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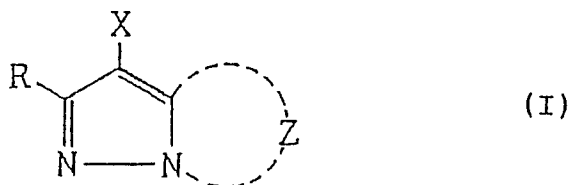
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(54) **Silver halide colour photographic material capable of improved colour reproduction and method of processing said photographic material.**

(57) A silver halide color photographic material and a method of processing said photographic material are disclosed, said photographic material having one or more silver halide emulsion layers on a support, at least one of said silver halide emulsion layers containing a compound of the following formula (I) and silver halide grains having fog centers on their surface or subsurface:



where Z represents a group of the non-metallic atoms necessary for forming a nitrogen-containing heterocyclic ring, provided that the ring formed by Z may have a substituent; X represents a hydrogen atom or a substituent capable of being eliminated upon reaction with the oxidation product of a color developing agent; and R represents a hydrogen atom or a substituent.

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SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL CAPABLE OF IMPROVED COLOR REPRODUCTION AND METHOD OF PROCESSING SAID PHOTOGRAPHIC MATERIAL

BACKGROUND OF THE INVENTION

The present invention relates to a silver halide color photographic material and a method of processing the same. More particularly, the present invention relates to a silver halide color reversal photographic material and a method of processing the same to produce an image with improved color reproduction.

Prior art silver halide color reversal photographic materials typically consist of a support on which are coated, in order from the support, a red-sensitive emulsion layer for forming a cyan dye image, a green-sensitive emulsion layer for forming a magenta dye image, and a blue-sensitive emulsion layer for forming a yellow dye image. Since it is desired that neither the green-sensitive emulsion layer nor the red-sensitive emulsion layer has sensitivity to blue light during exposure, a yellow filter is usually provided between these layers. In addition, for imparting improved performance, an anti-halation layer and an interlayer are commonly provided between the support and the red-sensitive emulsion layers and between the red-sensitive and green-sensitive emulsion layers, respectively, with a protective layer being provided as the topmost layer. It is also common practice for each of the red-, green-and blue-sensitive emulsion layers to be composed of two or three emulsion layers having different sensitivities.

As usual, processing of the silver halide color reversal photographic material having the structure described above starts with imagewise exposure followed by development with a black-and-white developer. If the photographic material contains a coupler capable of forming a color image, black-and-white development is followed by color development which is performed after or while fogging the residual silver halide either chemically or optically. In the next step, the silver that has formed in the photographic material as a result of black-and-white development and color development is bleached out to obtain a multi-color positive dye image. If no color-forming coupler is incorporated in the photographic material, the photographic layers are not fogged simultaneously and instead the individual emulsion layers are fogged independently by exposure to associated light and are subsequently processed with developers that contain couplers capable of forming dyes appropriate for the respective layers.

Couplers suitable for this purpose are compounds that are capable of entering into coupling reaction with the oxidation products of aromatic primary amino developing agents to form dyes. Typical couplers are acylacetamide compounds (as yellow couplers), 5-pyrazolone compounds (as magenta couplers), and naphtholic and phenolic compounds (as cyan couplers).

The dyes formed by these couplers have varying degrees of unwanted absorption that causes either mismatching of tone or reduced purity in color reproduction. Therefore, for the purpose of achieving improved color reproduction, it is desired to use couplers that are capable of forming dyes having a minimum amount of unwanted absorption. While studies have been conducted to develop such couplers, most active efforts have been directed to 5-pyrazolone based magenta couplers which form dyes that have a significant amount of unwanted absorption in the blue region of the spectrum.

Magenta couplers that have been developed to meet the requirement for reduction in unwanted absorption include pyrazolobenzimidazoles (U.S. Patent 3,369,897), pyrazolotriazoles (U.S. Patent 3,725,067), pyrazolotetrazoles (Research Disclosure No. 24220, June 1984), and pyrazolopyrazoles (Research Disclosure No. 24230, June 1984).

By using these magenta couplers, the unwanted absorption of blue light by magenta dyes can be appreciably reduced to provide improved color reproduction. However, these couplers are incapable of completely eliminating the unwanted absorption occurring in various dyes. Furthermore, color contamination by unwanted absorption cannot be completely prevented by simply improving the spectral absorption characteristics of dyes.

In many of the common color negative films, the color distortion that originates from the inherent spectral absorption characteristics of dyes is corrected by so-called "masking" techniques. While masking can be implemented by various methods, the most commonly employed method that is applied to modern multilayered color negative films is to use a "colored coupler" that initially takes on the color to be eliminated from an image dye of interest and which, upon coupling reaction with the oxidation product of a color developing agent, loses the initial color to form a desired image dye. If it is necessary to form a magenta color image that is free from the unwanted absorption in the blue region, a yellow-colored coupler is specifically employed for the formation of a magenta image.

However, the use of such colored couplers involves several disadvantages. First, colored couplers, as their name implies, are colored and absorb visible light so that they have a potential to reduce the sensitivity of the light-sensitive emulsion layer lying under the layer containing that coupler. Secondly, a colored coupler can only mask a certain range of unwanted absorption occurring in a certain type of image dye. For instance, a cyan-or green-colored magenta coupler reduces the red sensitivity of a layer containing a cyan coupler. On the other hand, a red-colored yellow coupler reduces the green sensitivity of a magenta layer. These colored couplers are in principle necessary for the purposes of masking the unwanted absorption occurring in a magenta dye in the red region of the spectrum, and of masking the unwanted absorption occurring in a yellow dye in the green region of the spectrum. However, with the ever increasing demand for higher sensitivity in photographic materials, any deleterious effects on sensitivity must be avoided no matter how minor they are. Therefore, it is impossible in practice to employ the aforementioned colored couplers in commercial products of high-sensitivity films.

A colored coupler presents a color even in unexposed areas and as compared to the case where no colored coupler is used, the minimum density (D_{min}) of the image taken as a whole is higher by the amount corresponding to the density of that color. For this reason, colored couplers can be effectively used in negative light-sensitive materials which allow for color correction during printing but not in positive or reversal light-sensitive materials intended for direct viewing.

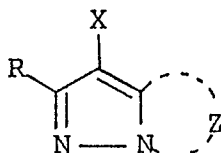
One of the methods proposed for providing improved color reproduction and which can be applied to reversal light-sensitive materials is the use of a fogged emulsion and this approach is described in, for example, Japanese Patent Publication No. 35011/1984. In this method, a surface-fogged silver halide emulsion is incorporated in a light-sensitive silver halide emulsion and the interimage effect is emphasized to achieve improved color reproduction. But one problem with this method is that the light-sensitive material has a tendency to experience fogging during prolonged storage before photographic processing is conducted, and the extent of fogging increases upon application of heat. If fogging occurs, the density of a positive image decreases and only color reproduction with low saturation can be attained.

Under the circumstances described above, it has been desired to develop a technique that is free from the problems involved in the prior art and which achieves remarkable improvements in color reproduction in silver halide color reversal photographic materials without impairing their ability to withstand storage before photographic processing.

SUMMARY OF THE INVENTION

An object, therefore, of the present invention is to provide a silver halide color reversal photographic material that achieves good color reproduction while exhibiting high stability during storage prior to photographic processing.

This object of the present invention can be attained by a silver halide color photographic material that has one or more silver halide emulsion layers on a support, at least one of said silver halide emulsion layers containing a compound of the general formula (I) noted below and silver halide grains having fog centers on their surface or subsurface:



(I)

where Z represents a group of the non-metallic atoms necessary for forming a nitrogen-containing heterocyclic ring, provided that the ring formed by Z may have a substituent; X represents a hydrogen atom or a substituent capable of being eliminated upon reaction with the oxidation product of a color developing agent; and R is a hydrogen atom or a substituent.

DETAILED DESCRIPTION OF THE INVENTION

In the magenta coupler of formula (I), Z represents a group of the non-metallic atoms necessary for forming a nitrogen-containing heterocyclic ring, provided that the ring formed by Z may have a substituent; X represents a hydrogen atom or a substituent capable of being eliminated upon reaction with the oxidation product of a color developing agent; and R is a hydrogen atom or a substituent. Example of the substituent represented by R include a halogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an alkynyl group, an aryl group, a heterocyclic group, an acyl group, a sulfonyl group, a sulfinyl group, a phosphonyl group, a carbamoyl group, a sulfamoyl group, a cyano group, a spiro-compound residue, a bridged hydrocarbon compound residue, an alkoxy group, an aryloxy group, a heterocycloxy group, a siloxy group, an acyloxy group, a carbamoyloxy group, an amino group, an acylamino group, a sulfonamide group, an imido group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkylthio group, an arylthio group and a heterocyclicthio group.

Exemplary halogen atoms include, for example, chlorine and bromine atoms, the chlorine atom being particularly preferable.

The alkyl group represented by R is preferably one having 1 to 32 carbon atoms; the alkenyl group and the alkynyl group are preferably those having 2 to 32 carbon atoms; and the cycloalkyl group and the cycloalkenyl group are preferably those having 3 to 12, particularly 5 to 7, carbon atoms, the alkyl, alkenyl and alkynyl groups each including those having a straight or branched chain.

These alkyl, alkenyl, alkynyl, cycloalkyl and cycloalkenyl groups each may have one or more substituents. Such substituents include, in addition to an aryl group, a cyano group, a halogen atom, a heterocyclic group, a cycloalkyl group, a cycloalkenyl group, a spiro-compound residue and a bridged hydrocarbon compound residue, for example, those substituted through the carbonyl group, such as acyl, carboxy, carbamoyl, alkoxycarbonyl and aryloxycarbonyl groups, and those substituted through the hetero atom, for example, those substituted through the oxygen atom, such as hydroxy, alkoxy, aryloxy, heterocycloxy, siloxy, acyloxy and carbamoyloxy groups, those substituted through the nitrogen atom, such as nitro, amino (including dialkylamino and the like), sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, acylamino, sulfonamido, imido and ureido groups, those substituted through the sulfur atom, such as alkylthio, arylthio, heterocyclicthio, sulfonyl, sulfinyl and sulfamoyl groups, and those substituted through the phosphorus atom, such as a phosphonyl group and the like.

Examples of the alkyl group represented by R include, for example, methyl, ethyl, isopropyl, t-butyl, pentadecyl, heptadecyl, 1-hexylnonyl, 1,1'-dipentylnonyl, 2-chloro-t-butyl, trifluoromethyl, 1-ethoxytridecyl, 1-methoxyisopropyl, methanesulfonyl, 2,4-di-t-amylphenoxy, anilino, 1-phenylisopropyl, 3-m-butanedisulfonaminophenoxypropyl, 3,4'-[α -(4''-(p-hydroxybenzenesulfonyl)phenoxy)dodecanoylamino]phenylpropyl, 3-[4'-[α -(2'',4''-di-t-amylphenoxy)butaneamido]phenyl]-propyl, 4-[α -(0-chlorophenoxy)-tetradecanamidophenoxy]propyl, allyl, cyclopentyl and cyclohexyl groups.

The aryl group represented by R is preferably a phenyl group, and may have a substituent such as an alkyl, alkoxy or acylamino group.

Examples of the aryl group include phenyl, 4-t-butyl phenyl, 2,4-di-t-amylphenyl, 4-tetradecaneamidophenyl, hexadecyl-oxyphenyl and 4'-[α -(4''-t-butylphenoxy)tetradecaneamido]phenyl groups.

The heterocyclic group represented by R is preferably a 5-to 7-membered heterocyclic ring, and may be substituted or may be condensed. Examples of the heterocyclic group include 2-furyl, 2-thietnyl, 2-pyrimidinyl and 2-benzothiazonyl groups.

Example of the acyl group represented by R include alkylcarbonyl groups such as acetyl, phenylacetyl, dodecanoyl and α -2,4-di-t-amylphenoxybutanoyl groups, and arylcarbonyl groups such as benzoyl, 3-pentadecycloxybenzoyl and p-chlorobenzoyl groups.

Examples of the sulfonyl group represented by R include alkylsulfonyl groups such as methylsulfonyl and dodecylsulfonyl groups, and arylsulfonyl groups such as benzenesulfonyl and p-toluenesulfonyl groups.

Examples of the sulfinyl group represented by R include alkylsulfinyl groups such as ethylsulfinyl, octylsulfinyl and 3-phenoxybutylsulfinyl groups, and arylsulfinyl groups such as phenylsulfinyl and m-pentadecylphenylsulfinyl groups.

Examples of the phosphonyl group represented by R include an alkylphosphonyl group such as butyloxyoctyl phosphonyl group, an alkoxyphosphonyl group such as octyloxyphosphonyl group, an aryloxyphosphonyl group such as phenoxyphosphonyl group and an arylphosphonyl group such as phenylphosphonyl group.

Examples of the carbamoyl group represented by R include those substituted with an alkyl or aryl (preferably phenyl) group, such as, N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-pentadecyloctylethyl)-carbamoyl, N-ethyl-N-dodecylcarbamoyl and N-{3-(2,4-di-t-amylphenoxy)propyl}carbamoyl group.

Examples of the sulfamoyl group represented by R include those substituted with an alkyl or aryl (preferably phenyl) group, such as N-propylsulfamoyl, N,N-diethylsulfamoyl, N-(2-pentadecyloxyethyl)-sulfamoyl, N-ethyl-N-dodecylsulfamoyl and N-phenylsulfamoyl groups.

Examples of the spiro-compound residue represented by R include spiro[3,3]heptan-1-yl and the like.

Examples of the bridged hydrocarbon compound residue represented by R include bicyclo[2,2,1]-heptan-1-yl, tricyclo[3,3,1,1^{3,7}]decan-1-yl and 7,7-dimethyl-bicyclo-[2,2,1]heptan-1-yl.

Examples of the alkoxy group represented by R include those substituted further with such a substituent(s) as is shown above with the alkyl group, such as methoxy, propoxy, 2-ethoxyethoxy, pentadecyloxy, 2-dodecyloxyethoxy and phenethyloxyethoxy.

The aryloxy group represented by R is preferably a phenyloxy group, and exemplified by those the aryl nucleus of which is further substituted with such a substituent(s) or an atom(s) as is shown above with the aryl group, such as phenoxy, p-t-butylphenoxy and m-pentadecylphenoxy groups.

The heterocycloxy group represented by R is preferably one having a 5-to 7-membered heterocyclic ring, and exemplified by those the heterocyclic ring of which has a substituent, such as 3,4,5,6-tetrahydropyran-2-oxy and 1-phenyltetrazol-5-oxy groups.

The siloxy group represented by R may be substituted with an alkyl group, as illustrated by trimethylsiloxy, triethylsiloxy, dimethylbutylsiloxy group, etc.

Examples of the acyloxy group represented by R include alkylcarbonyloxy and arylcarbonyloxy groups, and further include those having a substituent(s) such as acetyloxy, α -chloroacetyloxy and benzoyloxy groups.

Examples of the carbamoyloxy group represented by R include those substituted with an alkyl or aryl group, as illustrated by N-ethylcarbamoyloxy, N,N-diethylcarbamoyloxy and N-phenylcarbamoyloxy groups.

Examples of the amino group represented by R include those substituted with an alkyl or aryl (preferably phenyl) group, as illustrated by ethylamino, anilino, m-chloroanilino, 3-pentadecyloxy-carbonylanilino and 2-chloro-5-hexadecanamidoanilino groups.

Examples of the acylamino group represented by R include alkylcarbonylamino and arylcarbonylamino (preferably phenylcarbonylamino) groups, and further include those having a substituent(s), as illustrated by acetamido, α -ethylpropanamido, N-phenylacetamido, dodecanamido, 2,4-di-t-amylphenoxyacetamido and α -3-t-butyl-4-hydroxyphenoxybutanamido groups.

Examples of the sulfonamido group represented by R include alkylsulfonylamino and arylsulfonylamino groups, and further include those having a substituent(s), as illustrated by methylsulfonylamino, pentadecylsulfonylamino, benzensulfonamido, p-toluenesulfonamido and 2-methoxy-5-t-amylbenzenesulfonamido groups.

Examples of the imido group represented by R include those which are open-chained and close-chained, and further include those having a substituent(s), as illustrated by succinimido, 3-heptadecylsuccinimido, phthalimido and glutarimido groups.

Examples of the ureido group represented by R include those substituted with an alkyl or aryl (preferably phenyl) group, as illustrated by N-ethylureido, N-methyl-N-decylureido, N-phenylureido and N-p-tolylureido groups.

Examples of the sulfamoylamino group represented by R include those substituted with an alkyl or aryl (preferably phenyl) group, as illustrated by N,N-dibutylsulfamoylamino, N-methylsulfamoylamino and N-phenylsulfamoylamino groups.

Examples of the alkoxy-carbonylamino group represented by R include those having a substituent(s), as illustrated by methoxycarbonylamino, methoxyethoxycarbonylamino and octadecyloxy-carbonylamino groups.

Examples of the aryloxy-carbonylamino group represented by R include those having a substituent(s), as illustrated by phenoxy-carbonylamino and 4-methylphenoxy-carbonylamino groups.

Examples of the alkoxy-carbonyl group represented by R include those having a substituent(s), as illustrated by methoxycarbonyl, butyloxy-carbonyl, dodecyloxy-carbonyl, octadecyloxy-carbonyl, ethoxymethoxycarbonyloxy and benzyloxy-carbonyl groups.

Examples of the aryloxy-carbonyl group represented by R include those having a substituent(s), as illustrated by phenoxy-carbonyl, p-chlorophenoxy-carbonyl and m-pentadecyloxyphenoxy-carbonyl groups.

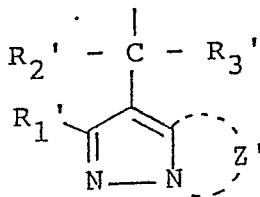
Examples of the alkylthio group represented by R include those having a substituent(s), as illustrated by ethylthio, dodecylthio, octadodecylthio, phenethylthio and 3-phenoxypropylthio groups.

The arylthio group represented by R is preferably a phenylthio group, and illustrative arylthio groups include those having a substituent(s), such as phenylthio, p-methoxyphenylthio, 2-t-octylphenylthio, 3-octadecylphenylthio, 2-carboxyphenylthio and p-acetaminophenylthio groups.

The heterocyclicthio group represented by R is preferably a 5-to 7-membered heterocyclicthio group, and may have a condensed ring or a substituent(s). Examples of such heterocyclicthio group include 2-pyridylthio, 2-benzothiazolylthio and 2,4-diphenoxy-1,3,5-triazole-6-thio groups.

Examples of the substituent represented by X that is capable of leaving upon reaction with the oxidized product of a color developing agent include those substituted through the carbon, oxygen, sulfur or nitrogen atom other than the halogen atom (e.g., chlorine, bromine or fluorine atom).

The groups which are substituted through the carbon atom include, in addition to the carboxyl group, a group represented by the following formula:



(wherein R₁' is the same in meaning as said R; Z' is the same in meaning as said Z; and R₂' and R₃' each represents a hydrogen atom, an aryl, alkyl or heterocyclic group), a hydroxymethyl group and a triphenylmethyl group.

The groups which are substituted through the oxygen atom include, for example, alkoxy, aryloxy, heterocycloxy, acyloxy, sulfonyloxy, alkoxycarbonyloxy, aryloxy carbonyl, alkyloxalyloxy and alkoxyoxalyloxy groups.

Illustrative alkoxy groups include those having a substituent(s), such as ethoxy, 2-phenoxyethoxy, 2-cyanoethoxy, phenethylloxy, and p-chlorobenzoyloxy groups.

