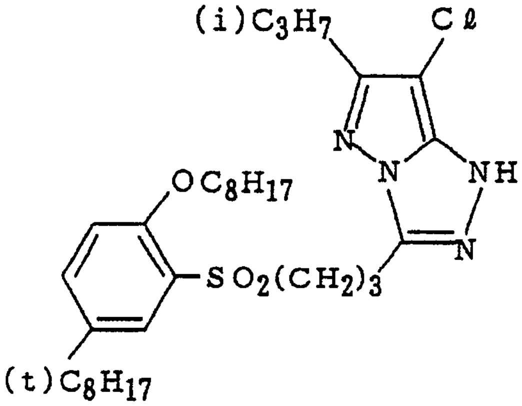
C－(54)



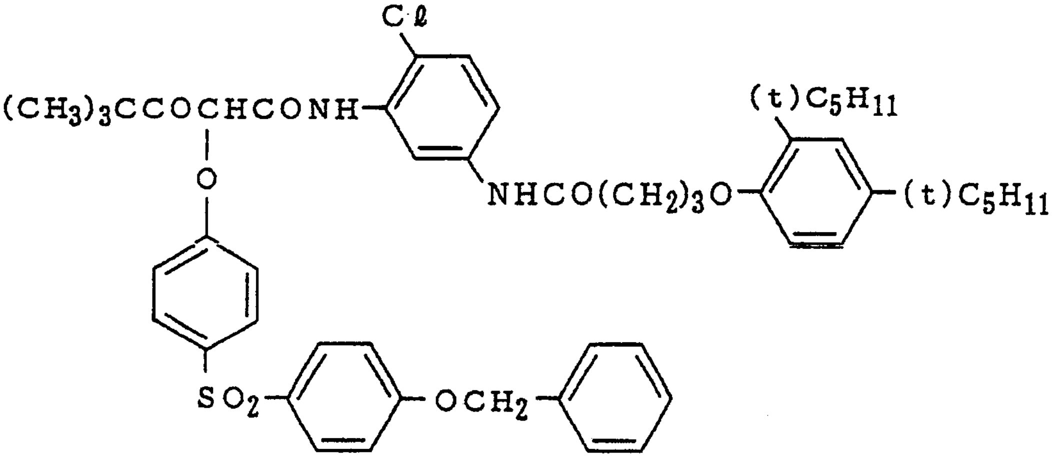
C－(55)



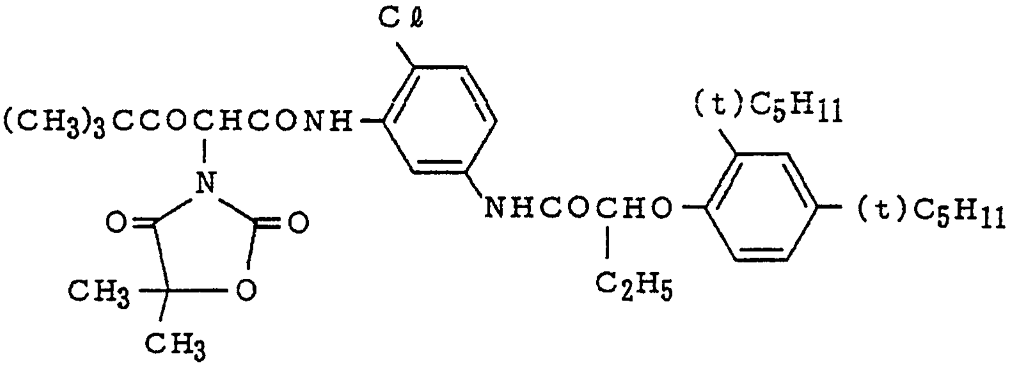
C – (56)


(i)C3H7
Cℓ
N
N
NH
N
OC8H17
SO2(CH2)3
(t)C8H17

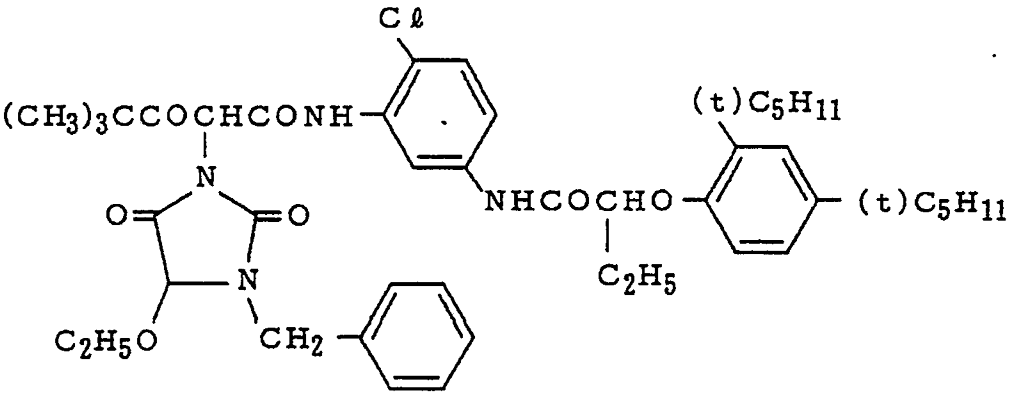
C – (57)


Cℓ
(CH3)3CCOCHCONH
O
NHCO(CH2)3O
(t)C5H11
(t)C5H11
SO2
OCH2

C－(58)


Cℓ
(CH3)3CCOCHCONH
N
O
O
CH3
O
CH3
NHCOCHO
C2H5
(t)C5H11
(t)C5H11

C－(59)


Cℓ
(CH3)3CCOCHCONH
N
O
O
N
C2H5O
CH2
NHCOCHO
C2H5
(t)C5H11
(t)C5H11

C－(60)

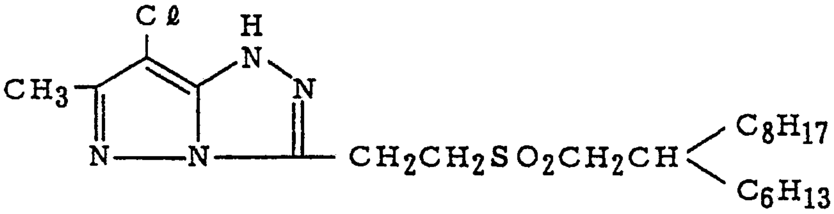
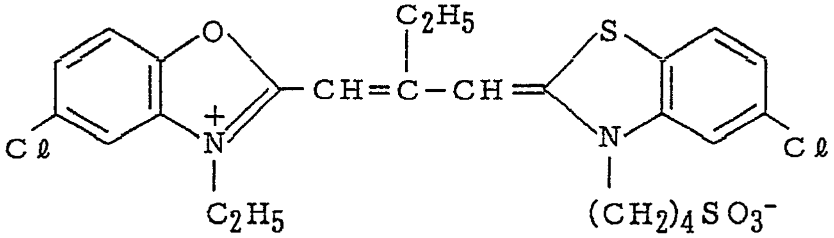
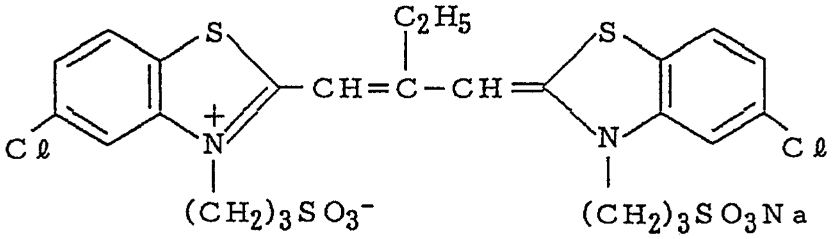

