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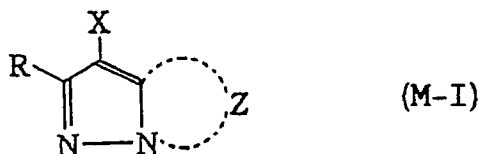
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EUROPEAN PATENT APPLICATION(21) Application number: **91108545.4**(51) Int. Cl.⁵: **G03C 7/30**(22) Date of filing: **25.05.91**(30) Priority: **28.05.90 JP 137455/90**(43) Date of publication of application:
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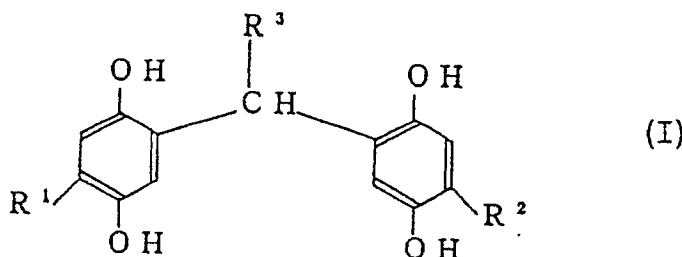
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W-4000 Düsseldorf 13(DE)(54) **Silver halide color photographic light-sensitive material.**

(57) A silver halide color photographic material suitable for making a color proof in photomechanical process is disclosed. The light-sensitive material comprises a silver halide emulsion layer containing a yellow coupler and a magenta coupler represented by Formula M-I and the silver halide emulsion layer or a layer adjacent to the emulsion layer contains a compound represented by Formula I:



wherein Z is a group of atoms necessary forming a nitrogen-containing heterocyclic ring; X is a hydrogen atom or a substituent capable of being split off upon coupling reaction; and R is a hydrogen atom or a substituent:



wherein R¹ and R² each a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group or an alkylamido

group, the alkyl group, alkoxy group, alkylthio group and alkylamido group each have 1 to 8 carbon atoms; and R^3 is a hydrogen atom or an alkyl group having 1 to 11 carbon atoms.

FIELD OF THE INVENTION

The present invention relates to a color photographic light-sensitive material improved in color tone, particularly to a silver halide color photographic light-sensitive material used in making a color proof from plural black-and-white dot images obtained by color separation and image conversion in the color photomechanical process.

BACKGROUND OF THE INVENTION

As a method to prepare a color proof from plural black-and-white dot images obtained through color separation and dot image conversion in the color photomechanical process, there have been known the overlay method and surprint method which form color images with a photopolymer or diazo compound.

The overlay method is very simple and low in manufacturing costs, and has an advantage that preparations for color proofing can be made by simply laying four color film sheets, the subtractive three primary colors and black, one over another; but overlaying of such film sheets yields gloss which causes a disadvantage of giving a texture different from that of printed matter.

The surprint method is to overlay colored images one over another on a support. In this surprint method, techniques to obtain colored images utilizing tackiness of photopolymerizable materials are disclosed in U.S. Patent Nos. 3,582,327, 3,607,264 and 3,620,726.

There are also known, in Japanese Patent Examined Publication No. 27441/1972 and Japanese Patent O.P.I. Publication No. 501217/1981, a method to prepare a color proof through repetition of steps of laminating a colored photosensitive sheet on a support, forming an image through exposure and development and then laminating another colored sheet thereon.

Further, Japanese Patent O.P.I. Publication No. 97140/1984 discloses a method to form colored images on a support by transfer, in which colored photosensitive sheets are used to expose corresponding color separation films and images obtained by development are transferred on a support. This method has an advantage of providing a color proof having a tone similar to that in printed matter, because a colorant used in an printing ink can be employed as a toner and colorant for the colored sheet to form these images.

In preparing a color proof, however, these methods need overlaying or transferring of images; therefore, it involves disadvantages of taking time in these processes and a rise in manufacturing costs.

As a means to eliminate these disadvantages, there is disclosed a method of preparing a color proof, which uses a silver halide color photographic light-sensitive material having a white support, in Japanese Patent O.P.I. Publication Nos. 11313/1981 and 104335/1981. But, this method can hardly reproduce a color of a printing ink since the colors of respective layers of yellow, magenta and cyan obtained by color separation exposure and development of the silver halide color photographic light-sensitive material are different from yellow, magenta and cyan colors used in a printing ink.

In case a color photographic light-sensitive material of negative type is used as a material for making a color proof, it is known through U.S. Patent No. 4,188,111 that an optimum color tone can be obtained by having color formation of dot images in yellow, magenta and cyan approximate to respective colors of printing inks by controlling the wavelength components of the light with filters during exposure and by appropriately mixing yellow, magenta and cyan of a color photographic light-sensitive material for a dot image.