The aryloxy group is preferably a phenoxy group, and may have a substituent(s). Examples of such aryloxy group include phenoxy, 3-methylphenoxy, 3-dodecylphenoxy, 4-methanesulfonamidophenoxy, 4-[α-(3'-pentadecylphenoxy)-butanamido]phenoxy, hexadecylcarbamoylmethoxy, 4-cyanophenoxy, 4-methanesulfonylphenoxy, 1-naphthylloxy and p-methoxyphenoxy groups.

The heterocycloxy group is preferably a 5-to 7-membered heterocycloxy group, and may be a condensed ring or may have a substituent(s). Examples of such heterocycloxy group include 1-phenyltetrazolylloxy and 2-benzothiazolylloxy groups.

Examples of the acyloxy group include alkylcarbonyloxy groups such as acetoxy and butanoyloxy groups, an alkenylcarbonyloxy group such as a cinnamoyloxy group, and an arylcarbonyloxy group such as a benzoyloxy group.

Examples of the sulfonyloxy group include butanesulfonyloxy and methanesulfonyloxy groups.

Examples of the alkoxycarbonyloxy group include ethoxycarbonyloxy and benzyloxycarbonyloxy groups.

Examples of the aryloxycarbonyloxy group includes a phenoxycarbonyloxy group and the like.

An example of the alkyloxalyloxy group is a methyloxalyloxy group.

Examples of the alkoxyoxalyloxy group include an ethoxyoxalyloxy group and the like.

Examples of the group which is substituted through the sulfur atom include alkylthio, arylthio, heterocyclicthio and alkyloxythiocarbonylthio groups.

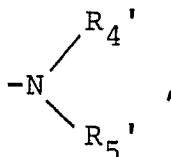
Examples of the alkylthio group include butylthio, 2-cyanoethylthio, phenethylthio and benzylthio groups.

Examples of the arylthio group include phenylthio, 4-methanesulfonamidophenylthio, 4-dodecylphenethylthio, 4-nonafluoropentanamidophenethylthio, 4-carboxyphenylthio and 2-ethoxy-5-t-butylphenylthio groups.

Examples of the heterocyclicthio group include 1-phenyl-1,2,3,4-tetrazolyl-5-thio and 2-benzothiazolylthio groups.

Examples of the alkyloxythiocarbonylthio group include a dodecyloxythiocarbonylthio group and the like.

An example of the group which is substituted through the nitrogen atom is one represented by the formula



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wherein R_4' and R_5' each represents a hydrogen atom, an alkyl, aryl, heterocyclic, sulfamoyl, carbamoyl, acyl, sulfonyl, aryloxy carbonyl or alkoxy carbonyl group, and R_4' and R_5' may cooperate to form a
10 heterocyclic ring, provided that R_4' and R_5' are not hydrogen atoms at the same time.

The alkyl group may be straight-chained or branched and is preferably one having 1 to 22 carbon atoms. Also, the alkyl group may have a substituent(s). Examples of such substituent include aryl, alkoxy, aryloxy, alkylthio, arylthio, alkylamino, arylamino, acylamino, sulfonamido, imino, acyl, alkylsulfonyl, arylsulfonyl, carbamoyl, sulfamoyl, alkoxy carbonyl, aryloxy carbonyl, alkoxy carbonylamino, aryloxy carbonylamino,
15 hydroxy, carboxyl and cyano groups and a halogen atom. Examples of such alkyl group include ethyl, octyl, 2-ethylhexyl and 2-chloroethyl groups.

The aryl group represented by R_4' or R_5' is preferably one having 6 to 32 carbon atoms, particularly a phenyl or naphthyl group, and may include those having a substituent(s). Such substituent includes a substituent for the alkyl group represented by R_4' or R_5' and an alkyl group. Examples of the aryl group
20 include phenyl, 1-naphthyl and 4-methylsulfonylphenyl groups.

The heterocyclic group represented by R_4' or R_5' is preferably a 5-or 6-membered ring, and may be a condensed ring or may have a substituent(s). Examples of such heterocyclic group include 2-furyl, 2-quinolyl, 2-pyrimidyl, 2-benzothiazolyl and 2-pyridyl groups.

Examples of the sulfamoyl group represented by R_4' or R_5' include N-alkylsulfamoyl, N,N-dialkylsulfamoyl, N-arylsulfamoyl and N,N-diarylsulfamoyl groups, and these alkyl and aryl groups may have such a substituent(s) as is mentioned with respect to the alkyl and aryl groups. Examples of such sulfamoyl group
25 include N,N-diethylsulfamoyl, N-methylsulfamoyl, N-dodecylsulfamoyl and N-p-tolylsulfamoyl groups.

Examples of the carbamoyl group represented by R_4' or R_5' include N-alkylcarbamoyl, N,N-dialkylcarbamoyl, N-arylcarbamoyl and N,N-diarylcarbamoyl groups, and these alkyl and aryl groups may have such a substituent(s) as is mentioned with respect to the alkyl and aryl groups. Specific examples of such carbamoyl group include N,N-diethylcarbamoyl, N-methylcarbamoyl, N-dodecylcarbamoyl, N-p-cyanophenylcarbamoyl and N-p-tolylcarbamoyl groups.
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Examples of the acyl group represented by R_4' or R_5' include alkylcarbonyl, arylcarbonyl and heterocyclic carbonyl groups, and the alkyl, aryl and heterocyclic groups may have a substituent(s). Specific examples of such acyl group include hexafluorobutanoyl, 2,3,4,5,6-pentafluorobenzoyl, acetyl, benzoyl, naphthoyl and 2-furylcarbonyl groups.
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Examples of the sulfonyl group represented by R_4' or R_5' include alkylsulfonyl, arylsulfonyl and heterocyclicsulfonyl groups, and may have a substituent(s). Specific examples of such sulfonyl group include ethanesulfonyl, benzenesulfonyl, octanesulfonyl, naphthalenesulfonyl and p-chlorobenzenesulfonyl
40 groups.

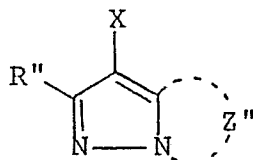
The aryloxy carbonyl group represented by R_4' or R_5' may have such a substituent(s) as is mentioned with respect to the aryl group, and specific examples include a phenoxy carbonyl group and the like.

The alkoxy carbonyl group represented by R_4' or R_5' may have such a substituent(s) as is mentioned with respect to alkyl group, and specific examples include methoxy carbonyl, dodecyloxy carbonyl and benzyloxy carbonyl groups.
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The heterocyclic ring which is formed through cooperation of R_4' and R_5' is preferably a 5-or 6-membered ring, may be saturated or unsaturated, may or may not be an aromatic ring, or may be a condensed ring. Examples of such heterocyclic ring include N-phthalimido, N-succinimide, 4-N-urazolyl, 1-N-hydantoinyl, 3-N-2,4-dioxooxazolidinyl, 2-N-1,1-dioxo-3-(2H)-oxo-1,2-benzthiazolyl, 1-pyrrolyl, 1-pyrrolidinyl, 1-pyrazolyl, 1-pyrazolidinyl, 1-piperidinyl, 1-pyrrolinyl, 1-imidazolyl, 1-imidazolinyl, 1-indolyl, 1-isindolyl, 2-isindolyl, 1-benzotriazolyl, 1-benzoimidazolyl, 1-(1,2,4-triazolyl), 1-(1,2,3-triazolyl), 1-(1,2,3,4-tetrazolyl), N-morpholinyl, 1,2,3,4-tetrahydroquinolyl, 2-oxo-1-pyrrolidinyl, 2-1H-pyridone, phthalazinone and 2-oxo-1-piperidinyl groups. These heterocyclic groups may be substituted by alkyl, aryl, alkoxy, aryloxy, acyl, sulfonyl, alkylamino, arylamino, acylamino, sulfonamino, carbamoyl, sulfamoyl, alkylthio, arylthio, ureido, alkoxy carbonyl, aryloxy carbonyl, imido, nitro, cyano, carboxyl groups as well as
55 by a halogen atom and the like.

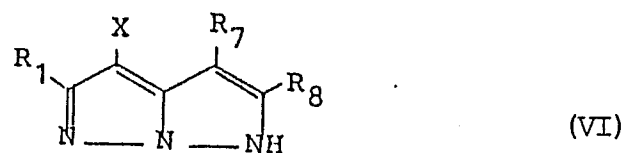
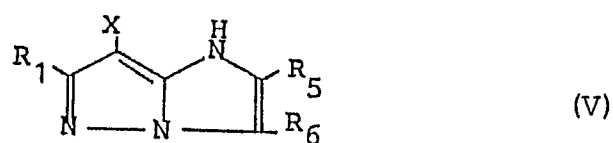
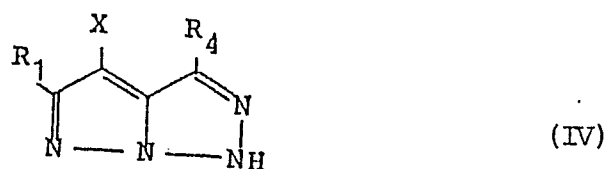
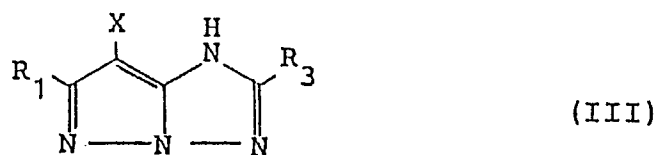
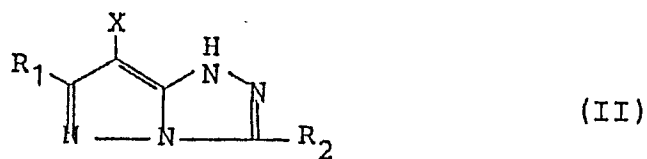
Examples of the nitrogen-containing heterocyclic ring which is formed by Z or Z' include pyrazole, imidazole, triazole and tetrazole rings, and may have such a substituent(s) as is mentioned with respect to R.

When the substituent(s) (for example, either of R and R₁ to R₈) on the heterocyclic ring in formula (I) and in formulas (II) to (VIII) to be mentioned later has the following formula:



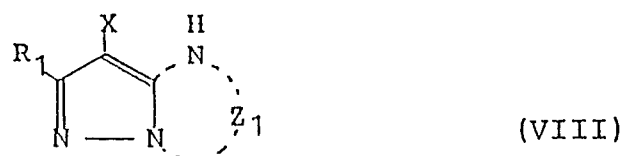
(wherein R'', X and Z'' are the same in meaning as R, X and Z in formula (I), respectively), the coupler formed is the so-called bis-type coupler, which is included in the present invention. The ring which is formed by Z, Z', Z'' as well by Z₁ to be stated later may be condensed with another ring (for example 5-to 7-membered cycloalkene). For example, in formula (V), R₅ and R₆, and in formula (VI), R₇ and R₈, may cooperate to form a ring (for example, 5-to 7-membered cycloalkene, or benzene), respectively.

Couplers represented by formula (I) are more specifically represented by the following formulas (II) to (VII):



wherein R₁ to R₈ and X are the same in meaning as R and X mentioned above.

50 The coupler of formula (I) is preferably one represented by the following formula (VIII):



wherein R₁, X and Z₁ are the same in meaning as R, X and Z in formula (I).

Of the magenta couplers represented by formulas (II) to (VII), those represented by formula (II) are particularly preferable.

With respect to the substituent(s) on the heterocyclic ring in formulas (I) to (VIII), R in formula (I) and R₁ in formulas (II) to (VIII) preferably satisfy the following requirement 1, more preferably satisfy the following requirements 1 and 2, and most preferably satisfy all of the following requirements 1, 2 and 3:

Requirement 1: The root atom bonded directly to the heterocyclic ring is a carbon atom.

Requirement 2: Said carbon atom has only one hydrogen atom or has no hydrogen atom at all, bonded thereto.

Requirement 3: The bonds between said carbon atom and adjacent atoms are all single bonds.

The most preferable substituents R and R₁ on the heterocyclic ring are those represented by the following formula (IX):



wherein R₉, R₁₀ and R₁₁ each represents a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an alkynyl group, an aryl group, a heterocyclic group, an acyl group, a sulfonyl group, a sulfinyl group, a phosphonyl group, carbamoyl group, a sulfamoyl group, a cyano group, a spiro-compound residue, a bridged hydrocarbon compound residue, an alkoxy group, an aryloxy group, a heterocycloxy group, a siloxy group, an acyloxy group, a carbamoyloxy group, an amino group, an acylamino group, a sulfonamido group, an imido group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkylthio group, an arylthio group or a heterocyclicthio group, provided that at least two of R₉, R₁₀ and R₁₁ are not hydrogen atoms.

Two of R₉, R₁₀ and R₁₁, for example, R₉ and R₁₀, may cooperate to form a saturated or unsaturated ring (e.g., cycloalkane, cycloalkene or heterocyclic ring), and further R₁₁ may cooperate with said ring to form a bridged hydrocarbon compound residue.

The group represented by R₉ to R₁₁ may have a substituent(s). Examples of said group and said substituent(s) are the same as the examples of the group represented by R in formula (I) and the substituent(s) mentioned with respect thereto.

Examples of the ring formed by the cooperation of, for example, R₉ and R₁₀, as well as of the bridged hydrocarbon compound residue which is formed by R₉ to R₁₁ and the substituent(s) which said residue may have, are the same as the examples of the cycloalkyl, cycloalkenyl, and heterocyclic groups represented by R in formula (I), and the substituent(s) mentioned with respect thereto.

The following are two preferable cases of the coupler represented by formula (IX):

(i) Two of R₉ to R₁₁ are alkyl groups.

(ii) One of R₉ to R₁₁, for example, R₁₁ is a hydrogen atom, and the other two, R₉ and R₁₀, cooperate with the root carbon atom to form a cycloalkyl group.

Further, the preferable substituent(s) in (i) above is such that two of R₉ to R₁₁ are alkyl group, and the other one is a hydrogen atom or an alkyl group.

The alkyl and cycloalkyl groups each may have a substituent(s). Examples of such alkyl and cycloalkyl groups as well as of their substituents are the same as the examples of the alkyl and cycloalkyl groups represented by R in formula (I) and the substituents mentioned with respect thereto.

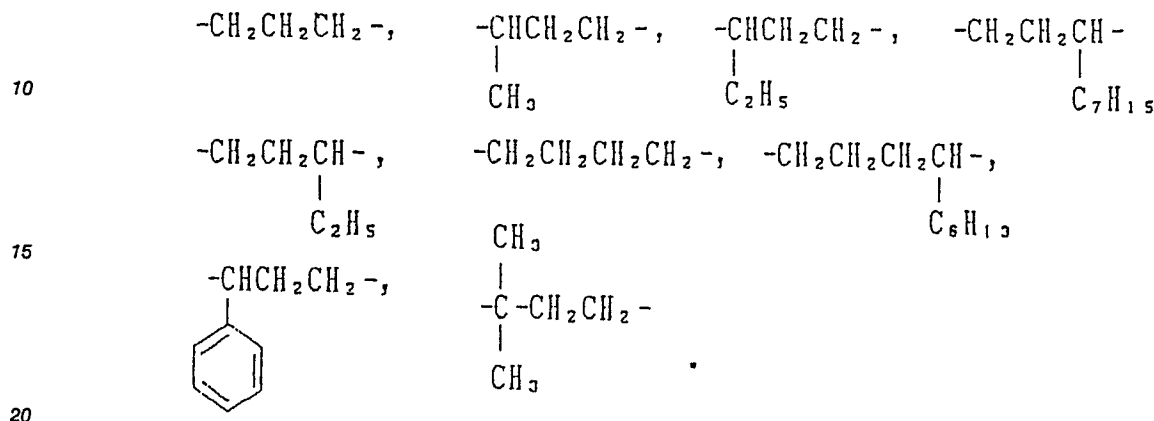
The substituent that may be possessed by the ring formed by Z in formula (I) or Z₁ in formula (VIII), and R₂ to R₈ in formulas (II) to (VI) are preferably represented by the following formula (X):



where R¹ is an alkylene, and R² is an alkyl, cycloalkyl or aryl.

The alkylene represented by R¹ preferably has at least two, more preferably 3 to 6, carbon atoms in the straight-chained portion. This alkylene which may be either straight-chained or branched may also have a substituent. Examples of the substituent are the same as those mentioned as the substituents that can be had by an alkyl group when R in formula (I) is an alkyl group. A preferable substituent is phenyl.

5 Preferable examples of the alkylene represented by R¹ are shown below:



The alkyl group represented by R² may be straight-chained or branched and illustrative examples include methyl, ethyl, propyl, iso-propyl, butyl, 2-ethylhexyl, octyl, dodecyl, tetradecyl, hexadecyl, octadecyl, and 2-hexyldexyl.

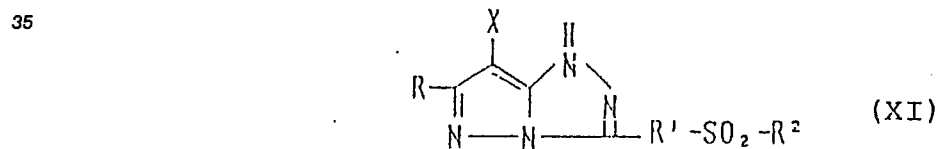
25 The cycloalkyl group represented by R² is preferably 5-or 6-membered, as illustrated by cyclohexyl.

Each of the alkyl and cycloalkyl represented by R² may have a substituent that is selected from among those listed for R¹.

Specific examples of the aryl represented by R² include phenyl and naphthyl. The aryl group may have a substituent such as a straight-chained or branched alkyl or any of the substituents already listed for R¹.

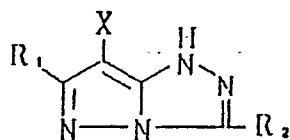
30 If R¹ and R² have two or more substituents, they may be the same or different.

Particularly preferable examples of the compound represented by formula (I) are those represented by the following formula (XI):



where R and X are the same in meaning as R and X, respectively, in formula (I), and R¹ and R² have the same meanings, as R¹ and R², respectively, in formula (X).

More specific examples of the compounds that can be used as couplers in the present invention are shown below.