Cℓ
H
N
N
CH3
N
N
CH2CH2SO2CH2CH
C8H17
C6H13

Table C

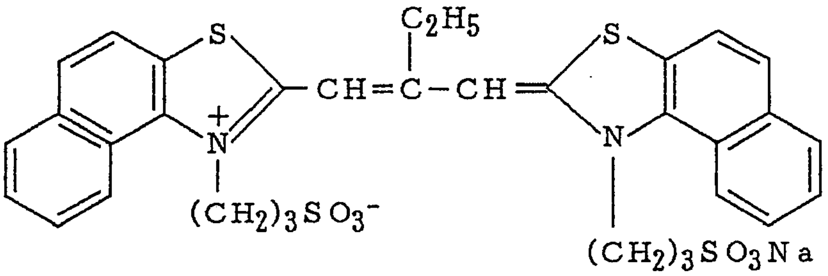
ExS-1



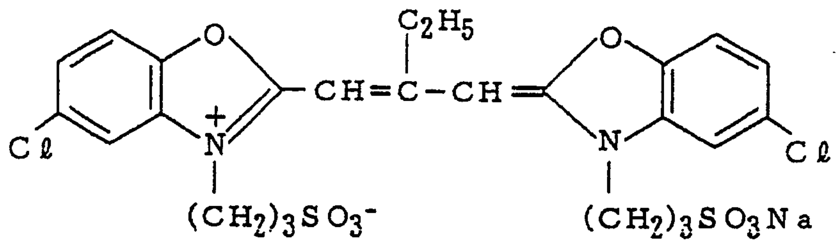
ExS-2



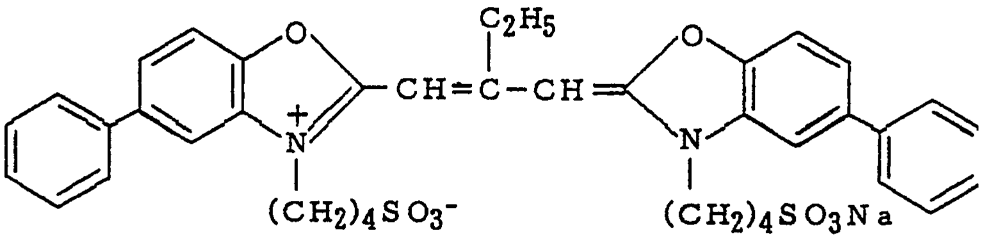
ExS-3



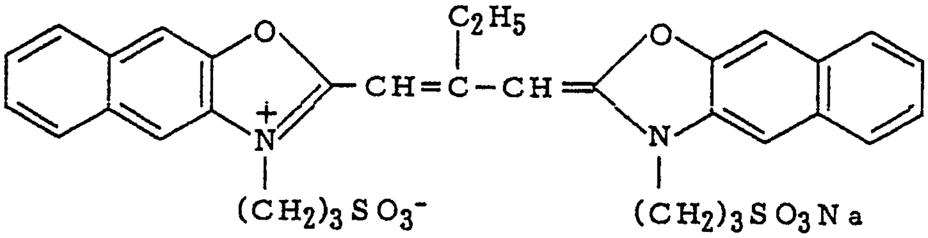
ExS−4



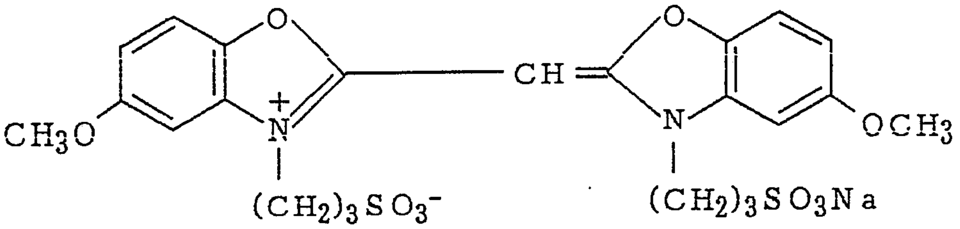
ExS−5



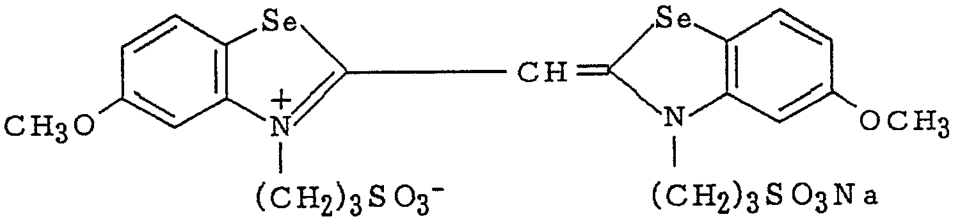
ExS−6



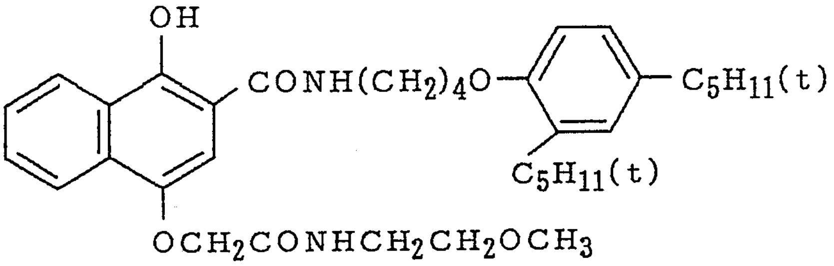
ExS-7



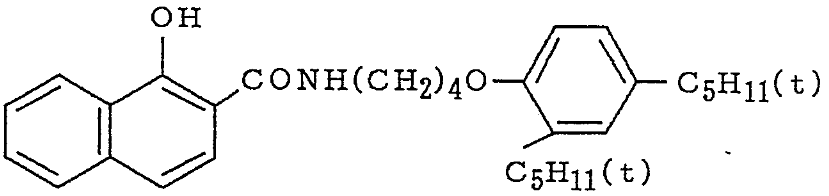
ExS-8



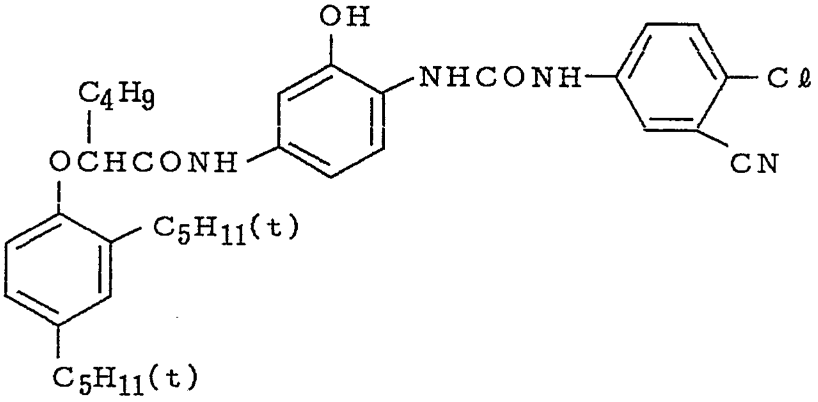
ExC-4



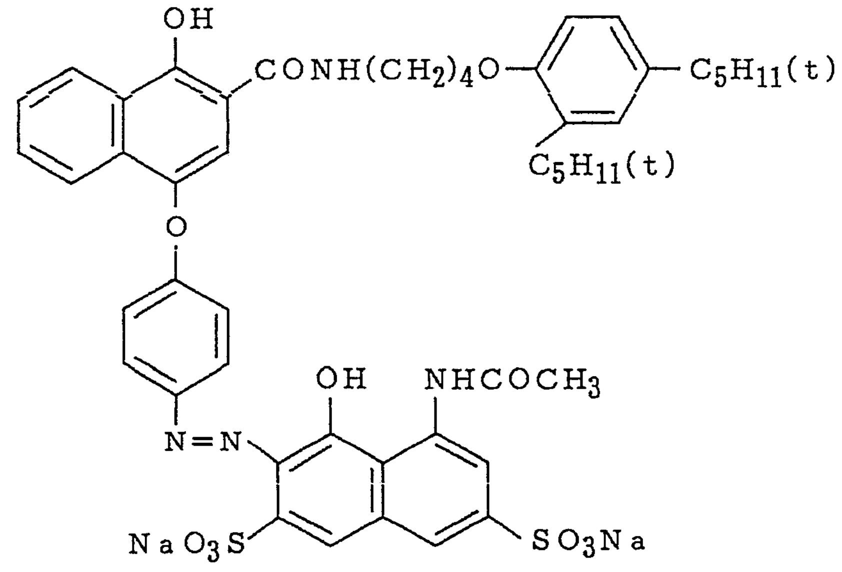
ExC－5


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)

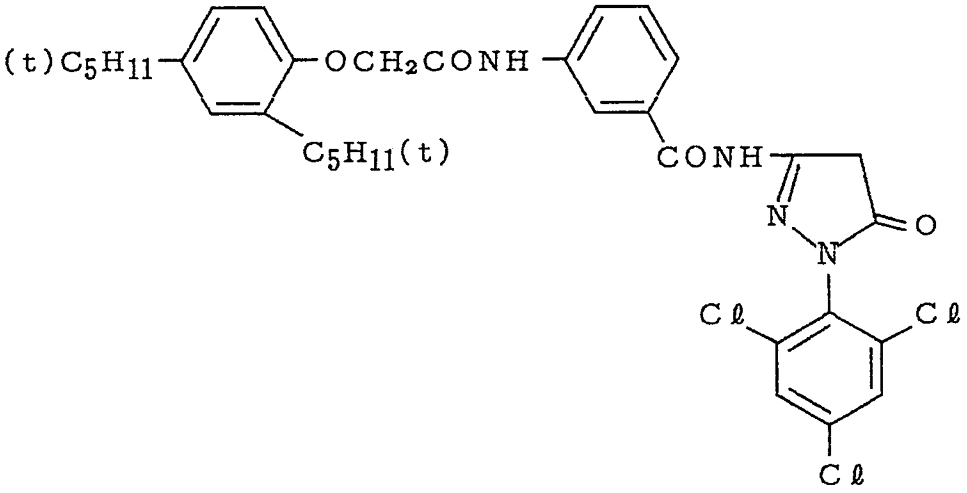
ExC－1


OH
NHCONH
Cℓ
CN
C4H9
OCHCONH
C5H11(t)
C5H11(t)

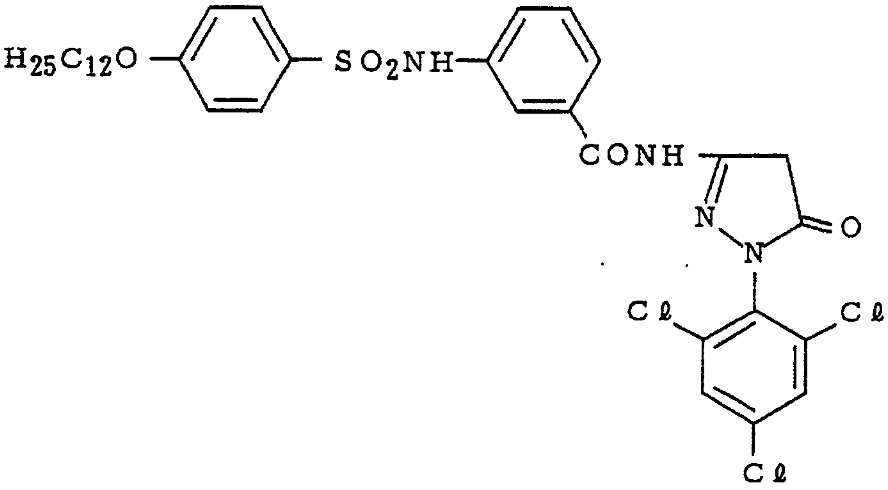
ExC－2


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)
O
OH
NHCOCH3
N=N
NaO3S
SO3Na