However, the color proof prepared by this method has been found to have a defect of causing a large variation in color tone of dots when dots are small; therefore, it cannot properly perform the function as a color proof.

Further, in the method to prepare a color proof by subjecting a positive type color photographic light-sensitive material to exposure from black-and-white positive dot images, there remains a difficulty in the process to control wavelength components of the light during exposure; that is, it is difficult to adjust optical densities of yellow, magenta and cyan of a color photographic material to an appropriate ratio which gives color tones approximate to those of printing inks. Therefore, adjusting a color tone takes a long time.

Under the circumstances, there is known, by Japanese Patent Application No. 306569/1988, a technique to approximate magenta, in which the color difference from an printing ink is most conspicuous, to a color tone of printing ink by incorporating a yellow coupler in a layer containing a magenta coupler.

Besides the color tone, reproducibility of dots is another important function demanded of a color proof.

For a color proof prepared by use of a photographic light-sensitive material, the so-called foot gradation must be hard. And as a measure to impart it, a technique to incorporate a hydroquinone compound in a photographic structural layer is proposed by Japanese Patent O.P.I. Publication No. 239153/1987.

However, when said hydroquinone compound is applied to the technique of Japanese Patent Applica-

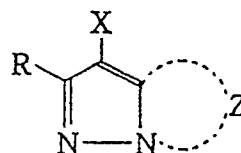
tion No. 306569/1988, an adequate dot quality cannot be obtained, because a quality difference comes about between large dots and small dots.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a silver halide color photographic light-sensitive material used to prepare a color proof from plural black-and-white dot images obtained by color separation and dot image conversion, which is capable of reproducing dots in good state and giving a color tone approximate to that of a printing ink.

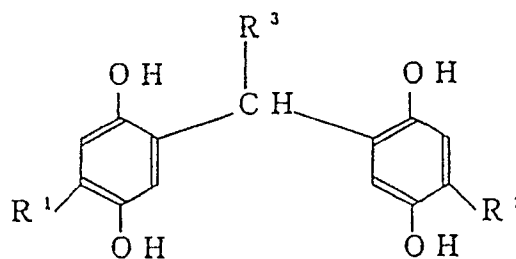
The silver halide color photographic light-sensitive material of the invention has, on a support, having thereon a silver halide emulsion layer containing a magenta coupler represented by the following Formula M-I and a yellow coupler, and the silver halide emulsion layer and/or a layer adjacent thereto contains at a compound represented by the following Formula I.

Formula M-I



In the formula, Z represents a group of atoms necessary to form 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 oxidized product of a color developing agent. R represents a hydrogen atom or a substituent.

Formula I

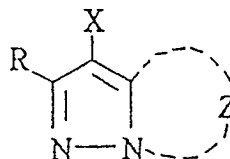


In the formula, R^1 and R^2 independently represent a hydrogen atom or an alkyl, alkoxy, alkylthio or alkylamide group each of which has 1 to 8 carbon atoms. R^3 represents a hydrogen atom or an alkyl group having carbon atoms of 1 to 11. The total number of carbon atoms in R^1 , R^2 and R^3 are 8 to 22.

DETAILED DESCRIPTION OF THE INVENTION

In the invention, preferred magenta dye forming couplers contained in a magenta dye image forming layer of the silver halide color photographic light-sensitive material are those pyrazoloazole couplers which are represented by the following Formula M-I.

Formula M-I



In Formula M-I, Z represents a group of atoms necessary to form a nitrogen-containing heterocyclic ring, and the ring formed by Z may have a substituent.

X represents a hydrogen atom or a group capable of being split off upon reaction with an oxidized product of a color developing agent.

R represents a hydrogen atom or a substituent.

The substituent represented by R is not particularly limited, but typical examples thereof include an alkyl, aryl, anilino, acylamino, sulfonamide, alkylthio, arylthio, alkenyl and cycloalkyl groups. Other usable examples are halogen atoms; a cycloalkenyl, alkynyl, heterocyclic, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imido, ureido, sulfamoylamino, alkoxy-carbonylamino, aryloxy-carbonylamino, alkoxy-carbonyl, aryloxy-carbonyl and heterocyclic thio groups; and spiro residues and bridged hydrocarbon residues.

The alkyl group represented by R is preferably one having 1 to 32 carbon atoms and may be a straight or branched chain.

The aryl group represented by R is preferably a phenyl group.

Examples of the acylamino group represented by R include alkylcarbonylamino and arylcarbonylamino groups.

