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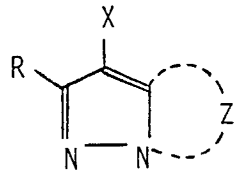
(54)
Direct positive silver halide light-sensitive photographic material.

(57) The material comprises a support and a silver halide emulsion layer thereon containing direct positive silver halide grains adapted to form an internal latent image upon imagewise exposure and being unpre-fogged, and a compound represented by general formula [I],

[I]



wherein Z represents a group of non-metallic atoms necessary to complete a nitrogen-containing heterocyclic ring which may have a substituent; X represents a hydrogen atom or a substituent capable of being split off upon reaction with an oxidation product of a color developing agent; and R represents a hydrogen atom or a substituent. The emulsion has a maximum density which is sufficiently large and a minimum density which is sufficiently small. The foot portion of the density/exposure curve can exhibit high contrast while the highlight portion shows little or no tendency towards magenta color.

DIRECT POSITIVE SILVER HALIDE LIGHT-SENSITIVE PHOTOGRAPHIC MATERIAL

This application claims the priority of Japanese Application 217,690/86, filed September 16, 1986.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a direct positive silver halide light-sensitive photographic material, and more particularly to a light-sensitive photographic material having an internal latent image-type silver halide emulsion layer which, after being imagewise exposed, is subjected to fogging treatment (such as an overall exposure or surface development treatment in the presence of a fogging agent), whereby a direct positive image can be obtained.

Description of the Prior Art

Those conventionally known direct positive image-obtaining methods are broadly divided into two types. One type uses a silver halide emulsion provided with fogging nuclei. The emulsion is imagewise exposed to destroy the fogging nuclei or latent image in the exposed area by utilizing the solarization or Herschel effect. It is then developed, thereby giving a positive image. The other type uses an unprefogged internal latent image-type silver halide emulsion which, after being imagewise exposed, is subjected to fogging treatment (developing nuclei forming treatment) and then to surface development or which, after being imagewise exposed, is subjected to surface development while being subjected to fogging treatment (developing nuclei forming treatment), thereby giving a positive image.

Of the foregoing methods for the formation of a positive image, the latter tends generally to give a higher sensitivity than the former, so that the latter is suitable for uses which require high sensitivity.

The above-mentioned fogging treatment (developing nuclei-forming treatment) may be carried out by an overall exposure, by using a chemical fogging agent, by using a high-energy developer solution, or by thermal treatment.

In this technological field, various techniques have been known to date. For example, there are conversion-type, core/shell-type or stratified-type silver halide emulsions as disclosed in U.S. Patent No. 2,592,250, Japanese Patent Examined Publication Nos. 34213/1977, 1412/1983 and 1415/1983. Also, as the grain-growing agent to be used therefor, suitable thioethers, imidazoles and the like are described in U.S. Patent No. 3,574,626, and Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 100717/1979.

On the other hand, in the color image forming process wherein an ordinary silver halide color photographic light-sensitive material is used, an oxidized p-phenylenediamine color developing agent is reacted with dye image-forming couplers to form a color image. To this method, generally, a color reproduction according to the subtractive color process is applied wherein a dye image is formed which is composed of cyan, magenta and yellow dyes corresponding to red, green and blue colors, respectively. Also, in a direct positive silver halide color photographic material, a color image may be formed in similar manner. However, where a direct positive emulsion is used, since its development is performed along with its fogging treatment, the treatment generally tends to lower its sensitivity as well as increase its minimum density. Particularly where a magenta color image-forming coupler is used, there is a tendency for the gradation at the foot portion of the density/exposure curve to become less dense (softening), and to lose its gradational balance with other layers, and thereby turn the color of the highlight portion pinkish. For example, Japanese Patent Examined Publication No. 12709/1970 discloses a method of incorporating a heterocyclic thione compound into the emulsion, and U.S. Patent No. 2,497,917 discloses a method of using an N-heterocyclic compound such as 5-methyl-benzoyl to correct this imbalance. In addition, Japanese Patent Examined Publication No. 9939/1983 discloses a method of using, for example, a specific magenta coupler and a mercapto compound. None of these methods, however, are effective to prevent the highlight portion from turning pinkish.

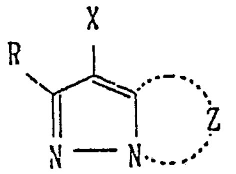
In the direct positive silver halide light-sensitive photographic material, removal of silver from the light-sensitive material is performed by bleaching and fixation processes or a bleach-fix process after development. If a fixing solution or bleach-fixing solution containing a silver halide solvent was mixed by mistake into the color developer solution in this process, softening of the magenta image gradation and increase in the minimum density thereof would occur. Accordingly, it is necessary to take measures to cope with the above-mentioned adverse effect upon the image in processing. Particularly, the above-mentioned softening of the gradation and increase in the minimum density appear conspicuously in the case in which unprefogged internal latent image-type silver halide grains for magenta image formation contain silver chloride. Thus, this matter is a great problem especially in making the effective use of the aptitude of silver chloride-containing emulsions for rapid machine processing.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide a direct positive silver halide light-sensitive photographic material comprising an internal latent image-type silver halide emulsion whose maximum density is sufficiently large and whose minimum density is sufficiently small. It is also an object of this invention to provide such photographic material wherein the foot portion of the density/exposure curve exhibits high contrast, and the highlight portion shows little or no tendency toward magenta color.

Also, even if fixing or bleach-fixing solution is mixed by mistake into the color developer solution, the material will show no substantial soft gradation or increase in minimum density, and will not be affected by fogging treatment, thereby providing excellent reliability in the processing thereof.

The above objects of the present invention are accomplished by the use of a direct positive silver halide light-sensitive photographic material comprising a support and a silver halide emulsion layer containing direct positive image-forming-type silver halide grains adapted to form an internal latent image upon imagewise exposure and without prefogging on the surface thereof, and a compound represented by Formula [1],



wherein Z represents a group of non-metallic atoms necessary to complete a nitrogen-containing heterocyclic ring which may have a substituent; X represents a hydrogen atom or a substituent capable of being split off upon reaction with an oxidation product of a color developing agent; and R represents a hydrogen atom or a substituent.

The substituent represented by the R is, for example, a halogen atom, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl, heterocyclic, acyl, sulfonyl, sulfinyl, phosphonyl, carbamoyl, sulfamoyl, cyano, spiro compound residue, cross-linked hydrocarbon compound residue, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, carbamoyloxy, amino, acylamino, sulfonamido, imido, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl, alkylthio, arylthio, or heterocyclic thio.

Out of these substituents the alkyl, alkenyl, alkynyl, cycloalkyl and cycloalkenyl groups each may have a further substituent. Typical substituents are an aryl group, cyano group, halogen atom, heterocyclic group, cycloalkyl group, cycloalkenyl group, spiro compound residue, cross-linked hydrocarbon compound residue, or a group substituting through a carbonyl group, such as acyl, carboxy, carbamoyl, alkoxycarbonyl or aryloxycarbonyl, or a group substituting through a hetero atom. Typical such groups (when the hetero atom is oxygen) are hydroxy, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy or carbamoyloxy group. When the hetero atom is nitrogen, nitro, amino (including dialkylamino, etc.), sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, acylamino, sulfonamido, imido, or ureido group are typically suitable. When the hetero atom is sulfur, alkylthio, arylthio, heterocyclic thio, sulfonyl, sulfinyl, or sulfamoyl group may be used, and when the hetero atom is phosphorus, a phosphonyl group is among the useful radicals of suitable groups.

Examples include methyl, ethyl, isopropyl, t-butyl, pentadecyl, heptadecyl, 1-hexylnonyl, 1,1′-dipentylnonyl, 2-chloro-t-butyl, trifluoromethyl, 1-ethoxytridecyl, 1-methoxyisopropyl, methanesulfonylethyl, 2,4-di-t-amylphenoxymethyl, anilino, 1-phenylisopropyl, 3-m-butanesulfonaminophenoxypropyl, 3-4′-{α-[4″(p-hydroxybenzenesulfonyl)phenoxy]dodecanoylamino}phenylpropyl, 3-{ 4′-[α-(2″,4″-di-t-amylphenoxy)butaneamido]-phenyl} propyl, 4-[α-(o-chlorophenoxy)tetradecaneamidophenoxy]propyl, allyl, cyclopentyl, cyclohexyl, and the like.

The preferred aryl group represented by R is phenyl, which may have a substituent such as alkyl, alkoxy, acylamino or the like. Examples of the aryl group include phenyl, 4-t-butylphenyl, 2,4-di-t-amylphenyl, 4-tetradecaneamidophenyl, hexadecyloxyphenyl, 4′-[α-(4″-t-butylphenoxy)tetradecaneamido]-phenyl, and the like.

The preferred heterocyclic group represented by R has 5 to 7 members, may have a substituent, or which may also be condensed. Examples of the group include 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl, and the like.

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

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

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

Examples of the phosphonyl group represented by R include alkylphosphonyl groups such as butylphosphonyl; alkoxyphosphonyl groups such as octyloxyphosphonyl; aryloxy phosphonyl groups such as phenoxyphosphonyl; arylphosphonyl groups such as phenylphosphonyl; and the like.

The carbamoyl group represented by R may have a substituent such as alkyl, aryl (preferably phenyl) or the like, and examples of the carbamoyl group include N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-pentadecyloctylethyl)carbamoyl, N-ethyl-N-dodecylcarbamoyl, N-[3-(2,4-di-t-amylphenoxy)propyl]carbamoyl, and the like.

The sulfamoyl group represented by R may have a substituent such as alkyl, aryl (preferably phenyl) or the like, and examples of the sulfamoyl group include N-propylsulfamoyl, N,N-diethylsulfamoyl, N-(2-pentadecyloxyethyl)sulfamoyl, N-ethyl-N-dodecylsulfamoyl, N-phenylsulfamoyl, and the like.

Examples of the spiro compound residue represented by R include spiro [3.3]heptane-1-yl and the like.

Examples of the cross-linked hydrocarbon compound residue represented by R include bicyclo[2.2.1]-heptane-1-yl, tricyclo[3.3.1.$1^{3,7}$]decane-yl, 7,7-dimethylbicyclo[2.2.1]heptane-1-yl, and the like.

The alkoxy group represented by R may have a further substituent such as one of those previously defined as a substituent for the foregoing alkyl group represented by R. Examples of the alkoxy group include methoxy, propoxy, 2-ethoxyethoxy, pentadecyloxy, 2-dodecyloxyethoxy, phenethyloxyethoxy, and the like.

The aryloxy group represented by R is preferably phenyl, and the nucleus may be substituted by one of those defined as the substituent or atom to the aryl group represented by R. Examples of the aryloxy group include phenoxy, p-t-butylphenoxy, m-pentadecylphenoxy, and the like.

The heterocyclic oxy group represented by R preferably has a 5 to 7-member heterocyclic ring, and the heterocyclic ring may have a further substituent. Examples of the heterocyclic oxy group include 3,4,5,6-tetrahydropyranyl-2-oxy, 1-phenyltetrazole-5-oxy, and the like.

The siloxy group represented by R may be further substituted by an alkyl group or the like, and examples of the siloxy group include trimethylsiloxy, triethylsiloxy, dimethylbutylsiloxy, and the like.

The acyloxy group represented by R is, for example, alkylcarbonyloxy, arylcarbonyloxy, or the like, which may have a further substituent. Examples of the acyloxy group include acetyloxy, α-chloroacetyloxy, benzoyloxy, and the like.

The carbamoyloxy group represented by R may be substituted by an alkyl or aryl group, and examples thereof include N-ethylcarbamoyloxy, N,N-diethylcarbamoyloxy, N-phenylcarbamoyloxy, and the like.

The amino group represented by R may be substituted by alkyl or aryl (preferably phenyl) group, and examples thereof include ethylamino, anilino, m-chloroanilino, 3-pentadecyloxycarbonylanilino, 2-chloro-5-hexadecaneamidoanilino, and the like.

The acylamino group represented by R is alkylcarbonylamino, arylcarbonylamino (preferably phenylcarbonylamino) of the like, which may have a further substituent. Examples of the acylamino group include acetamido, α-ethylpropaneamido, N-phenylacetamido, dodecaneamido, 2,4-di-t-amylphenoxyacetamido, α-3-t-butyl-4-hydroxyphenoxybutaneamido, and the like.

The sulfonamido group represented by R is alkylsulfonylamino, arylsulfonylamino or the like, which may have a further substituent. Examples of the sulfonamido group include methylsulfonylamino, pentadecylsulfonylamino, benzenesulfonamido, p-toluenesulfonamido, 2-methoxy-5-t-amylbenzenesulfonamido, and the like.

The imido group represented by R may be either in the open-chain form or in the cyclic form, and may have a further substituent. Examples of the imido group include succinic acid imido, 3-heptadecyl-succinic acid imido, phthalimido, glutarimido, and the like.

The ureido group represented by R may be substituted by alkyl or aryl (preferably phenyl), and examples of the ureido group include N-ethylureido, N-methyl-N-decylureido, N-phenylureido, N-p-tolylureido, and the like.

The sulfamoylamino group represented by R may be substituted by alkyl or aryl (preferably phenyl), and examples of the sulfamoylamino group include N,N-dibutylsulfamoylamino, N-methylsulfamoylamino, N-phenylsulfamoylamino, and the like.

The alkoxycarbonylamino group represented by R may have a further substituent, and examples of the group include methoxycarbonylamino, methoxyethoxycarbonylamino, octadecyloxycarbonylamino, and the like.

The aryloxycarbonylamino group represented by R may have a further substituent, and examples of the group include phenoxycarbonylamino, 4-methylphenoxycarbonylamino, and the like.

The alkoxycarbonyl group represented by R may have a further substituent, and examples of the group include methoxycarbonyl, butyloxycarbonyl, dodecyloxycarbonyl, octadecyloxycarbonyl, ethoxymethoxycarbonyloxy, benzyloxycarbonyl, and the like.

The aryloxycarbonyl group represented by R may have a further substituent, and examples of the group include phenoxycarbonyl, p-chlorophenoxycarbonyl, m-pentadecyloxyphenoxycarbonyl, and the like.

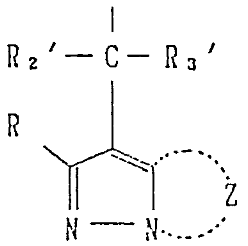
The alkylthio group represented by R may have a further substituent, and examples of the group include ethylthio, dodecylthio, octadecylthio, phenethylthio, 3-phenoxypropylthio, and the like.

The arylthio group represented by R is preferably a phenylthio, which may have a further substituent, and examples of the group include phenylthio, p-methoxyphenylthio, 2-t-octylphenylthio, 3-octadecylphenylthio, 2-carboxyphenylthio, p-acetaminophenylthio, and the like.

The heterocyclic thio group represented by R is preferably one having 5 to 7 members, and may have a further condensed ring and may also have a further substituent. Examples of the group include 2-pyridylthio, 2-benzothiazolylthio, 2,4-diphenoxy-1,3,5-triazolo-6-thio, and the like.

The substituent represented by X which can be split off by the reaction with the oxidized product of a color developing agent is a group substituting through, e.g., a halogen atom (chlorine, bromine, fluorine, etc.), carbon atom, oxygen atom, sulfur atom or nitrogen atom.

Examples of the group substituting through the carbon atom include carboxyl, hydroxymethyl group, triphenylmethyl group, and those groups having the general formula:

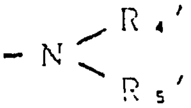


wherein R_2' and R_3' each is hydrogen, aryl, alkyl, or a heterocyclic group.

The group substituting through the above-mentioned oxygen group is alkoxy, aryloxy, heterocyclic oxy, acyloxy, sulfonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, alkyloxalyloxy, or alkoxyoxalyloxy. The foregoing alkoxy group may have a further substituent, and examples of the group include ethoxy, 2-phenoxyethoxy, 2-cyanoethoxy, phenethyloxy,p-chlorobenzyloxy, and the like. The foregoing aryloxy group is preferably phenoxy, and may have a further substituent. Examples of the group include phenoxy, 3-methylphenoxy, 3-dodecylphenoxy, 4-methanesulfonamidophenoxy, 4-[-(3'pentadecylphenoxy)-butaneamido]phenoxy, hexydecylcarbamoylmethoxy, 4-cyanophenoxy, 4-methanesulfonylphenoxy, 1-naphthyloxy, p-methoxyphenoxy, and the like. The foregoing heterocyclic oxy group preferably has 5 to 7 members and may be a condensed ring and also may have a further substituent. Examples of this group include 1-phenyltetrazolyloxy, 2-benzothiazolyl, and the like. Examples of the foregoing acyloxy group include alkylcarbonyloxy groups such as acetoxy, butanoloxy, etc.; alkenylcarbonyloxy groups such as cinnamoyloxy: and arylcarbonyloxy groups such as benzoyloxy. Examples of the foregoing sulfonyloxy group include butanesulfonyloxy, methanesulfonyloxy, and the like. Examples of the foregoing alkoxycarbonyloxy group include ethoxycarbonyloxy, benzyloxycarbonyloxy, and the like. Examples of the foregoing aryloxycarbonyl group include phenoxycarbonyloxy and the like. Examples of the foregoing alkyloxalyloxy group include methyloxalyloxy, and the like. Examples of the foregoing alkoxyoxalyloxy group include ethoxyoxalyloxy, and the like.