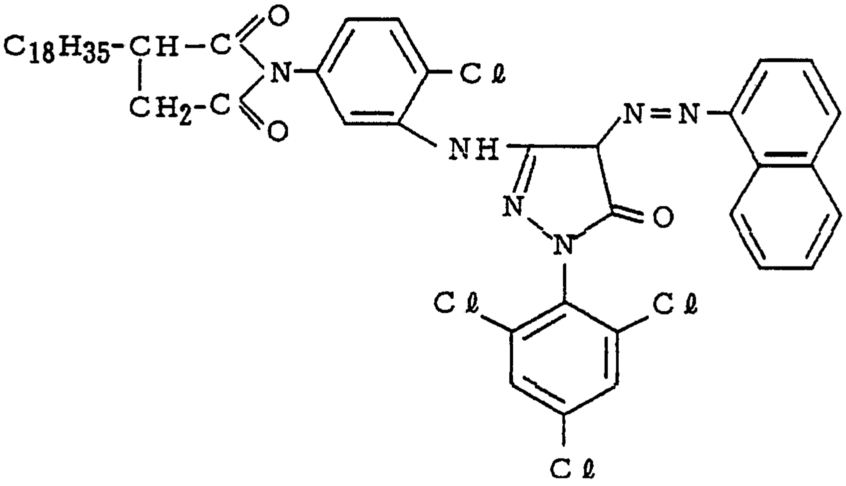
ExM－6


(t)C5H11
OCH2CONH
C5H11(t)
CONH
N
N
O
Cℓ
Cℓ
Cℓ

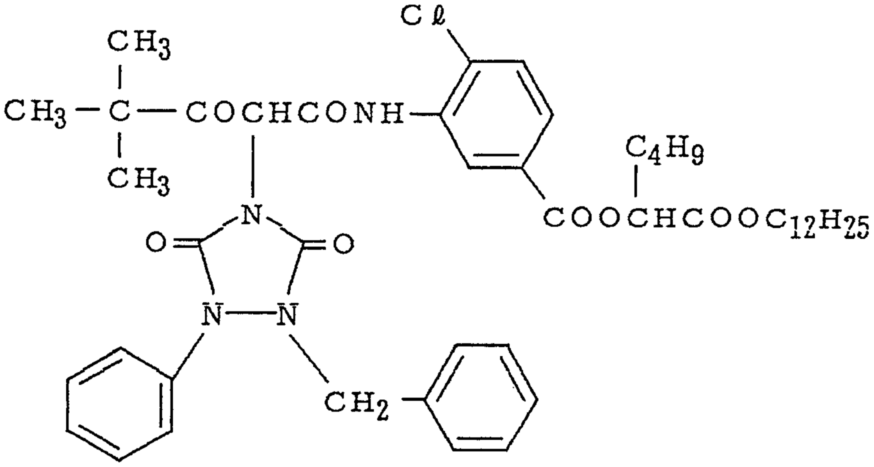
ExM-7


H25C12O
SO2NH
CONH
N
N
O
Cℓ
Cℓ
Cℓ

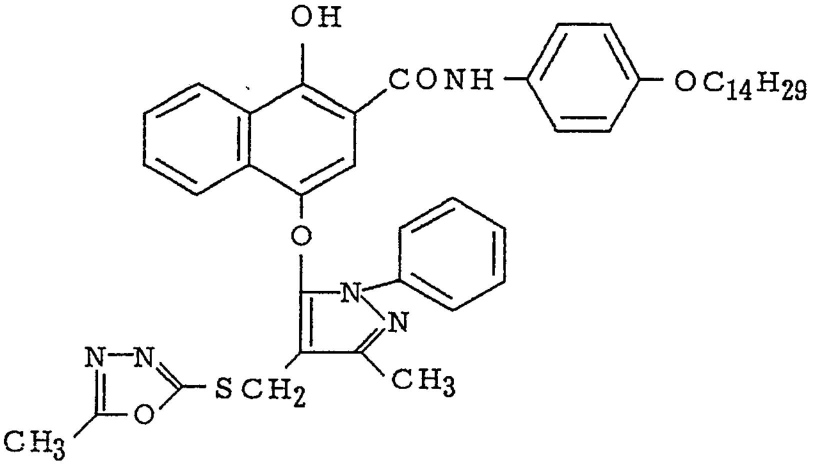
ExM-8


C18H35-CH-C
CH2-C
O
O
N
Cℓ
NH
N=N
N
N
O
Cℓ
Cℓ
Cℓ

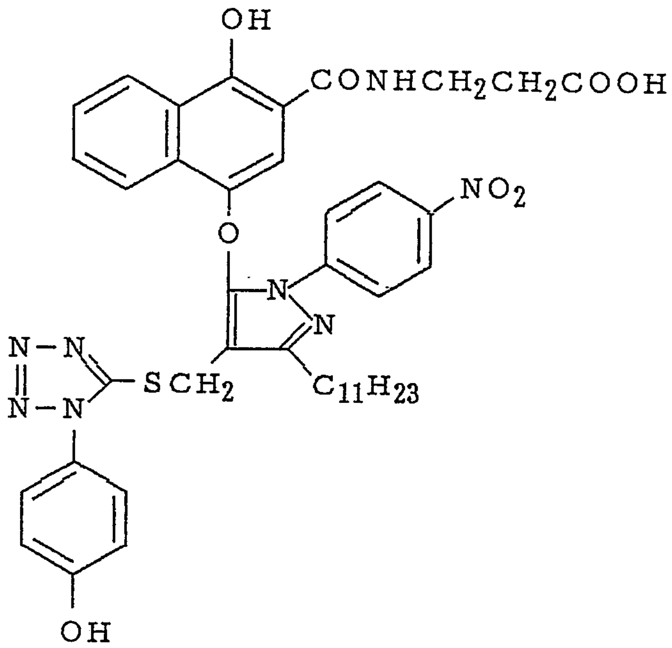
ExY-10



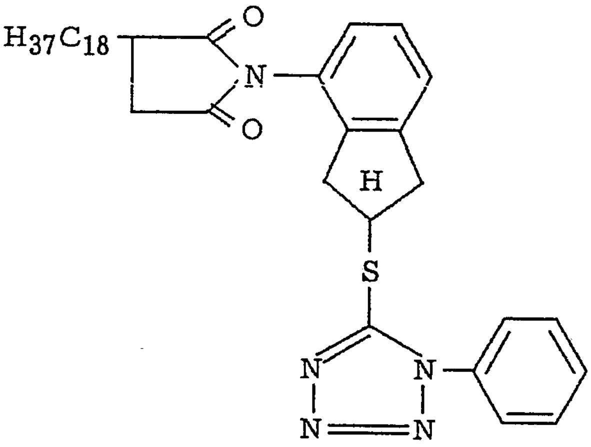
ExC-3



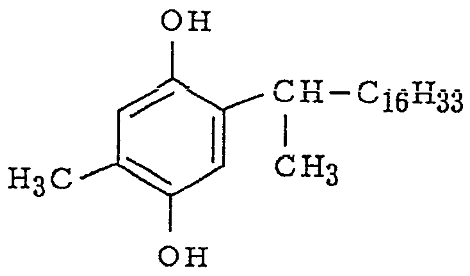
ExC-9



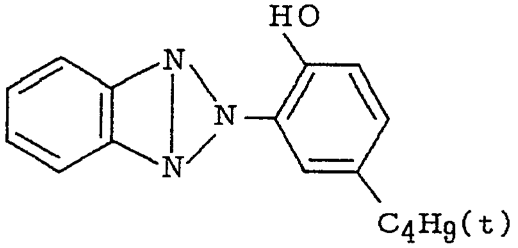
Cpd-1



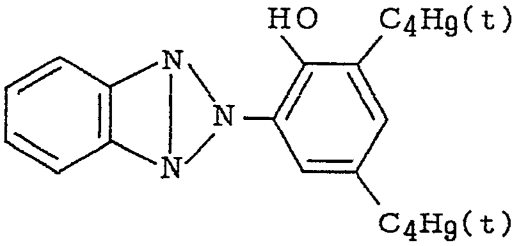
Cpd−2



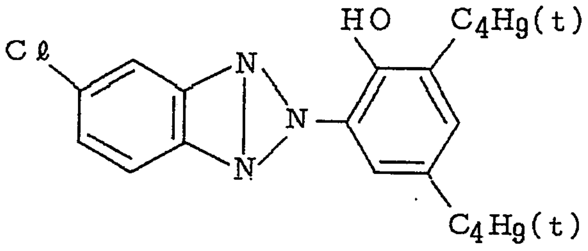
Cpd−3



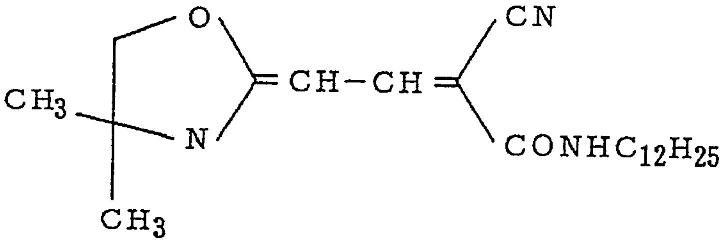
Cpd−4



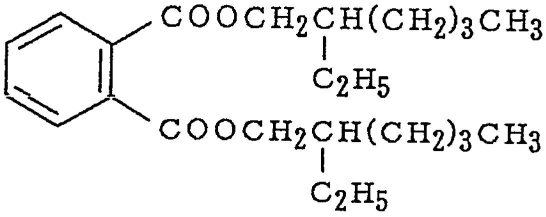
Cpd-5



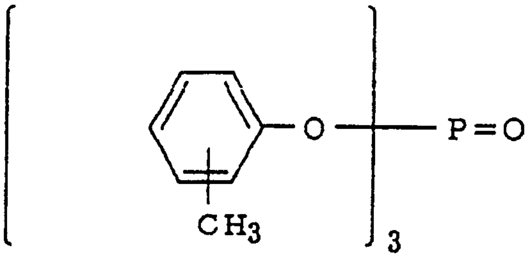
Cpd-6



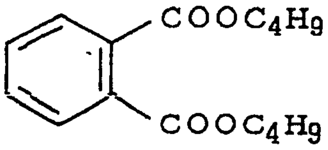
Solv-1



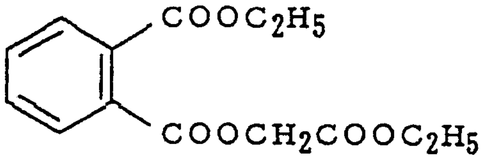
Solv-2



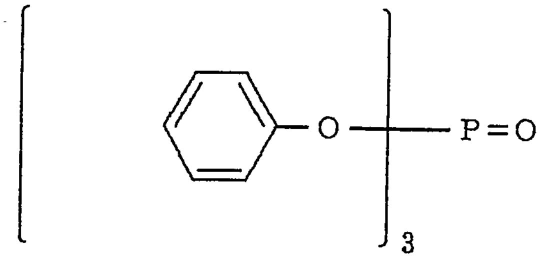
Solv-3



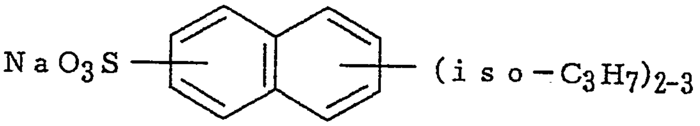
Solv-4



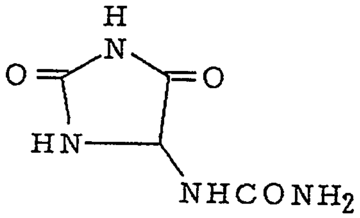
Solv-5



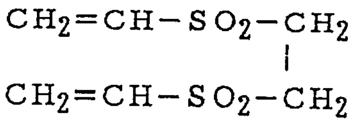
Cpd-7



Cpd-8



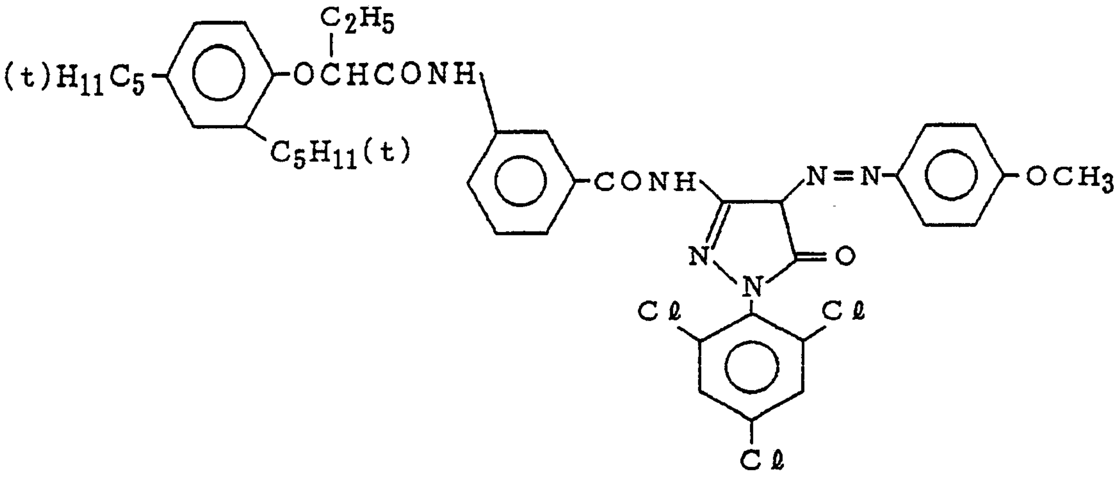
H-1



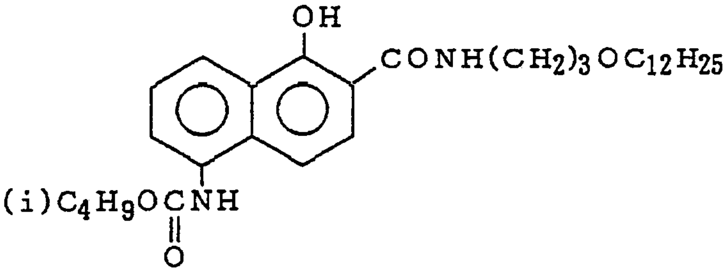
$$\begin{array}{l} CH_2=CH-SO_2-CH_2 \\ \qquad\qquad\qquad\qquad\quad | \\ CH_2=CH-SO_2-CH_2 \end{array}$$