Examples of the sulfonamide group represented by R are alkylsulfonylamino and arylsulfonylamino groups.

Examples of the alkyl and aryl components in the alkylthio and arylthio groups represented by R are the alkyl and aryl groups each represented by R.

The alkenyl group represented by R is preferably one having 2 to 32 carbon atoms; the cycloalkyl group represented by R is preferably one having 3 to 12, particularly 5 to 7 carbon atoms; and the alkenyl group may be of straight or branched chain.

The cycloalkenyl group represented by R is preferably one having 3 to 12 carbon atoms, more preferably 5 to 7 carbon atoms.

Examples of the sulfonyl group represented by R include alkylsulfonyl and arylsulfonyl groups.

Examples of the sulfinyl group include alkylsulfinyl and arylsulfinyl groups.

Examples of the phosphonyl group include alkylphosphonyl, alkoxyphosphonyl, aryloxyphosphonyl and arylphosphonyl groups.

Examples of the acyl group include alkylcarbonyl and arylcarbonyl groups.

Examples of the carbamoyl group include alkylcarbamoyl and arylcarbamoyl groups.

Examples of the sulfamoyl group include alkylsulfamoyl and arylsulfamoyl groups.

Examples of the acyloxy group include alkylcarbonyloxy and arylcarbonyloxy groups.

Examples of the carbamoyloxy group include alkylcarbamoyloxy and arylcarbamoyloxy groups.

Examples of the ureido group include alkylureido and arylureido groups.

Examples of the sulfamoylamino group include alkylsulfamoylamino and arylsulfamoylamino groups.

The heterocyclic group is preferably a five- to seven-membered one, and examples thereof include 2-furyl, 2-thienyl, 2-pyrimidinyl and 2-benzothiazolyl groups.

The heterocyclic oxy group is preferably one having a five- to seven-membered heterocycle, and examples thereof include 3,4,5,6-tetrahydropyran-2-yl and 1-phenyltetrazole-5-yl groups.

The heterocyclic thio group is preferably one having a five- to seven-membered heterocycle, and examples thereof include 2-pyridylthio, 2-benzothiazolylthio and 2,4-diphenoxy-1,3,5-triazole-6-thio groups.

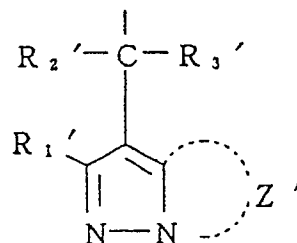
Examples of the siloxy group include trimethylsiloxy, triethylsiloxy and dimethylbutylsiloxy groups.

Examples of the imido group include succinimido, 3-heptadecyl succinimido, phthalimido and glutarimido groups.

Examples of the spiro residue include [3.3]heptane-1-yl.

Examples of the bridged hydrocarbon residue include bicyclo[2.2.1]heptane-1-yl, tricyclo[3.3.1,^{3,7}]decane-1-yl and 7,7-dimethyl-bicyclo[2.2.1]heptane-1-yl.

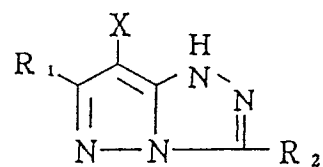
Examples of the substituent that is represented by X and is capable of being split off upon reaction with an oxidation product of a color developing agent include halogen atoms, e.g., chlorine, bromine and fluorine atoms; alkoxy, aryloxy, heterocyclic oxy, acyloxy, sulfonyloxy, alkoxycarbonyloxy, aryloxycarbonyl, alkylox-
 5 alkyloxy, alkoxyoxalyloxy, alkylthio, arylthio, heterocyclic thio, alkyloxythiocarbonylthio, acylamino, sulfon-
 amide, N-atom bonded nitrogen-containing heterocycle, alkyloxycarbonylamino, aryloxycarbonylamino and
 carboxyl groups; and



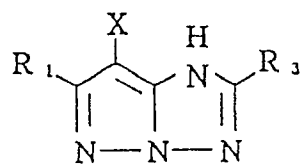
where R₁' is the same as the above R, Z' is the same as the above Z; and R₂' and R₃' are independently a
 20 hydrogen atom, or an aryl, alkyl or heterocyclic group. Among these examples, the preferred is a halogen
 atom, especially a chlorine atom. Examples of the nitrogen-containing heterocycle formed by Z or Z'
 include pyrazole, imidazole, triazole and tetrazole rings. The substituent which any of these rings may have
 is the same as that defined for R.