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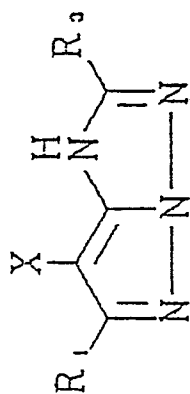
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Compound	X	R ₁	R ₂	Compound	X	R ₁	R ₂	Compound	X	R ₁	R ₂
1	2	11	52	39	189	15	89	77	3	15	181
2	2	11	71	40	2	15	22	78	2	15	298
3	3	11	37	41	2	15	108	79	2	15	298
4	2	11	80	42	2	15	102	80	211	15	52
5	2	11	82	43	2	15	194	81	218	15	52
6	184	11	48	44	2	15	128	82	11	15	52
7	2	11	108	45	2	15	136	83	2	18	52
8	2	11	124	46	2	15	134	84	2	21	52
9	2	11	121	47	2	15	132	85	2	21	44
10	2	11	115	48	2	15	135	86	2	21	116
11	184	11	82	49	2	15	127	87	2	24	110
12	2	11	136	50	2	15	133	88	2	24	55
13	2	11	142	51	2	15	138	89	2	24	32
14	H	11	88	52	2	15	131	90	2	153	71
15	2	11	102	53	2	15	130	91	2	153	75
16	2	13	52	54	2	15	139	92	222	153	52
17	217	14	52	55	2	15	137	93	2	151	89
18	2	11	79	56	2	15	129	94	2	153	141
19	2	22	80	57	2	15	140	95	284	153	106
20	2	22	20	58	2	15	142	96	2	153	125
21	234	11	166	59	2	15	121	97	2	152	89
22	2	15	71	60	2	15	120	98	2	151	121
23	2	15	52	61	2	15	118	99	2	16	71
24	2	15	51	62	2	15	115	100	2	16	52
25	2	15	38	63	2	15	105	101	2	16	56
26	2	15	36	64	2	15	126	102	2	16	54
27	2	15	59	65	184	15	113	103	2	16	85
28	2	15	82	66	2	15	123	104	2	16	69
29	2	15	47	67	221	15	107	105	2	16	66
30	184	15	31	68	2	15	112	106	3	16	43
31	3	15	88	69	2	15	117	107	2	16	39
32	2	15	79	70	182	15	119	108	183	16	29
33	2	15	77	71	3	15	109	109	184	16	59
34	217	15	78	72	2	15	114	110	2	16	81
35	2	15	49	73	204	15	121	111	227	16	85
36	199	15	42	74	2	15	111	112	2	16	88
37	286	15	105	75	2	15	104	113	200	16	45
38	2	15	88	76	2	15	189	114	2	16	101

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Compound	X	R ₁	R ₂	Compound	X	R ₁	R ₂	Compound	X	R ₁	R ₂
115	182	16	108	127	2	16	136	139	2	25	36
116	2	16	27	128	2	16	143	140	2	155	51
117	2	16	79	129	2	16	144	141	2	154	52
118	214	16	74	130	2	16	121	142	2	16	164
119	2	16	41	131	2	16	115	143	197	16	44
120	2	16	72	132	2	16	123	144	2	161	55
121	2	16	73	133	H	16	122	145	2	168	11
122	2	16	128	134	236	16	231	146	2	171	128
123	3	16	136	135	2	26	52	147	2	171	45
124	2	16	135	136	2	16	24	148	197	232	40
125	214	16	136	137	199	19	52				
126	203	16	136	138	2	23	52				



Compound	X	R ₁	R ₃	Compound	X	R ₁	R ₃	Compound	X	R ₁	R ₃
149	2	16	42	160	187	23	11	171	201	63	11
150	2	15	66	161	2	11	58	172	235	11	89
151	2	16	193	162	186	11	58	173	232	167	11
152	2	62	11	163	2	67	11	174	191	70	11
153	2	76	11	164	2	16	93	175	223	195	11
154	2	89	11	165	1	H	94	176	220	11	11
155	198	27	11	166	2	196	33	177	190	11	58
156	2	193	11	167	225	188	11	178	2	16	90
157	2	11	34	168	2	11	81	179	224	11	95
158	2	56	11	169	2	11	84	180	2	11	65
159	192	56	11	170	2	11	82	181	2	64	11

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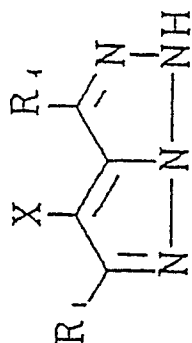
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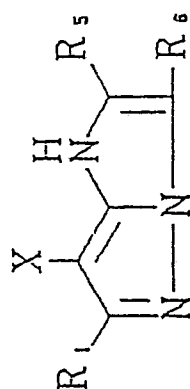
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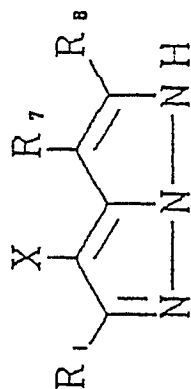
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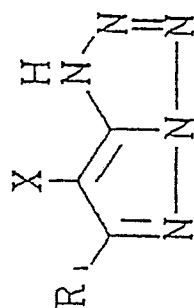
Compound	X	R ₁	R ₄	Compound	X	R ₁	R ₄
182	2	16	53	185	218	96	11
183	2	52	11	186	219	99	172
184	2	92	11	187	215	15	89
				188	224	98	11
				189	184	13	83
				190	H	52	11



Compound	X	R ₁	R ₅	R ₆	Compound	X	R ₁	R ₅	R ₆
191	2	16	11	52	197	185	12	162	11
192	2	15	H	52	198	3	11	11	.89
193	2	16	60	H	199	H	226	H	H
194	2	174	11	H	200	2	23	173	17
195	184	11	30	H	201	2	23	H	H
196	2	152	H	57	202	H	23	H	H



Compound	X	R ₁	R ₇	R ₈	Compound	X	R ₁	R ₇	R ₈
203	2	11	H	91	209	H	11	H	91
204	2	11	H	92	210	2	16	H	52
205	219	172	H	100	211	2	16	H	42
206	235	15	H	87	212	184	15	H	66
207	2	11	H	62	213	2	203	H	163
208	202	13	11	97	214	204	212	H	50



Compound	X	R ₁	Compound	X	R ₁
215	2	20	221	2	86
216	184	88	222	235	43
217	2	69	223	2	103

The numerals under the headings other than "compound" denote the following:

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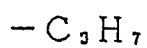
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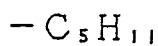
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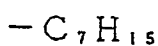
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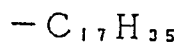
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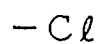
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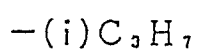
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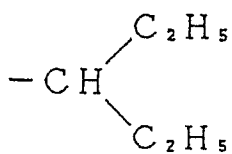
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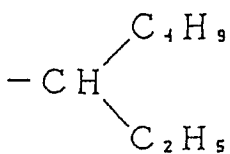
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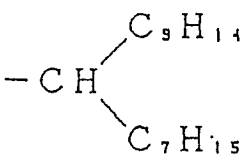
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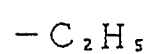
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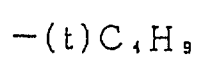
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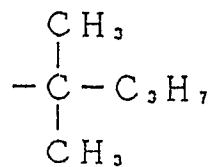
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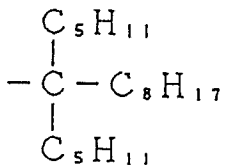
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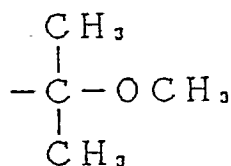
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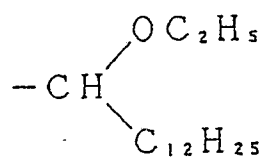
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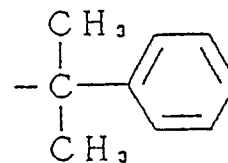
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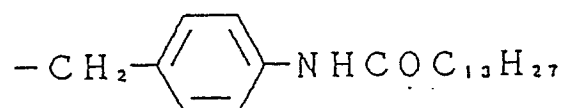
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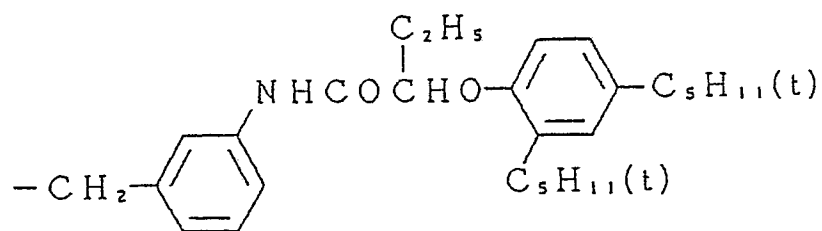
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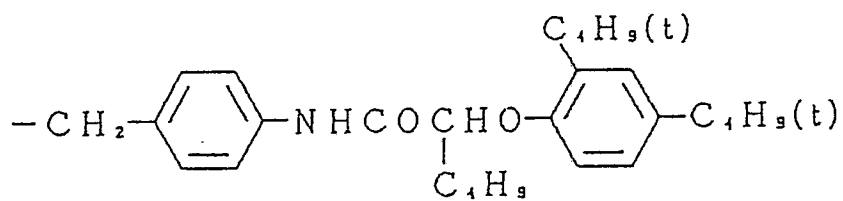
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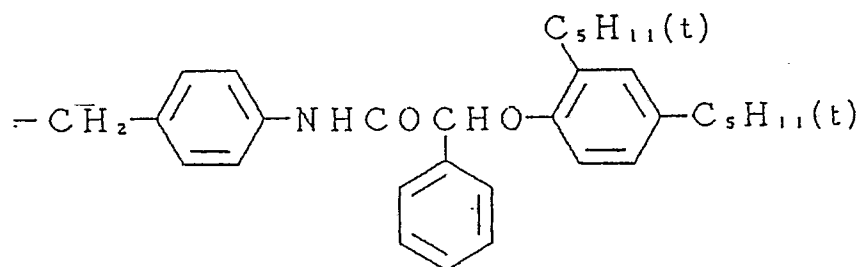
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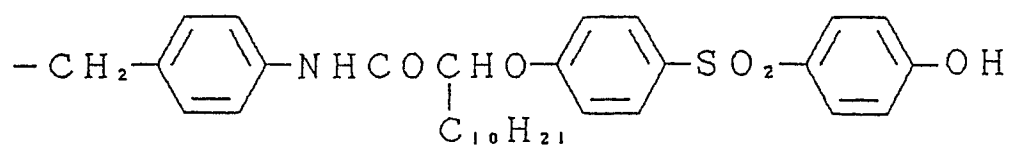


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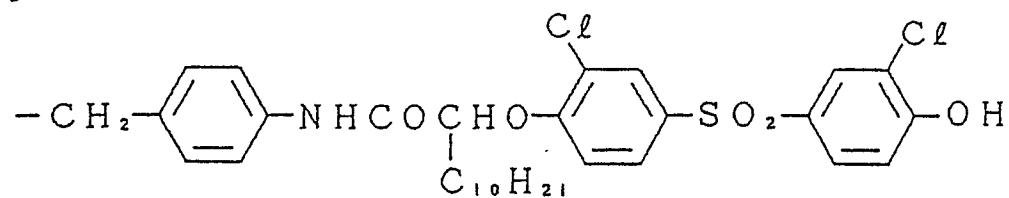
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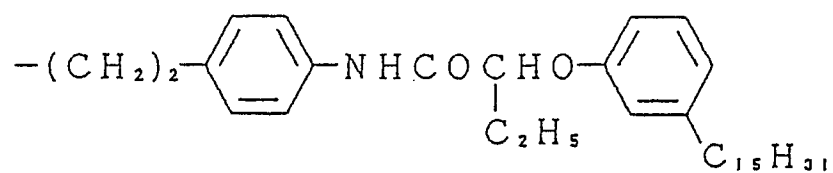
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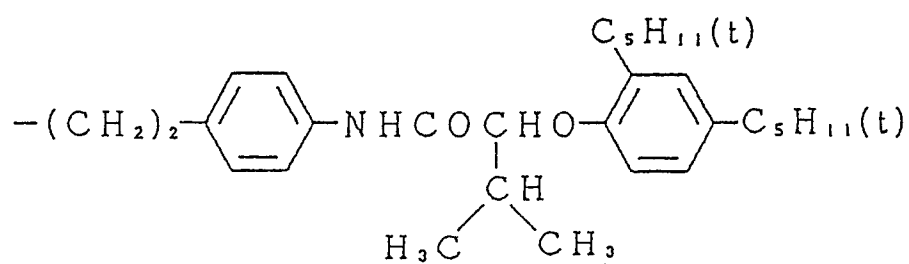
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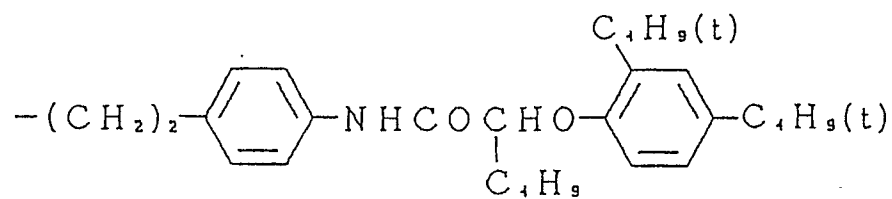
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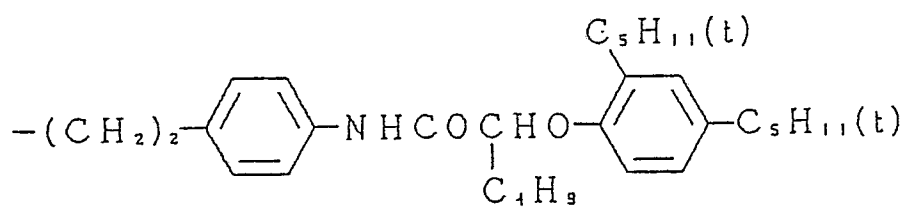


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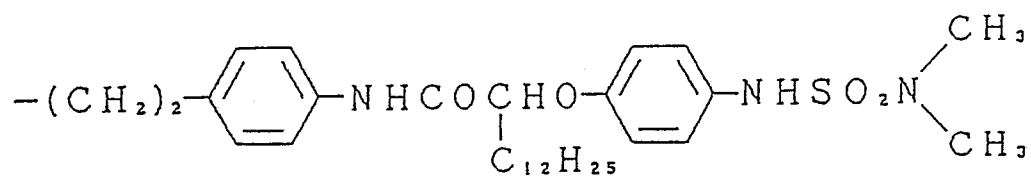
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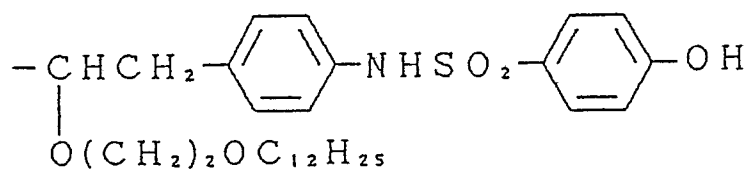
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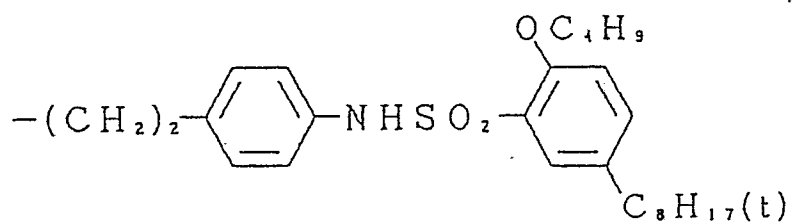
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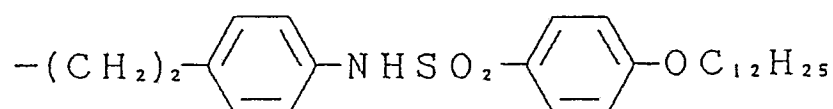
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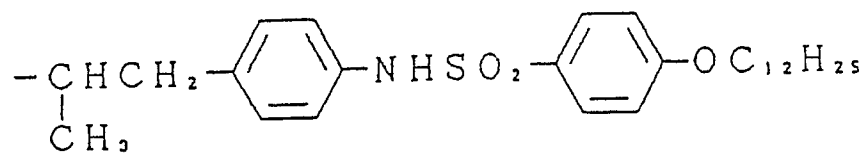


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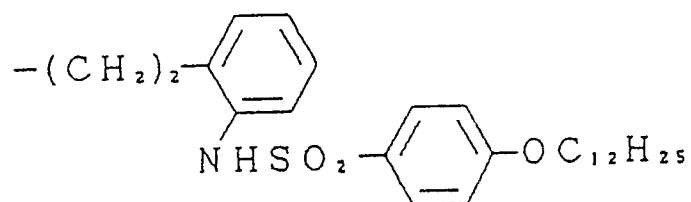
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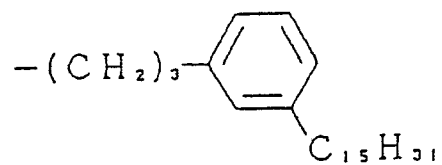
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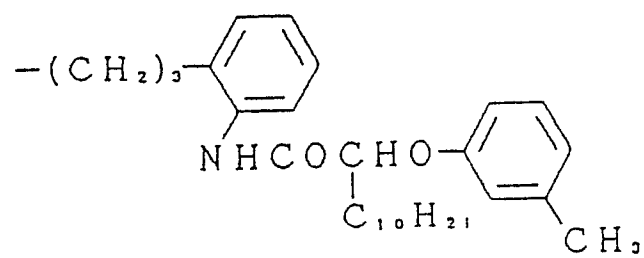
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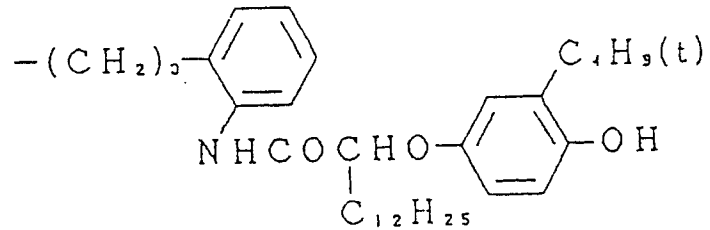
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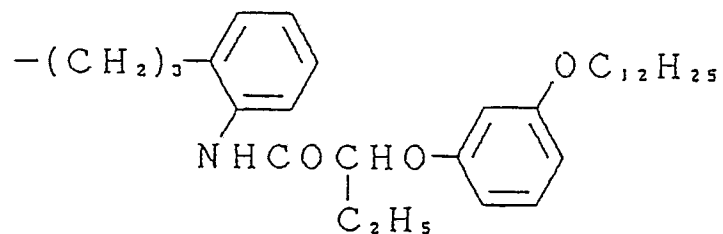