Table D

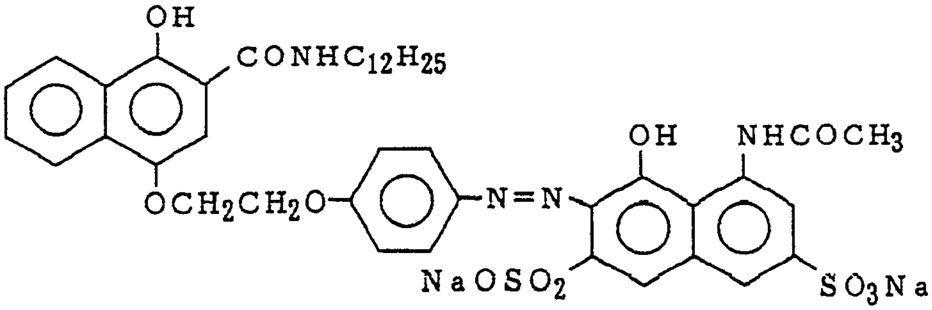
EX-1



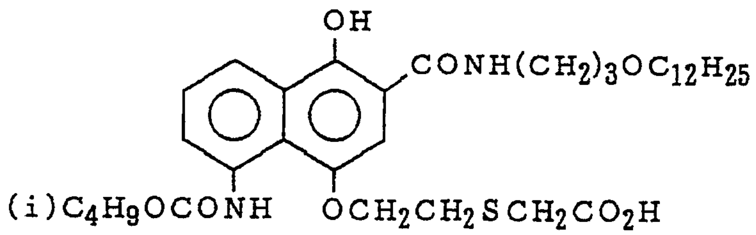
EX-2



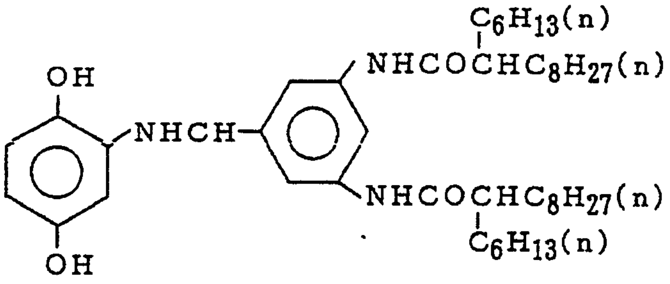
EX-3



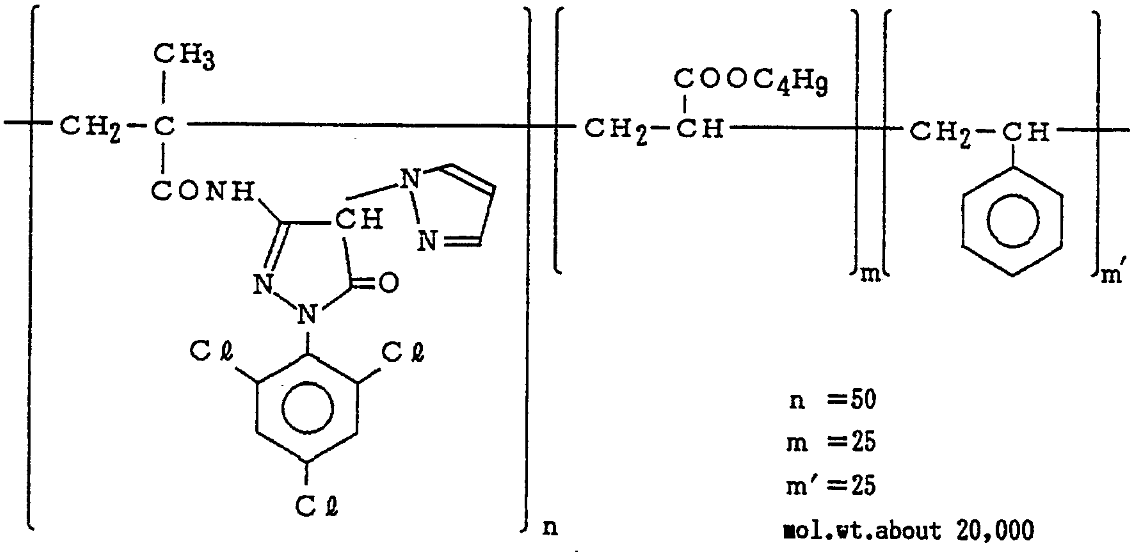
EX-4



EX-5

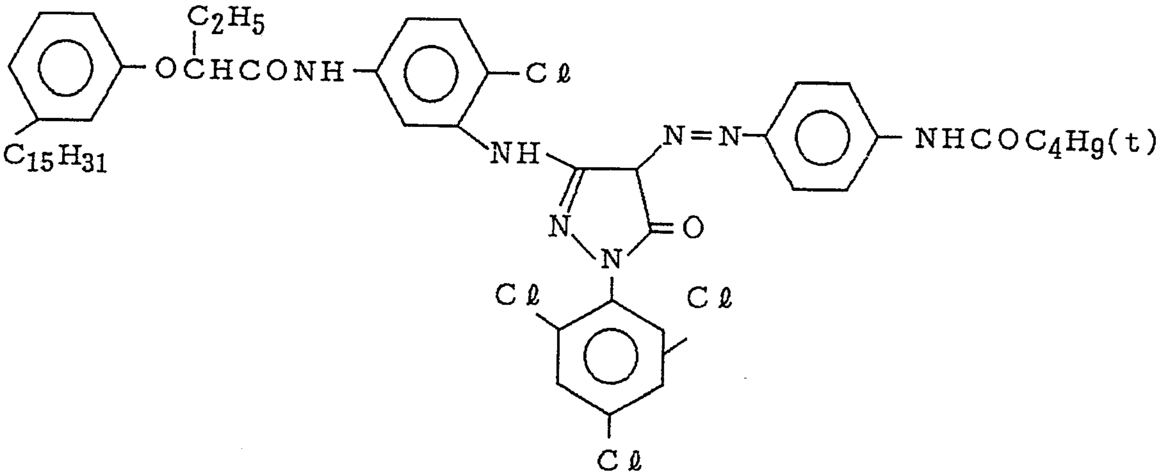


EX-6

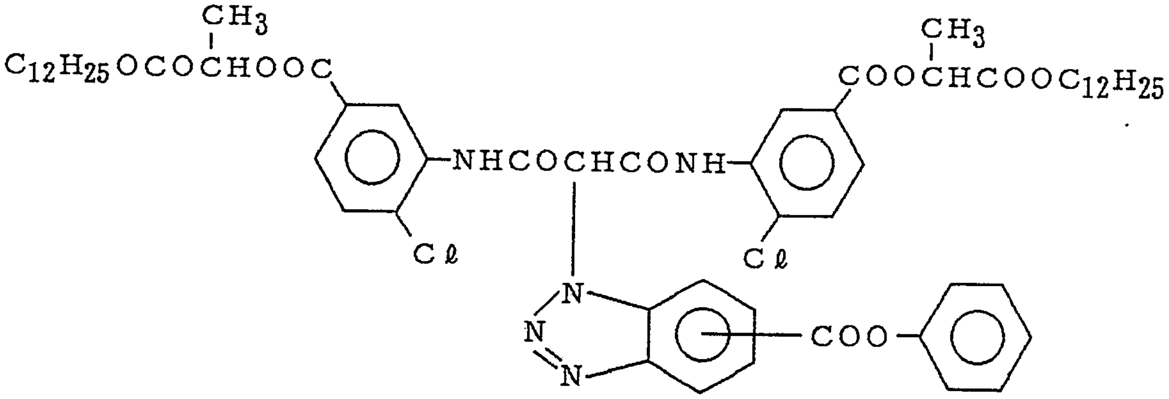


n =50
m =25
m′ =25
mol.wt.about 20,000

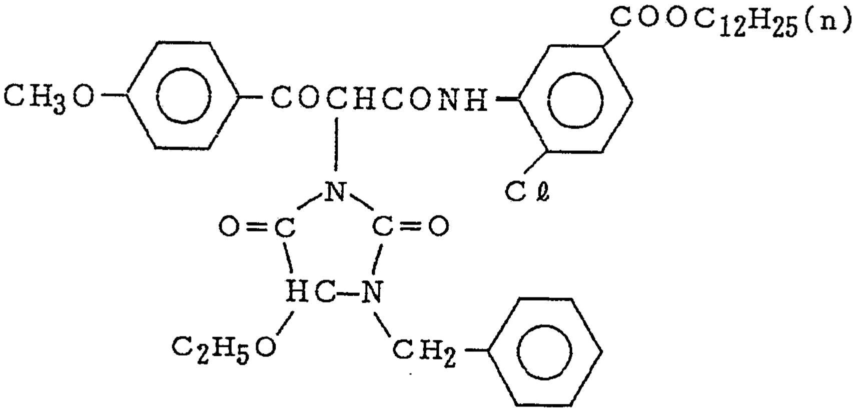
EX−7


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

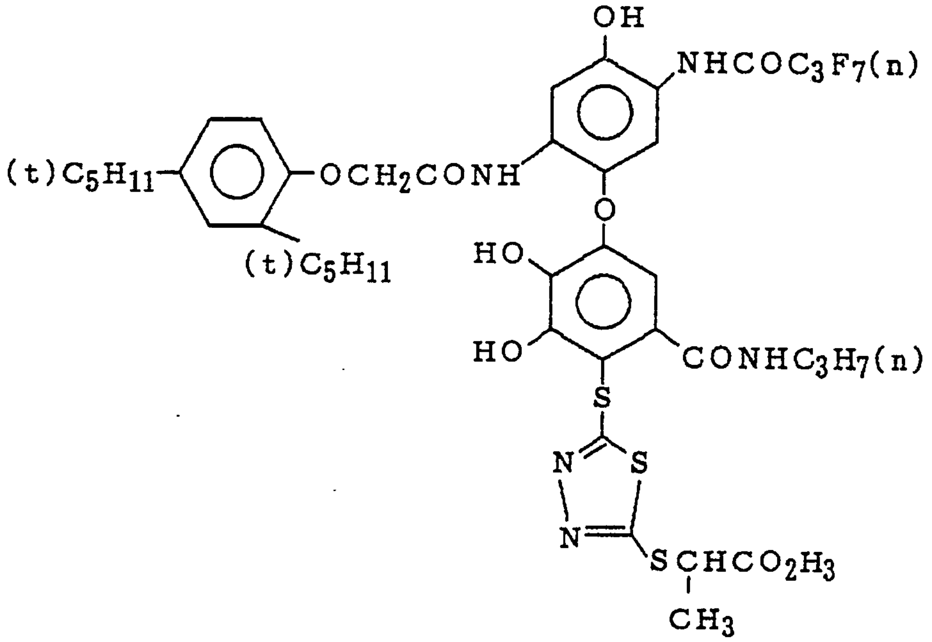
EX−8


CH3
C12H25OCOCHOOC
CH3
COOCHCOOC12H25
NHCOCHCONH
Cℓ
Cℓ
N
N
N
COO

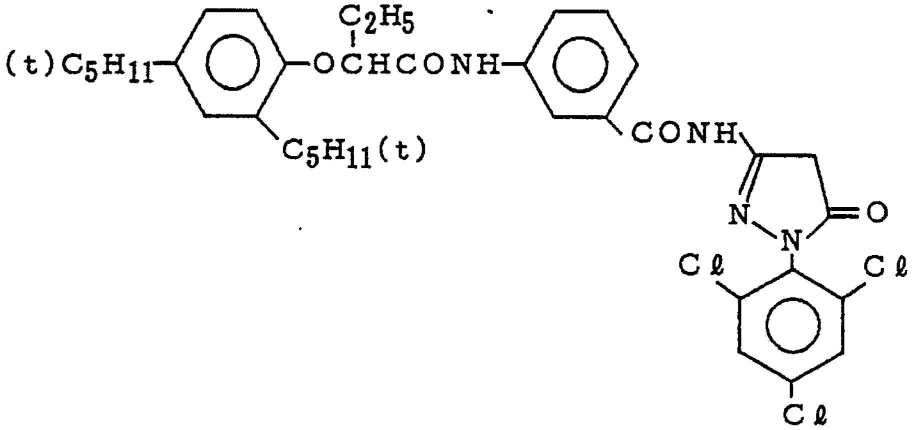
EX−9


COOC12H25(n)
CH3O
COCHCONH
Cℓ
N
O=C
C=O
HC−N
C2H5O
CH2

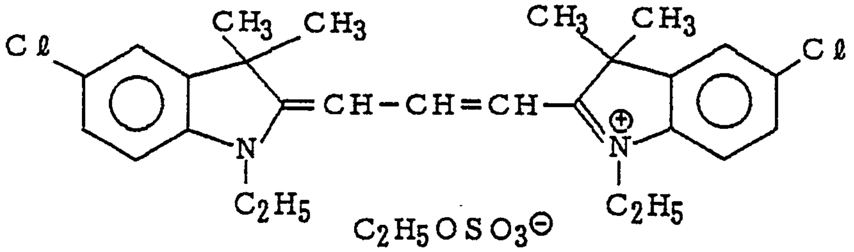
E X − 10



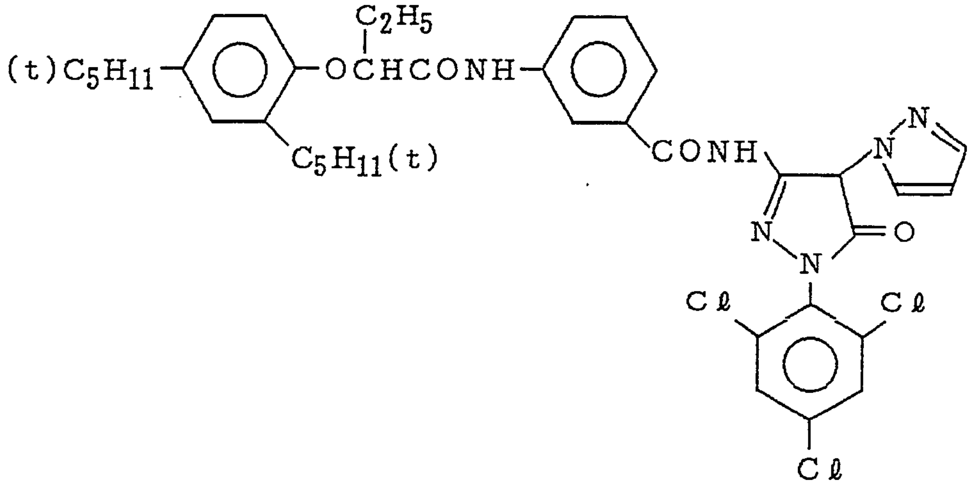
E X − 11



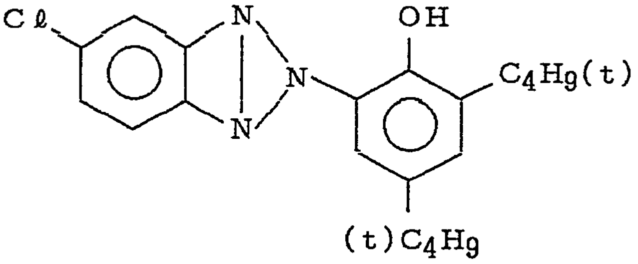
E X − 12



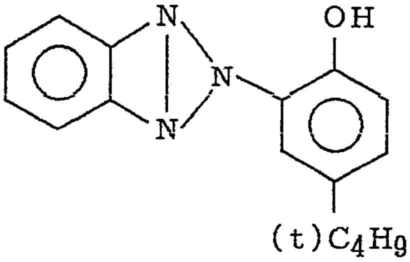
EX-13


(t)C5H11
C2H5
OCHCONH
C5H11(t)
CONH
N
N
N
N
O
Cℓ
Cℓ
Cℓ

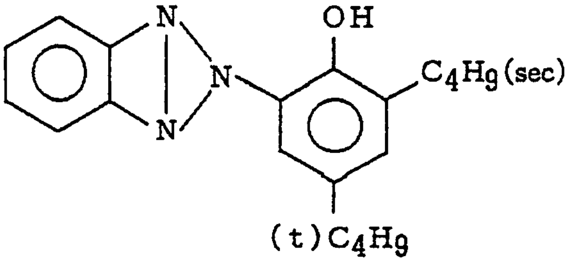
U-1


Cℓ
N
N
N
OH
C4H9(t)
(t)C4H9