The couplers represented by Formula M-I are more specifically expressed by the following Formulas
 25 M-II to M-VII :

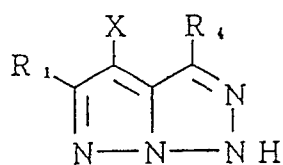
Formula M-II



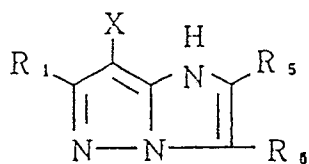
Formula M-III



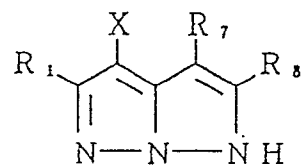
Formula M-IV



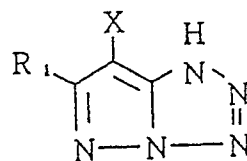
Formula M-V



Formula M-VI



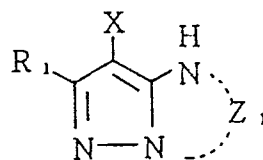
Formula M-VII



In the above Formulas [M-II] to [M-VII], R_1 to R_8 and X are the same as those defined for R and X previously.

Of those represented by Formula [M-I], the particularly preferred are those represented by the following Formula M-VIII :

Formula M-VIII



In the formula, R_1 , X and Z_1 are the same as those defined for R, X and Z previously.

Among the magenta couplers represented by Formulas M-II to M-VII, the particularly preferred are those represented by Formula M-II or Formula III.

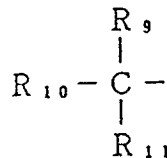
In the light-sensitive material used to form positive images, it is preferable for the substituents on the heterocycles in Formulas M-I to M-VIII that R in Formula M-I or R_1 in Formulas M-II to M-VIII meet the following requisite 1; the more preferred is that they meet the following requisites 1; and the most preferred is that they meet the following requisites 1 and 2.

Requisite 1: The atom directly bonding with the heterocycle is a carbon atom.

Requisite 2: The bonds between said carbon atom and the adjacent atoms are single bonds.

The preferred substituents, which are represented by R and R_1 and meet the above requisites, are those represented by the following Formula M-IX.

Formula M-IX



In the formula, R_9 , R_{10} and R_{11} are the same as those defined for R previously; two of these R_9 , R_{10} and R_{11} , for example, R_9 and R_{10} , may form a saturated or unsaturated ring such as cycloalkane, cycloalkene or heterocycle; and the rings may link with R_{11} to form a bridged hydrocarbon residue.

With Formula M-IX, it is preferable that (i) at least two of R_9 to R_{11} be alkyl groups, or that (ii) one of R_9 to R_{11} , for example, R_{11} be a hydrogen atom and the other two, namely R_9 and R_{10} , link with each other to form a cycloalkyl residue in conjunction with the root carbon atom.

Further, in the above case (i), it is preferable that two of R_9 to R_{11} be alkyl groups, while the other one be a hydrogen atom or an alkyl group.

As the substituent which a ring formed by Z in Formula M-I or a ring formed by Z_1 in Formula M-VIII may have, or as any of R_2 to R_8 in Formulas M-II to M-VI, those represented by the following Formula M-X

are preferred.

Formula M-X $-R^1-SO_2-R^2$

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In the formula, R^1 represents an alkylene group, and R^2 represents an alkyl, cycloalkyl or aryl group.

The alkylene group represented by R^1 possesses a straight chain portion having preferably 2 or more carbon atoms, more preferably 3 to 6 carbon atoms, and may be of either straight or branched structure.

The cycloalkyl group represented by R^2 is preferably a five- to six-membered one.

10 In case the light-sensitive material is used for negative image formation, it is preferable for the substituents on heterocycles in Formulas M-I to M-VIII that R in Formula M-I or R_1 in Formulas M-II to M-VIII meet the following requisite 1; it is more preferable that they meet the following requisites 1 and 2.

Requisite 1: The atom directly bonding with the heterocycle is a carbon atom.

Requisite 2: At least two hydrogen atoms bond with said carbon atom.

15 As the substituents R and R_1 which meet the above requisite, those represented by the following Formula [M-XI] are particularly preferred.

Formula M-XI $R_{12}-CH_2-$

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In the formula, R_{12} is the same as that defined for R previously.

R_{12} is preferably a halogen atom or an alkyl group.