The group substituting through the foregoing sulfur atom is, for example, an alkylthio, arylthio, heterocyclic thio or alkyloxythiocarbonylthio. Examples of the foregoing alkylthio group include butylthio, 2-cyanoethylthio, phenethylthio, benzylthio, and the like. Examples of the foregoing arylthio group include phenylthio, 4-methanesulfonamidophenylthio, 4-dodecylphenethylthio, 4-nonafluoropentaneamidophenethylthio, 4-carboxyphenylthio, 2-ethoxy-5-t-butylphenylthio, and the like. Examples of the foregoing heterocyclic thio group include 1-phenyl-1,2,3,4-tetrazolyl-5-thio, 2-benzothiazolylthio, and the like. Examples of the foregoing alkyloxythiocarbonylthio group include dodecyloxythiocarbonylthio, and the like.

The group substituting through the foregoing nitrogen atom is, for example, one having the general formula:



$$-N\begin{cases} R_4' \\ R_5' \end{cases}$$

wherein R_4' and R_5' each is hydrogen, alkyl, aryl, heterocyclic, sulfamoyl, carbamoyl, acyl, sulfonyl, aryloxycarbonyl, or alkoxycarbonyl; provided that R_4' and R_5' may combine with each other to form a heterocyclic ring, but are not both hydrogen atoms at the same time.

The alkyl group represented by R_4' and R_5' may be either straight-chain or branched-chain, and is preferably one having from 1 to 22 carbon atoms. The alkyl group may have a substituent such as aryl, alkoxy, aryloxy, alkylthio, arylthio, alkylamino, arylamino, acylamino, sulfonamido, imino, acyl, alkylsulfonyl, arylsulfonyl, carbamoyl, sulfamoyl, alkoxycarbonyl, aryloxycarbonyl, alkloxycarbonylamino, aryloxycarbonylamino, hydroxyl, carboxyl, cyano or halogen. Examples of the above alkyl group include ethyl, octyl, 2-ethylhexyl, 2-chloroethyl, and the like.

The aryl group represented by R_4' or R_5' has 6 to 32 carbon atoms, and is preferably phenyl or naphthyl. The aryl group may have a substituent such as one represented by R_4' or R_5' or an alkyl group. Examples of the aryl group include phenyl, 1-naphthyl, and 4-methylsulfonylphenyl.

The heterocyclic group represented by R_4' or R_5' has 5 to 6 members, may be a condensed ring, and may also have a substituent. Examples of the group include 2-furyl, 2-quinolyl, 2-pyrimidyl, 2-benzothiazolyl, 2-pyridyl, and the like.

The sulfamoyl group represented by R_4' or R_5' is a N-alkylsulfamoyl, N, N-dialkylsulfamoyl, N-arylsulfamoyl, N,N-diarylsulfamoyl, or the like, and these alkyl and aryl groups each may have one of those substituents as defined in the above-mentioned alkyl and aryl groups represented by R_4' or R_5'. Examples of the sulfamoyl group include N-diethylsulfamoyl, N-methylsulfamoyl, N-dodecylsulfamoyl, and N-p-tolylsulfamoyl.

The carbamoyl group represented by the R_4' or R_5' is N-alkylcarbamoyl, N,N-dialkylcarbamoyl, N-arylcarbamoyl, N,N-diarylcarbamoyl or the like; and these alkyl and aryl groups each may have one of those substituents as defined in the foregoing alkyl and aryl groups represented by R_4' and R_5'. Examples of the carbamoyl group include N,N-diethylcarbamoyl, N-methylcarbamoyl, dodecylcarbamoyl, N-p-cyanophenylcarbamoyl, and N-p-tolylcarbamoyl.

The acyl group represented by R_4' or R_5' is, for example, alkylcarbonyl, arylcarbonyl, or heterocyclic carbonyl, and these alkyl, aryl and heterocyclic groups each may have a substituent. Examples of the acyl group include hexafluorobutanoyl, 2,3,4,5,6-pentafluorobenzoyl, acetyl, benzoyl, naphthoyl, 2-furylcarbonyl, and the like.

The sulfonyl group represented by R_4' or R_5' is alkylsulfonyl, arylsulfonyl or heterocyclic sulfonyl, and may have a substituent. Examples of the group include ethanesulfonyl, benzenesulfonyl, octanesulfonyl, naphthalenesulfonyl, p-chlorobenzenesulfonyl, and the like.

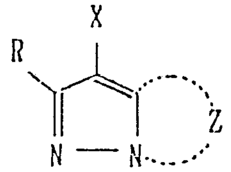
The aryloxycarbonyl group represented by the R_4' or R_5' may have one of those substituents as defined in the above aryl group represented by R_4' and R_5', and is, for example, phenoxycarbonyl, or the like.

The alkoxycarbonyl group represented by R_4' and R_5' may have one of those substituents as defined in the above alkyl group, and examples of the group include methoxycarbonyl, dodecyloxycarbonyl, benzyloxycarbonyl, and the like.

The heterocyclic group formed by the combination of the R_4' and R_5' preferably has 5 to 6 members, which may be either saturated or unsaturated, may or may not be aromatic, and also may be a condensed ring. Examples of the heterocyclic group include N-phthalimido, N-succinic acid imido, 4-N-urazolyl, 1-N-hydantoinyl, 3-N-2,4-dioxooxazolidinyl, 2-N-1,1-dioxo-3-(2H)-oxo-1,2-benzothiazolyl, 1-pyrrolyl, 1-pyrrolidinyl, 1-pyrazolyl, 1-pyrazolidinyl, 1-piperidinyl, 1-pyrrolinyl, 1-imidazolyl, 1-imidazolinyl, 1-indolyl, 1-isoindolinyl, 2-isoindolyl, 2-isoindolinyl, 1-benzotriazolyl, 1-benzimidazolyl, 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, phthaladione, 2-oxo-1-piperidinyl, and the like. These heterocyclic groups each may have a substituent such as an alkyl, aryl, alkyloxy, aryloxy, acyl, sulfonyl, alkylamino, arylamino, acylamino, sulfonamino, carbamoyl, sulfamoyl, alkylthio, arylthio, ureido, alkoxycarbonyl, aryloxycarbonyl, imido, nitro, cyano or carboxyl, or halogen.

The nitrogen-containing heterocyclic ring represented by Z is pyrazole, imidazole, triazole, or tetrazole, and the substituent which the above ring may have includes those as defined in the previously mentioned R.

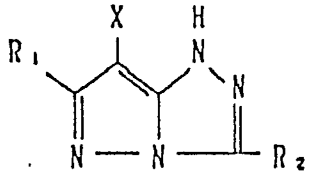
Where the substituents (e.g., R and R_1 through R_8) on the heterocyclic rings of Formula [I] and the hereinafter described Formulas [II] through [VII] have a part having the formula:



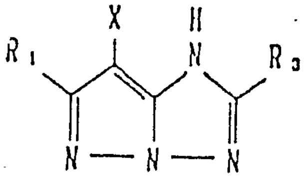
they form bis-type couplers, which are included in the present invention. The rings formed by Z and the hereinafter described Z_1 may each be condensed with another ring, e.g., 5 to 7 member cycloalkene. For example, R_5 and R_6 in Formula [V] and R_7 and R_8 in Formula [VI] may combine with each other to form rings such as 5 to 7 member cycloalkene and benzene, respectively.

Those magenta color image forming couplers having Formula [I] may be more particularly represented by the following general Formulas [II] through [VII]:

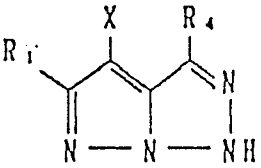
Formula [II]



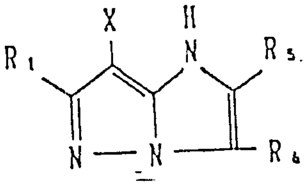
Formula [III]



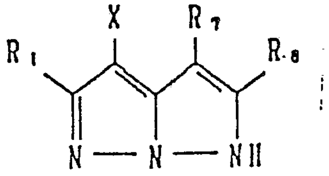
Formula [IV]



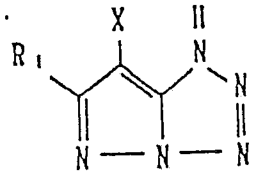
Formula [V]



Formula [VI]

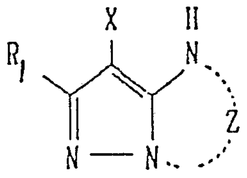


Formula [VII]



The most preferred among those compounds having Formula [I] are ones represented by the following Formula [VIII]:

Formula [VIII]



The particularly preferred magenta color image forming couplers having Formulas [II] through [VII] are represented by Formula [II].

As regards the substituents to the heterocyclic rings of Formulas [I] through [VIII], R and R_1 preferably should satisfy Condition 1, more desirably should satisfy Conditions 1 and 2, and most desirably should satisfy Conditions 1, 2 and 3.

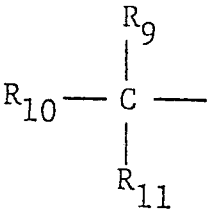
Condition 1: The immediate atom directly bound to the heterocyclic ring is a carbon atom.

Condition 2: Only one hydrogen atom or no hydrogen atom is bonded to the carbon atom.

Condition 3: The bonds between the carbon atoms and the adjacent atoms are all single bonds.

The most preferred as the substituents for R or R_1 on the above heterocyclic ring are:

Formula [IX]



$$R_{10}-\overset{\displaystyle R_9}{\underset{\displaystyle R_{11}}{\overset{|}{\underset{|}{C}}}}-$$

wherein each of R_9, R_{10} and R_{11} is hydrogen, halogen, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl, heterocyclic, acyl, sulfonyl, sulfinyl, phosphonyl, carbamoyl, sulfamoyl, cyano, spiro compound residue, cross-linked hydrocarbon compound residue, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, carbamoyloxy, amino, acylamino, sulfonamido, imido, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl, alkylthio, arylthio or heterocyclic thio; provided that at least two of R_9, R_{10} and R_{11} are not hydrogen at the same time.

Any two of the above R_9, R_{10} and R_{11} (e.g., R_9 and R_{10}), may combine with each other to form a saturated or unsaturated ring (e.g., cycloalkane, cycloalkene or heterocyclic), and further the third (e.g. R_{11}) may combine with this ring to form a cross-linked hydrocarbon compound residue.

Any of the groups represented by R_9 through R_{11} may have a substituent, and specific examples of the groups represented by R_9 through R_{11} and of the substituent which they may have are the same as those examples of the groups represented by R and of the substituents thereon.

Also, examples of the ring formed by the combination of, e.g., R_9 and R_{10}, and of the cross-linked hydrocarbon compound residue formed by R_9 through R_{11}, and of the substituents which they may have, are the same as those examples of the cycloalkyl, cycloalkenyl and heterocyclic cross-linked hydrocarbon compound residue represented by R of the Formula [I] and of the substituents thereon.

The preferred substituents having Formula [IX] are those in which:

(i) two of R_9 through R_{11} are alkyl groups, or

(ii) one of R_9 through R_{11}, e.g., R_{11}, is a hydrogen atom, and the others, e.g. R_9 and R_{10}, are linked to the adjacent carbon atom to form a cycloalkyl.

Particularly preferred among (i) are those groups in which two of R_9 through R_{11} are alkyl and the third is hydrogen or alkyl. The alkyl and the cycloalkyl herein each may have a further substituent. Examples of the alkyl, cycloalkyl and substituent thereto are the same as those examples of the alkyl and cycloalky represented by R of Formula [I] and of the substituents thereon.

The preferred groups as the substituent which may be carried by the rings formed by Z of Formulas [I] and [VIII] and as the R_2 through R_8 of Formulas [II] through [VI] are:

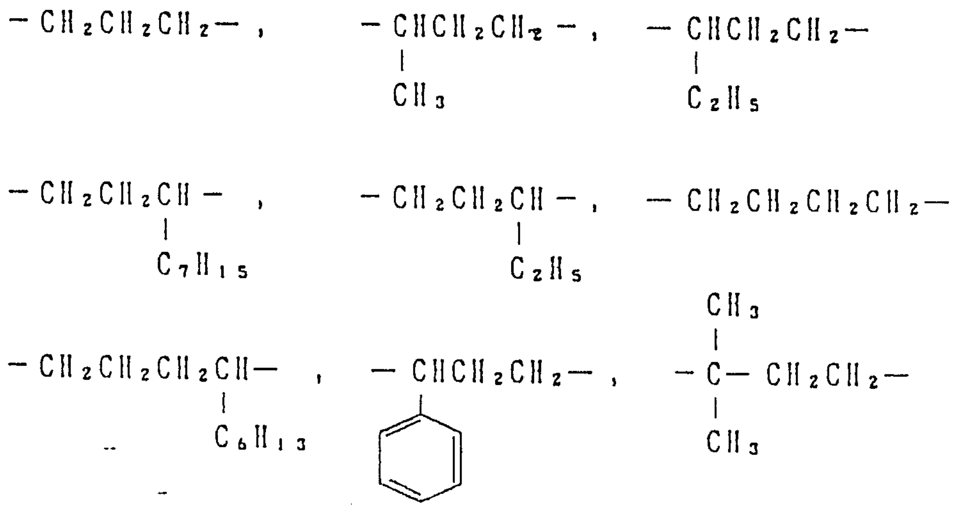
Formula [X]

$-R_{12}-SO_2-R_{13}$

wherein R_{12} is alkylene, and R_{13} is alkyl, cycloalkyl or aryl.

The alkylene represented by R_{12} has a straight chain portion preferably having not less than two carbon atoms, and more preferably from 3 to 6 carbon atoms, and may be in the straight-chain or branched-chain form, and also may have a further substituent. Examples of the substituent are the same as those exemplified for the substituent which may be carried by the alkyl represented by R of Formula [I]. The substituent is preferably a phenyl group.

The preferred examples of the alkylene represented by the R_{12} are as follows:



$-CH_2CH_2CH_2-$, $-\underset{CH_3}{\underset{|}{CH}}CH_2CH_2-$, $-\underset{C_2H_5}{\underset{|}{CH}}CH_2CH_2-$

$-CH_2CH_2\underset{C_7H_{15}}{\underset{|}{CH}}-$, $-CH_2CH_2\underset{C_2H_5}{\underset{|}{CH}}-$, $-CH_2CH_2CH_2CH_2-$

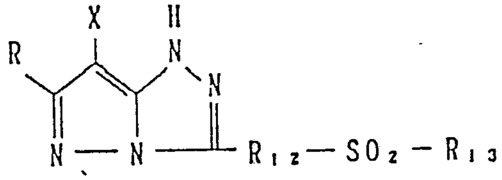
$-CH_2CH_2CH_2\underset{C_6H_{13}}{\underset{|}{CH}}-$, $-\underset{C_6H_5}{\underset{|}{CH}}CH_2CH_2-$, $-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2CH_2-$

The alkyl group represented by R_{13} may be either straight or branched chain. Examples include methyl, ethyl, propyl, iso-propyl, butyl, 2-ethylhexyl, octyl, dodecyl, tetradecyl, hexadecyl, octadecyl, 2-hexyldecyl, and the like. The cycloalkyl group represented by R_{13} preferably has 5 to 6 members, e.g. cyclohexyl. The alkyl or cycloalkyl group represented by R_{13} may have a substituent, examples of which are the same as those exemplified as the substituent on R_1.

Examples of the aryl group represented by R_{13} include phenyl and naphthyl and may have a substituent such as straight or branched chain alkyl groups as well as those exemplified as substituents on R_{12}. In addition, where the group has two or more substituents, these substituents may be either the same or different.

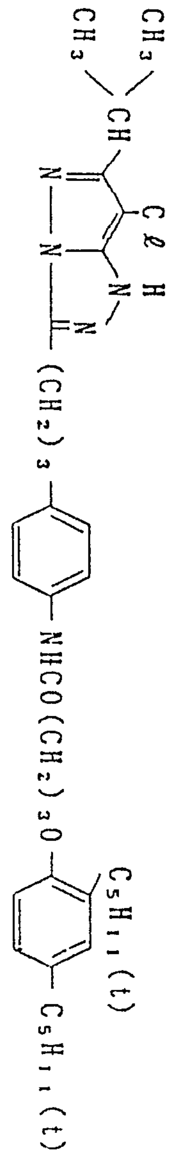
The most preferred compounds of Formula [I] are:

Formula [XI]



The following are non-limiting examples representative of the magenta dye image forming couplers of this invention.