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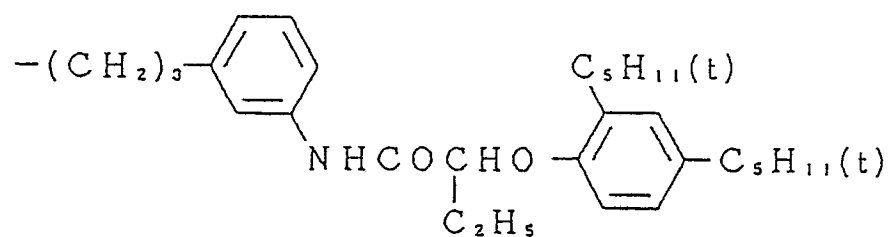
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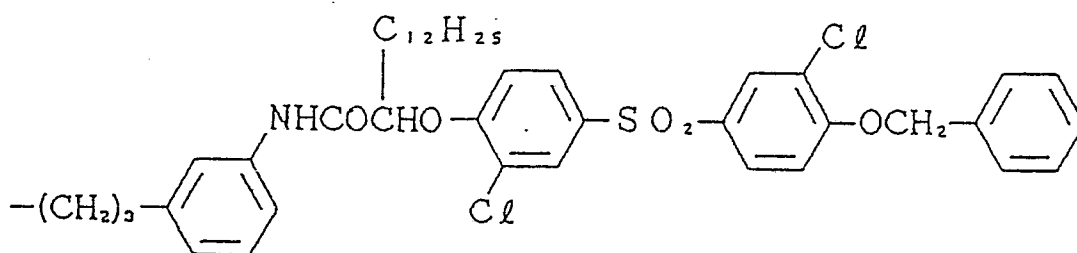
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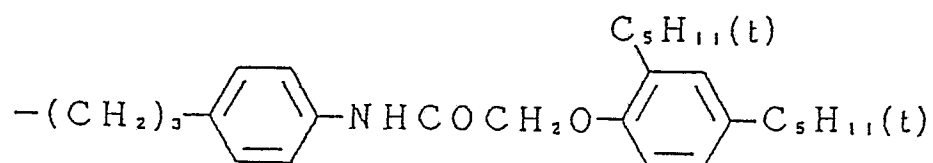
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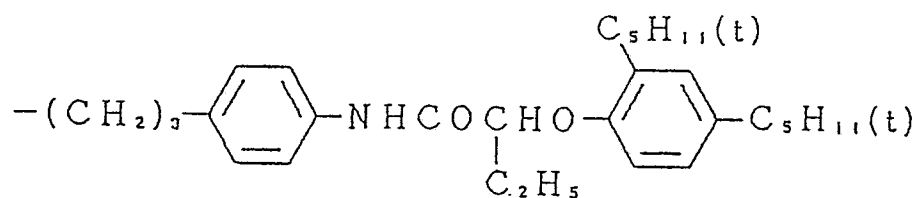
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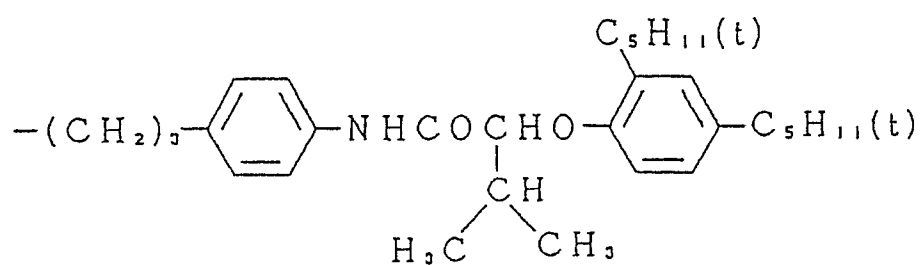
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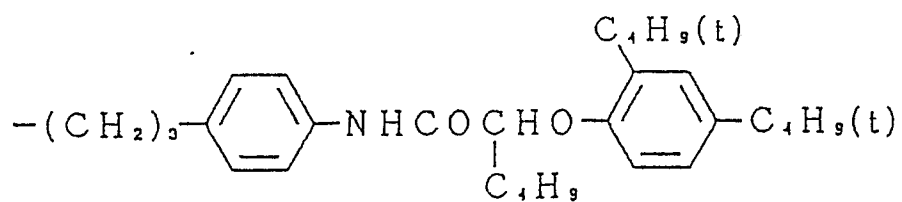
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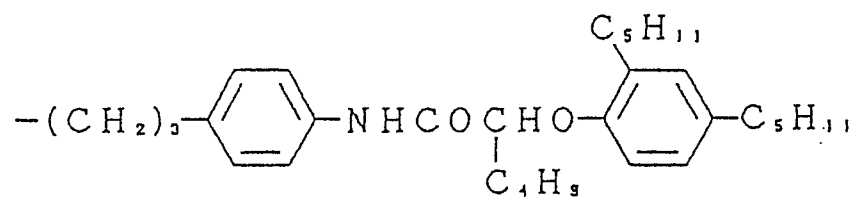
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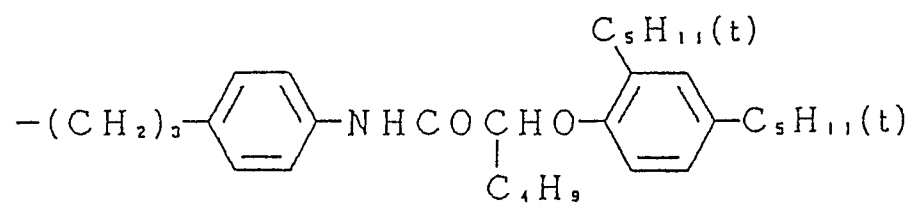
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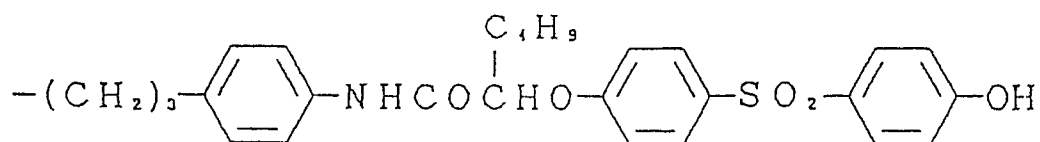
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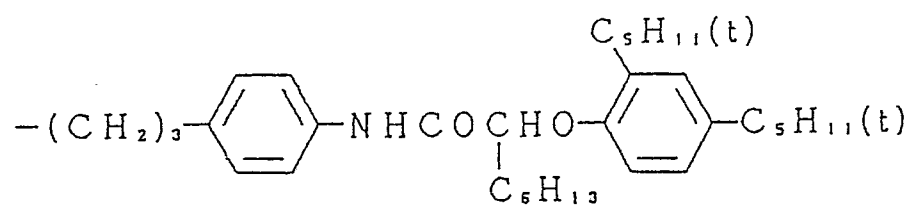
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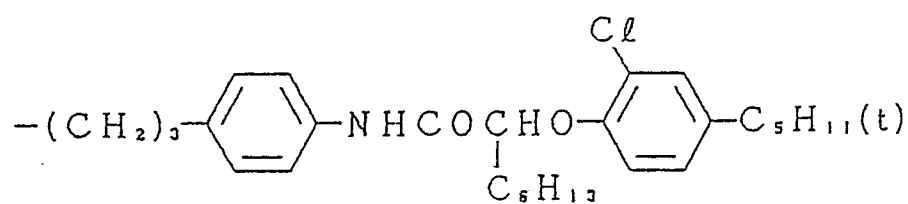
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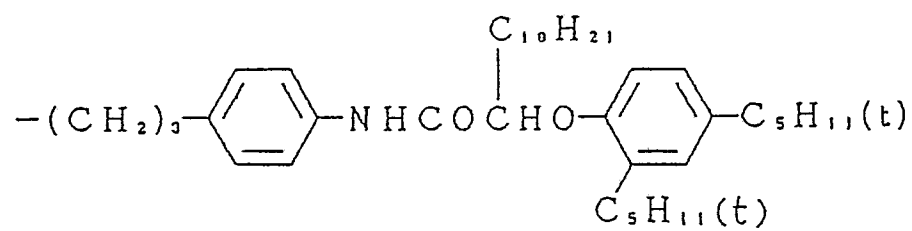
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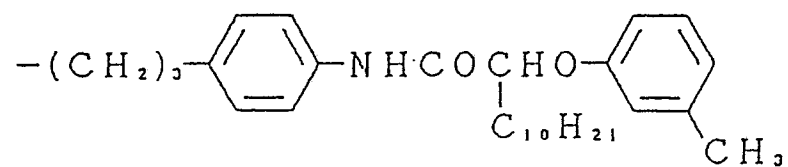
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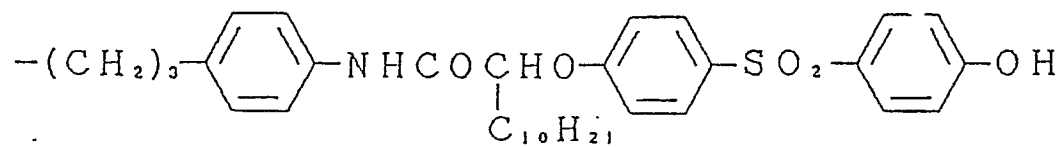
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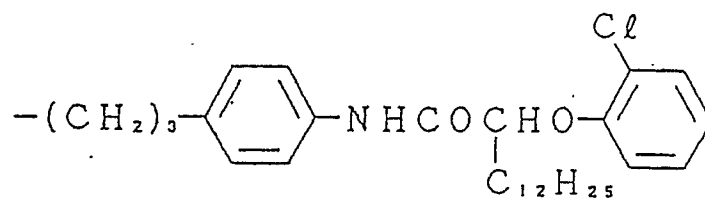


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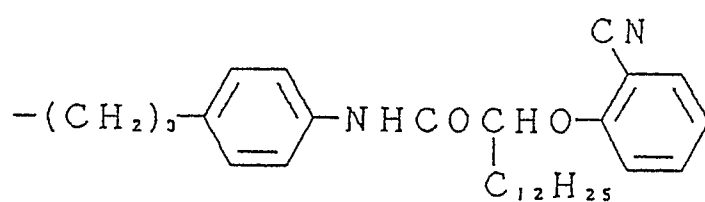
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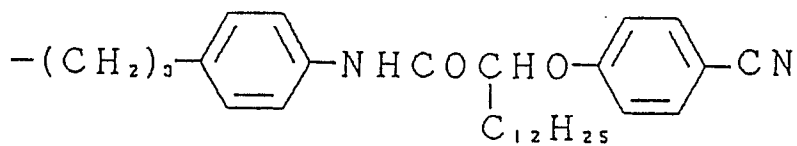
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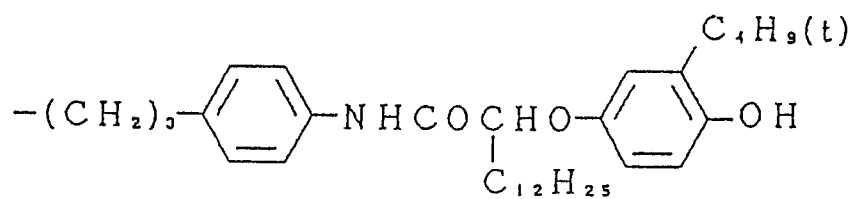
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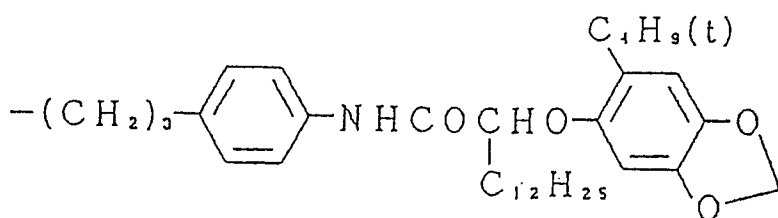
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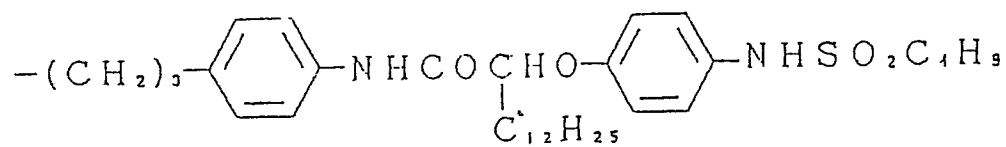
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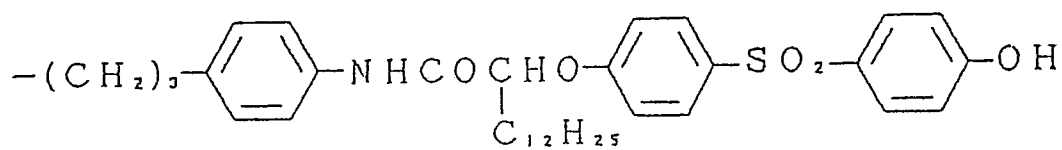
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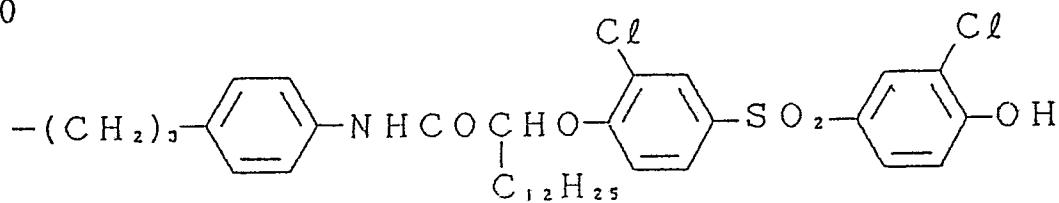
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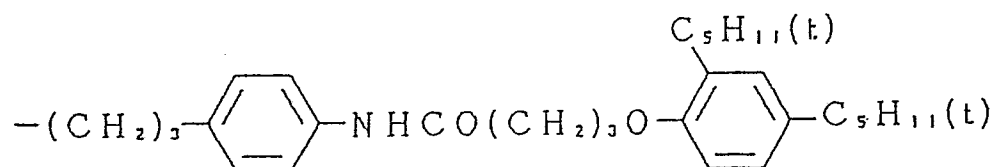
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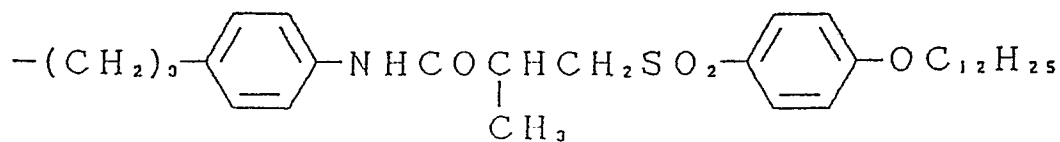
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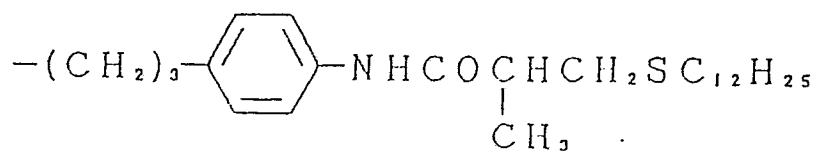
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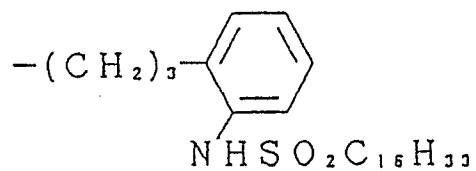
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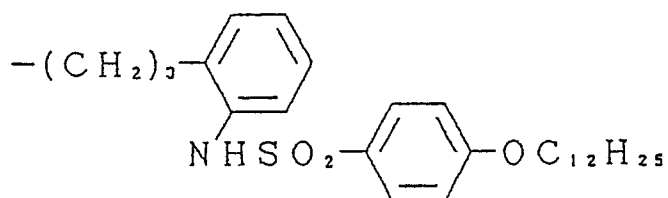
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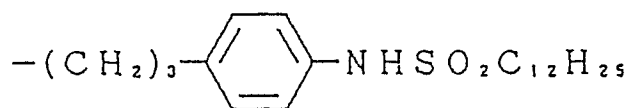
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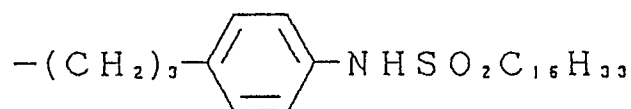
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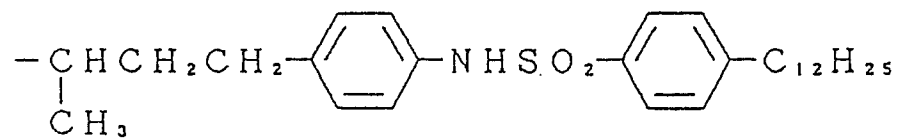
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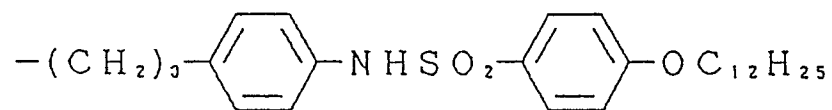
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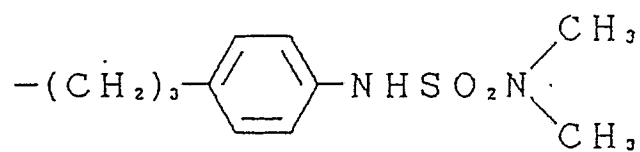


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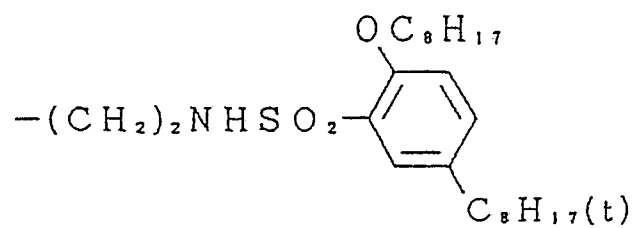
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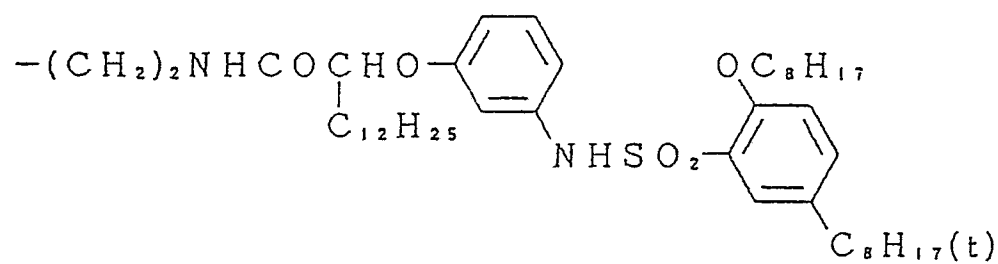
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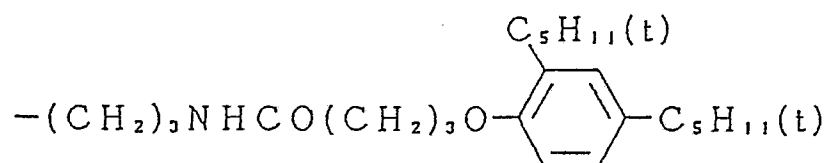
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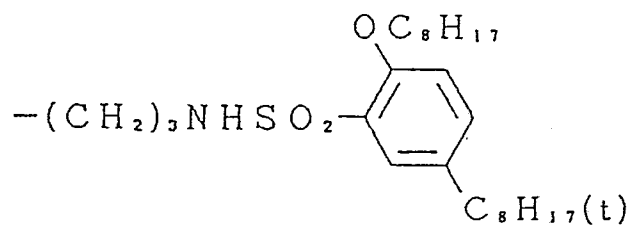
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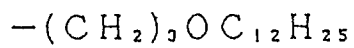
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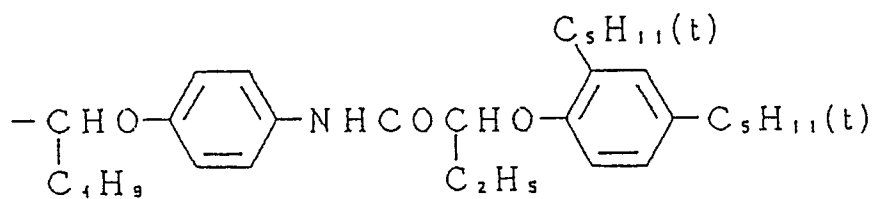
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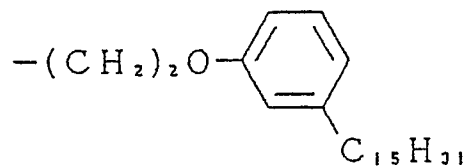
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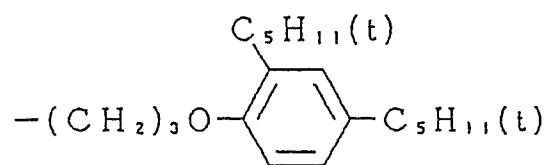
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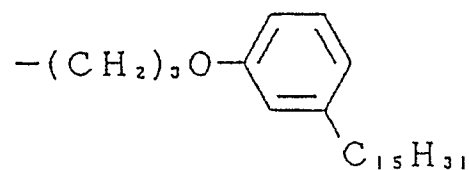
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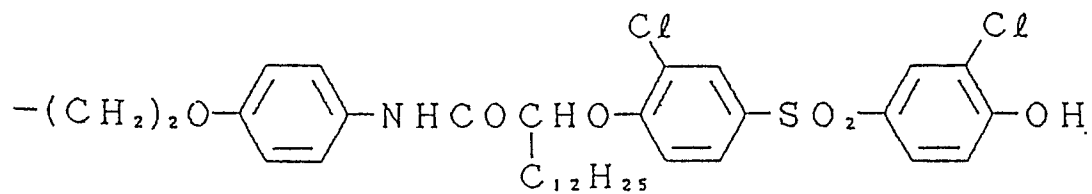
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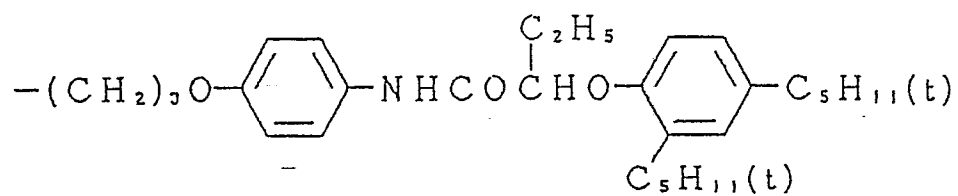