Typical examples of the compounds according to the invention are as follows:

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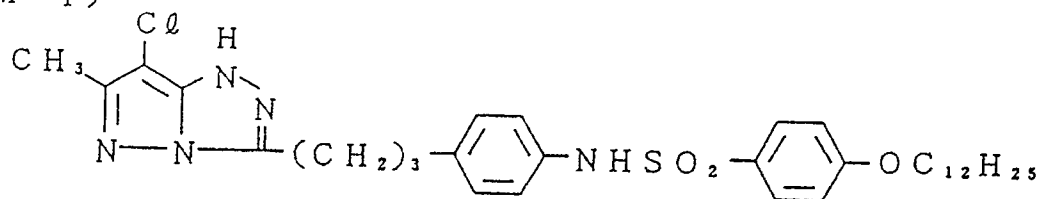
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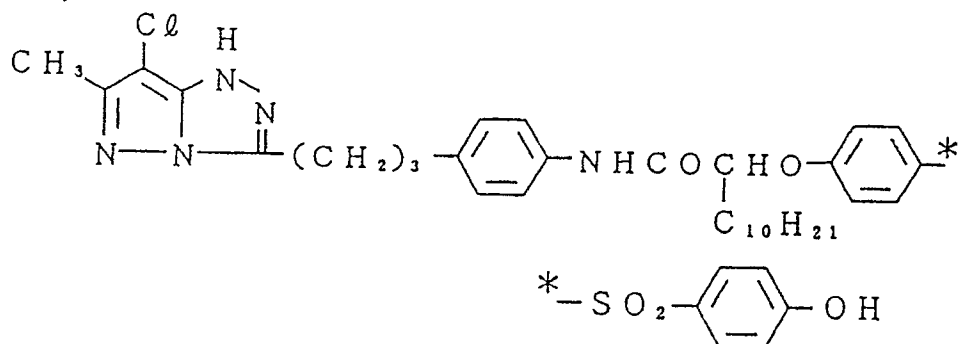
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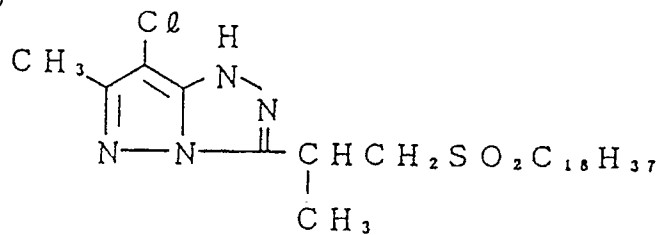
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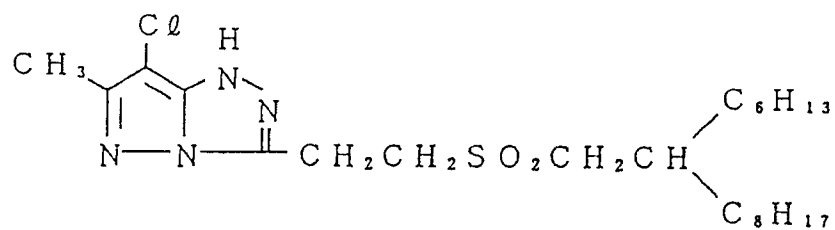
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(M-3)



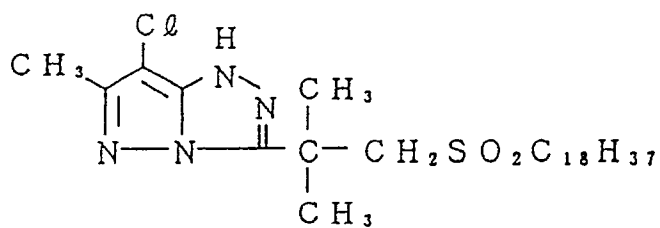
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(M-5)

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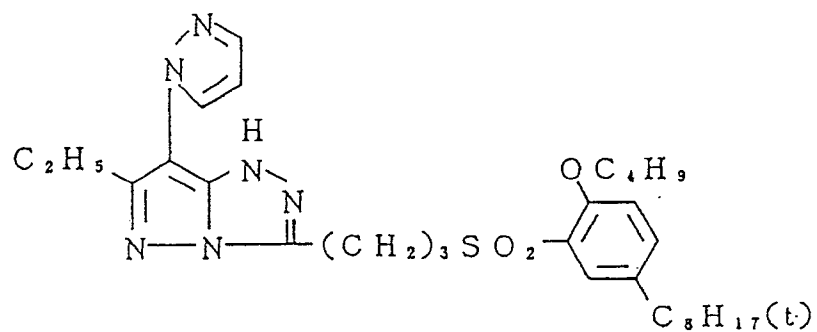


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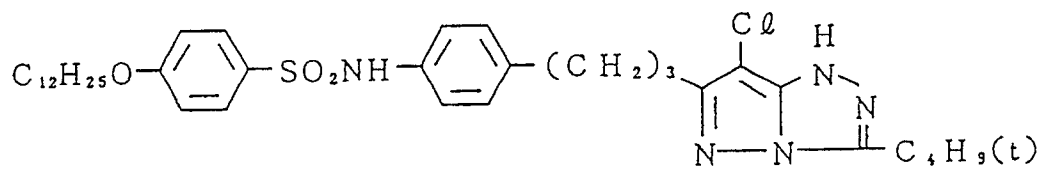
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(M-7)