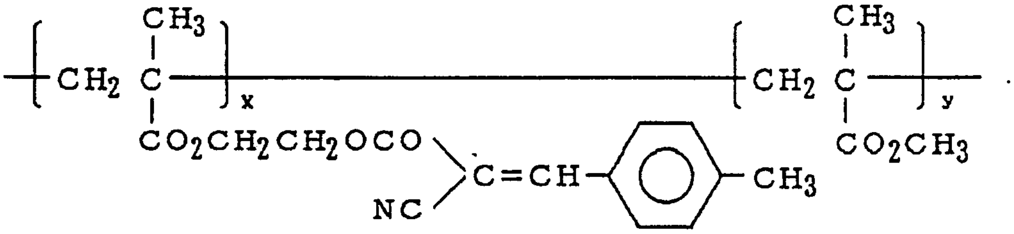
U-2


N
N
N
OH
(t)C4H9

U－3

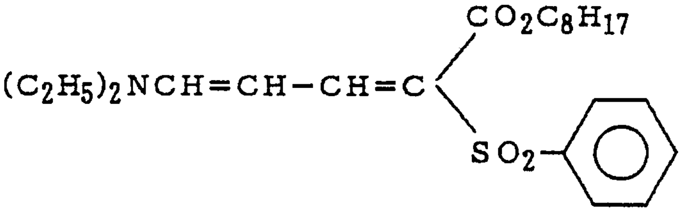


U－4



x : y =70 : 30 (wt%)

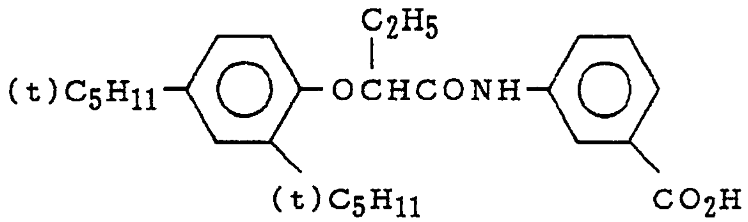
UV－5



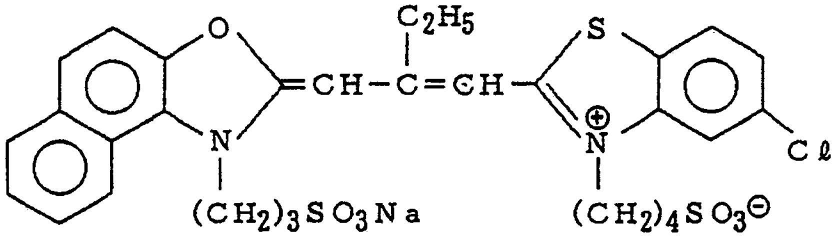
HBS−1 tricresyl phosphate

HBS−2 di-n-butylphtalate

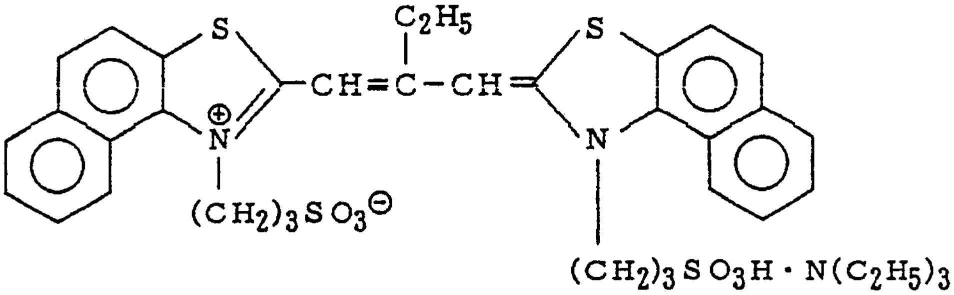
HBS−3



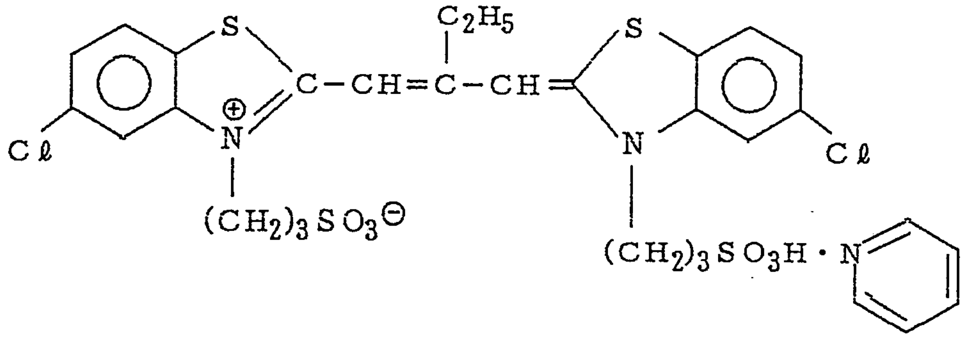
sensitizing dye I



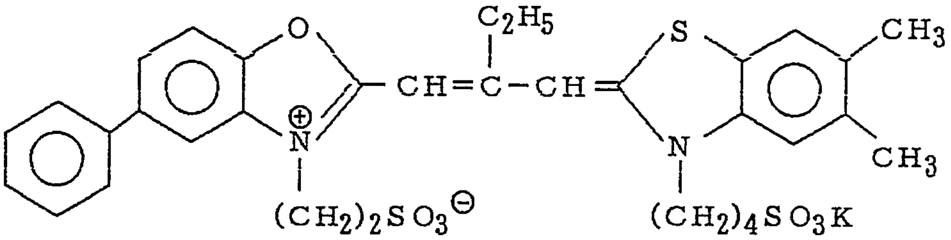
sensitizing dye II



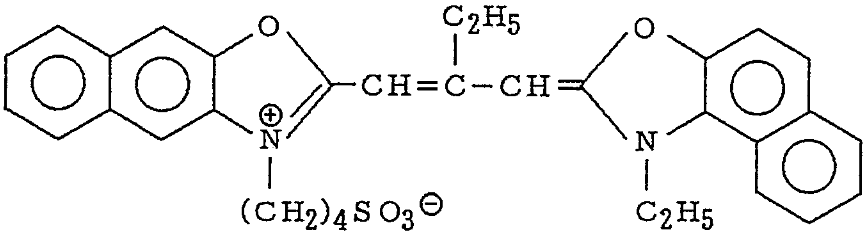
senritizing dye III



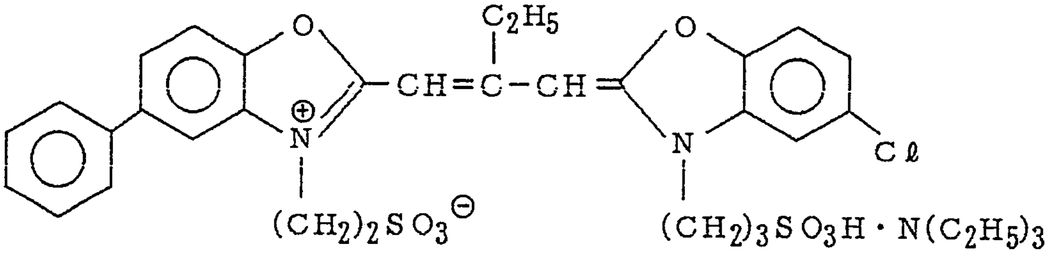
senritizing dye V



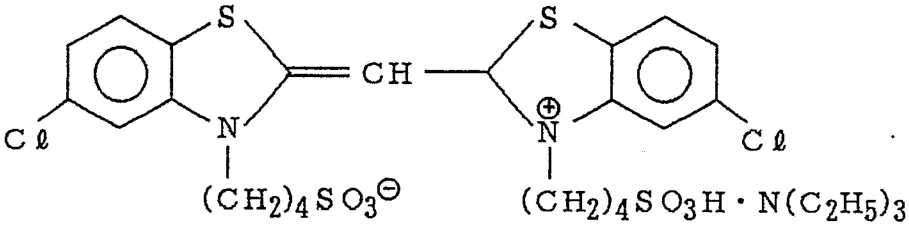
senritizing dye VI



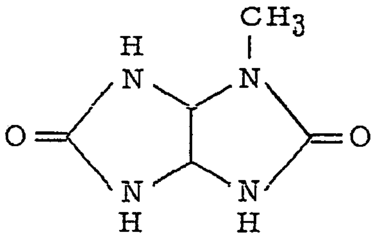
senritizing dye VII



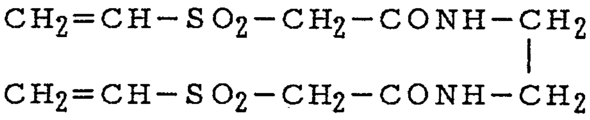
senritizing dye VIII



S－1



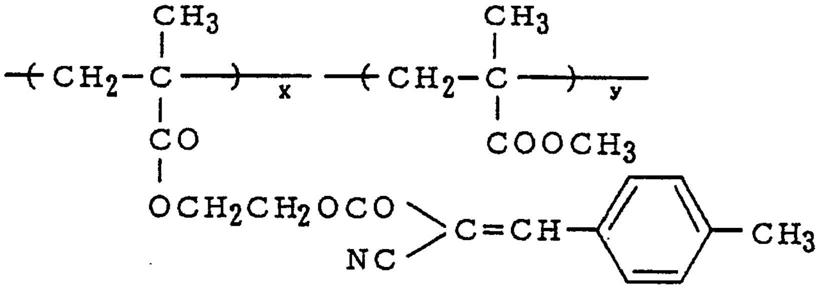
H－1



$$\begin{array}{rc} \mathrm{CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}} & \mathrm{CH_2} \\ & | \\ \mathrm{CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}} & \mathrm{CH_2} \end{array}$$