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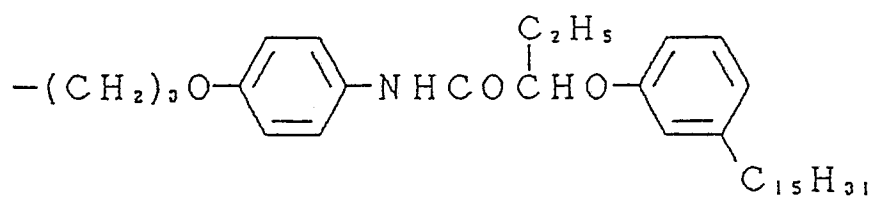
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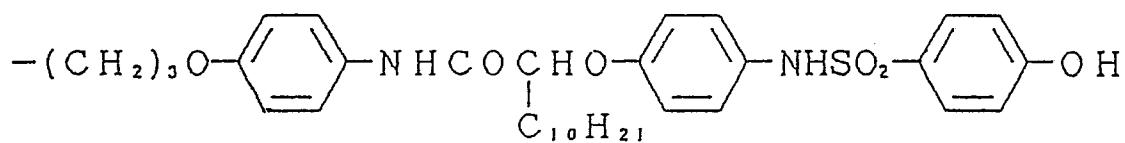
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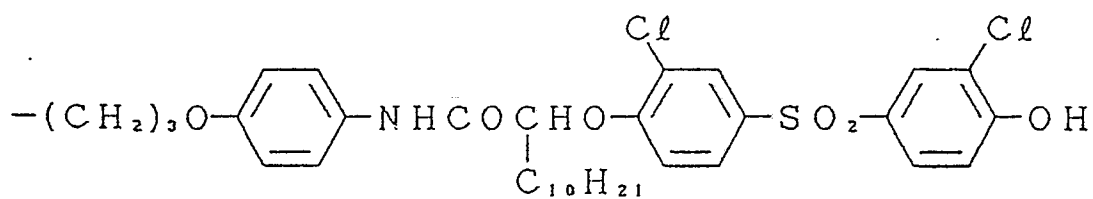
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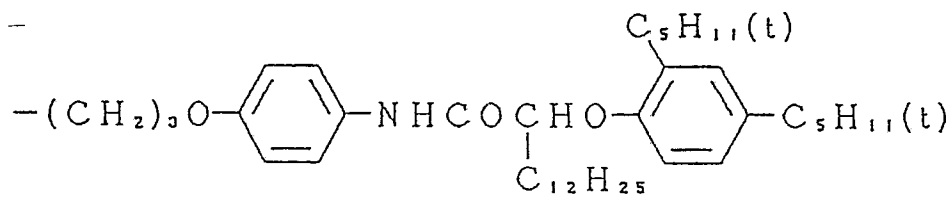
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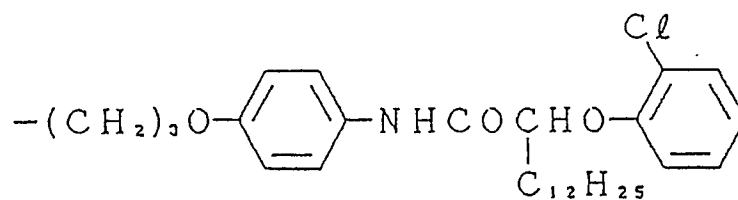
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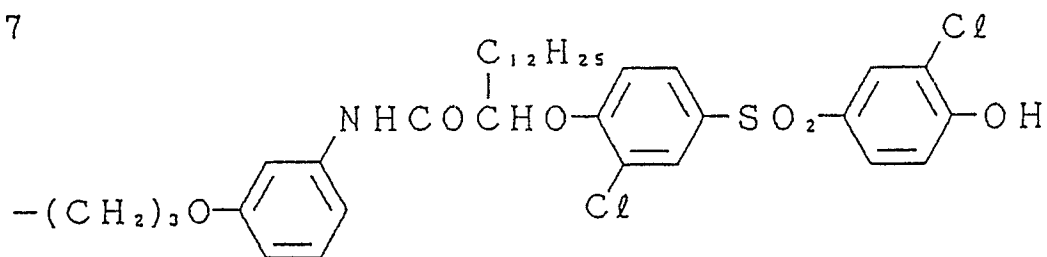
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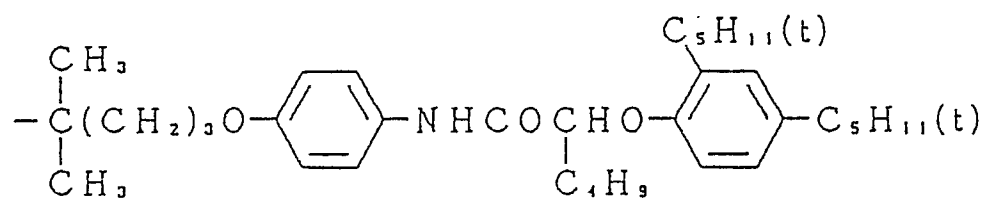
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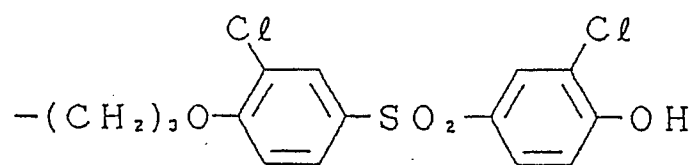
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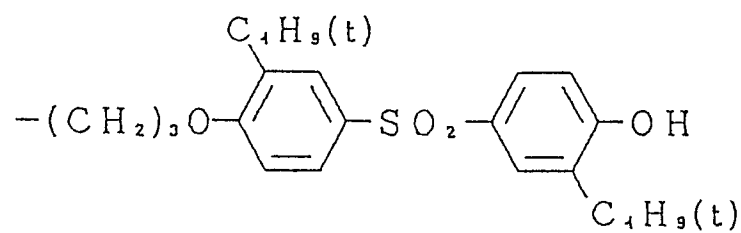
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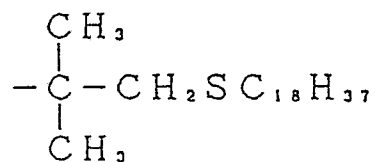
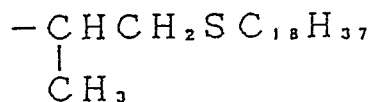
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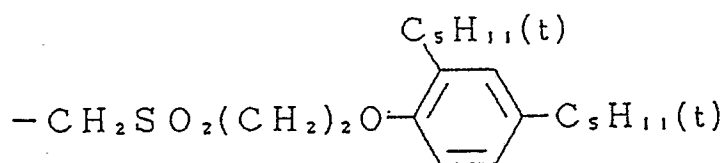
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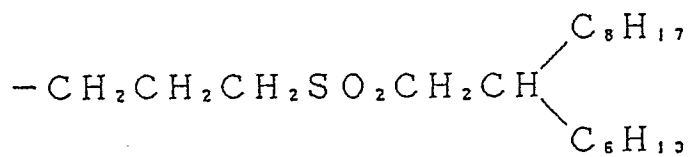
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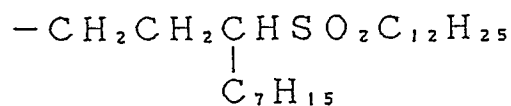
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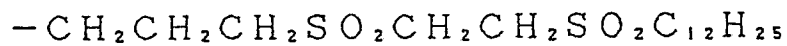
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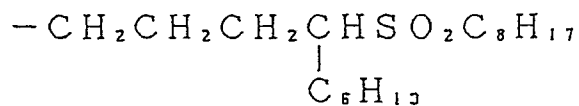
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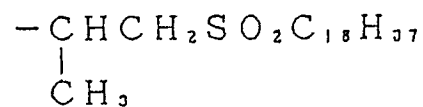


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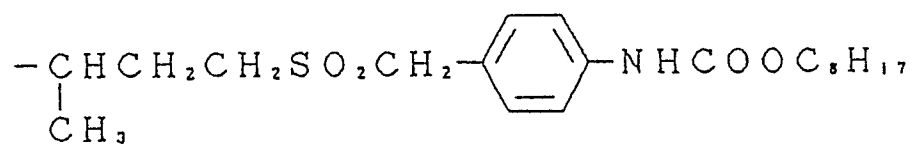
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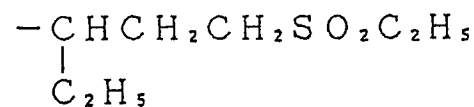
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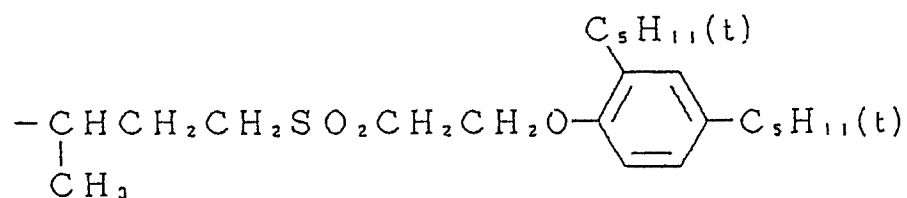
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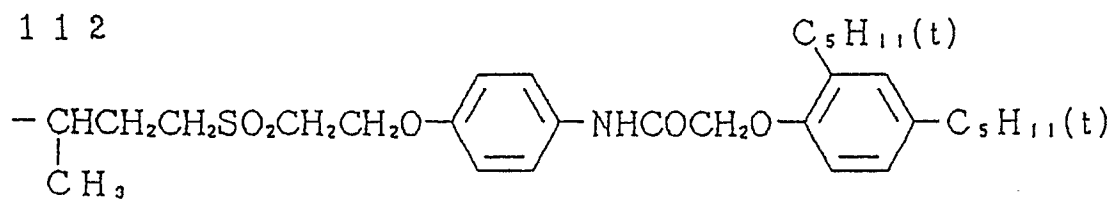
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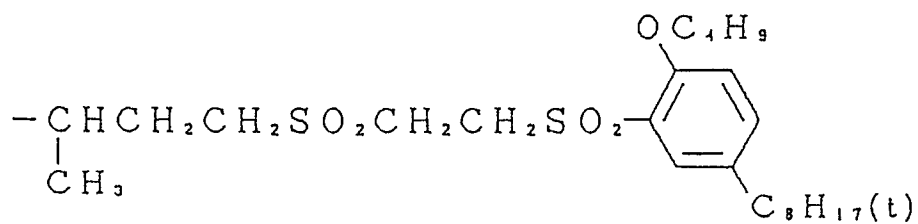
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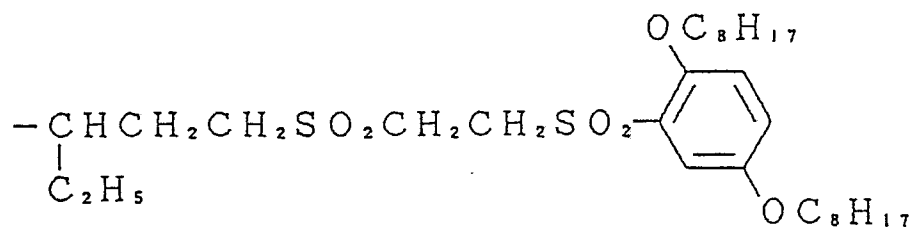
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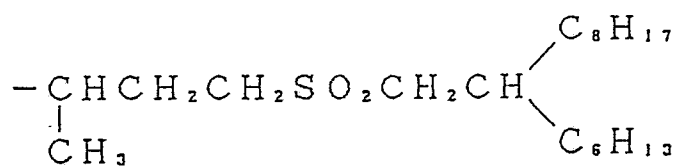
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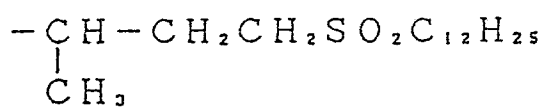
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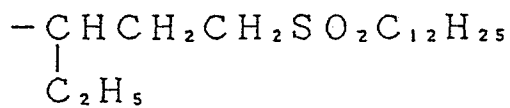
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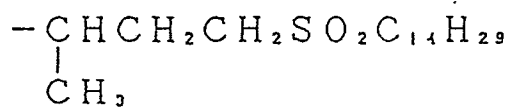
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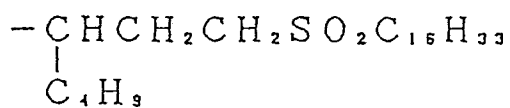
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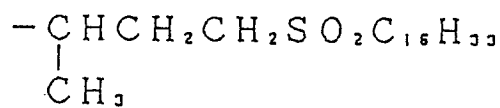


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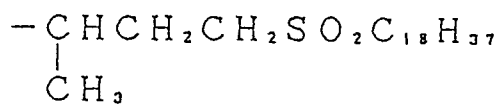
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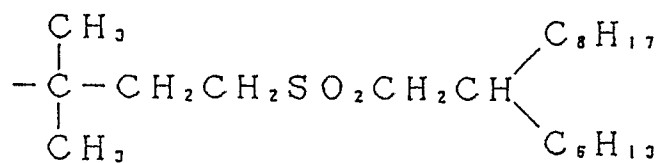
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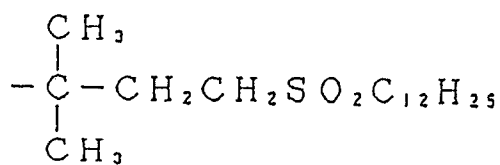
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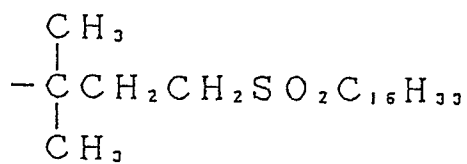
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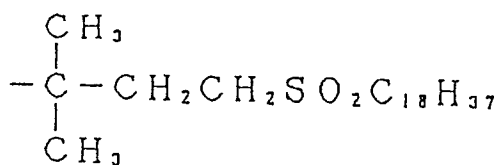
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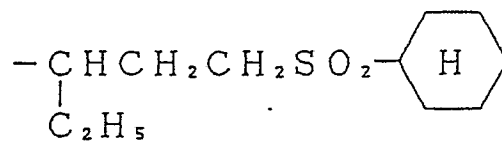
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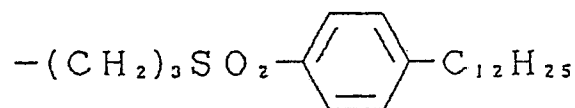
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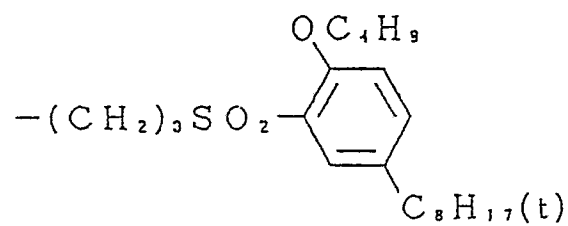
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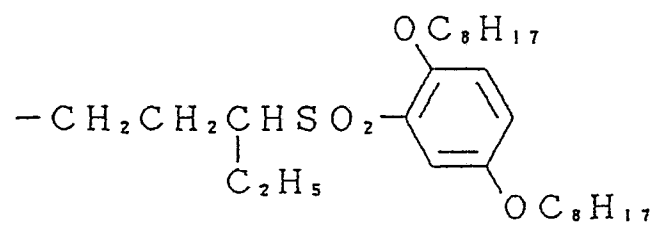
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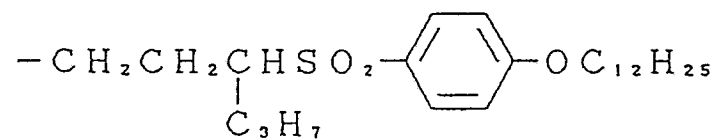
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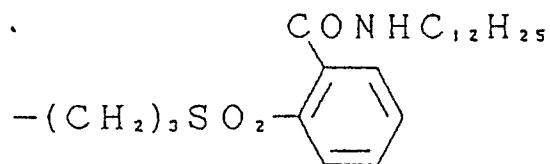


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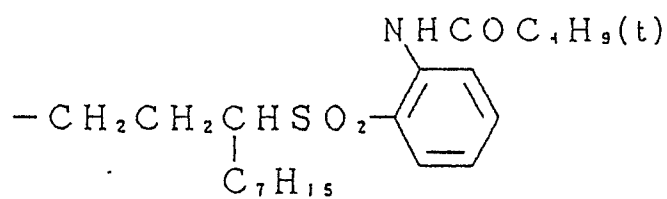
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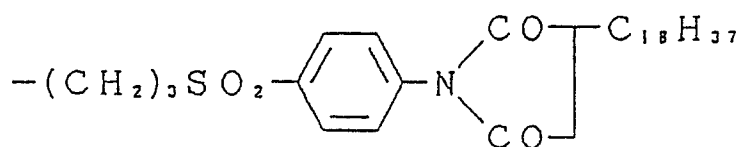
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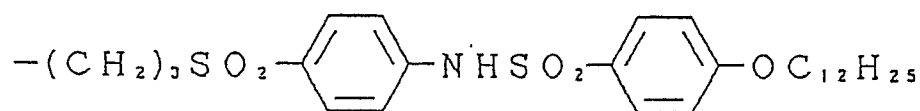
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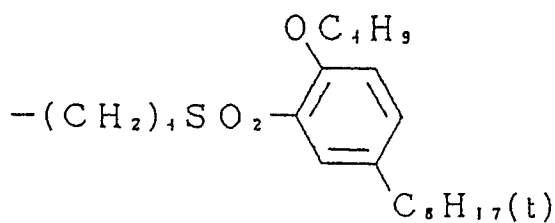
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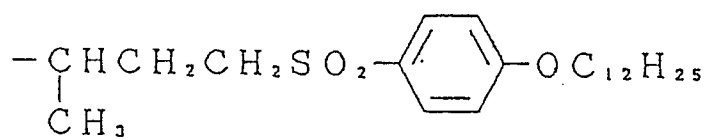
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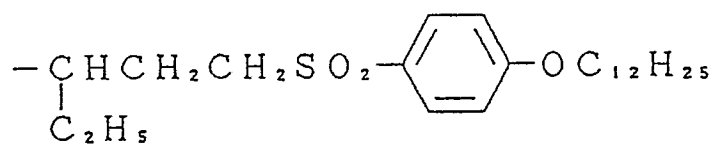