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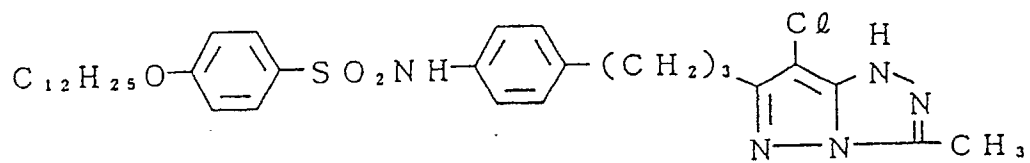
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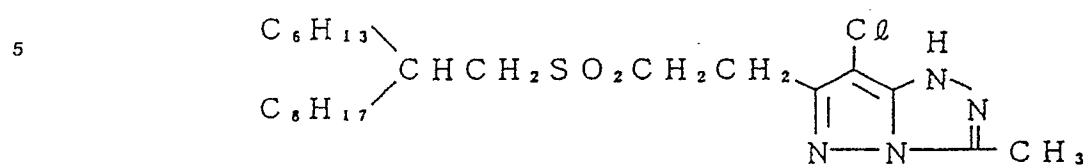
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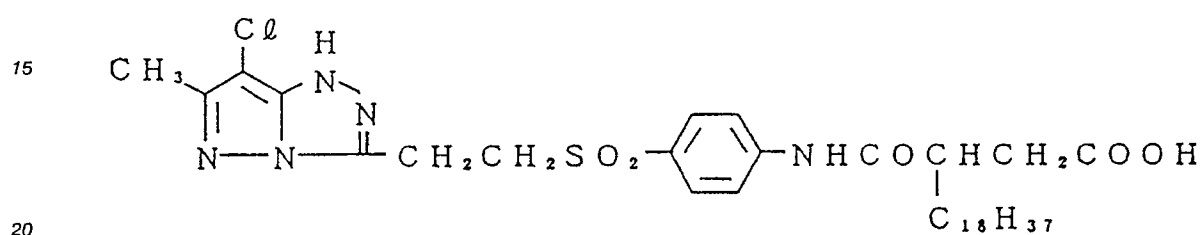


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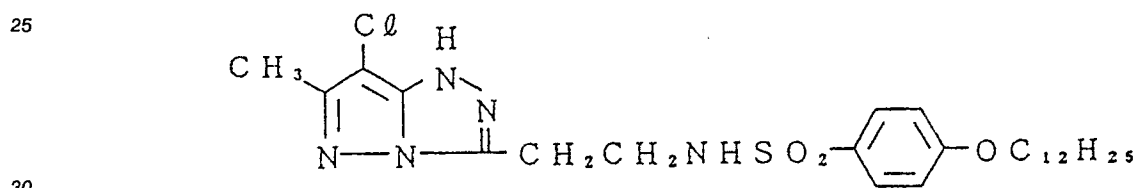