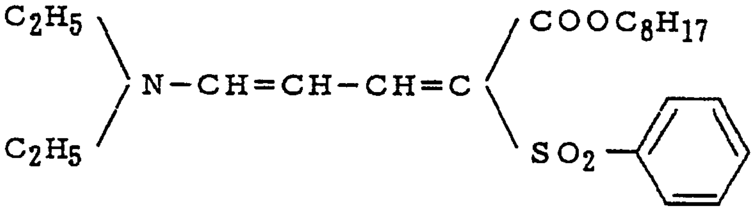
Table E

UV-1

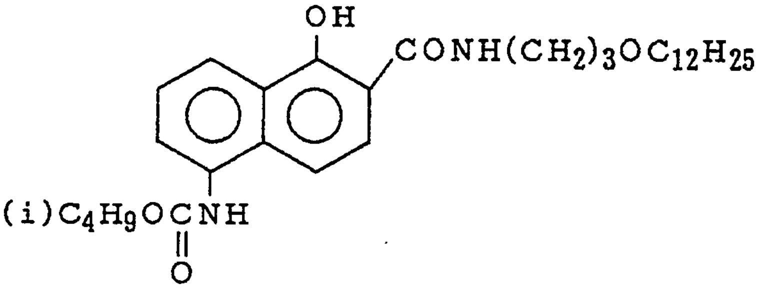


x/y = 7/3 (weight ratio)

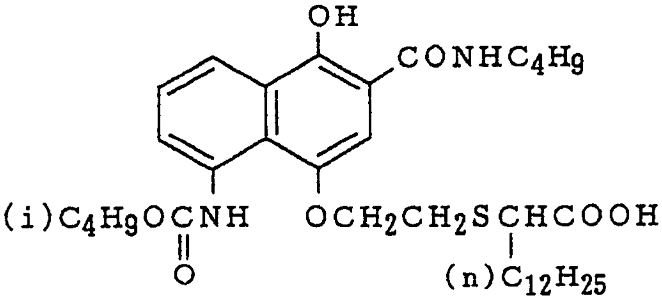
UV-2



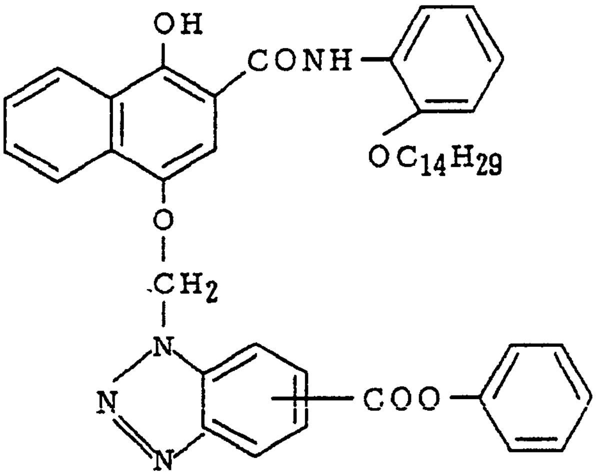
ExC-1



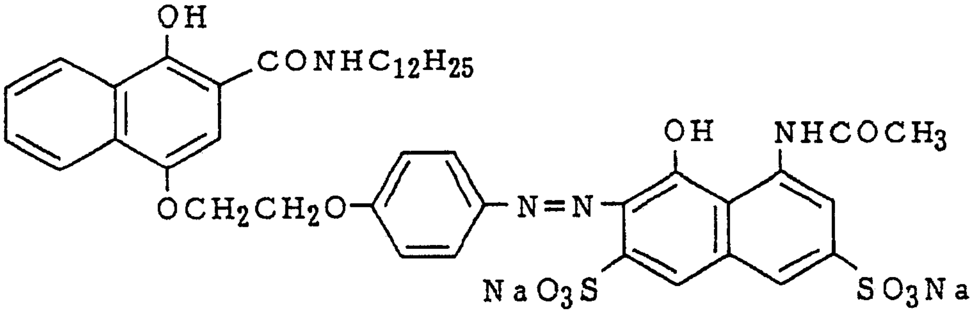
ExC−2



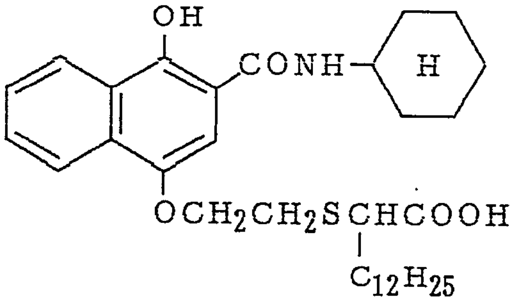
ExC−3



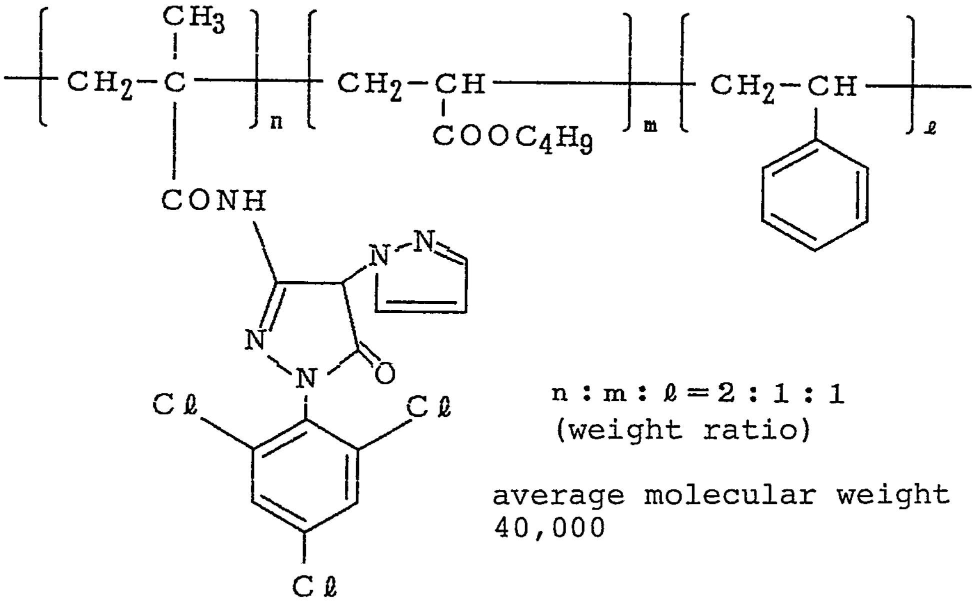
ExC−4



ExC-5



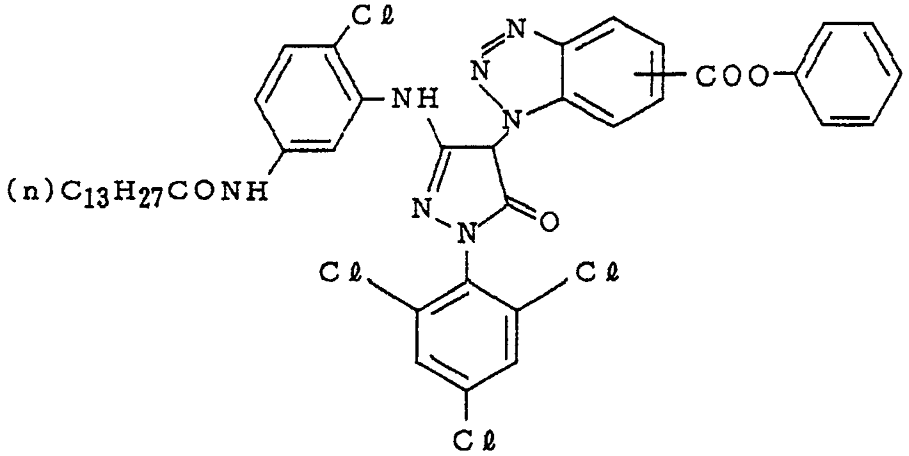
ExM-1



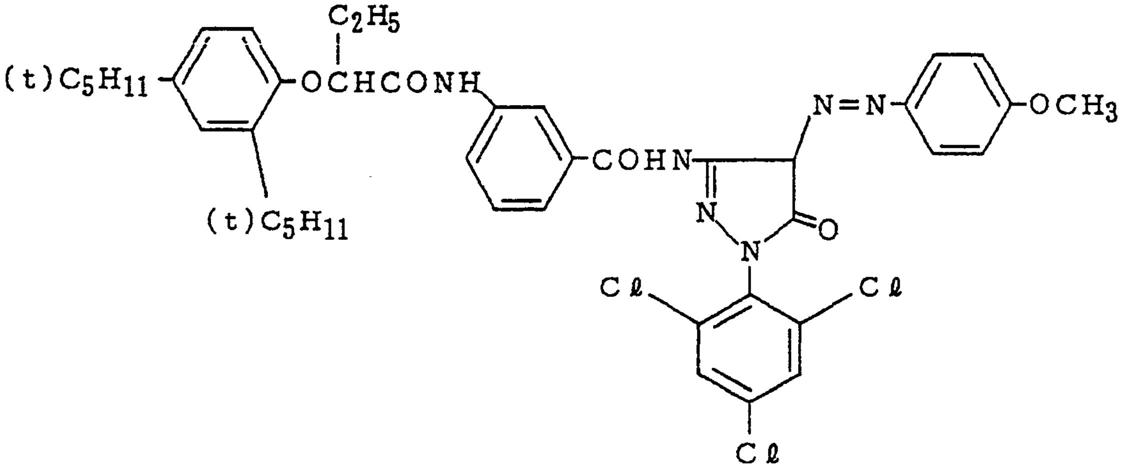
n : m : ℓ = 2 : 1 : 1
(weight ratio)