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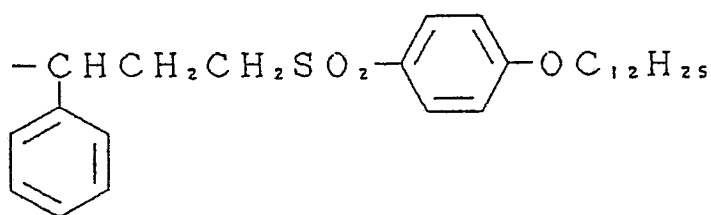
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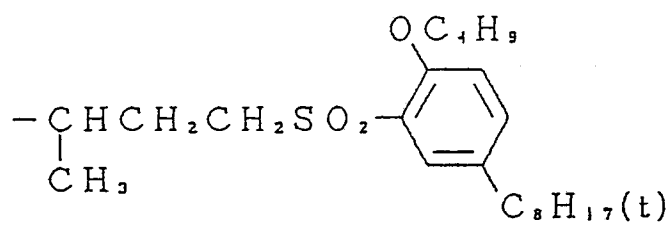
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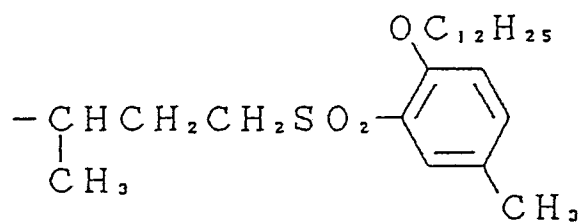
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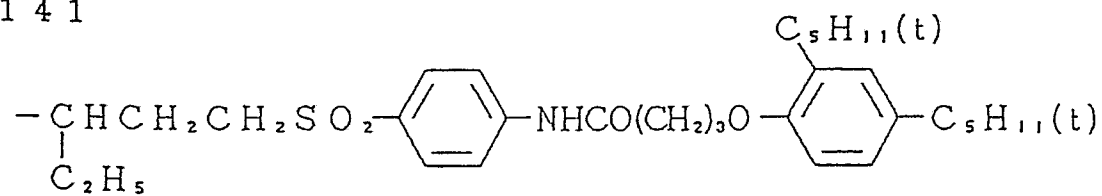
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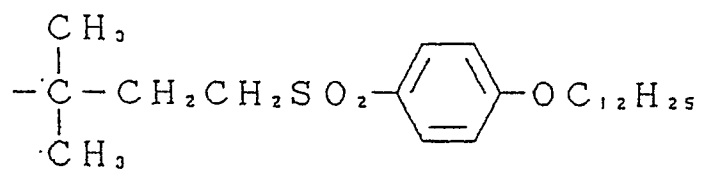


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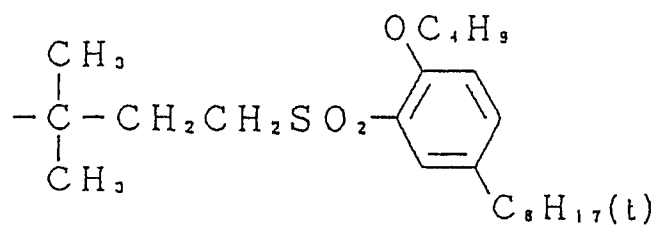
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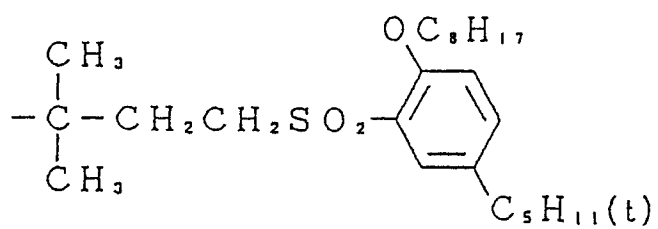
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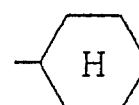
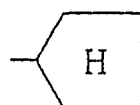
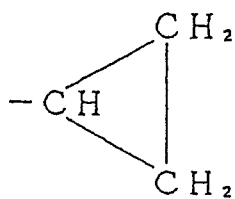
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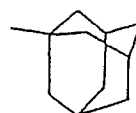
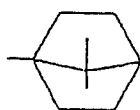


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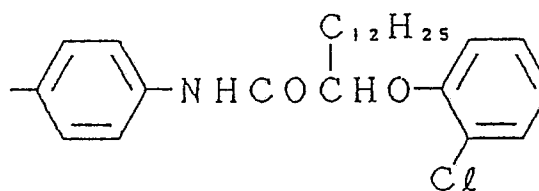
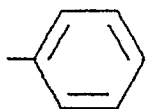
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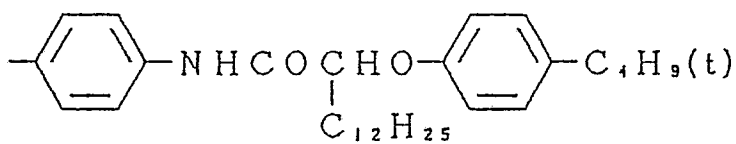
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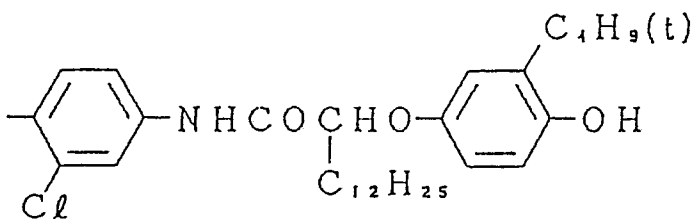
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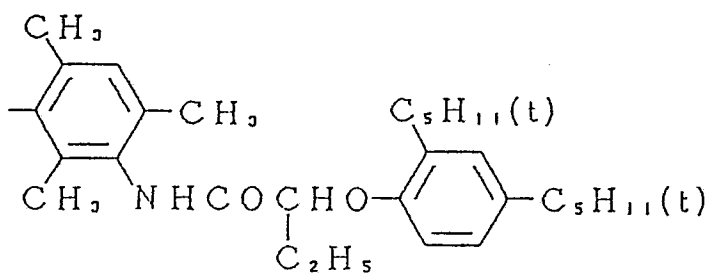
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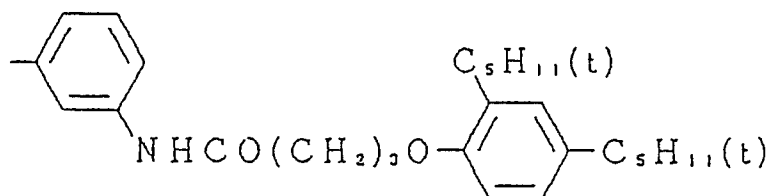
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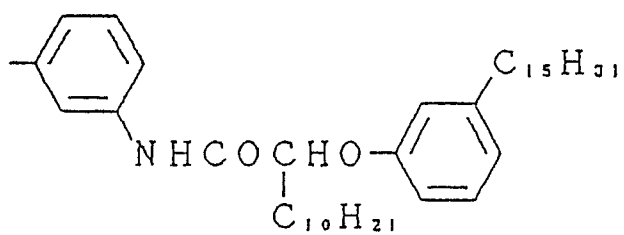
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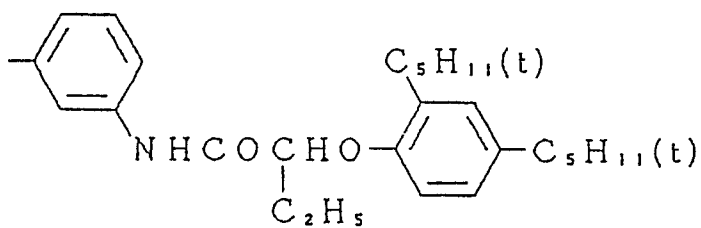
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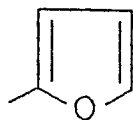
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-CN

-COCH₃

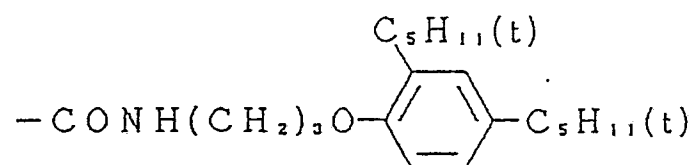
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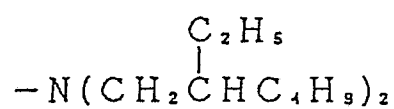


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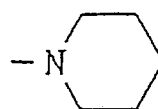
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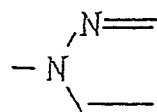
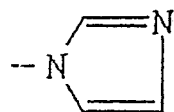
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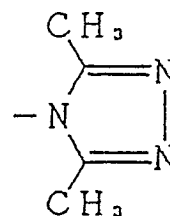
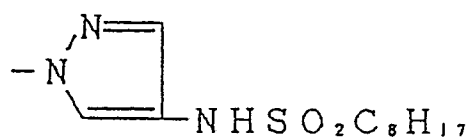
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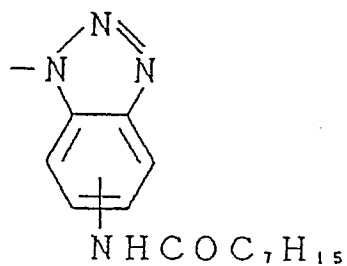


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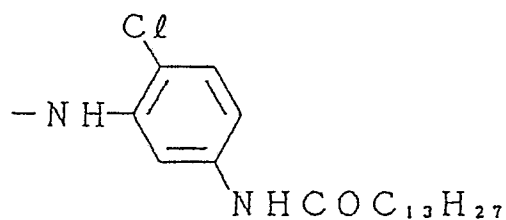
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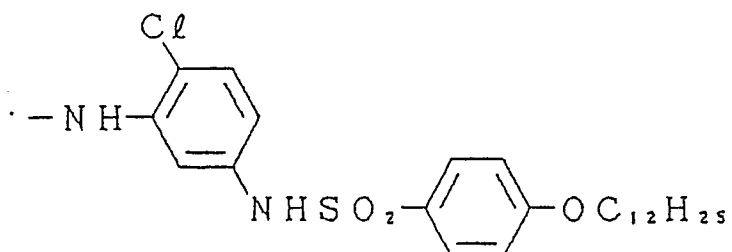
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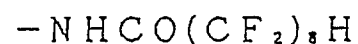


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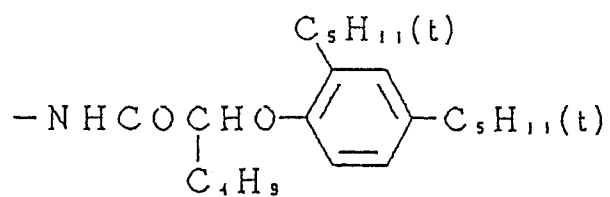
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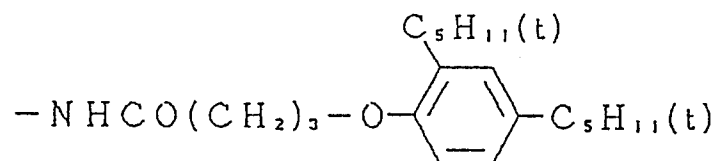
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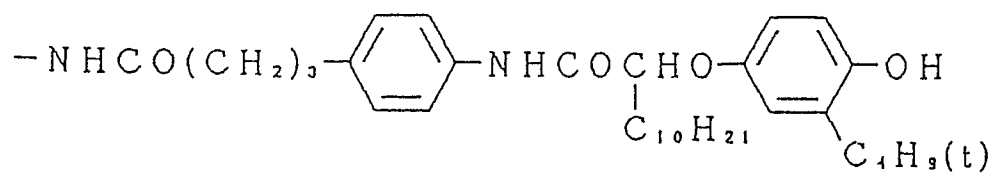
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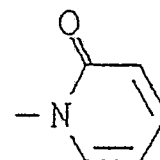
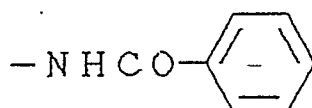
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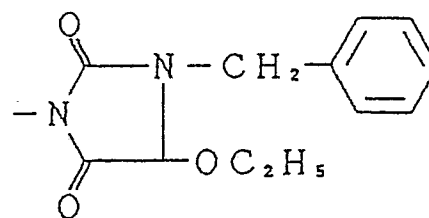
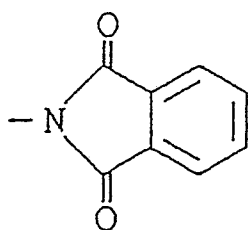


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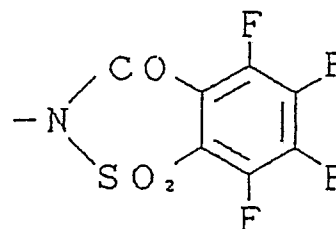
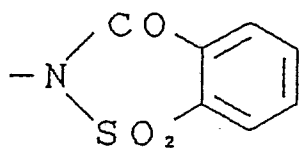


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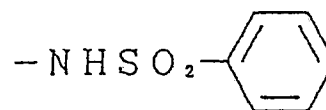
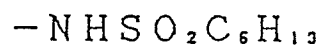


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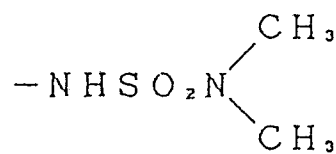
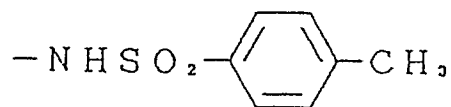


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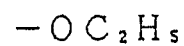
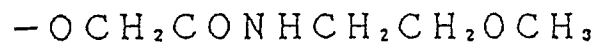
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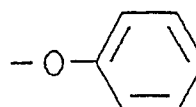
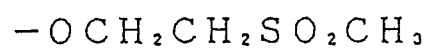
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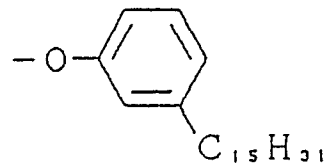
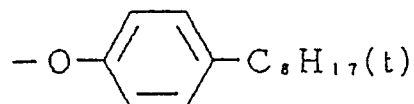


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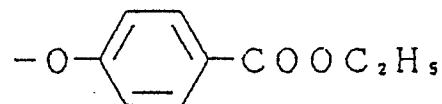
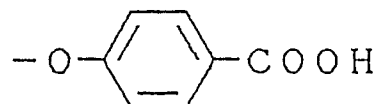
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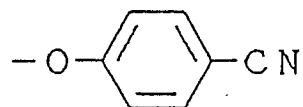
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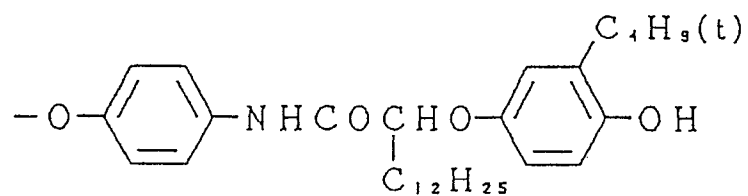
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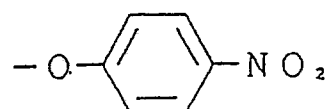


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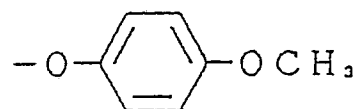
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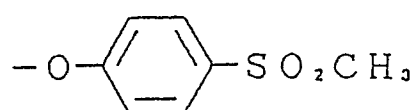


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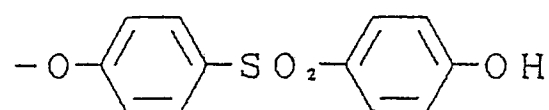


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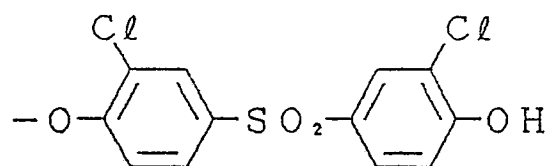
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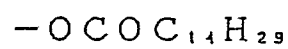
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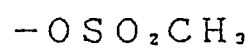
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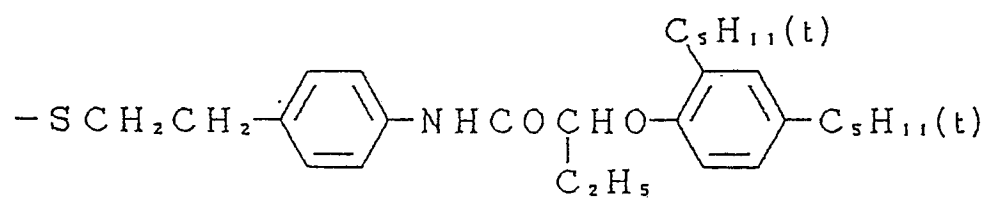


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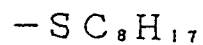
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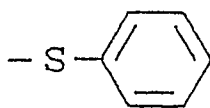


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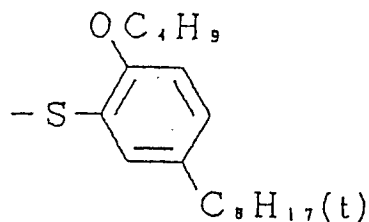


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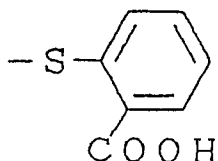
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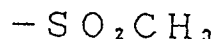
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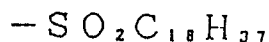
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2 3 7



2 3 8



These couplers were synthesized by reference to Journal of the Chemical Society, Perkin I (1977), pages 2047 to 2052, U. S. Patent No. 3,725,067 and Unexamined Published Japanese Patent Application Nos. 99437/1984, 42045/1983, 162548/1984, 171956/1984, 33552/1985, 43659/1985, 172982/1985 and 190779/1985.

The coupler of the present invention is preferably incorporated in an amount within the range of 1×10^{-5} mole to 1×10^{-1} per mole of silver.

The coupler of the present invention may be used in combination with any other type of magenta coupler.

The silver halide emulsion comprised of silver halide grains having fog centers on their surface or subsurface is defined as such an emulsion that, when a photographic sample coated with it for a silver deposit of 0.5 g/m^2 is developed at 38°C for 6 minutes with a developer having the formulation indicated below, at least 60%, preferably at least 70%, more preferably at least 80%, of the coated silver is developed. Measurement of the amount of developed silver can be conducted by any known method such as potentiometry or X-ray fluorimetry.

Formulation of developer

5:	Water	700	ml
	Sodium tetrapolyphosphate	2	g
	Sodium sulfite	20	g
10	Hydroquinone monosulfonate	30	g
	Sodium carbonate (monohydrate)	30	g
15	1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	2	g
	Potassium bromide	2.5	g
	Potassium thiocyanate	1.2	g
20.	Potassium iodide (0.1% aq. sol.)	2	ml
	Water	to make 1,000	ml

25 The silver halide emulsion that has fog centers on the surface of silver halide grains and which is suitable for use in the present invention can be prepared by irradiating growing or grown silver halide grains with light. A foggant may be employed to cause simultaneous chemical fogging. For specific procedures of chemical fogging, see U.S. Patent 4,082,553 and 4,036,646. Fogging is usually conducted prior to the coating of emulsions but it may be effected during or after the coating operation.

30 The silver halide emulsion having fog centers on the subsurface of silver halide grains that can be used in the present invention is defined as such an emulsion that the coated silver is little developed with a surface developer of the Methol-ascorbic acid type but that at least 60% of the coated silver is developed with a developer having the formulation indicated above. A desired emulsion can be prepared by forming a very thin layer of silver halide shell over grains having fog centers on their surface. The method that can be used to form such a shell layer is not limited in any way and the method described in Unexamined
35 Published Japanese Patent Application No. 133542/1984 may be employed.