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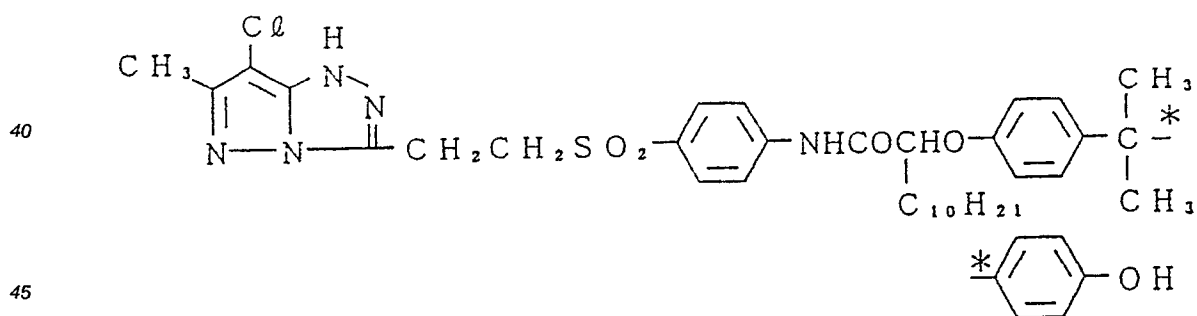
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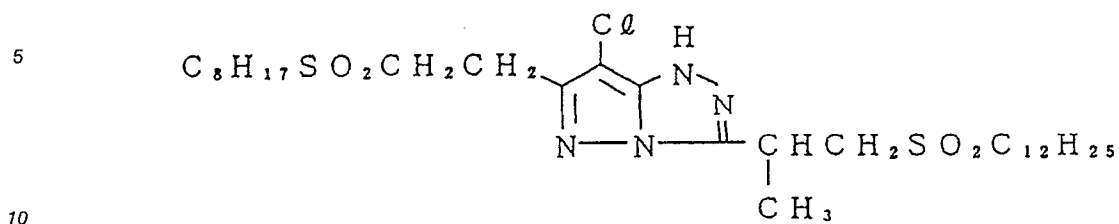
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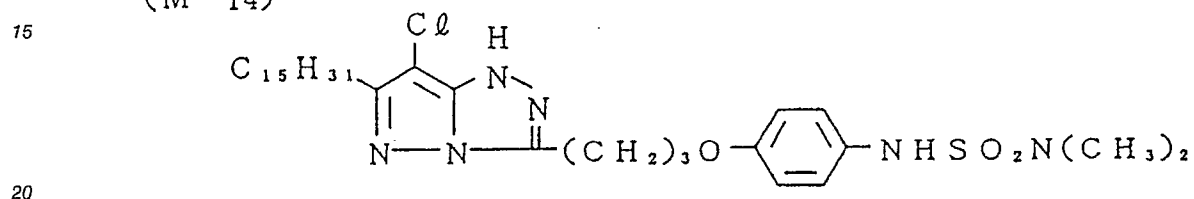
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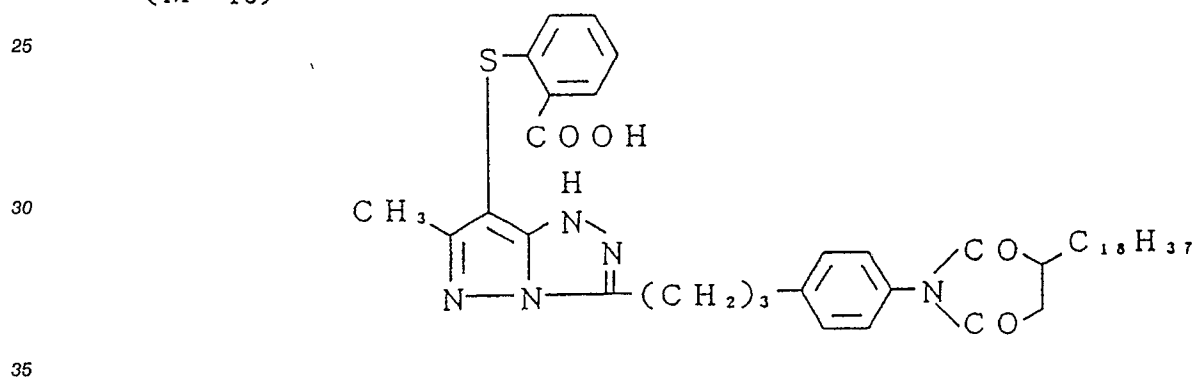
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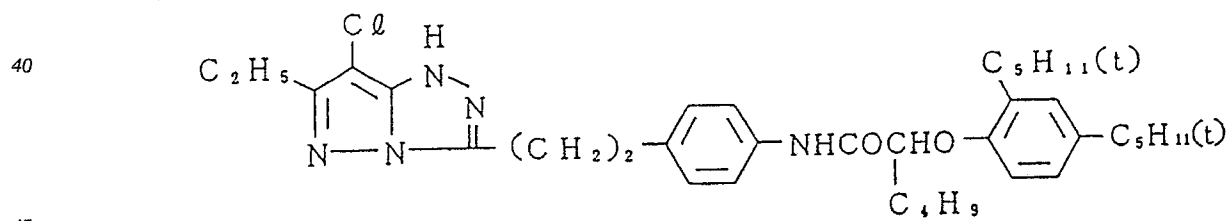
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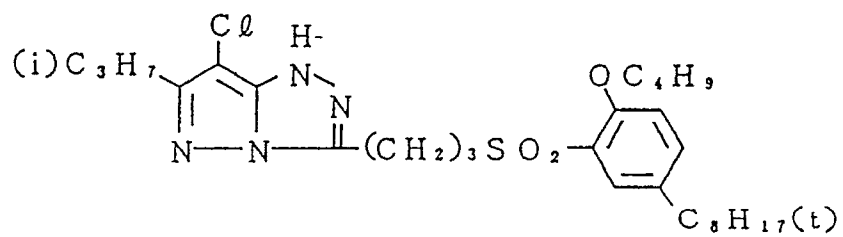