(1)



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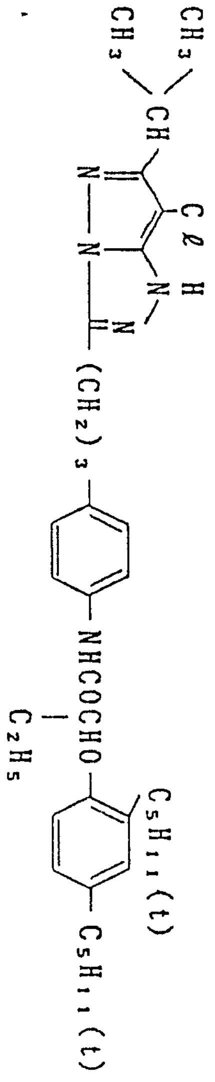

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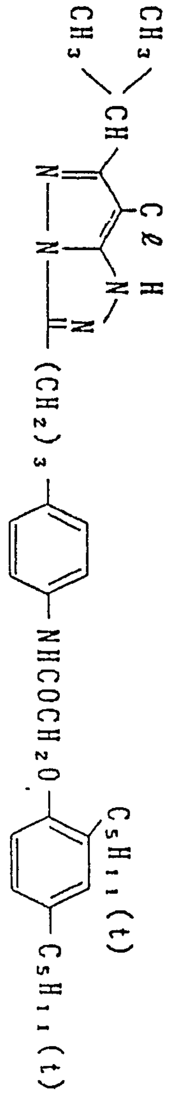

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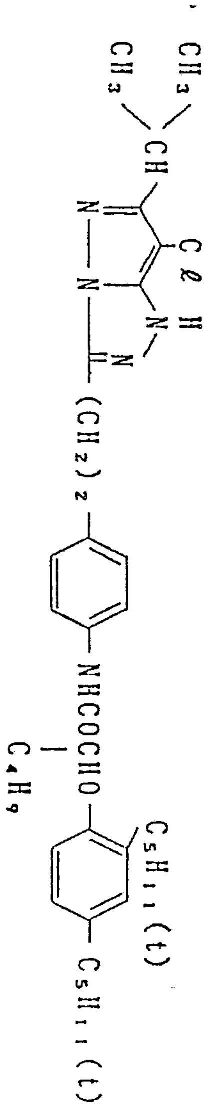

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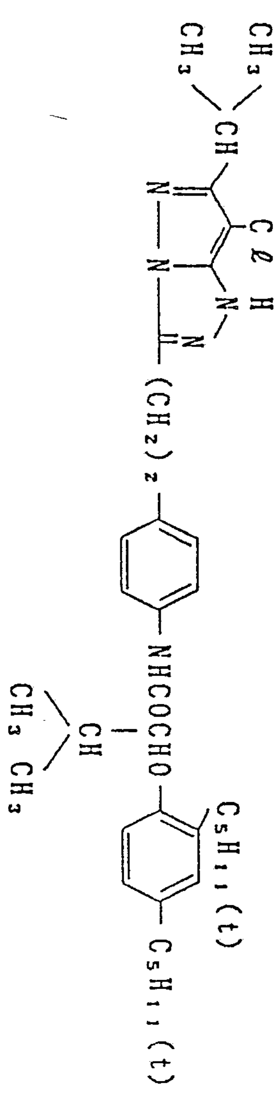

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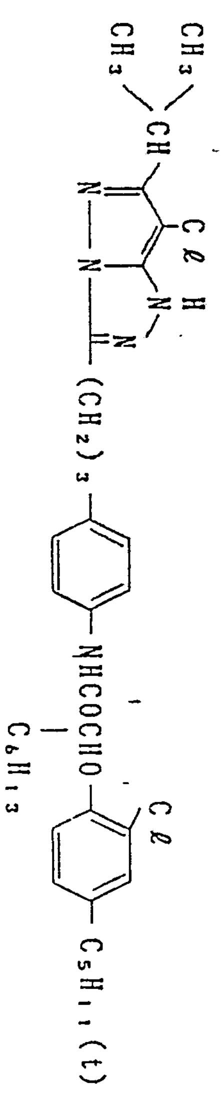

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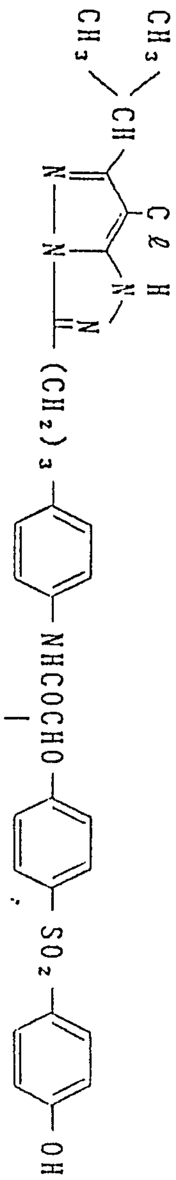

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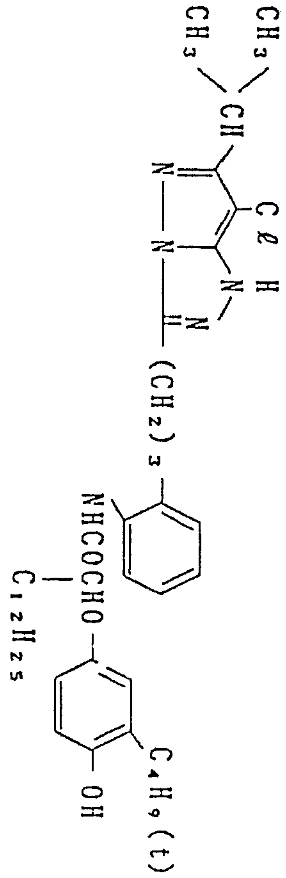

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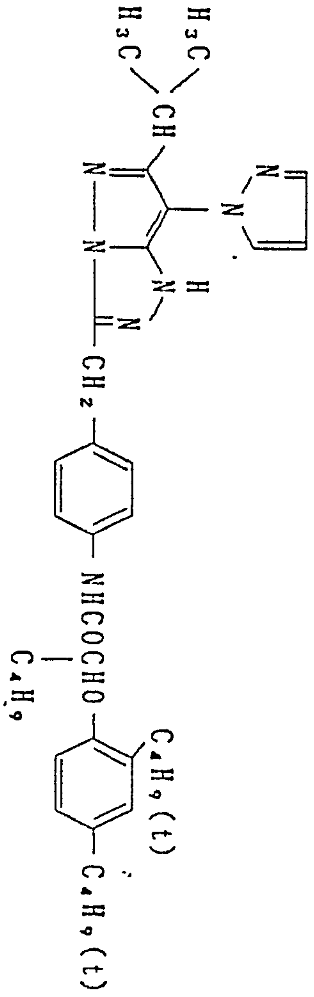

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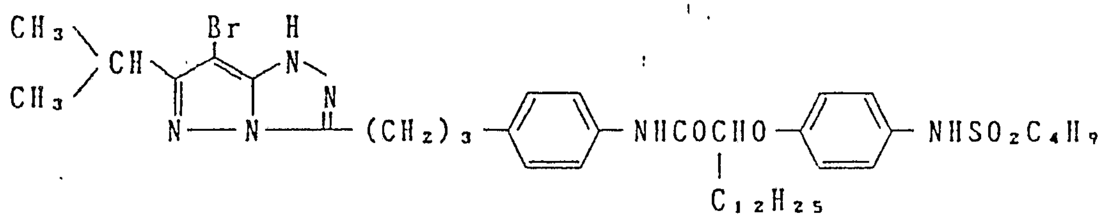

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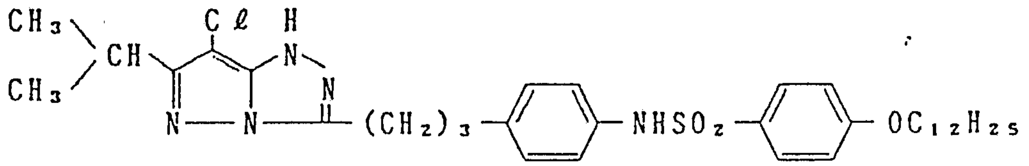

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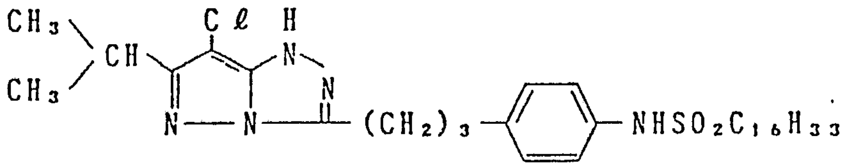

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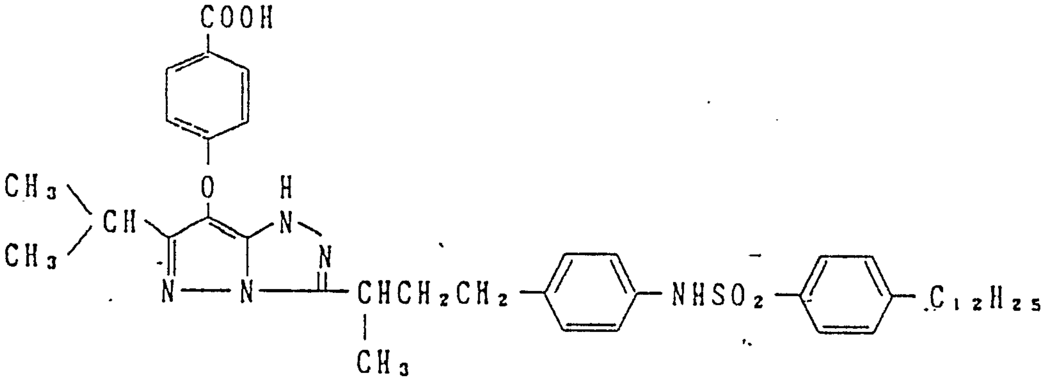

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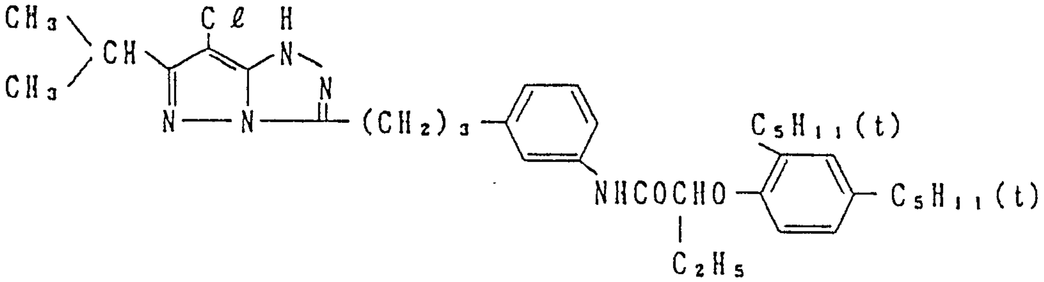

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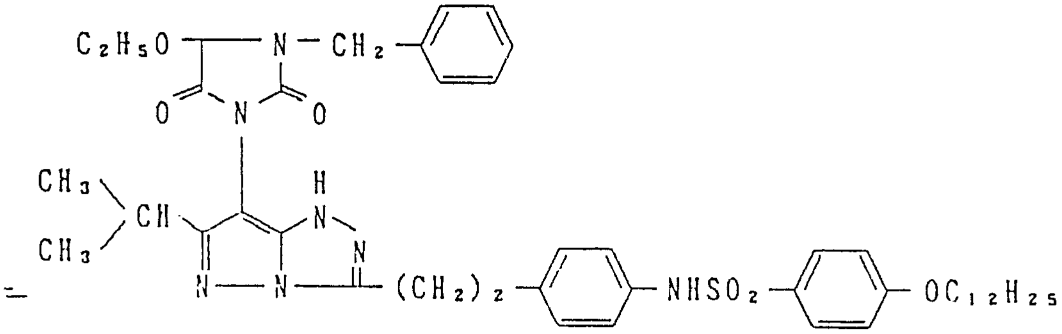

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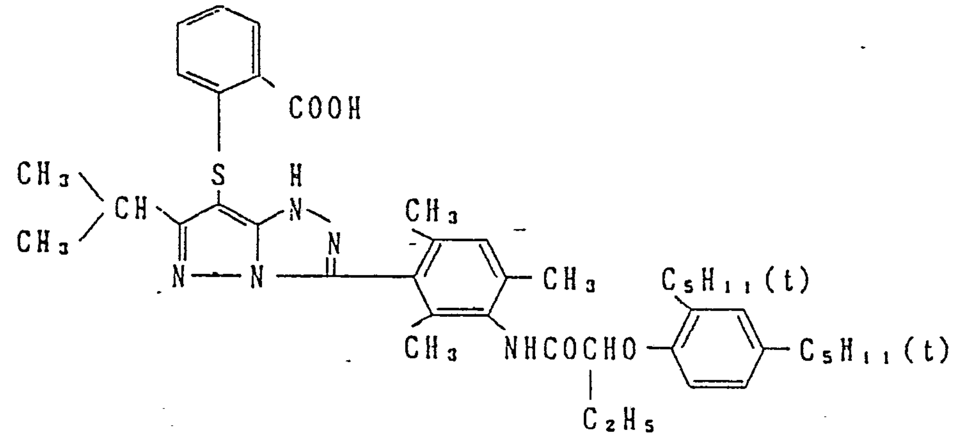

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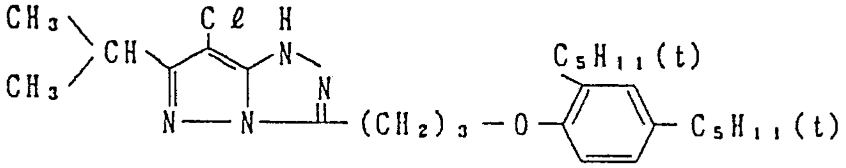

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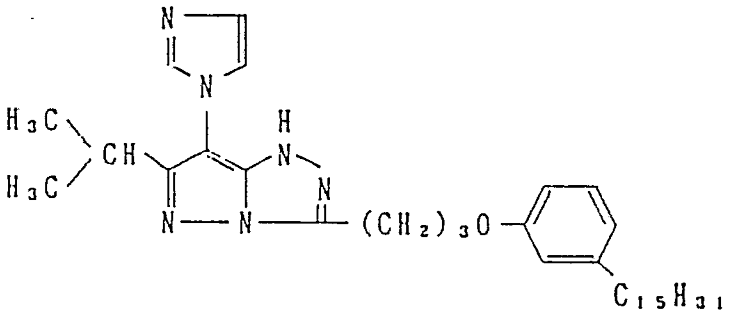

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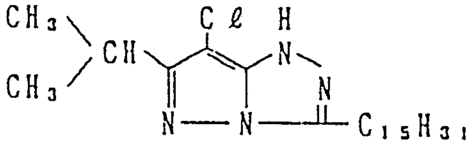

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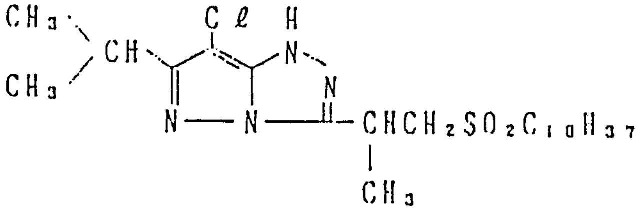

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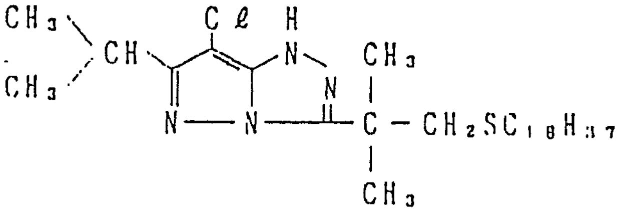

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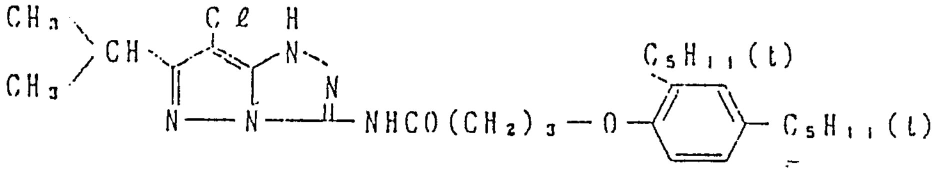