average molecular weight
40,000

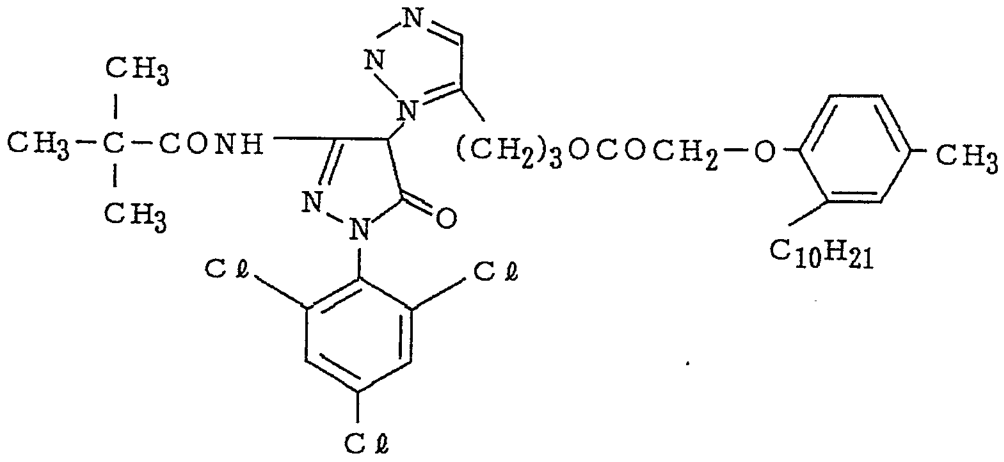
ExM-2


Cℓ
NH
N
N
N
COO
(n)C13H27CONH
N
N
O
Cℓ
Cℓ
Cℓ

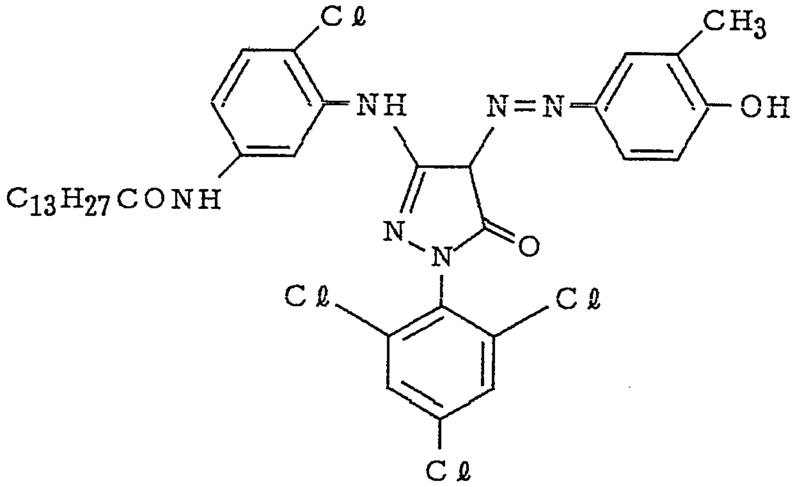
ExM-3


C2H5
(t)C5H11
OCHCONH
N=N
OCH3
COHN
(t)C5H11
N
N
O
Cℓ
Cℓ
Cℓ

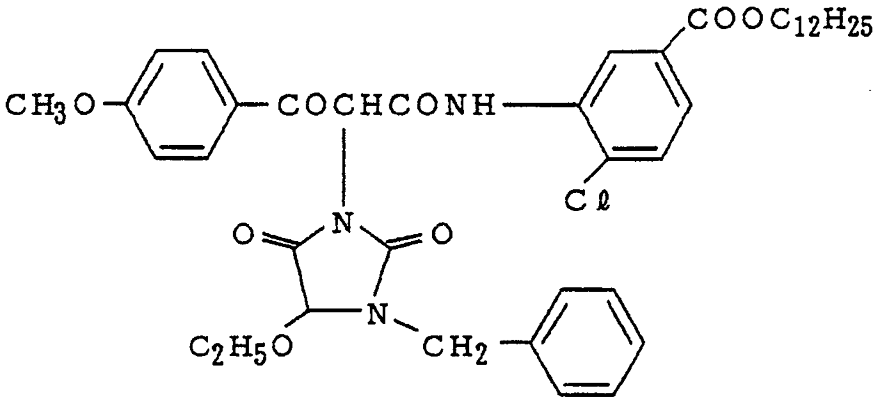
ExM-4


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

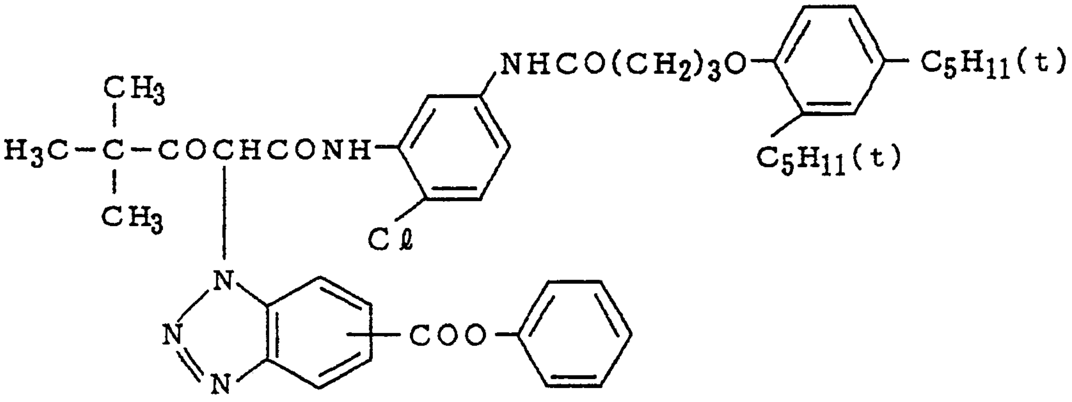
ExM-5


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

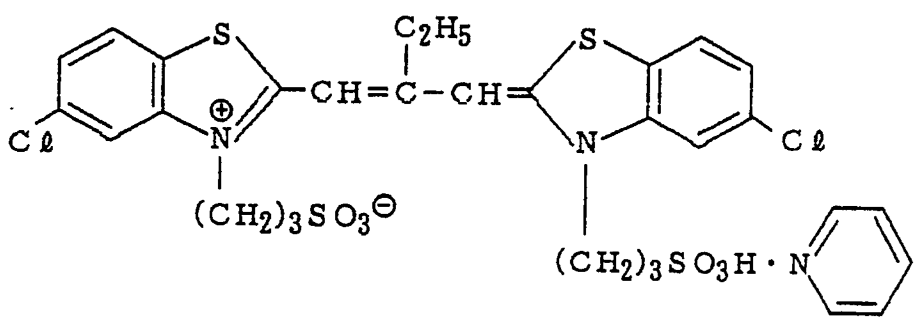
ExY-1



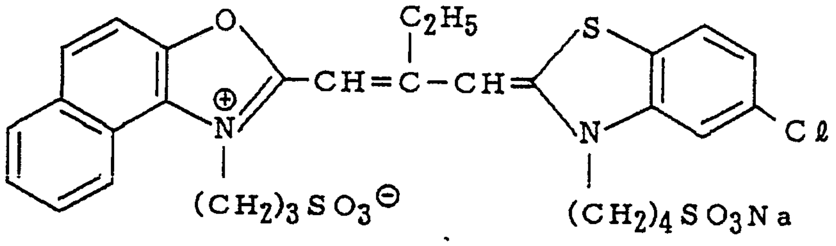
ExY-2



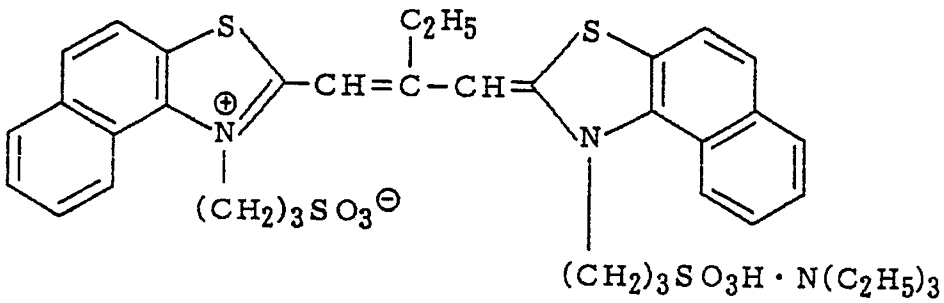
ExS－1



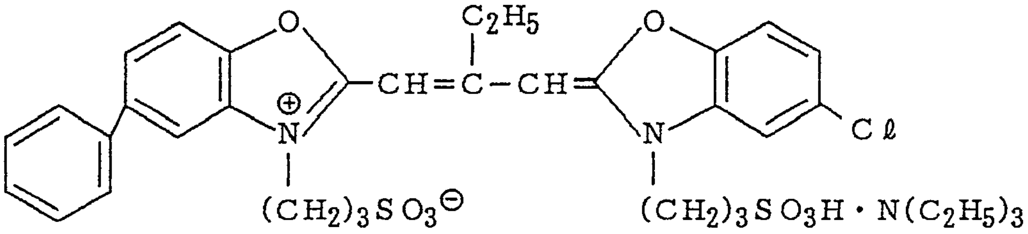
ExS－2



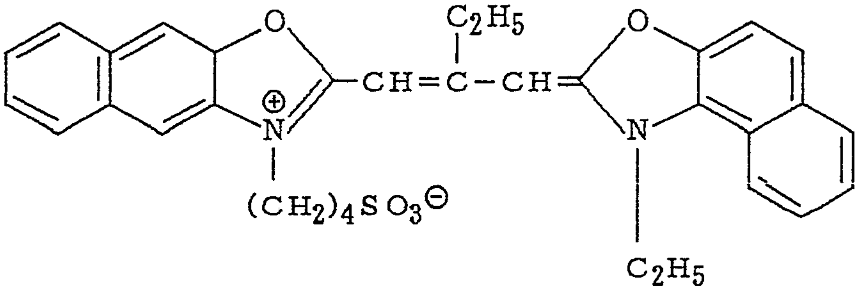
ExS－3



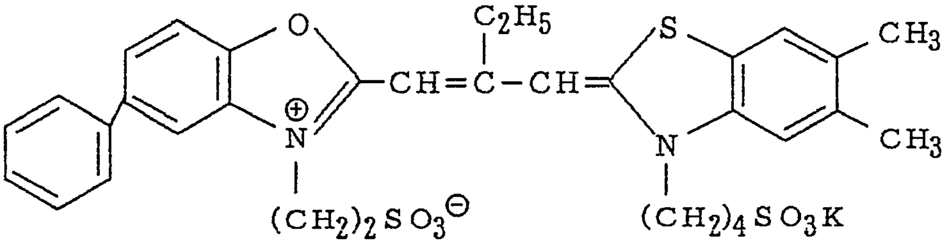
ExS－5



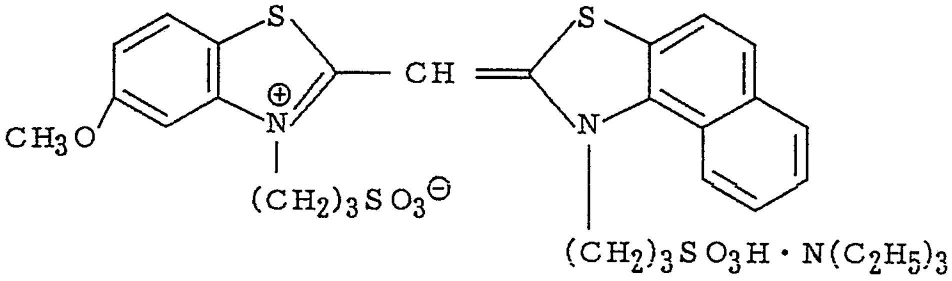
ExS－6



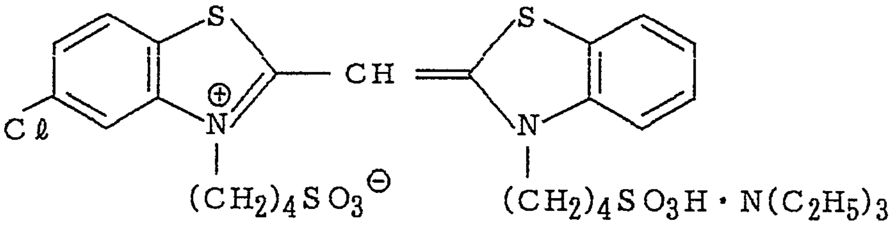
ExS－7



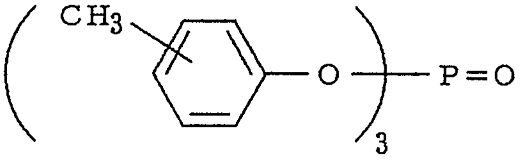
ExS−8



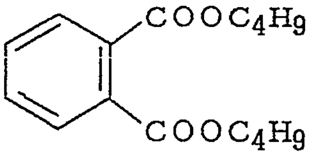
ExS−9



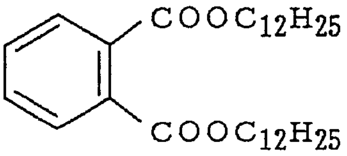
Solv−1



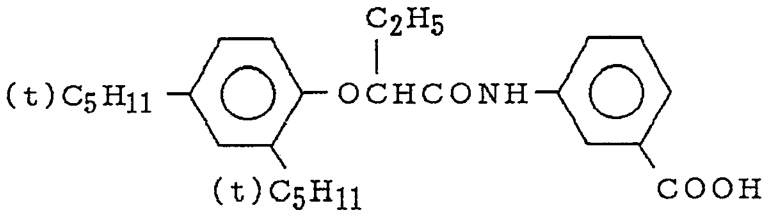
Solv−2



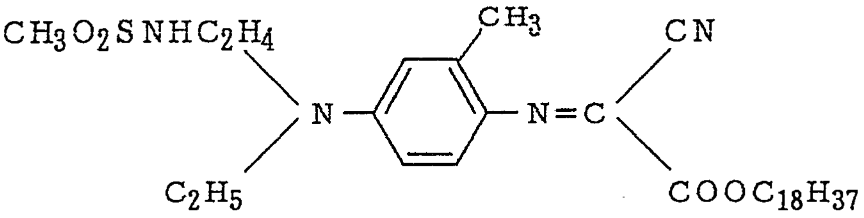
Solv−3



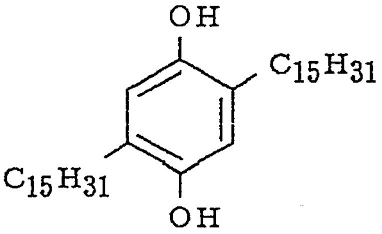
Solv−4



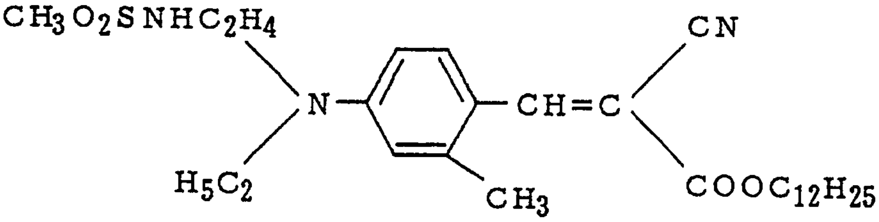
Cpd−1



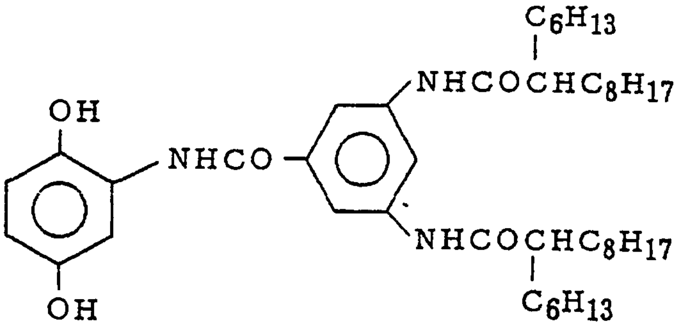
Cpd−2



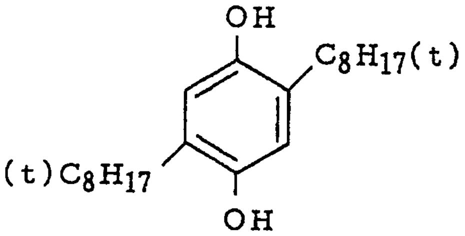
Cpd-3



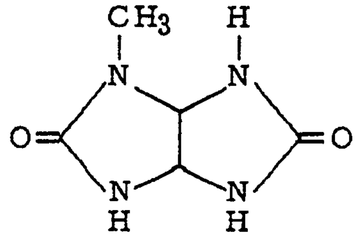
Cpd-4



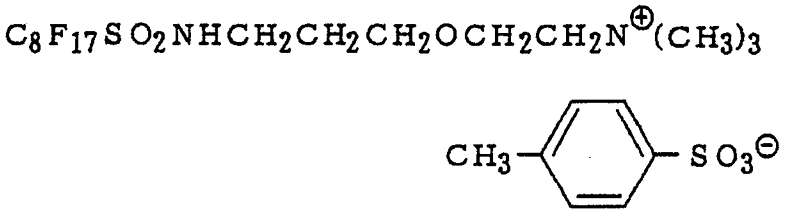
Cpd-5



Cpd-6

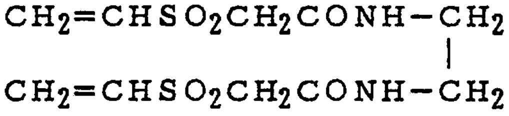


W-1



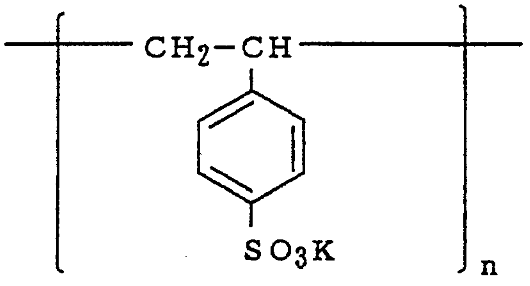
$C_8F_{17}SO_2NHCH_2CH_2CH_2OCH_2CH_2N^{\oplus}(CH_3)_3$

H-1



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

B-1



Claims

1. A silver halide photographic light-sensitive material comprising a support and at least one silver halide emulsion layer thereon, said silver halide emulsion layer containing a monodisperse silver halide emulsion manufactured in the presence of at least one type of thiosulfonic acid compounds represented by formulas [I], [II], and [III]:
[I] $R\text{-}SO_2S\text{-}M$

[II] $R\text{-}SO_2S\text{-}R^1$

[III] $RSO_2S\text{-}Lm\text{-}SSO_2\text{-}R^2$

characterized in that R, R^1, and R^2 may be the same or different and represent an aliphatic group, an aromatic group, or a heterocyclic group, M represents a cation, L represents a divalent linking group, m represents 0 or 1, compounds represented by formulas [I] to [III] can be polymers containing, as a repeating unit, divalent groups derived from compounds represented by formulas [I] to [III], and if possible, R, R^1, R^2, and L can be bonded with each other to form a ring.

2. A silver halide photographic light-sensitive material according to claim 1, characterized in that said monodisperse silver halide emulsion is reduction-sensitized during precipitation of silver halide grains in the presence of at least one type of thiosulfonic acid compounds represented by formulas [I], [II], and [III].

3. A silver halide photographic light-sensitive material according to claim 2, characterized in that said thiosulfonic acid compound present during precipitation of the silver halide grains is a compound represented by formula [I].

4. A silver halide photographic light-sensitive material comprising a support and at least one silver halide emulsion layer thereon, said silver halide emulsion layer containing a monodisperse silver halide emulsion reduction-sensitized by ascorbic acid or at least one type of derivatives of the ascorbic acid in a process of manufacturing a silver halide emulsion.

5. A silver halide photographic light-sensitive material according to claim 4, characterized in that said silver halide emulsion is a monodisperse silver halide emulsion reduction-sensitized in the presence of at least one type of thiosulfonic acid compounds represented by formulas [I], [II], and [III].

6. A silver halide photographic light-sensitive material according to claim 5, characterized in that said thiosulfonic acid compound is a compound represented by formula [I].

7. A silver halide photographic light-sensitive material according to claim 2, characterized in that an amount of a reduction sensitizer added upon reduction sensitization is 10^{-7} to 10^{-3} mol per mol of a silver halide.

8. A silver halide photographic light-sensitive material according to claim 1, characterized in that an addition amount of said thiosulfonic acid compound is 10^{-6} to 10^{-2} mol per mol of a silver halide.