The silver halide grains having fog centers on their surface or subsurface are incorporated in at least one of the silver halide emulsion layers in the silver halide color photographic material of the present invention. Preferably, these grains are incorporated in the silver halide emulsion layer that contains a
40 compound of formula (I). If desired, such grains may be divided into two portions, one of them being incorporated in the emulsion layer containing a compound of formula (I) while the remainder is incorporated in other layers. The emulsion comprised of grains having fog centers on their surface or subsurface is used in an amount generally ranging from 0.05 to 50 wt%, preferably from 0.1 to 25 wt%, more preferably from 0.5 to 10 wt%, of the total silver in the emulsion layers in which the fogged emulsion is incorporated.

45 Any silver halide that are conventionally used in silver halide emulsions such as silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide, silver chloriodobromide and silver chloride can be incorporated in the silver halide emulsion for use in the present invention. Of these silver halides, silver bromide, silver iodobromide and silver chloriodobromide are preferred.

The silver halide grains to be used in the silver halide emulsions of the present invention may have a
50 homogeneous structure throughout the crystal, or the structure of the core may be different from that of the shell.

These silver halide grains may be of the surface type where latent images are predominantly formed on the grain surface or of the internal type where latent images are formed within the grain.

55 The silver halide grains used in the silver halide emulsion in accordance with the present invention may have regular crystal shapes such as cubic, octahedral and tetradecahedral forms. The grains may have anomalous crystal shapes such as spherical and tabular forms.

The average size of the silver halide grains used in the present invention is preferably within the range of 0.05 ~ 30 μm , with the range of 0.1 ~ 20 μm being more preferable.

The silver halide emulsion used in the present invention may have any pattern of grain size distribution, broad or narrow. Emulsions having a broad distribution (referred to as polydispersed emulsions) may be used. Also, suitable for use are emulsions having a narrow distribution.

5 The silver halide emulsion of the present invention may be chemically sensitized by an ordinary method, such as sulfur sensitization, selenium sensitization, reduction sensitization, or noble metal sensitization using gold and other noble metal compounds. Such methods may be used each independently or in combination.

The silver halide emulsion of the present invention may be optically sensitized to a desired range of wavelength, using dyes known as sensitizing dye in the photographic industry.

10 Compounds that are known as antifoggants or stabilizers in the photographic industry may be incorporated in the silver halide emulsion during or upon completion of chemical ripening and/or before coating of the silver halide emulsion following chemical ripening, for the purpose of preventing fogging during preparation of the light-sensitive material, during its storage or photographic processing or for the purpose of stabilizing its photographic performance characteristics.

15 Known acyl acetanilide based couplers may preferably be used as yellow dye forming couplers in the present invention. Benzoyl acetanilide and pivaloyl acetanilide based compounds are advantageous.

Compounds of formula (I) may be used as magenta-dye forming couplers either independently or in combination with known couplers such as 5-pyrazolone couplers, pyrazolobenzimidazole couplers, open-chain acylacetone nitrile couplers and indazolone couplers.

20 Phenol-or naphthol-based couplers are generally used for cyan-dye forming couplers.

The silver halide photographic material of the present invention may use an image stabilizer. Preferable image stabilizer is a compound that is described in RD 17643, VII, J.

Color reversal processing is performed after exposure to obtain reversal dye images using the light-sensitive material of the present invention. Color reversal processing consists basically of a black-and-white development step, a fogging step, a color development step, bleach step, fixing step, and washing step.

Additional steps may be included if desired.

Two or more steps may be grouped and conducted at a time.

30 A prehardening step, neutralizing step, stop-fix step or posthardening step may be performed in combination with the above-listed processing steps. An activator processing step may be performed instead of the color development step where a color developing agent or its precursor is incorporated in the photographic material and development is performed in an activator bath. Alternatively, activator processing may be applied to the monobath processing in the above-described color processing.

The processing temperature is usually selected from the range of 10 to 65°C, but may exceed 65°C. A preferable processing temperature is in the range from 25 to 45°C.

35 The black-and-white developer generally comprises an alkaline aqueous solution containing a black-and-white developing agent. Illustrative black-and-white developing agents include aminophenolic derivatives, polyhydroxyphenolic derivatives, and 1-phenyl-3-pyrazolidone derivatives.

40 The black-and-white developer may incorporate a variety of additives that are commonly employed in developing solutions, such as an alkali agent, a restrainer, an alkali metal halide, an auxiliary developing agent, a silver halide solvent, a preservative, an anti-foaming agent, and a surfactant.

The black-and-white developer generally has a pH of at least 7, with a preferable value being within the range of from about 8 to 12.

The black-and-white developer may also contain a variety of chelating agents as metal ion sequestering agents.

45 Fogging is achieved either by treatment with a solution containing a chemical foggant or by irradiation with light or by both. Illustrative foggants are stannous chloride and tertiary butylaminoborane. Fogging is effected either prior to or simultaneously with color development. In the latter case, the foggant is incorporated in the color developer.

50 The color developer generally comprises an aqueous alkali solution containing a color developing agent. The color developing agent is an aromatic primary amine color developing agent, such as aminophenol-based and p-phenylene-diamine derivatives. These color developing agents may be used in the form of organic or inorganic acid salts such as hydrochloride, sulfate, p-toluenesulfonate, sulfite, oxalate and benzenesulfonate.

55 These compounds are generally used in amounts in the range from about 0.1 to 30 g, more preferably in amounts in the range from about 1 to 15 g, per 1,000 ml of color developer.

The color developer may contain a variety of additives that are usually incorporated in developers, such as an alkali agent, benzyl alcohol, an alkali metal halide, a conditioner, a preservative, an anti-foaming agent, a surfactant, and an organic solvent.

The color developer used in the present invention usually has a pH of 7 or higher, preferably a pH of about 9 to 13.

The color developer may further contain an anti-oxidation agent.

The bleach step may be performed simultaneously with the fixing step or separately. Exemplary bleaching agents include metal complex salts of organic acids such as polycarboxylic acid, aminopolycarboxylic acid, oxalic acid and citric acid that are coordinated to metal ions such as iron, cobalt and copper ions.

These bleaching agents are added in amounts in the range from 5 to 450 g/1,000 ml, more preferably in the range from 20 to 250 g/1,000 ml.

Fixers of generally employed compositions may be employed.

Exemplary bleaching agents that may be used in the bleaching fix bath include the metal complex salts of organic acids described in the in the aforementioned bleach step.

The fixing agents described in the aforementioned fixing step can be incorporated in the bleach-fix bath as silver halide fixing agents.

After fixation, the silver halide color photographic material of the present invention may be subjected to a stabilizing treatment. For the purpose of improving the storage stability of photographic images, aldehyde derivatives are incorporated in the stabilizer.

The following examples are provided for the purpose of further illustrating the preferred embodiment of the present invention but are in no way to be taken as limiting.

EXAMPLES

A subbed triacetyl cellulose base was coated with emulsion layers and auxiliary layers, in the order shown below, so as to prepare Sample No. 1.

Firstlayer: Anti-halation layer

Four grams of an UV absorber 1 and 6g of an UV absorber 2 were dissolved in 8 ml of dibutyl phthalate and 10 ml of ethyl acetate. To the resulting solution, 300 ml of an aqueous solution of 5% gelatin and 20 ml of an aqueous solution of 5% surfactant 1 were added and 150 ml of a dispersion was formed by subsequent emulsification and dispersing. This dispersion was mixed with 600 ml of an aqueous solution of 5% gelatin containing 3 g of black colloidal silver. To the mixture, 20 ml of a methanol solution of 0.5% hardener 1 was added and the resulting fluid was coated to give a silver deposit of 0.1 g/m².

Second layer: Intermediate layer

Three grams of 2,5-di-t-octyl hydroquinone was dissolved in 3 g of tricresyl phosphate and 3 ml of ethyl acetate. To the resulting solution, 100 ml of an aqueous solution of 5% gelatin and 5 ml of an aqueous solution of 5% surfactant 1 were added and the mixture was subjected to emulsification and dispersion. The resulting dispersion was added to 600 ml of an aqueous solution of 5% gelatin to make a coating fluid which was applied to give a 2,5-di-t-octyl hydroquinone deposit of 0.1 g/m².

Third layer: Less red-sensitive emulsion layer

A monodispersed emulsion having a silver iodide content of 4 mol%, an average grain size of 0.3 μ m and a core-shell structure in which the grain surface had a lower iodine content than the interior was sensitized with sensitizing dyes, 1, 2 and 3. To 1 kg of the so prepared red-sensitive silver iodobromide emulsion (0.5 mol Ag), 400 ml of a dispersion of coupler 1 (for the procedure of its preparation, see below) and 10 ml of a methanol solution of 0.1% restrainer 1 were added and the resulting coating solution was applied to give a silver deposit of 0.5 g/m².

Preparation of dispersion of coupler 1

Fifty grams of coupler 1 was dissolved in 10 ml of dibutyl phthalate and 150 ml of ethyl acetate and the resulting solution was mixed with 600 ml of an aqueous solution of 5% gelatin and 100 ml of an aqueous solution of 5% surfactant 1, followed by emulsification and dispersion.

Fourth layer: Moderate red-sensitive emulsion layer

A red-sensitive silver iodobromide emulsion was prepared by the same method as used to prepare the emulsion incorporated in the third layer, except that the silver iodide content was 3 mol% and that the average grain size was $0.5\mu\text{m}$. To 1 kg of the so prepared red-sensitive silver iodobromide emulsion (0.5 mol Ag), 600 ml of a dispersion of coupler 1 was added and the resulting coating solution was applied to give a silver deposit of 0.4 g/m^2 .

Fifth layer: Highly red-sensitive emulsion layer

A red-sensitive silver iodobromide emulsion was prepared by the same method as used to prepare the emulsion incorporated in the third layer, except that the silver iodide content was 3 mol% and that the average grain size was $0.7\mu\text{m}$. To 1 kg of the so prepared red-sensitive silver iodobromide emulsion (0.5 mol Ag), 900 ml of a dispersion of coupler 1 was added and the resulting coating solution was applied to give a silver deposit of 0.4 g/m^2 .

Sixth layer: Intermediate layer

Same as the second layer.

Seventh layer: Less green-sensitive emulsion layer

A monodispersed emulsion having a silver iodide content of 4 mol%, an average grain size of $0.3\mu\text{m}$ and a core-shell structure in which the grain surface had a lower iodine content than the interior was sensitized with sensitizing dyes 4 and 5. To 1 kg of the so prepared red-sensitive silver iodobromide emulsion (0.5 mol Ag), 400 ml of a dispersion of coupler 2 (for the procedure of its preparation, see below), 30 ml of a methanol solution of 0.1% restrainer 2, and 100 ml of a methanol solution of 1% hardener 2 were added and the resulting coating solution was applied to give a silver deposit of 0.5 g/m^2 .

Preparation of dispersion of coupler 2

Fifty grams of coupler 2 was dissolved in 10 g of tricresyl phosphate and 150 ml of ethyl acetate and the resulting solution was mixed with 600 ml of an aqueous solution of 5% gelatin and 100 ml of an aqueous solution of 5% surfactant 1, followed by emulsification and dispersion.

Eighth layer: Moderate green-sensitive emulsion layer

A green-sensitive silver iodobromide emulsion was prepared by the same method as used to prepare the emulsion incorporated in the seventh layer, except that the silver iodide content was 3 mol% and that the average grain size was $0.5\mu\text{m}$. To 1 kg of the so prepared green-sensitive silver iodobromide emulsion (0.5 ml Ag), 600 ml of a dispersion of coupler 2 was added and the resulting coating solution was applied to give a silver deposit of 0.5 g/m^2 .

Ninth layer: Highly green-sensitive emulsion layer

5 A green-sensitive silver iodobromide emulsion was prepared by the same method as used to prepare the emulsion incorporated in the seventh layer, except that the silver iodide content was 3 mol% and that the average grain size was 0.7 μ m. To 1 kg of the so prepared green-sensitive silver iodobromide emulsion (0.5 mol Ag), 900 ml of a dispersion of coupler 2 was added and the resulting coating solution was applied to give a silver deposit of 0.5 g/m².

10 Tenth layer: Intermediate layer

Same as the second layer.

15 Eleventh layer: Yellow filter layer

Same as the second layer except that yellow colloidal silver was incorporated in such an amount as to give silver deposit of 0.1 g/m².

20

Twelfth layer: Less blue-sensitive emulsion layer

25 A monodispersed emulsion having a silver iodide content of 3 mol%, an average grain size of 0.6 μ m and a core-shell structure in which the grain surface had a lower iodine content than the interior was sensitized with a sensitizing dye 6. To 1 kg of the so prepared blue-sensitive silver iodobromide emulsion (0.5 mol Ag), 1,300ml of a dispersion of coupler 3 (for the procedure of its preparation, see below), 30 ml of a methanol solution of 0.1% restrainer 3 and 300 ml of an aqueous solution of 5% hardener 3 were added and the resulting coating solution was applied to give a silver deposit of 0.6 g/m².

30

Preparation of dispersion of coupler 3

35 Eighty grams of coupler 3 was dissolved in 20 g of tricresyl phosphate and 250 ml of ethyl acetate and the resulting solution was mixed with 800 ml of an aqueous solution of 5% gelatin and 150 ml of an aqueous solution of 5% surfactant 1, followed by emulsification and dispersion.

Thirteenth layer: Moderate blue-sensitive emulsion layer

40 A blue-sensitive silver iodobromide emulsion was prepared by the same method as used to prepare the emulsion incorporated in the twelfth layer, except that the silver iodide content was 3 mol% and that the average grain size was 0.7 μ m. To 1 kg of the so prepared blue-sensitive silver iodobromide emulsion (0.5 mol Ag), 1,300ml of a dispersion of coupler 3 and 300 ml of an aqueous solution of 5% hardener 3 were added and the resulting coating solution was applied to give a silver deposit of 0.3 g/m².

45

Fourteenth layer: Highly blue-sensitive emulsion layer

50 A blue-sensitive silver iodobromide emulsion was prepared by the same method as used to prepare the emulsion incorporated in the twelfth layer, except that the silver iodide content was 3 mol% and that the average grain size was 0.8 μ m. To 1 kg of the so prepared blue-sensitive silver iodobromide emulsion (0.5 mol Ag), 1,300 ml of a dispersion of coupler 3 and 300 ml of an aqueous solution of 5% hardener 3 were added and the resulting coating solution was applied to give a silver deposit of 0.3 g/m².

55

Fifteenth layer: UV absorbing layer

Four grams of UV absorber 1, 6 g of UV absorber 2, and 3 g of 2,5-di-t-octylhydroquinone were dissolved in a mixture of dioctyl phthalate (5 ml), tricresyl phosphate (5 ml) and ethyl acetate (10 ml). To the resulting solution, 300 ml of an aqueous solution of 5% gelatin and 20 ml of an aqueous solution of 5% surfactant 1 were added, followed by emulsification and dispersion. To the dispersion, 500 ml of an aqueous solution of 5% gelatin and 100 ml of an aqueous solution of 5% hardener 3 were added. The resulting fluid was coated to give a 2,5-di-t-hydroquinone deposit of 0.1 g/m².

10

Sixteenth layer: Protective layer

To a substantially non-light-sensitive, fine-grained silver halide emulsion (AgI/Br emulsion with an average grain size of 0.06 μ m and AgI content of 1 mol%), an inorganic matting agent, an alkali-soluble organic matting agent, and surfactant 2 were added to prepare a coating solution which was applied to give a silver deposit of 0.5 g/m².

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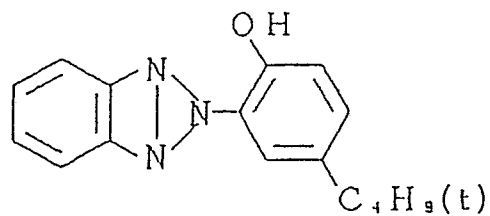
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UV absorber 1

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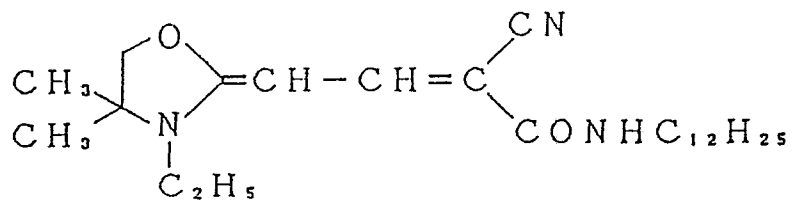
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UV absorber 2

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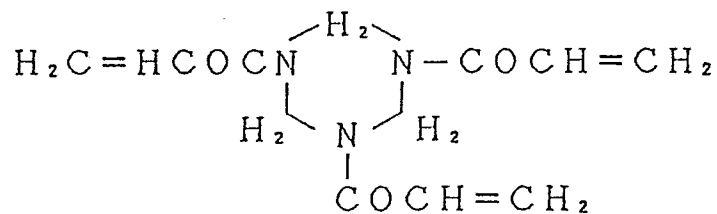
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Hardener 1

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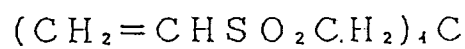


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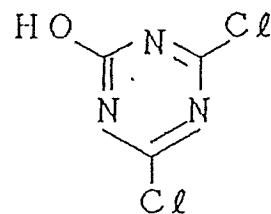
Hardener 2

Hardener 3

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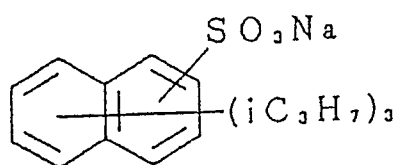
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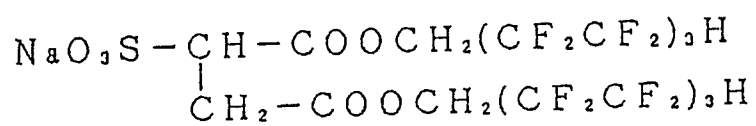
Surfactant 1

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Surfactant 2

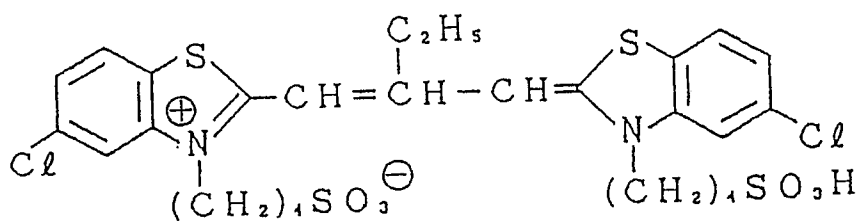


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Sensitizing dye 1

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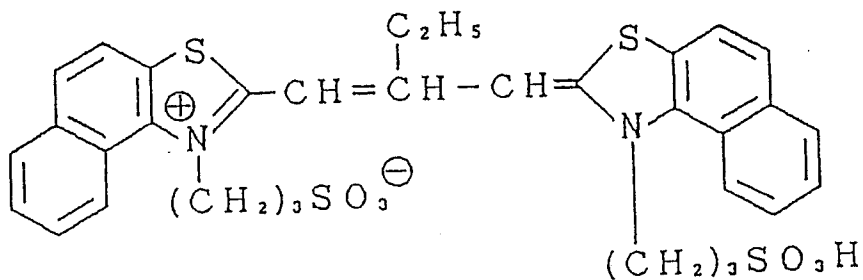
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Sensitizing dye 2