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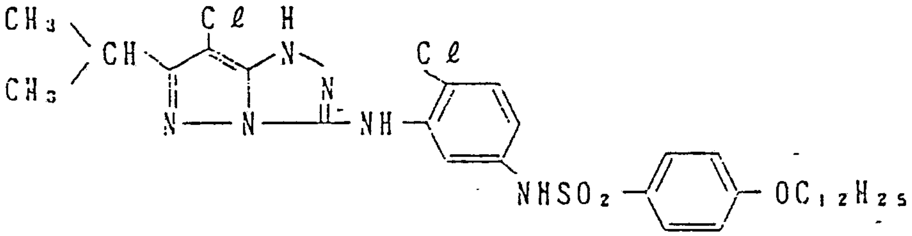
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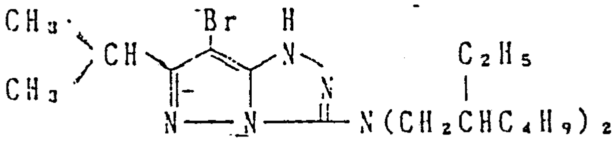
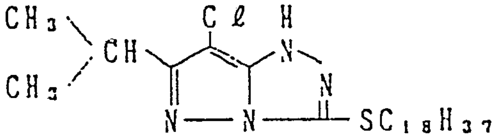
CH
CH3
Cℓ
H
N
N
N
N
NH
Cℓ
NHSO2
OC12H25

(24)


CH3
CH
CH3
Br
H
N
N
N
N
C2H5
N(CH2CHC4H9)2

(25)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CH
CH3
Cℓ
H
N
N
N
N
SC18H37

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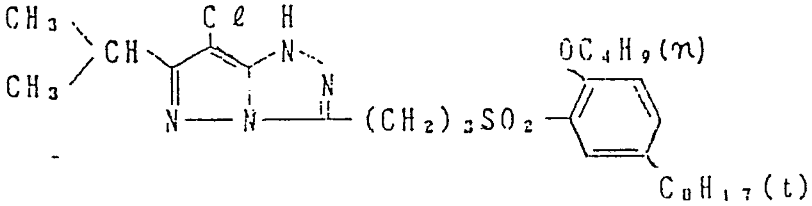
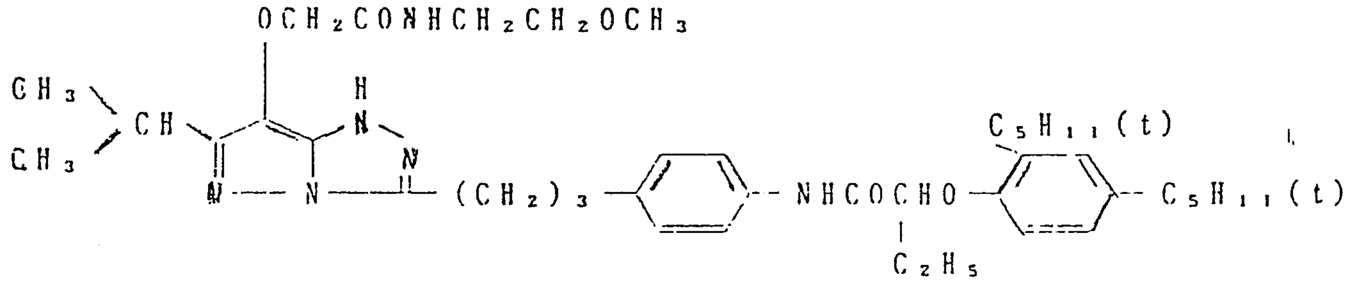

CH3
CH
CH3
Cℓ
H
N
N
N
N
(CH2)3SO2
OC4H9(n)
C8H17(t)

(27)



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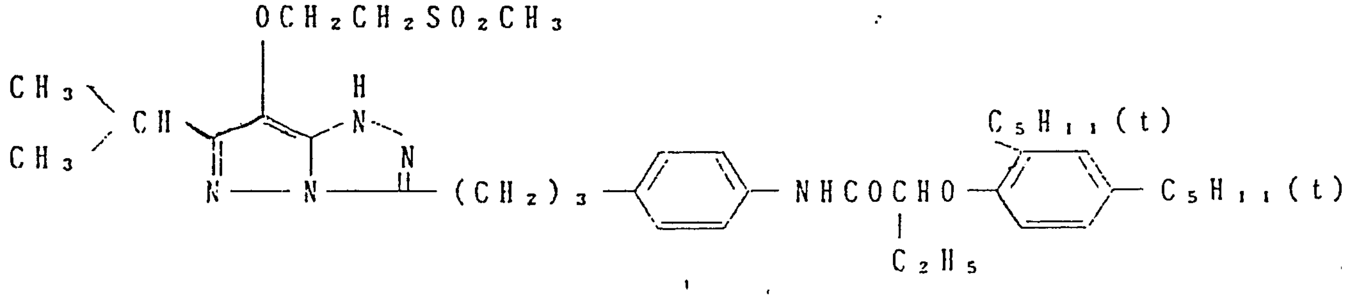

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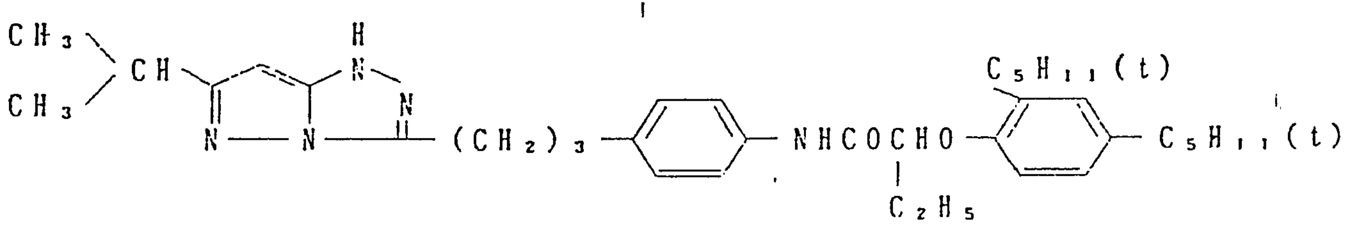

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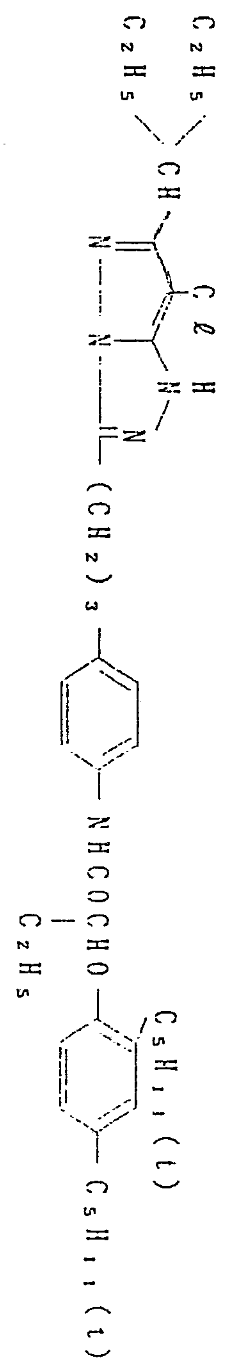

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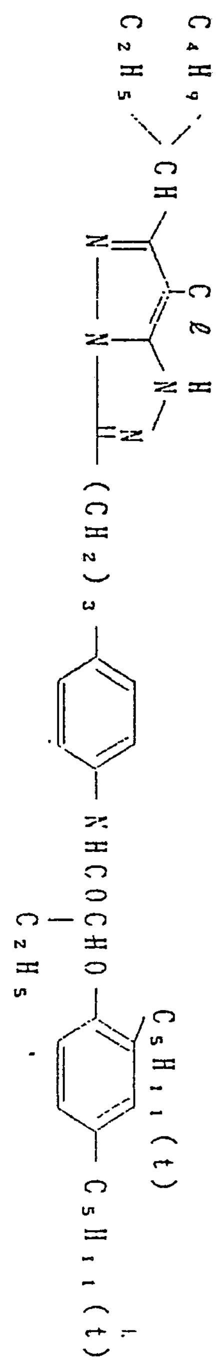

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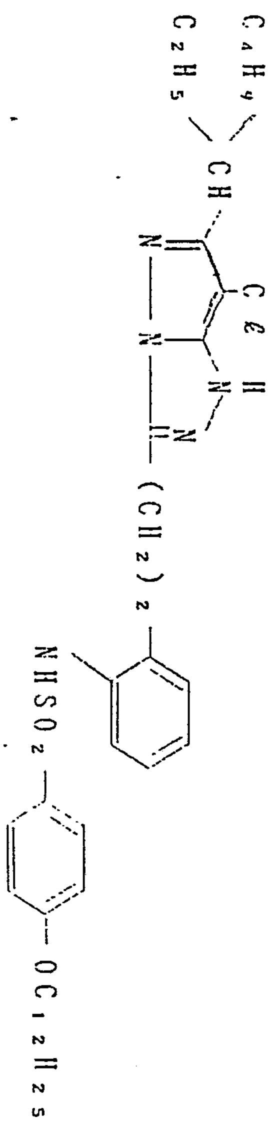

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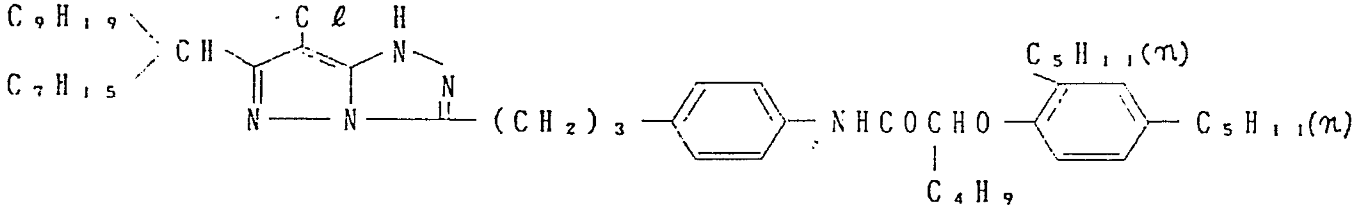

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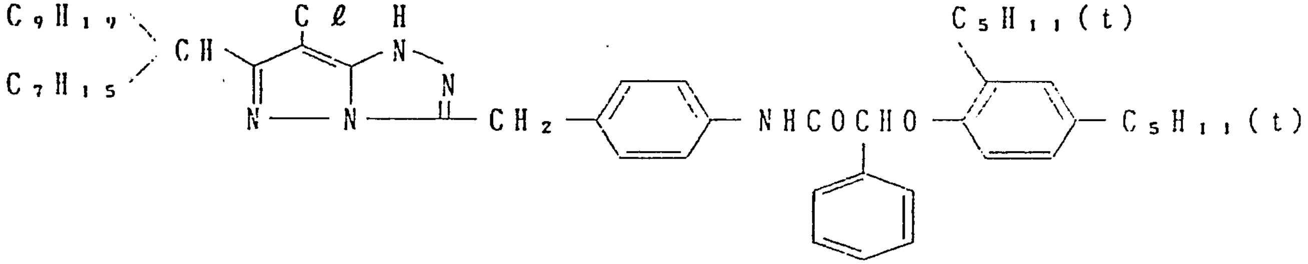

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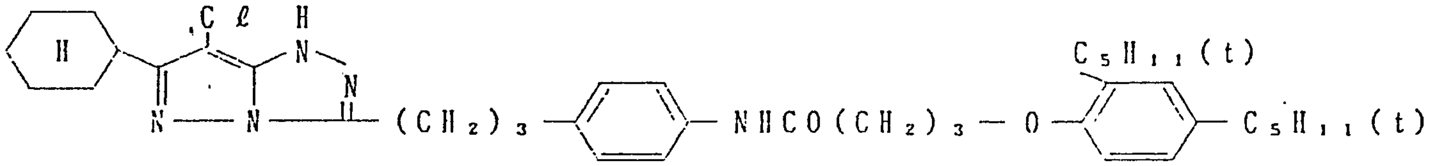

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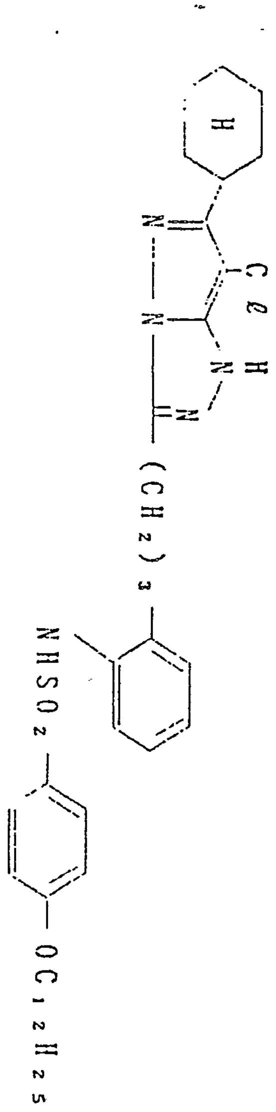

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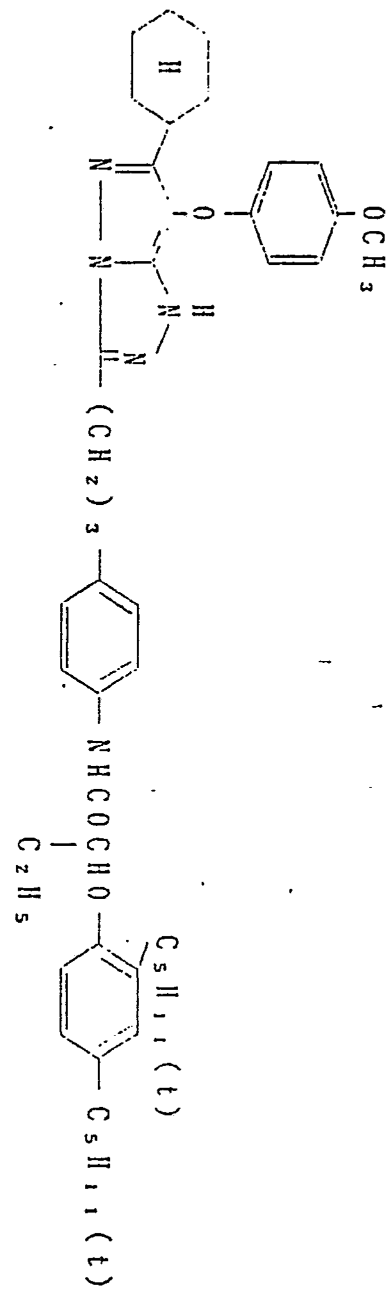

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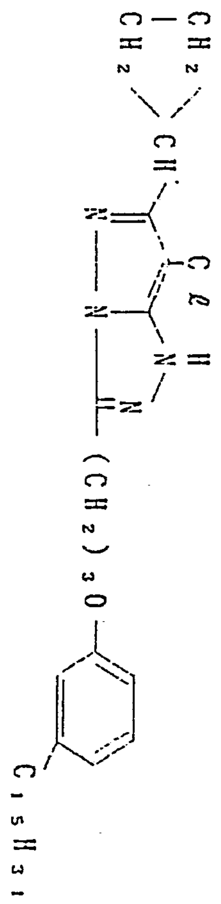

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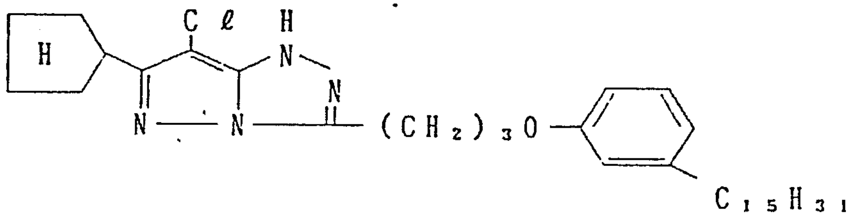

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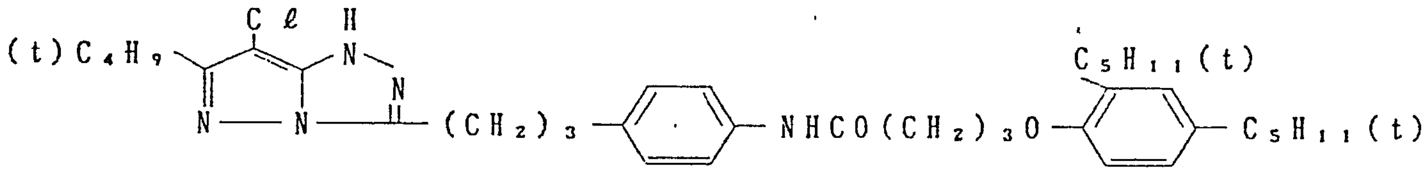