9. A silver halide photographic light-sensitive material according to claim 1, characterized in that an addition amount of said thiosulfonic acid compound is 10^{-5} to 10^{-3} mol per mol of a silver halide.

10. A silver halide photographic light-sensitive material according to claim 4, characterized in that an addition amount of said ascorbic acid or derivative thereof is 5×10^{-4} to 1×10^{-2} mol per mol of a silver halide.

11. A silver halide photographic light-sensitive material according to claim 4, characterized in that an addition amount of said ascorbic acid or derivative thereof is 1×10^{-3} to 1×10^{-2} mol per mol of a silver halide.

12. A silver halide photographic light-sensitive material according to claim 1, characterized in that said monodisperse silver halide emulsion comprises octahedral grains having a (111) face and tetradecahedral grains having both of a (100) face and a (111) face in a single grain.

13. A silver halide photographic light-sensitive material according to claim 4, characterized in that said monodisperse silver halide emulsion comprises octahedral grains having a (111) face and tetradecahedral grains having both of a (100) face and a (111) face in a single grain.

14. A silver halide photographic light-sensitive material according to claim 6, characterized in that ascorbic acid is used as a reduction sensitizer.

15. A silver halide photographic light-sensitive material according to claim 10, characterized in that ascorbic acid is used as a reduction sensitizer.

16. A silver halide photographic light-sensitive material according to claim 1, characterized in that in said monodisperse silver halide emulsion, a weight of silver halide grains falling within the grain size region ranging from -20% to +20% of a maximum grain size $\bar{r}$ account for not less than 60% of a total silver halide grain weight.

17. A silver halide photographic light-sensitive material according to claim 1, characterized in that in said monodisperse silver halide emulsion, a weight of silver halide grains falling within the grain size region ranging from -20% to +20% of a maximum grain size $\bar{r}$ account for not less than 70% of a total silver halide grain weight.

18. A silver halide photographic light-sensitive material according to claim 1, characterized in that in said monodisperse silver halide emulsion, a weight of silver halide grains falling within the grain size region ranging from -20% to +20% of a maximum grain size $\bar{r}$ account for not less than 80% of a total silver halide grain weight.

19. A silver halide photographic light-sensitive material according to claim 1, characterized in that two or

more types of monodisperse silver halide emulsions having different maximum-frequency grain sizes are mixed in a single layer or coated on different layers.

20. A silver halide photographic light-sensitive material according to claim 1, characterized in that said monodisperse silver halide emulsion comprises coreshell type grains or double structure grains having different halogen compositions in an interior and a surface of a grain.

21. A silver halide photographic light-sensitive material according to claim 1, characterized in that said material is a color photographic light-sensitive material.

22. A silver halide photographic light-sensitive material according to claim 1, containing at least one coupler selected from the group consisting of a DIR coupler, a DIR coupler releasing coupler, and a DIR redox compound releasing coupler.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 12 1214

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	Zeitschrift für wissenschaftliche Photographi vol. 63, no. 7-9, 1969, Berlin,DD pages 133 - 148; S.Gahler: "Benzolthiosulfonsäure und Reduktionssensibilisierung" * the whole document *	1-22	G03C1/10 G03C1/34 G03C1/035
Y	FR-A-2169360 (AGFA-GEVAERT AG) * page 3, lines 32 - 34; claims 1-9 *	1-22	
Y	PATENT ABSTRACTS OF JAPAN vol. 9, no. 37 (P-335)(1760) 16 February 1985. & JP-A-59 178447 (KONISHIROKU PHOTO INDUSTRY COMPANY LIMITED) 09 October 1984, * the whole document *	1-22	
A	DE-A-2824082 (FUJI PHOTO FILM COMPANY LIMITED) *claims*	1-22	
A	US-A-4775617 (FUJI PHOTO FILM COMPANY LIMITED) * the whole document *	1-22	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 MARCH 1990	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family; corresponding document