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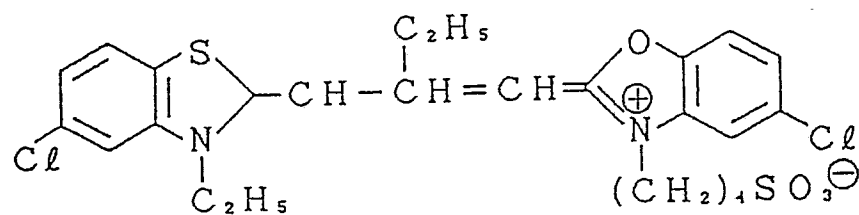
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Sensitizing dye 3

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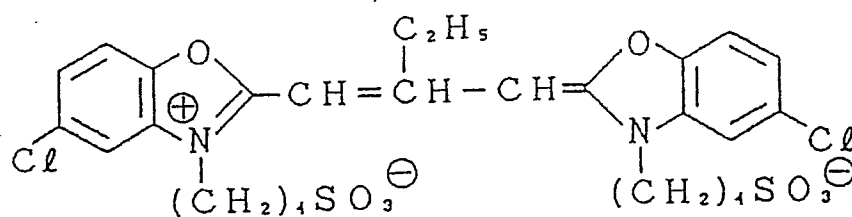
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Sensitizing dye 4

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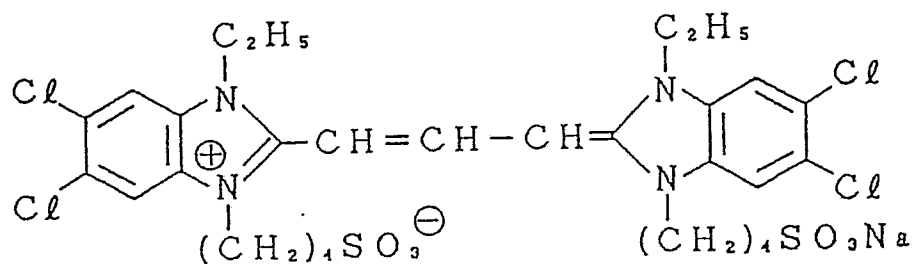


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Sensitizing dye 5

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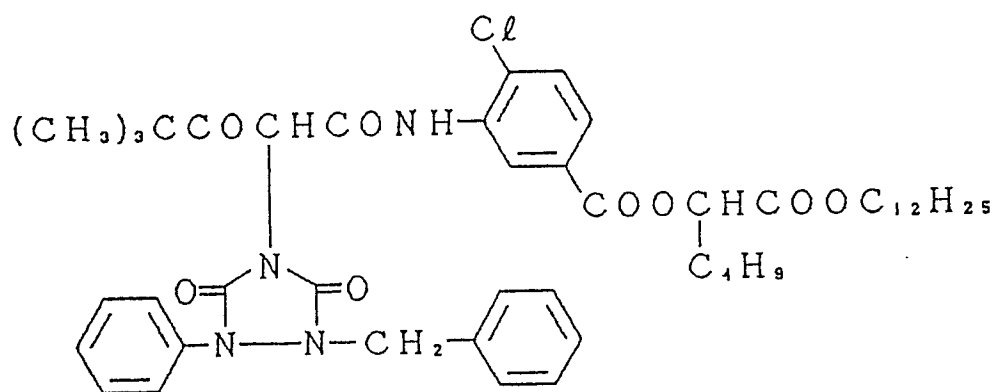
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Coupler 3

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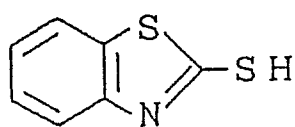
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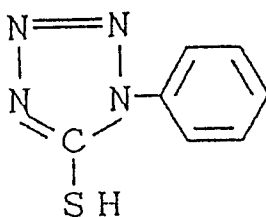
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Restrainer 1

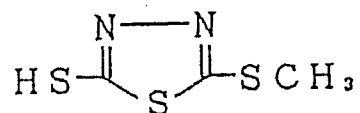
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Restrainer 2



Restrainer 3

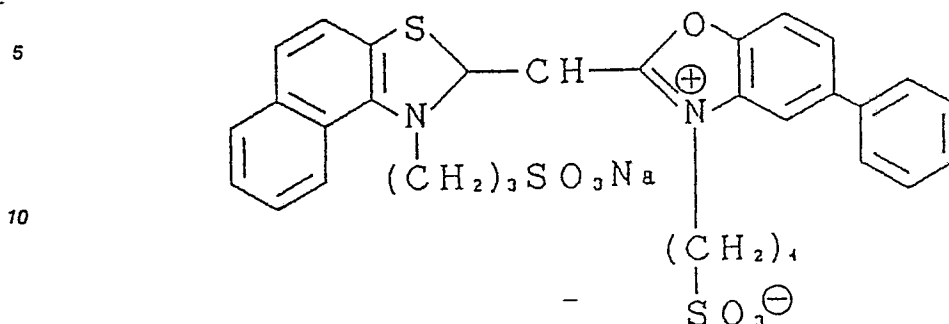


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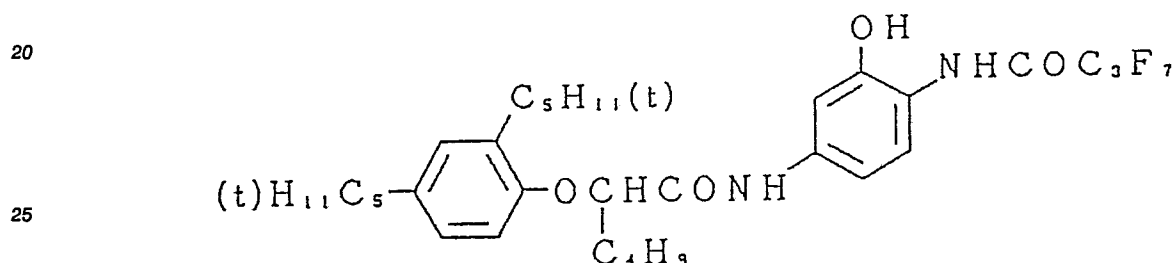
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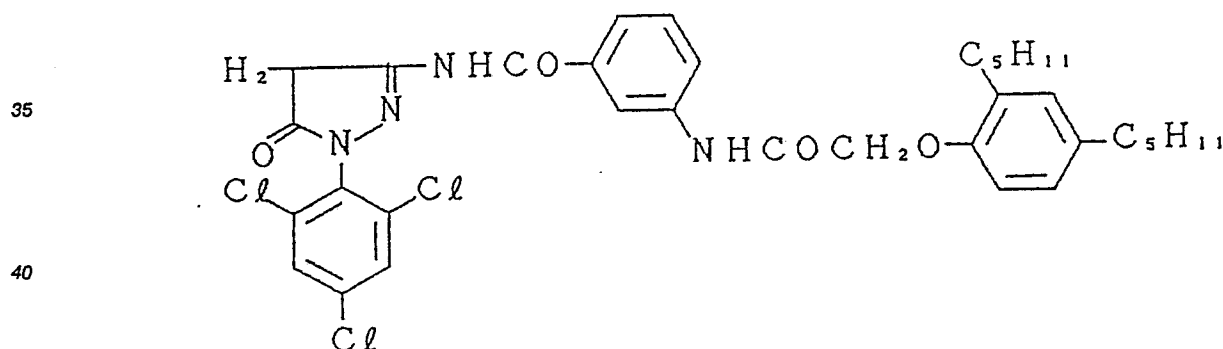
Sensitizing dye 6



Coupler 1



Coupler 2



45 Sample Nos. 8 to 22 of multilayer coated film were prepared as described above except that coupler 2 used in layers 7, 8 and 9 was replaced by equimolar amounts of the couplers listed in Table 1. Sample Nos. 2 - 7 and 10 - 22 were also prepared as above except that the fine grained silver halide emulsion incorporated in layer 16 was replaced by a surface-fogged emulsion or a subsurfacefogged emulsion was incorporated in the layers noted in Table 1 in the amounts also indicated in Table 1: the surface-fogged emulsion was prepared by chemically fogging said fine-grained silver halide emulsion with diacidic thiourea and a gold complex salt at pH 6.5, pAg 6.6 and at 40°C; the subsurface-fogged emulsion was prepared by coating the surface of the grains in said surface-fogged emulsion with a silver bromide shell 100 Å thick.

50 The color reproducing qualities of these samples were evaluated by the following procedure: pictures were taken of blue, green and red color charts and subjected to a color reversal processing by the schedule shown below and the color reproduced were compared with those on the original color charts to determine the values of color difference, ΔE_{ab}^* , according to the CIE 1976 (L^* , a^* , b^*) color system. The results are summarized in Table 1; the smaller the values of ΔE_{ab}^* , the more faithful the color reproduction was.

In order to evaluate the keeping quality during storage prior to processing, each of the samples was caused to deteriorate by exposure to 50°C × 60% RH for 14 days and thereafter subjected to imagewise exposure and the necessary steps of color reversal processing (see below for the processing schedule). The results are also shown in Table 1 in terms of ΔS , or the difference in sensitivity at density 1.0 between the accelerated samples and those which were not accelerated.

Further, with respect to Samples 12, 16, 17, 18, 19 and 20, the RMS granularity was evaluated. This RMS granularity was shown with relative values with the value of Sample 12 as a reference (100), with the standard deviation value taken from the average value of the variations of density measured by scanning the density 1.0 area with microdensitometer with a scanning area 250 μm^2 .

Processing schedule

	<u>Steps</u>	<u>Time (min)</u>	<u>Temperature (°C)</u>
15	First development	6	38 (± 0.3)
	Washing	2	38 (± 0.3)
20	Reversal	2	38 (± 0.3)
	Color development	6	38 (± 0.3)
	Conditioning	2	38 (± 0.3)
25	Bleaching	6	38 (± 0.3)
	Fixing	4	38 (± 0.3)
30	Washing	4	38 (± 0.3)
	Stabilizing	1	RT
35	Drying		

First development

40 Water 700 ml
 Sodium tetrapolyphosphate 2 g
 Sodium sulfite 20 g

First development

45
 Hydroquinone monosulfonate 30g
 Sodium carbonate (monohydrate) 30g
 50 1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone 2g
 Potassium bromide 2.5g
 Potassium thiocyanate 1.2g
 Potassium iodide (0.1% aq. sol.) 2ml
 Water to make 1,000ml

Reversal

Water 700ml
 Nitrilo-N,N,N,-trimethylene phosphonic acid 6Na salt 3g
 5 Stannous chloride (dihydrate) 1g
 p-Aminophenol 0.1g
 Sodium hydroxide 8g
 Glacial acetic acid 15ml
 Water to make 1,000ml
 10

Color development

15 Water 700ml
 Sodium tetrapolyphosphate 2g
 Sodium sulfite 7g
 Sodium tertiary phosphate (dihydrate) 36g
 Potassium bromide 1g
 20 Potassium iodide (0.1% aq. sol.) 90ml
 Sodium hydroxide 3g

25 Color development

Citrazinic acid 1.5g
 N-Ethyl-N-(ss-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate 11g
 Ethylenediamine 3g
 30 Water to make 1,000 ml

Conditioning

35 Water 700ml
 Sodium sulfite 12g
 Ethylenediaminetetraacetic acid sodium salt (dihydrate) 8g
 Thioglycerin 0.4ml
 40 Glacial acetic acid 3ml
 Water to make 1,000 ml

45 Bleaching

Water 800ml
 Ethylenediaminetetraacetic acid-sodium salt (dihydrate) 2.0g
 Ethylenediaminetetraacetic acid iron (II) ammonium (dihydrate) 120.0g
 50 Potassium bromide 100.0g
 Water to make 1.0g

55

Fixing

Water 800ml
 Ammonium thiosulfate 80.0g
 5 Sodium sulfite 5.0g
 Sodium bisulfite 5.0g

10 Fixing

Water to make 1.0g

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Stabilizing

Water 800ml
 Formaldehyde (37 wt% aq. sol.) 5.0ml
 20 Surfactant solution (Drywell®) 5.0ml
 Water to make 1,000ml

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Table 1

Sample No.	Coupler	Fogged emulsion		ΔE_{ab}^*			Storage stability ΔS	R M S Granularity	Remarks
		Fogged area	Description of layer in which fogged emulsion was added	Dose mg/m ²	blue	green	red		
1	coupler-2	-	-	-	20	25	23	-	Outside the scope of the invention
2	coupler-2	surface	7	60	20	25	22	-	do.
3	coupler-2	do.	7, 8, 9	each 30	19	25	20	-	do.
4	coupler-2	do.	7, 8, 9	each 60	17	24	16	-	do.
5	coupler-2	subsurface	7	60	20	25	22	-	do.
6	coupler-2	do.	7, 8, 9	each 30	19	25	20	-	do.
7	coupler-2	do.	7, 8, 9	each 60	17	24	17	-	do.
8	compound 1	-	-	-	15	20	16	-	do.
9	compound 22	-	-	-	14	20	16	-	do.
10	compound 1	surface	7	60	15	20	15	-	do.
11	compound 1	do.	7, 8, 9	each 30	14	20	13	-	do.
12	compound 1	do.	7, 8, 9	each 60	12	19	9	100	do.
13	compound 1	subsurface	7	60	15	20	15	-	do.
14	compound 1	do.	7, 8, 9	each 30	14	20	13	-	do.
15	compound 1	do.	7, 8, 9	each 60	12	19	10	-	do.
16	compound 22	surface	7, 8, 9	each 60	11	19	10	105	do.
17	compound 66	do.	7, 8, 9	each 60	12	20	11	110	do.
18	compound 82	do.	7, 8, 9	each 60	12	20	11	70	do.
19	compound 133	do.	7, 8, 9	each 60	10	19	9	65	do.
20	compound 178	do.	7, 8, 9	each 60	10	19	9	120	do.
21	compound 22	do.	3,4,5,7,8,9	each 60	8	12	9	-	do.
22	compound 133	do.	3,4,5,7,8,9	each 60	7	11	9	-	do.

As is clear from the data shown in Table 1, sample No. 1 containing neither the coupler nor the fogged emulsion specified by the present invention did not provide good color reproduction as manifested by large values of ΔE_{ab} for blue, green and red colors. This sample was also poor in keeping quality for storage before processing (its ΔS was great).

Sample Nos. 2 - 7 containing fogged emulsions in a magenta coupler that was outside the scope of the present invention had slightly better values of ΔE for red and blue colors and lower values of a ΔS than sample No. 1 because of the presence of fogged emulsions. But the improvements were still unsatisfactory and the reduction in ΔE for green color was either zero or negligible.

Sample Nos. 8 and 9 in which magenta couplers that were within the scope of the present invention were used in the absence of any fogged emulsion were much more improved in ΔE compared to sample Nos. 1 and 2 - 7 but the improvements were still unsatisfactory. Furthermore, these samples did not have any good keeping quality. Sample Nos. 10 - 20 in which magenta couplers and fogged emulsions within the scope of the present invention were employed in combination attained good color reproduction as manifested by small values of ΔE for all of the blue, green and red colors. In addition, these samples had good keeping qualities. Further improvements in color reproduction (especially of green color) were attained by sample Nos. 21 and 22 in which the fogged emulsions used in sample Nos. 14 - 20 were incorporated not only in the green-sensitive emulsion layers but also in the red-sensitive layers.

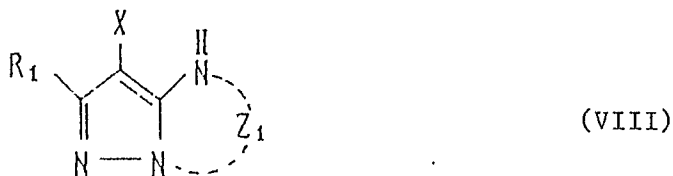
Claims

1. A silver halide color photographic material that has one or more silver halide emulsion layers on a support, at least one of said silver halide emulsion layers containing a compound of following formula (I) and silver halide grains having fog centers on their surface or subsurface:



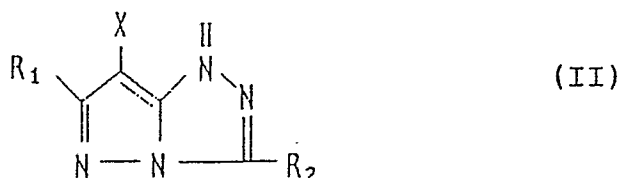
where Z represents a group of the non-metallic atoms necessary for forming a nitrogen-containing heterocyclic ring, provided that the ring formed by Z may have a substituent; X represents a hydrogen atom or a substituent capable of being eliminated upon reaction with the oxidation product of a color developing agent; and R represents hydrogen atom or a substituent.

2. A silver halide color photographic material according to Claim 1, wherein said compound of formula (I) is a compound of the following formula (VIII):



where Z₁ represents a group of the non-metallic atoms necessary for forming a nitrogen-containing heterocyclic ring, provided that the ring formed by Z₁ may have a substituent; X represents a hydrogen atom or a substituent capable of being eliminated upon reaction with the oxidation product of a color developing agent; and R₁ represents a hydrogen atom or a substituent.

3. A silver halide color photographic material according to Claim 2, wherein said compound of formula (I) is a compound of the following formula (II):



where X represents a hydrogen atom or a substituent capable of being eliminated upon reaction with the oxidation product of color developing agent; and R₁ and R₂ each represents a hydrogen atom or a substituent.

4. A silver halide color photographic material according to Claim 1, wherein said silver halide emulsion layer contains said compound of formula (I) in an amount of 1×10^{-5} to 1×10^{-1} mole per mole of silver halide.

5. A silver halide color photographic material according to Claim 1, wherein said silver halide grains are such that, when a photographic sample coated with said silver halide emulsion layer containing said grains for a silver deposit of 0.5 g/m² is developed at 38°C for 6 minutes with a developer having the formulation indicated below, at least 60% of the coated silver is developed.

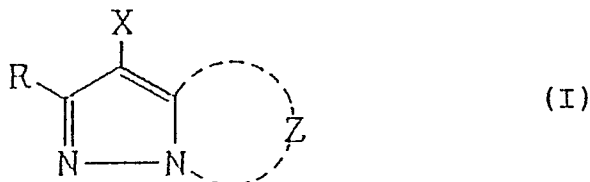
Formulation of developer

Water 700 ml
Sodium tetrapolyphosphate 2 g
sodium sulfite 20 g
Hydroquinone monosulfonate 30 g
Sodium carbonate (monohydrate) 30 g
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone 2 g
Potassium bromide 2.5 g
Potassium thiocyanate 1.2 g
Potassium iodide (0.1% aq. sol.) 2 ml
Water to make 1,000 ml

6. A silver halide color photographic material according to Claim 1, wherein said silver halide grains having fog centers on their surface or subsurface are chemically fogged.

7. A silver halide color photographic material according to Claim 1, wherein said silver halide emulsion layer contains said silver halide grains in an amount of 0.05 to 50 wt% with respect to the total amount of silver in said emulsion layer.

8. A method of processing an imagewise exposed silver halide color photographic material by the steps including, in sequence, at least black and white development, fogging, color forming development, bleaching and fixing, said silver halide color photographic material having one or more silver halide emulsion layers on a support, at least one of said silver halide emulsion layers containing a compound of the following formula (I) and silver halide grains having fog centers on their surface or subsurface:



where Z represents a group of the non-metallic atoms necessary for forming a nitrogen-containing heterocyclic ring, provided that the ring formed by Z may have a substituent; X represents a hydrogen atom or a substituent capable of being eliminated upon reaction with the oxidation product of a color developing agent; and R represents a hydrogen atom or a substituent.