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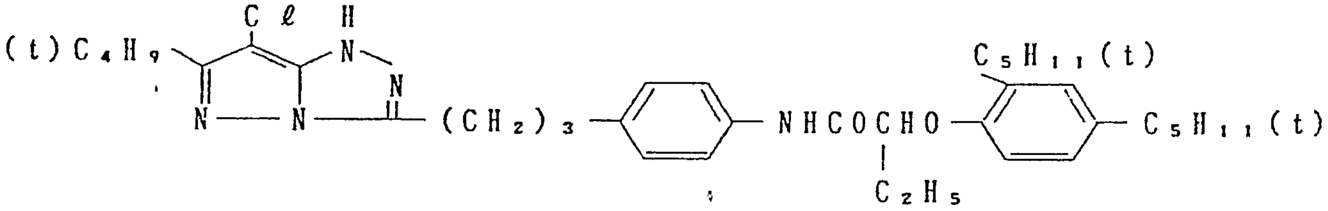

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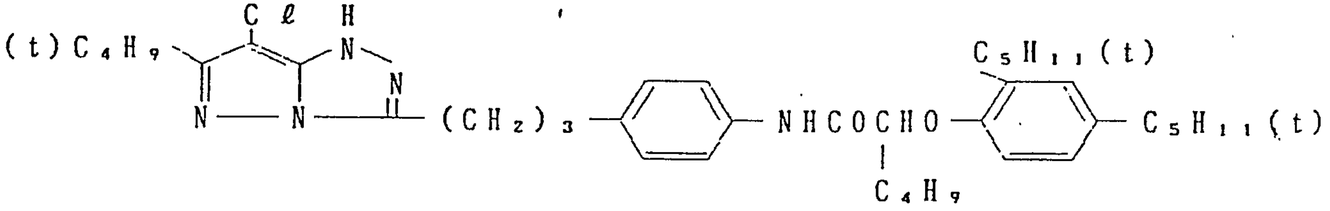

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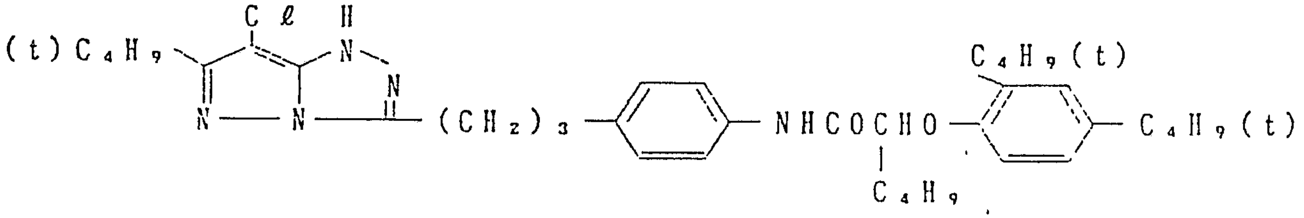

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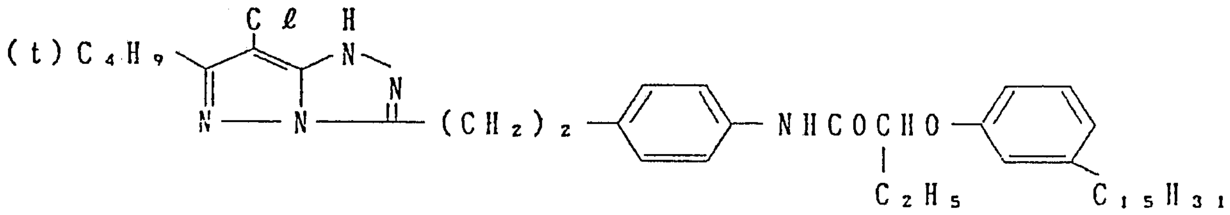

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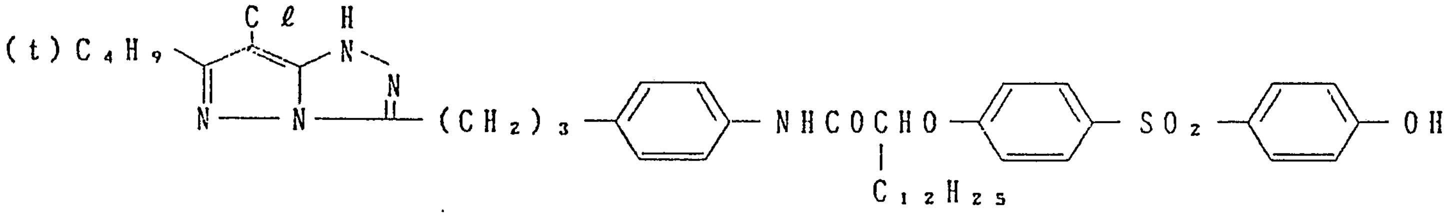

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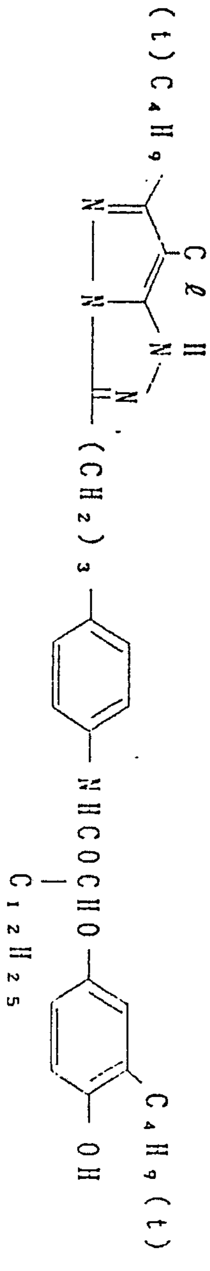

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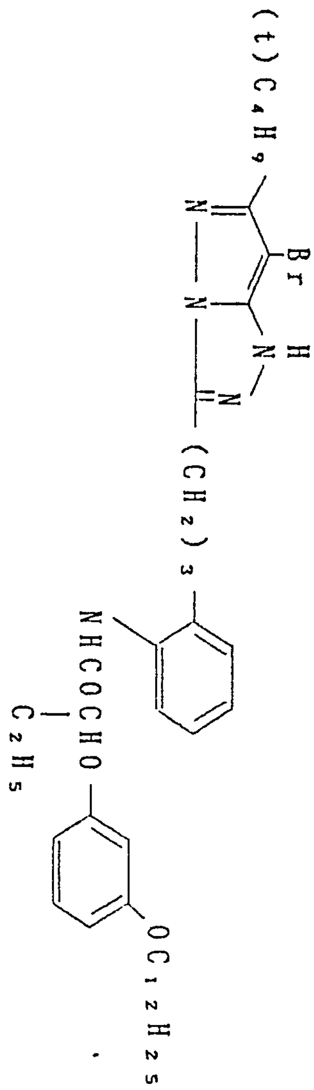

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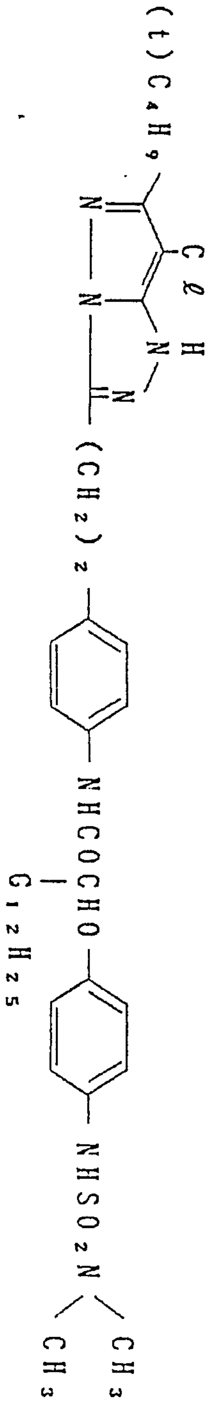

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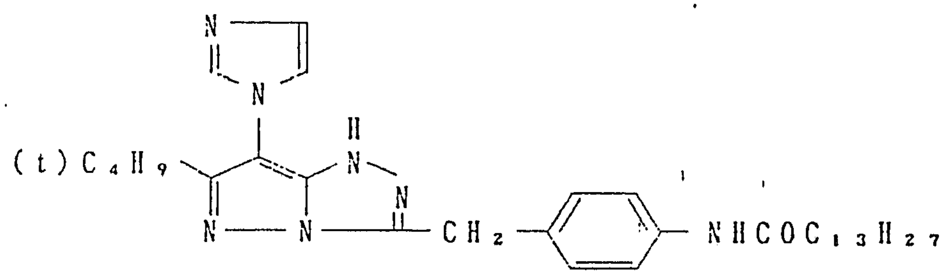

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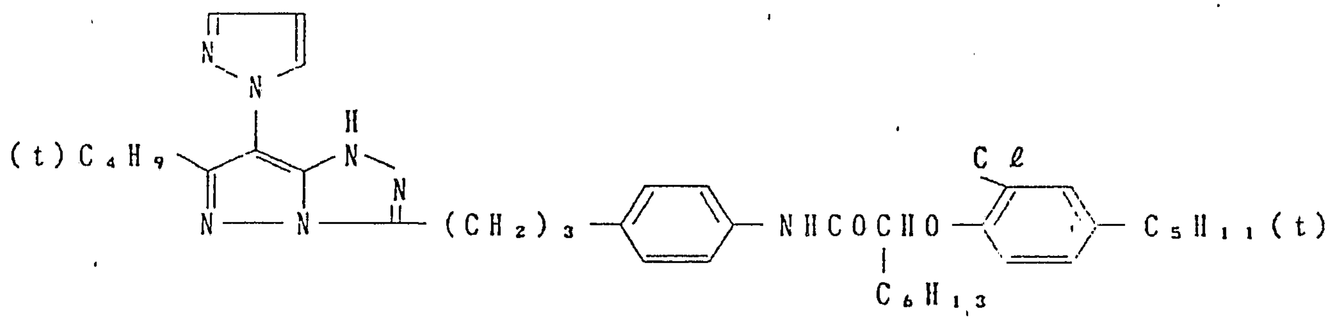

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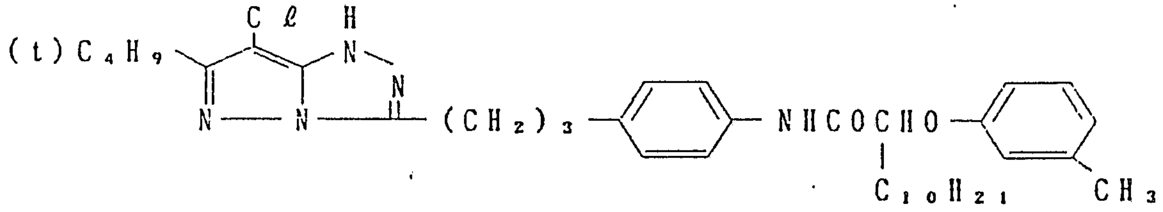

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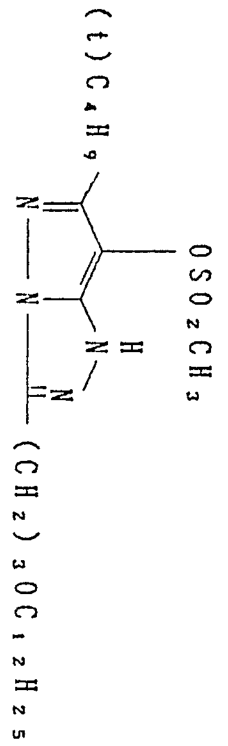

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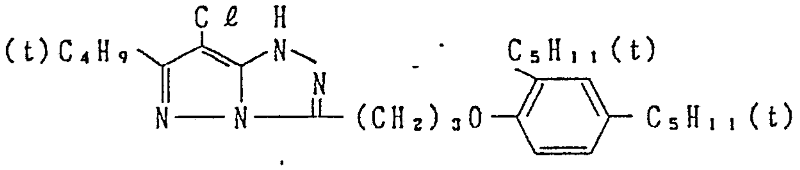

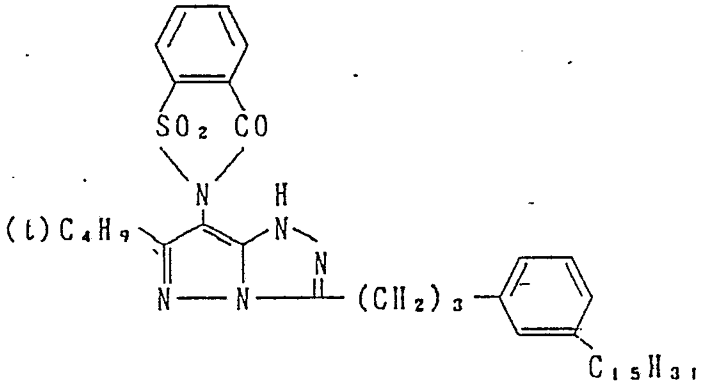

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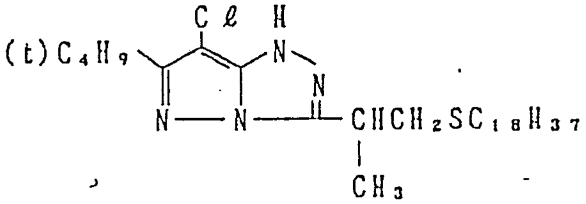

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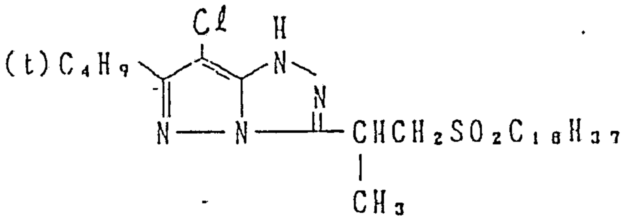

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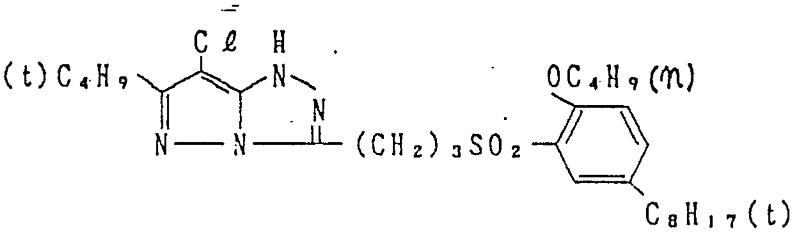

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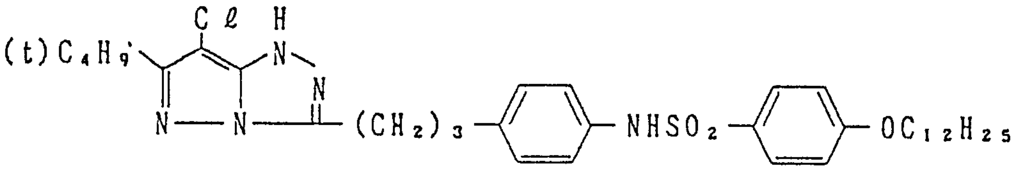

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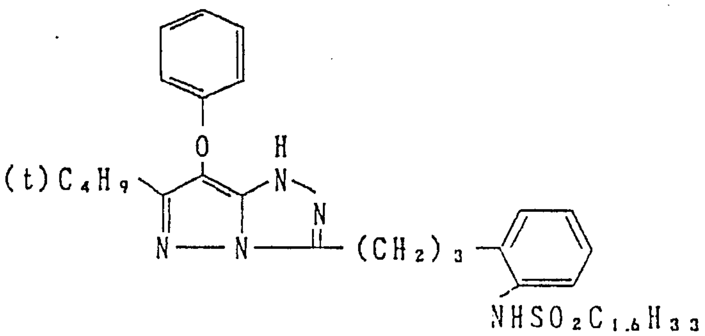

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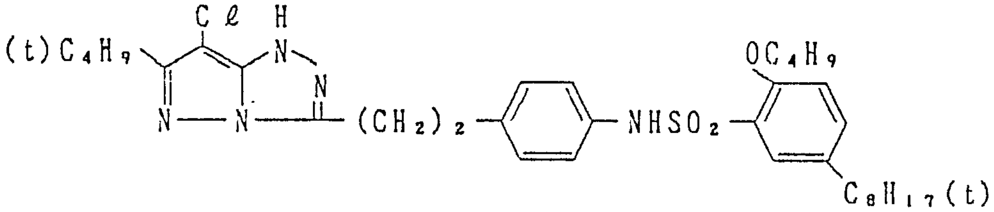

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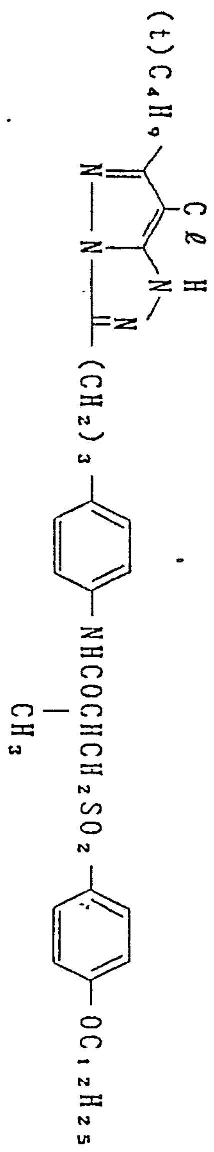

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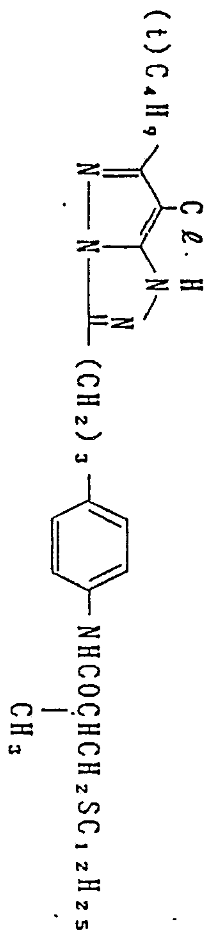

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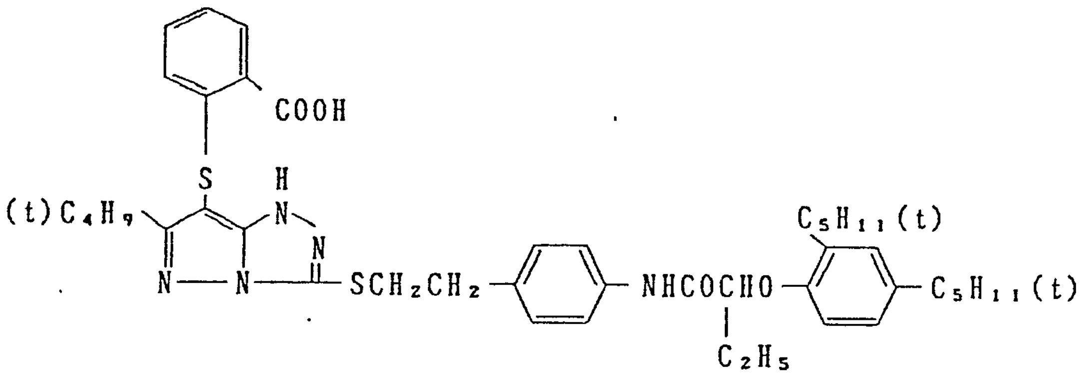

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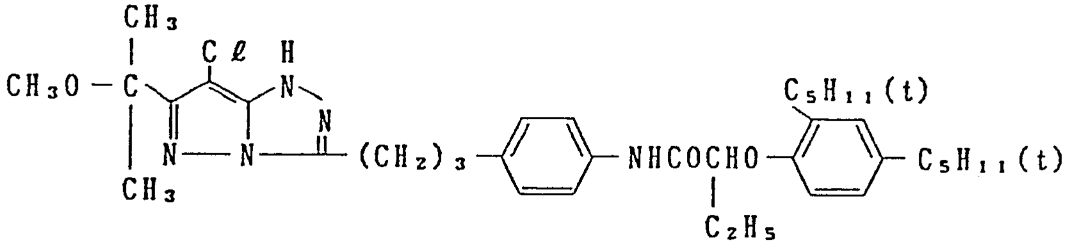

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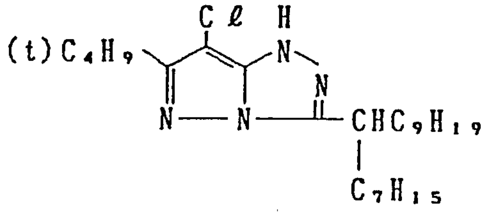

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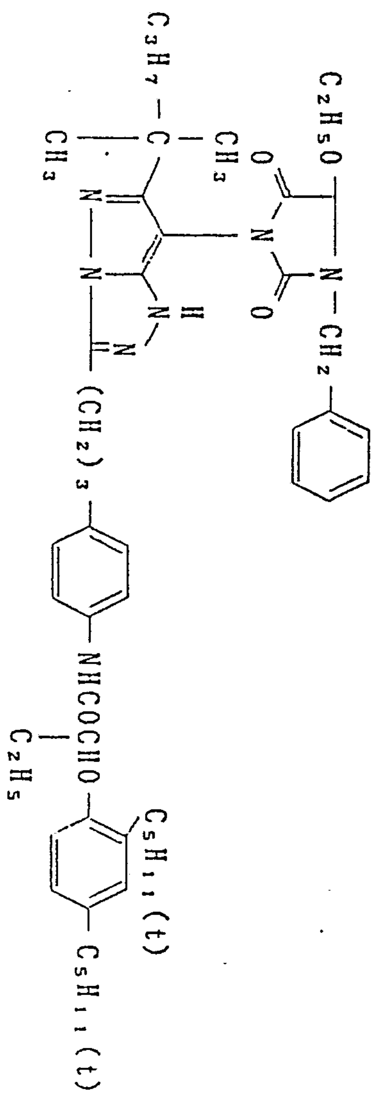

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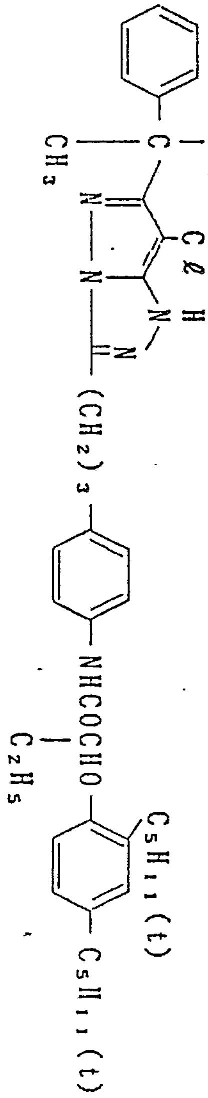

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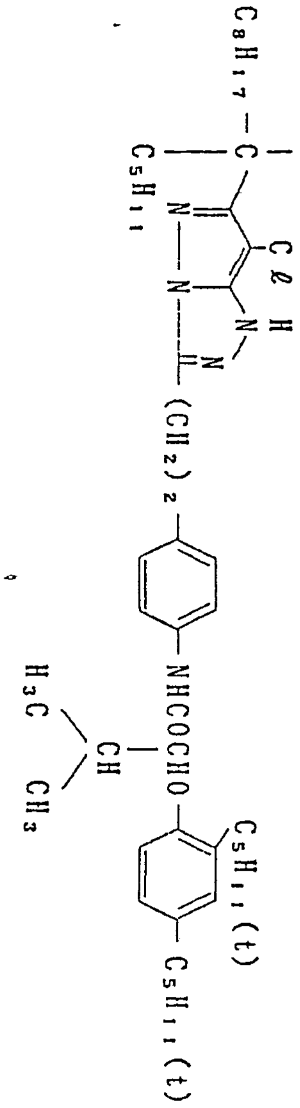

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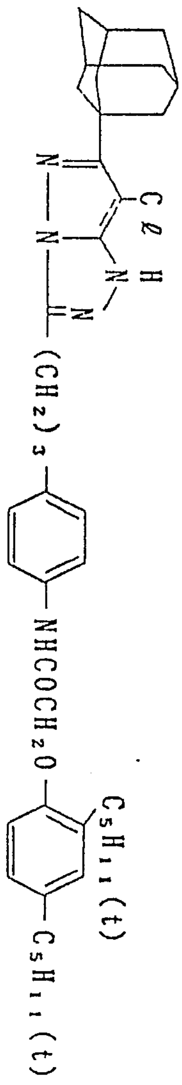

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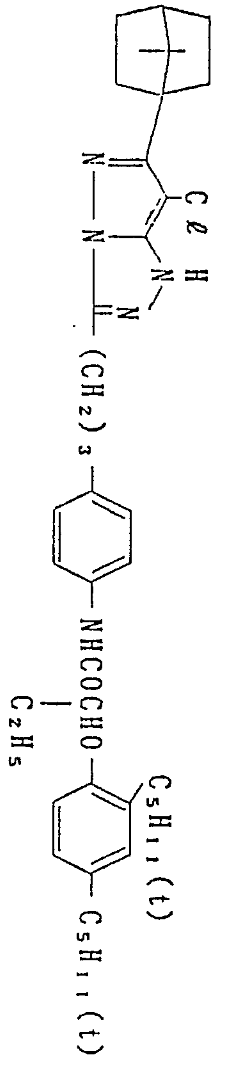

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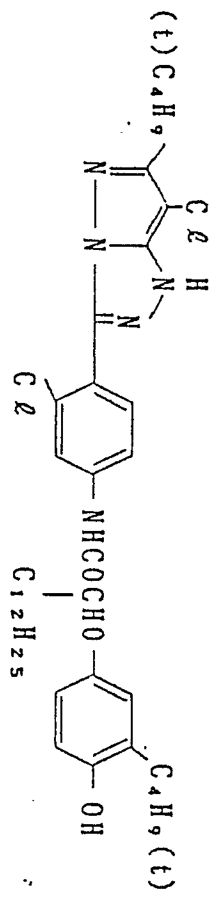

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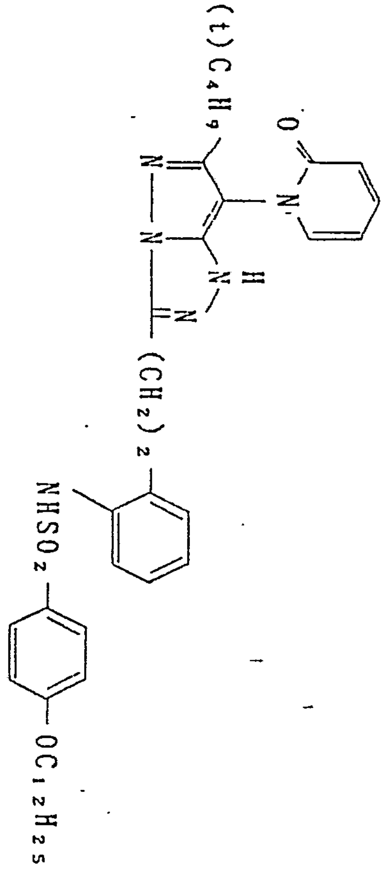

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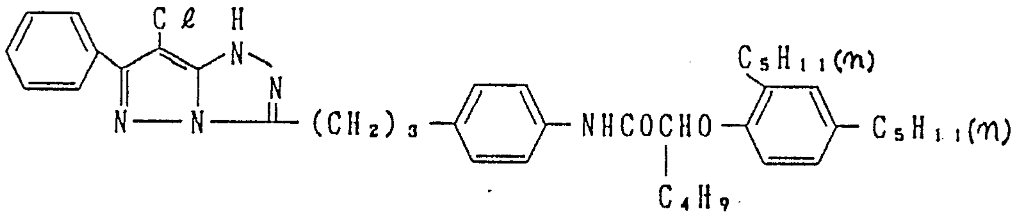

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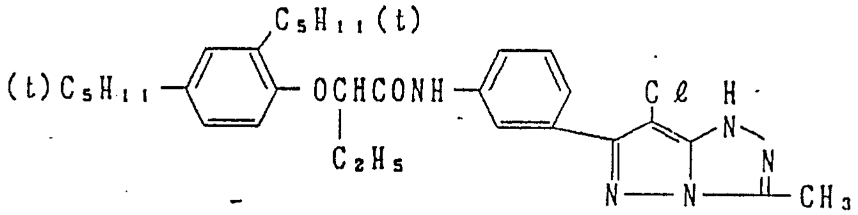

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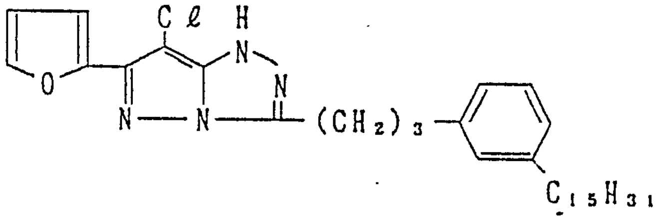


In the present invention, as the emulsion for use in forming the emulsion layer, known internal latent image-type silver halide emulsions may be used. These include conversion-type silver halide emulsions described in U.S. Patent No. 2,592,250, stratified structure-type silver halide emulsions described in Japanese Patent Examined Publication No. 1412/1983, internally chemically sensitized core/shell-type silver halide emulsions described in Japanese Patent Examined Publications 34213/1977 and 55821/1985, core/shell-type emulsions described in Japanese Examined Publication 55820/1985, and the like. The core/shell type emulsions are preferably used in the present invention.

The silver halide composition of the internal latent image-type silver halide to be used in the present invention is discretionary; for example, any of silver chloride, silver chlorobromide, silver chloroiodobromide, silver bromide, silver iodobromide, and silver chloroiodide may be used alone or in combination. The silver chloride content of the silver halide is preferably not less than 5 mole %, and more preferably not less than 30 mole %. The grains of the silver halides may be in any form such as cubic, regular octahedral, or dodecahedral, or mixtures thereof; or may also be spherical, tabular, or irregular. The average grain size and the grain size distribution thereof can vary widely according to the photographic characteristics required, but it is desirable to have the grain size distribution as narrow as possible: That is, the silver halide grains of this invention preferably contain silver halide grains whose sizes are plus or minus 20% of the average grain size thereof and which account for not less than 60% by weight of the total silver halide grains, and more preferably not less than 70% by weight.

Further, the silver halide emulsion of the present invention may be one comprising a mixture of silver halide grains of different average grain size. Such emulsions are produced by blending two or more individual emulsions, each of which has an average grain size substantially different from the others. The 'difference in the average grain size' herein means that the average grain size of smaller-size grains is not more than 80% of the average grain size of larger-size grains, and preferably not more than 70%. The grains of larger average size and the grains of smaller average size may be either the same or different in silver halide composition as well as grain form. The proportion of the larger grains to the smaller grains may be quite freely selected. In this instance, two or three or more different size silver halide grains may be mixed.

The internal latent image-type silver halide of this invention, in order to widen the exposure latitude thereof, may be used in the form of superposed emulsion layers different in sensitivity or may be mixed to be used in an emulsion layer. In this instance, the proportions of the amounts of silver in the respective emulsion layers is determined according to the photographic characteristics required.

In this invention, unprefogged internal latent image-type silver halide grains are used as the internal latent image-type silver halide. The term 'unprefogged' (i.e., the grain surface is not prefogged), as used herein, means that, when an unexposed test piece made by coating an emulsion on a transparent film support so that the amount of silver coated is 35 mg Ag/cm^2, is developed in the following surface developer solution A at 20°C for 10 minutes, the density obtained does not exceed 0.6, and preferably does not exceed 0.4.

Surface Developer Solution A:Metol	2.5 g
ℓ-Ascorbic acid	10.0 g
$NaBO_2.4H_2O$	35.0 g
KBr	1.0 g
Water to make	1 liter

Also, the silver halide emulsion of this invention provides an adequate density when the test piece prepared in the above manner, after being exposed, is developed in the following internal developer solution B.

Internal Developer Solution B:Metol	2.0 g
Anhydrous sodium sulfite	90.0 g
Hydroquinone	8.0 g
Sodium carbonate, monohydrated	52.5 g
KBr	5.0 g
KI	0.5 g
Water to make	1 liter

To be more specific, when part of the above test piece is subjected to a light-intensity scale exposure over a given period of time up to about 1 second, and then developed in Internal Developer Solution B at 20°C for 10 minutes, the part shows a maximum density at least 5 times, and preferably at least 10 times, the maximum density obtained when the other part is exposed under the same conditions and is developed in Surface Developer Solution A at 20°C for 10 minutes.

The silver halide emulsion of this invention may be optically sensitized by the usual sensitizing dyes. Such combinations of these sensitizing dyes as are used for supersensitization of internal latent image-type silver halide emulsions, negative-type silver halide emulsions, and the like, are useful also for the silver halide emulsion of this invention. For such sensitizing dyes, reference can be made to Research Disclosures 15162 and 17643.

A direct positive image can be easily obtained by surface development of an imagewise exposed (photographed) light-sensitive material of this invention. The primary process of making a direct positive image is such that a photgraphic light-sensitive material comprising the unprefogged internal latent image-type silver halide emulsion layer of this invention is imagewise exposed and then subjected to a treatment for producing fog nuclei chemically or optically. In other words, the imagewise exposed light-sensitive material is surface-developed after and/or during a fogging treatment. The fogging treatment may be carried out either by giving an overall exposure (by exposing the entire area of the light-sensitive material) or by using a fog nucleus-producing compound; i.e., a fogging agent.

The overall exposure is carried out so that the imagewise exposed light-sensitive material is immersed in or wetted by a developer or other solution and then uniformly exposed. The light source for the overall exposure may be any light, as long as it is in the wavelength region to which the light-sensitive material is sensitive. It may be a short-period-emitting high-intensity light like an electronic flash, or may also be a weak light exposed over a long period of time. The time may be widely varied according to the photographic light-sensitive material, developing conditions, type of the light source, and the like, to obtain the best-quality positive image. It is most desirable that the exposure required for the overall exposure be given in a certain specific range in combination with the light-sensitive material. Generally speaking, the use of excessive exposure increases or decreases the maximum density, thus resulting in deterioration of the resulting image quality. However, where the light-sensitive material of this invention is used, it reduces the degree of deterioration of the image quality to thereby produce a stable image.

A large variety of compounds may be used as the fogging agents of this invention. The fogging agent needs only to be present at the time of development; for example, the agent may be present in the nonsupport component layers of the photographic material (the silver halide emulsion layer is especially preferred), or may be contained in a developer or in a processing solution used prior to the developer. The amount of agent used may be varied widely according to known parameters. The preferred amount of fogging agent, when incorporated into the silver halide emulsion layer, is from 1 to 1,500 mg per mole of silver halide, and preferably from 10 to 1,000 mg, and, when incorporated into a processing solution such as a developer solution, is from 0.01 to 5 g/liter, and more preferably from 0.05 to 1 g/liter.

Compounds usable as the fogging agents of this invention include those hydrazines described in U.S. Patents 2,563,785 and 2,588,982, or those hydrazides or hydrazine compounds described in U.S. Patent 3,227,552; those heterocyclic quaternary nitrogen salt compounds described in U.S. Patents 3,615,615; 3,718,479; 3,719,494; 3,734,738; and 3,759,901; and compounds having a group adsorbable onto the silver halide surface such as those acylhydrazinophenylthioureas described in U.S. Patent 4,030,925. These fogging agents may be used in combination. For example, Research Disclosure 15162 describes the combined use of a nonadsorption-type fogging agent and an adsorption-type fogging agent; this combined-use technique is useful also in this invention. The invention allows the use of both nonadsorption-type and adsorption-type fogging agents and also their combined use.

Examples of suitable fogging agents are hydrazine compounds such as hydrazine hydrochloride, phenylhydrazine hydrochloride,
4-methylphenylhydrazine hydrochloride,
1-formyl-2-(4-methylphenyl)hydrazine,
1-acetyl-2-phenylhydrazine,
1-acetyl-2-(4-acetamidophenyl)hydrazine,
1-methylsulfonyl-2-phenylhydrazine,
1-benzoyl-2-phenylhydrazine,
1-methylsulfonyl-2-(3-phenylsulfonamidophenyl)-hydrazine,
formaldehydophenyl-hydrazine, etc.; N-substituted quaternary cycloammonium salts such as
3-(2-formylethyl)-2-methylbenzothiazolium bromide,
3-(2-formylethyl)-2-propylbenzothiazolium bromide,
3-(2-acetylethyl)-2-benzylbenzoselenazolium bromide,
3-(2-acetylethyl)-2-benzyl-5-phenyl-benzoxazolium bromide,
2-methyl-3-[3-(phenylhydrazino)propyl]benzothiazolium bromide,
2-methyl-3-[3-(p-tolylhydrazino)propyl]benzothiazolium bromide,
2-methyl-3-[3-(p-sulfophenylhydrazino)propyl]benzothiazolium bromide,
2-methyl-3-[3-(p-sulfophenylhydrazino)pentyl]-benzothiazolium iodide;1,2-dihydro-3-methyl-4-phenylpyrido-[2,1-b]benzothiazolium bromide, 1,2-dihydro-3-methyl-4-phenylpyrido[2,1-b]-5-phenylbenzothiazolium bromide,
4,4'-ethylenebis(1,2-dihydro)-3-methylpyrido[2,1-b]benzothiazolium bromide,
1,2-dihydro-3-methyl-4-phenylpyrido[2,1-b]benzoselenazolium bromide, etc.; and
5-[1-ethylnaphtho(1,2-b)thiazoline-2-ylidenethylidene]-1-(2-phenylcarbozoyl)methyl-3-(4-sulfamoylphenyl)-2-thiohydantoin, 5-(3-ethyl-2-benzothiazolinidene)-3-[4-(2-formylhydrazino)phenyl] rhodamine, 1-[4-(2-formylhydrazino)phenyl]-3-phenylthiourea, 1,3-bis[4-(2-formylhydrazino)phenyl]thiourea, and the like.

The photographic light-sensitive material comprising the silver halide emulsion layer of this invention provides a direct positive image which is formed so that the material, after being imagewise exposed, is either overall-exposed and then surface-developed or surface-developed in the presence of a fogging agent. Surface-developed implies that the light-sensitive material is processed in a developer solution substantially free of silver halide solvent.

Developing agents usable in the surface developer of the present invention include ordinary silver halide developing agents; e.g., polyhydroxybenzenes such as hydroquinone, aminophenols, 3-pyrazolidones, ascorbic acid and derivatives thereof, reductones, phenylenediamines, and mixtures thereof. Examples include hydroquinone, aminophenol,
N-methylaminophenol, 1-phenyl-3-pyrazolidone,
1-phenyl-4,4-dimethyl-3-pyrazolidone,
1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, ascorbic acid, N,N-diethyl-p-phenylenediamine,

diethylamino-o-toluidine, 4-amino-3-methyl-N-ethyl-N-(β-methanesulfonamidoethyl)aniline, 4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline, and the like. Any of these developing agents may be incorporated into the emulsion in advance, and the photographic material immersed in a high-pH aqueous solution to make the emulsion react with the agent.

The developer solution of this invention may contain further specific fogging agents and development restraining agents; alternatively these additives may be incorporated into the constituent layer of the photographic material.

In the direct positive silver halide photographic material of this invention, due to the addition of the magenta color image forming coupler having Formula [I] therein, even if a fixing or bleach-fixing solution is mixed by mistake into the color developer solution, almost no noticeable softening of the gradation at the foot of the density/exposure curve appears and increase in the minimum density is kept to a minimum. Accordingly, even if fixing or bleach-fixing solution is mixed accidentally into the color developer solution due to some operational error, or, for example, when pulling a jammed paper out of the processor, or during the belt-transport-type automatic processor operation, as long as the above-mentioned light-sensitive material is used, the processing can be reliably carried out. Therefore, the use of the light-sensitive material of this invention makes it unnecessary to renew the color developer solution each time accidental mixing occurs, thus reducing costs and saving time.

The substantial deterioration of image quality due to the gradation softening at the foot of the density/exposure curve and the increase in minimum density due to mixing of a silver halide solvent-containing processing solution into the color developer tends to occur when the developing takes place at a high temperature exceeding 35°C. Accordingly, the light-sensitive material of this invention is also useful for rapid processing which is carried out at a high temperature exceeding 35°C.

The silver halide emulsion of this invention may contain the usual photographic additives such as wetting agents, physical property improving agents for the layers, coating aids, and the like. Examples of the wetting agent are dihydroxyalkanes and the like. Physical property improving agents include water-dispersed particulate high-molecular materials obtained by emulsion polymerization, such as copolymers of alkyl acrylates or alkyl methacrylates with acrylic acid or methacrylic acid, styrene-maleic acid copolymers, styrene-maleic anhydride-half alkyl ester copolymers, and the like. Coating aids include saponin, polyethylene glycol-lauryl ether, etc. Other photographic additives may also be used which include gelatin plasticizers, surface active agents, ultraviolet absorbing agents, pH control agents, oxidation inhibitors, antistatic agents, viscosity increasing agents, graininess improving agents, dyes, mordants, brightening agents, developing speed control agents, matting agents, developing speed control agents, matting agents, and the like.

The above-prepared silver halide emulsion is coated, if necessary, through a subbing layer, antihalation layer, filter layer, etc., on a support, whereby the direct positive silver halide photographic material of this invention is obtained.

The photographic material of this invention is useful in color photgraphic processing. In this instance, it is desirable to incorporate cyan, magenta and yellow dye image forming couplers into the silver halide emulsion. The couplers can be those ordinarily used.

In order to prevent the resulting dye image from being discolored by short-wavelength active rays, it is advantageous to include, alone or in combination, an ultraviolet absorbing agent such as thiazolidone, benzotriazole, acrylonitrile, or a benzophenone-type compound, particularly Tinuvin PS, Tinuvin 320, Tinuvin 326, Tinuvin 327 and Tinuvin 328 (all manufactured by Ciba Geigy).

Materials suitable as the support of the photographic material of this invention include polyethylene terephthalate film, polycarbonate film, polystyrene film, polypropylene film, cellulose acetate film, glass plates, baryta paper, polyethylene-laminated paper, and the like. These may be subbed if needed.

The silver halide emulsion layer of this invention may contain appropriate gelatin derivatives in addition to gelatin as the protective colloid or binder thereof. Examples of the appropriate gelatin derivates include acylated gelatin, guanidylated gelatin, carbamylated gelatin, cyano-ethanolated gelatin, esterified gelatin, and the like.

Also, the silver halide emulsion layer of this invention may contain other hydrophilic binder materials, such as colloidal albumin, agar-agar, gum arabic, dextran, alginic acid, cellulose derivatives such as cellulose acetate hydrolyzed to 19 to 20% acetyl content, polyacrylamide, imidated polyacrylamide, casein, vinyl alcohol, vinyl alcohol polymers containing a urethanecarboxylic acid group or cyanoacetyl group such as vinylaminoacetate copolymer, polyvinyl alcohol, polyvinyl pyrolidone, hydrolyzed polyvinyl acetate, polymers obtained by the polymerization of protein or saturated acylated protein with monomers having vinyl groups, polyvinyl pyridine, polyvinyl amine, polyaminoethyl methacrylate, polyethyleneamine, etc. These may be incorporated into the constituent layers of the photographic material, e.g. the emulsion layer, intermediate layer, protective layer, filter layer, subbing layer, and the like. Further, the above-mentioned hydrophilic binder may contain appropriate plasticizers, wetting agents, etc.

These constituent layers of the photographic material of this invention may be hardened by using any appropriate hardening agent. Examples include chromium salts, zirconiums, aldehyde-type compounds such as formaldehyde, mucohalogenic acid, etc., and halotriazine-type, polyepoxy compound-type, ethyleneimine-type, vinyl-sulfone-type and acryloyl-type hardening agents.

The photographic material of this invention may have on the support various photographic constituent layers such as filter layers, intermediate layers, protective layers, subbing layers, backing layers, antihalation layers, and the like in addition to at least one light-sensitive emulsion layer containing the internal latent image-type silver halide grains of this invention.

Where the photographic material of this invention is for full-color use, on the support thereof are coated at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one blue-sensitive silver halide emulsion layer. In this instance, at least one light-sensitive silver halide emulsion layer must contain the internal latent image-type silver halide grains of this invention. It is desirable, however, that all the light-sensitive silver halide layers contain the internal latent image-type silver halide grains of this invention. Each of these light-sensitive silver halide emulsion layers may be separated into two or more layers having the same color sensitivity but differing in the speed. In this instance, at least one layer having the same color sensitivity but different in speed must contain the internal latent image-type silver halide grains of this invention. It is desirable, however, that all the emulsion layers contain the internal latent image-type silver halide grains of the present invention.

The photographic material of this invention may be effectively applied to various uses, such as black-and-white general use, X-ray, color photography, false-color, graphic arts, infrared photography, micrographics, silver-dye bleach process, and the like. It may also be applied to the colloid transfer process, silver salt diffusion transfer process, and those color image transfer processes and color transfer processes described in Rodgers' U.S. Patents 3,087,817; 3,185,567; and 2,983,606; Weyerts' U.S. Patent 3,253,915; Whitmore's U.S. Patent 3,227,550; Barr's U.S. Patent 3,227,551; Whitmore's U.S. Patent 3,227,552,; and Land's U.S. Patents 3,415,644; 3,415,645; and 3,415,646.

EXAMPLES

The present invention will be illustrated in detail with the following examples. Embodiments of the invention are not limited to the examples.

Example-1

An octahedral silver bromide-crystalline internal latent image-type core/shell emulsion, whose average grain size is 0.6 μ, was prepared in accordance with the method described in Japanese Patent Examined Publication No. 34213/1977, and this emulsion was used to prepare the following silver halide photographic material Sample No. 1.

To the above emulsion was added a magenta color image forming coupler (Exemplified Compound (3)) dissolved in dioctyl phthalate, and a coating aid and hardening agent were also added. This liquid mixture was coated on a support and dried, whereby Sample 1 was obtained. The coated amount of the above internal latent image-type emulsion on the support of Sample 1 was 1.0 g/m^2 in silver equivalent. The above magenta color image forming coupler was incorporated into the above emulson so that the coating amount thereof was 1.8 g/m^2.

Samples 2 to 8 were prepared in the same manner as Sample 1 except that the magenta color image forming coupler was replaced by those compounds described in Table 1.

The above-prepared light-sensitive material Samples 1 to 8 were exposed through an optical wedge, and then processed in the following manner:

Procedure (at 35°C)

Color developing	4 minutes
Bleach-fix	2 minutes
Stabilizing	2 minutes

During the above procedure, the entire area of each sample was exposed to 1-lux white light for a period of 10 seconds between 10 seconds and 20 seconds after the commencement of the color development.

The processing solutions used in the above processes are of the following compositions:

Color Developer Solution An aqueous solution of the following chemicals in concentrations (g/liter):

Potassium carbonate	28.9
Potassium sulfite	2.6
Sodium bromide	0.26
Benzyl alcohol	12.8
Ethylene glycol	3.4
Hydroxylamine sulfate	2.6
1,8-Dihydroxy-3,6-dithiooctane	0.1
Diaminopropanol-tetraacetic acid	0.09
Sodium chloride	3.2
Nitrilotriacetic acid	0.4
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate	4.25
pH (controlled by potassium hydroxide)	10.20

Bleach-Fix Bath An aqueous solution of the following chemical in concentrations (g/liter):

Ammonium thiosulfate	110
Sodium hydrogensulfite	10
Iron-ammonium ethylenediaminetetraacetate	60
Diammonium ethylenediaminetetraacetate	5
Bis-thiourea	2
pH (controlled by aqueous ammonia)	6.5

Stabilizer Solution

Glacial acetic acid	20
Anhydrous sodium acetate	5

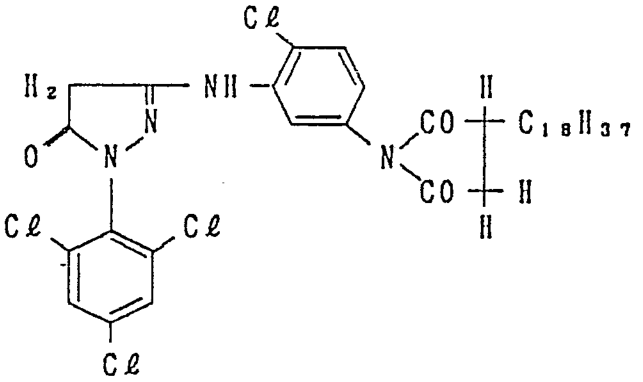
Each of the above samples processed in the above processing solutions was subjected to sensitometry to thereby find the gradation at the foot of the density/exposure curve in terms of gamma (γ) and the minimum density (Dmin). The γ represents the inclination of the characteristic curve for each sample in the density range given in Table 1.

Table 1

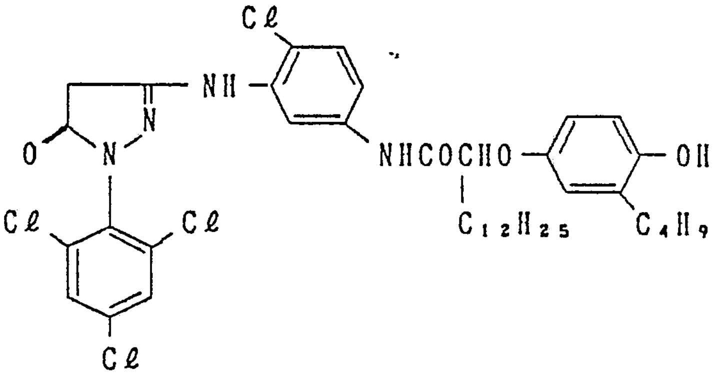
Sample No.	Magenta color image forming Coupler	γ	Dmin	Remarks
1	Exemplified Compound (3)	1.72	0.09	Invention
2	Exemplified Compound (20)	1.59	0.08	Invention
3	Exemplified Compound (21)	1.61	0.08	Invention
4	Exemplified Compound (26)	1.61	0.09	Invention
5	Exemplified Compound (55)	1.65	0.08	Invention
6	Exemplified Compound (57)	1.70	0.10	Invention
7	Comparative Compound (A)	1.25	0.12	Comparative
8	Comparative Compound (B)	1.39	0.13	Comparative

Note: γ: Absolute value of the inclination of a line connected between the density point of Dmin+0.1 and the density point of Dmin+0.5.

(A)



(B)



As is apparent from the results given in Table 1, Samples 1 through 6 for this invention show their γ's as the index of the gradation at the foot of the density/exposure curve as being higher than those of Comparative Samples 7 and 8. Each gave a clear, satisfactory image, while Samples 7 and 8 exhibited their γ's as being lower, thus producing an obscure image.

Example-2

The photographic material in this example was formed by preparing and coating the emulsions of the respective constituent layers thereof as follows:

In accordance with the method described in Japanese Patent Examined Publication No. 55820/1985, two different internal latent image-type silver halide emulsions having average grain sizes of 0.9 μ and 0.6 μ, respectively, were prepared. Each of the emulsions obtained contained AgBr/AgCl + = 60/40. These two emulsions, different in the average grain size, were mixed in a molar ratio of 1:1, whereby a blue-sensitive emulsion was prepared. Also, a mixed green-sensitive emulsion in a molar ratio of 1:1 made green-sensitive by using a green-sensitizing dye and a mixed red-sensitive emulsion in a molar ratio of 1:1 made red-sensitive by using a red-sensitizing dye were similarly prepared.

On a paper support, laminated on both sides with polyethylene, were coated the following emulsion and other layers in the described order, to prepare Sample 9.

(1) Red-sensitive emulsion layer:

A red-sensitive emulsion layer comprising 0.4 g/m^2 of the above red-sensitive emulsion, 0.8 g/m^2 of oil-protect-dispersed cyan coupler C-1, and 1.5 g/m^2 of gelatin.

(2) Intermediate layer:

A layer containing an oil-protected 2,5-di-tert-octyl-hydroquinone, and 8 mg/m² of gelatin.

(3) Green-sensitive emulsion layer:

A green-sensitive layer comprising 0.4 g/m² of the above green-sensitive emulsion, 0.8 g/m² of oil-protected Exemplified Compound (7) as a magenta color image forming coupler, and 1.5 g/m² of gelatin.

(4) Yellow filter layer:

A layer containing 0.12 g/m² of yellow colloidal silver, oil-protect-dispersed 2,5-di-tert-octyl-hydroquinone, and 1.5 g/m² of gelatin.

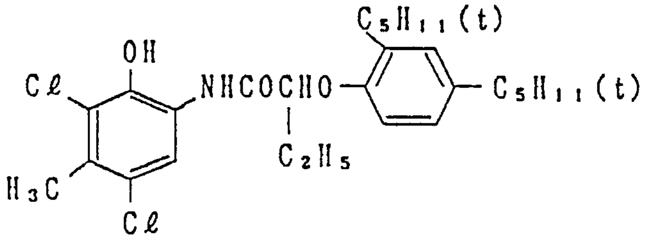
(5) Blue-sensitive emulsion layer:

A blue-sensitive emulsion layer comprising 0.5 g/m² of the above blue-sensitive emulsion. 0.7 g/m² of oil-protected yellow coupler Y-1, and 1.5 g/m² of gelatin.

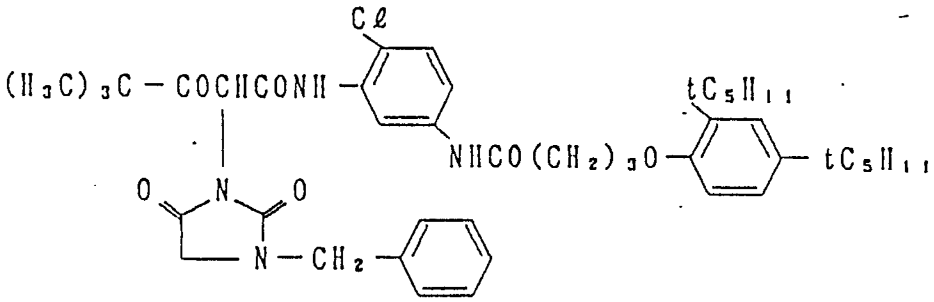
(6) Protective layer:

A layer containing 1.5 g/m² of gelatin.
The compounds used in these layers are as follows:

C - 1



Y - 1



Further, Samples 10 through 16 were prepared in the same manner as Sample 9 except that the magenta color image forming coupler in the green-sensitive emulsion layer was replaced as shown in Table 2.

Samples 9 through 16 were exposed through an optical wedge and then processed in the following procedure using the same processing solutions as in Example 1.

Procedure (at 38°C)Color developing 2 minutes and 30 seconds
Bleach-fix 1 minute and 30 seconds
Stabilizing 1 minute and 30 seconds

The entire area of each sample was exposed to 2 luxes of white light for a period of 10 seconds between 10 seconds and 20 seconds after the commencement of the color developing process. This processing was regarded as Processing 1.

Subsequently, a similar processing to Processing 1 was performed and this was regarded as Processing 2. In Processing 2, a color developer solution having 0.1% of bleach-fix solution was used.

Each of the samples processed in above was subjected to sensitometry, and the γ and minimum density (Dmin) of the magenta color image were determined with respect to both Processing 1 and Processing 2. The results obtained are shown in Table 2.

Table 2

Sample No.	Magenta color image forming coupler	Processing-1		Processing-2		Remarks
		γ	Dmin	γ	Dmin	
9	Exemplified Compound (7)	1.44	0.15	1.34	0.17	Invention
10	Exemplified Compound(11)	1.38	0.16	1.33	0.19	Invention
11	Exemplified Compound(26)	1.44	0.14	1.30	0.16	Invention
12	Exemplified Compound(48)	1.37	0.15	1.29	0.16	Invention
13	Exemplified Compound(55)	1.32	0.16	1.25	0.17	Invention
14	Exemplified Compound(57)	1.30	0.17	1.21	0.19	Invention
15	Exemplified Compound(71)	1.41	0.15	1.33	0.17	Invention
16	Comparative Compound (1)	1.14	0.16	0.85	0.29	Comparative

As is apparent from the results shown in Table 2, Samples 9 through 15 for this invention, even where a bleach-fix solution is mixed into the color developer solution (Processing 2), show only slight lowering of the γ and show no remarkable increase in the minimum density (Dmin); whereas Comparative Sample 16 shows magenta color stain on the background evidencing an increase in the minimum density (Dmin). Thus the resulting image was substantially deteriorated.

Example-3

Samples 9, 11, and 16 of the samples obtained in Example 2 were used and Processing 1 was repeated. In addition to Processing 1, Processing 3 and Processing 4 were performed with respect to Samples 9, 11, and 16.

Processing 3 was carried out in the same manner as Processing 1 except that the illumination in the overall exposure was 4 luxes and Processing 4 was performed in the same manner as Processing 1 except that the illumination in the overall exposure light was 8 luxes.

Each of the samples thus processed was subjected to sensitometry, and the sensitivity (S) and the minimum density (Dmin) of the magenta color image were found. The results obtained are shown in Table 3.

Table 3

Sample No.	Processing-1 S	Processing-1 Dmin	Processing-3 S	Processing-3 Dmin	Processing-4 S	Processing-4 Dmin	Remarkds
9	100	0.15	95	0.15	84	0.17	Invention
11	99	0.15	98	0.16	90	0.17	Invention
16	94	0.16	60	0.17	42	0.19	Comparative

As is apparent from the results shown in Table 3, Samples 9 and 11 of this invention show little lowering of sensitivity (S)-due to the change in the illumination in the overall exposure, thus showing a wide tolerance for this variable.

In contrast, it is apparent that the sensitivity (S) of Sample 16 is drastically lowered by the change in the illumination in the overall exposure.

Example 4

In this example, each of Samples 9, 11 and 16 which were obtained in Example 2 was exposed through an optical wedge, and then processed according to the following procedure. This processing was regarded as Processing 5.

Procedure (at 38°C)	
Color developing	2 minutes
Bleach-fix	1 minute and 30 seconds
Stabilizing	1 minute and 30 seconds

For the bleach-fix and stabilizing, the same solutions as in Example 1 were used, but a color developer solution having the following composition was used.

3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate	4.5 g
Potassium sulfite	5.0 g
Potassium carbonate	40.0 g
Potassium bromide	1.0 g
5-Methylbenzotriazole	10 mg
Benzyl alcohol	5.0 g
1-Formyl-2-phenylhydrazine (fogging agent)	0.2 g
Water to make	1 liter

(Use potassium hydroxide to adjust the pH to 12.0)

Another processing similar to Processing 5 except that 0.3 g/liter of 1-formyl-2-phenylhydrazine was used as the fogging agent in the color developer solution; this was regarded as Processing 6.

Each of the above samples thus processed was subjected to sensitometry, and the sensitivity (S) and the minimum density (Dmin) of the magenta color image were found. The results as shown in Table 4 were obtained.

Table 4

Sample No.	Processing-5 S	Processing-5 Dmin	Processing-6 S	Processing-6 Dmin	Remarks
9	100	0.14	104	0.14	Invention
11	98	0.14	99	0.15	Invention
16	89	0.15	78	0.17	Comparative

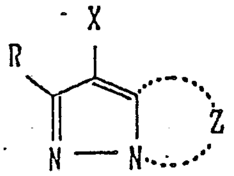
As is apparent from the results shown in Table 4, Samples 9 and 11, even when the amount of the fogging agent added is changed from 0.2 g/liter to 0.3 g/liter, almost no change in sensitivity (S), is shown. Comparative Sample 16 shows a large change in its sensitivity (S), thus being unstable.

Accordingly, it is understood that Samples 9 and 11 (the present invention) produce a satisfactory image stable to change in the developer composition, particularly change in the fogging agent.

Claims

1. A direct positive silver halide light-sensitive photographic material comprising a support and a silver halide emulsion layer thereon containing direct positive silver halide grains adapted to form an internal latent image upon imagewise exposure and being unpre-fogged, and a compound represented by general formula [I],

[I]

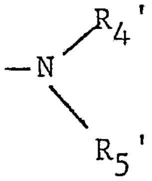


wherein Z represents a group of non-metallic atoms necessary to complete a nitrogen-containing heterocyclic ring which may have a substituent; X represents a hydrogen atom or a substituent capable of being split off upon reaction with an oxidation product of a color developing agent; and R represents a hydrogen atom or a substituent.

2. The material of Claim 1 wherein said substituent for R is selected from the group consisting of halogen, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl, heterocyclic, acyl, sulfonyl, sulfinyl, phosphonyl, carbamoyl, sulfamoyl, cyano, spiro residue, bridged hydrocarbon residue, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, carbamoyloxy, amino, acylamino, sulfonamide, imide, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl, alkylthio, arylthio, and heterocyclic thio.

3. The material of Claim 1 wherein X is selected from the group consisting of hydrogen, halogen, and and organic group having a carbon atom, an oxygen atom, a sulfur atom, a nitrogen atom or phosphorus atom through which said organic group is connected with the remainder of the compound.

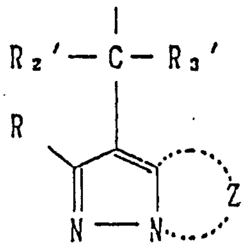
4. The material of Claim 1 wherein X is selected from the group consisting of halogen; alkoxy; aryloxy; heterocyclic oxy; acyloxy; sulfonyloxy; alkoxycarbonyloxy; aryloxycarbonyloxy; alkyloxalyloxy; alkoxyoxalyloxy; alkylthio; arylthio; heterocyclicthio; alkyloxythiocarbonylthio; a group represented by the formula



$$-N\begin{matrix} R_4' \\ R_5' \end{matrix}$$

wherein R_4'

wherein R_4' and R_5' independently represent hydrogen, alkyl, aryl, heterocyclic, sulfamoyl, carbamoyl, acyl, sulfonyl, aryloxycarbonyl, or alkoxycarbonyl, provided that R_4' and R_5' are not simultaneously hydrogen atoms and R_4' and R_5' may combine with each other to form a nitrogen-containing heterocyclic group; carboxy; hydroxymethyl; triphenylmethyl; and a group represented by the formula,

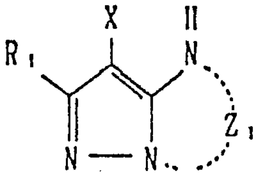


wherein R_2' and R_3' are independently selected from the group consisting of hydrogen, aryl, alkyl, and a heterocyclic group.

5. The material of Claim 1 wherein said nitrogen-containing heterocyclic ring is selected from the group consisting of pyrazole, imidazole, triazole, and tetrazole, each of which may have the same substituent as defined for R.

6. The material of Claim 1 wherein said compound represented by general formula [I] is a magenta dye-forming coupler.

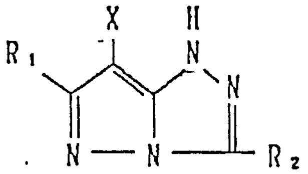
7. The material of Claim 6 wherein said magenta dye forming coupler is selected from a compound represented by formula [VIII]:



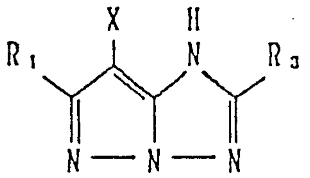
wherein R_1, X and Z_1 have the same meaning as R, X and Z.

8. The material of Claim 6 wherein said magenta dye forming coupler is selected from a compound represented by formulas [II] to [VII]:

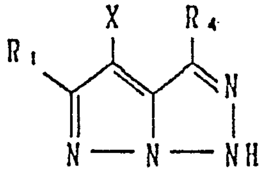
[II]



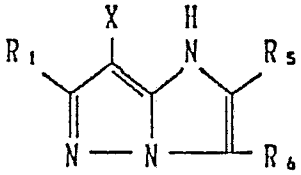
[III]



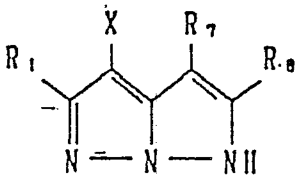
〔IV〕



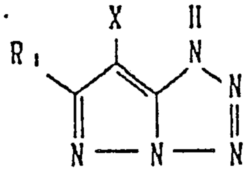
〔V〕



〔VI〕



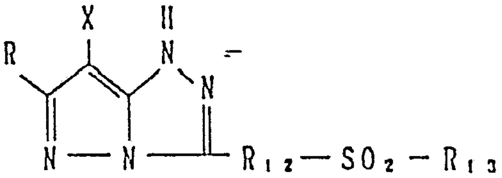
〔VII〕



wherein R_1 to R_8 have the same meaning as R.

9. The material of Claim 6 wherein said magenta dye forming coupler is selected from a compound represented by formula [XI]:

〔XI〕



wherein R_{12} is an alkylene group and R_{13} is selected from the group consisting of alkyl, cyclo alkyl, and aryl.

10. The material of Claim 1 wherein said silver halide grains are core/shell silver halide grains.

11. The material of Claim 10 wherein said shell contains at least 30 mol % of silver chloride.

12. The material of Claim 1 wherein the silver chloride content of the silver halide grains is not less than 5 mol %.

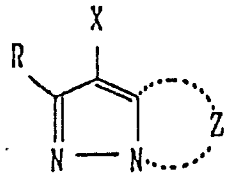
13. The material of Claim 1 wherein the silver chloride content of the silver halide grains is not less than 30 mol %.

14. The material of Claim 1 wherein said silver halide grains consisting essentially of a mixture of at least two sizes of silver halide grains each of which has a different average grain size.

15. The material of Claim 14 wherein the size of the smaller of said two sizes is no more than 80% of the size of the larger of said two sizes.

16. A method for the formation of a direct positive image which comprises imagewise exposing a direct positive silver halide light-sensitive photographic material, and
subjecting said exposed direct positive silver halide light-sensitive photographic material to surface development after or with a fogging treatment, said material comprising a support and a silver halide emulsion layer thereon containing direct positive silver halide grains adapted to form an internal latent image upon imagewise exposure and being unpre-fogged, and a compound represented by general formula [1],

[I]



wherein Z represents a group of non-metallic atoms necessary to complete a nitrogen-containing heterocyclic ring which may have a substituent; X represents a hydrogen atom or a substituent capable of being split off upon reaction with an oxidation product of a color developing agent; and R represents a hydrogen atom or a substituent.