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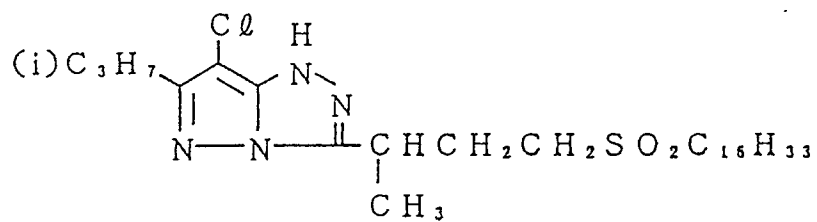
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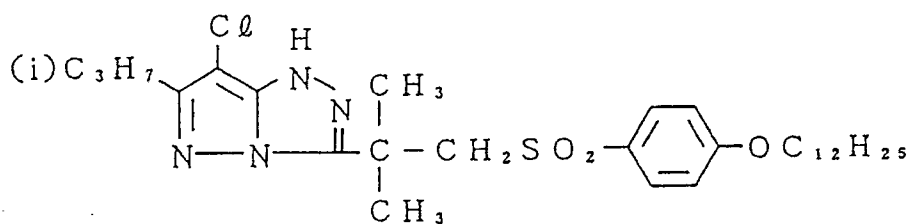
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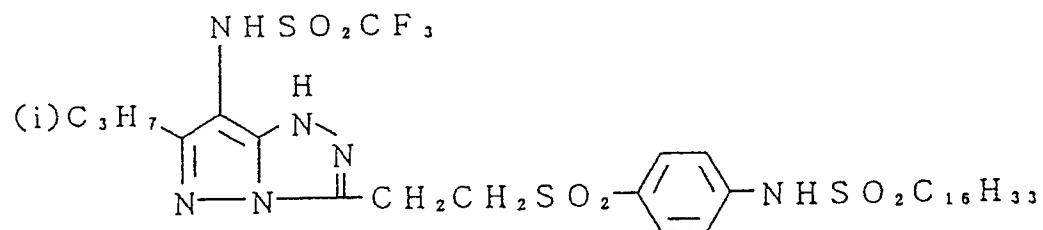
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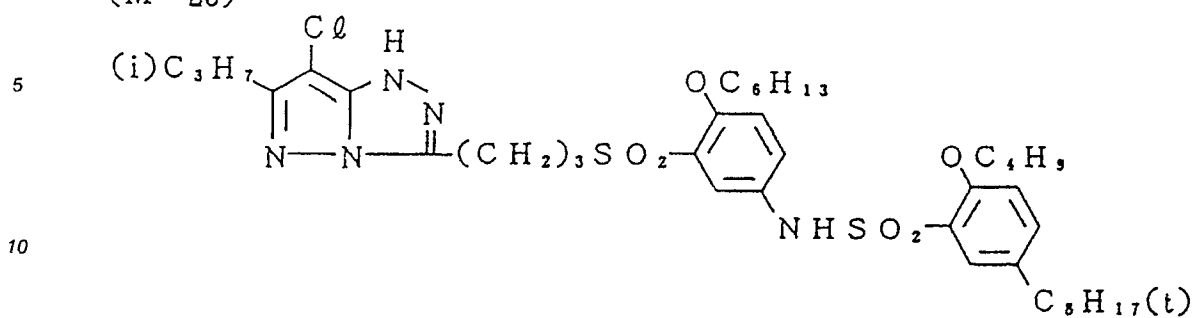
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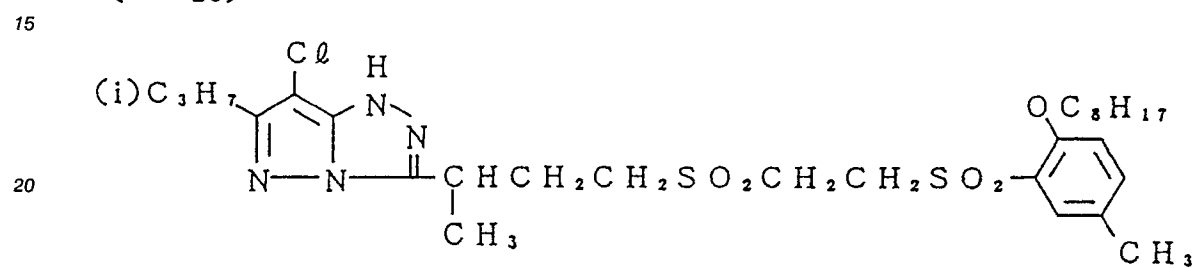
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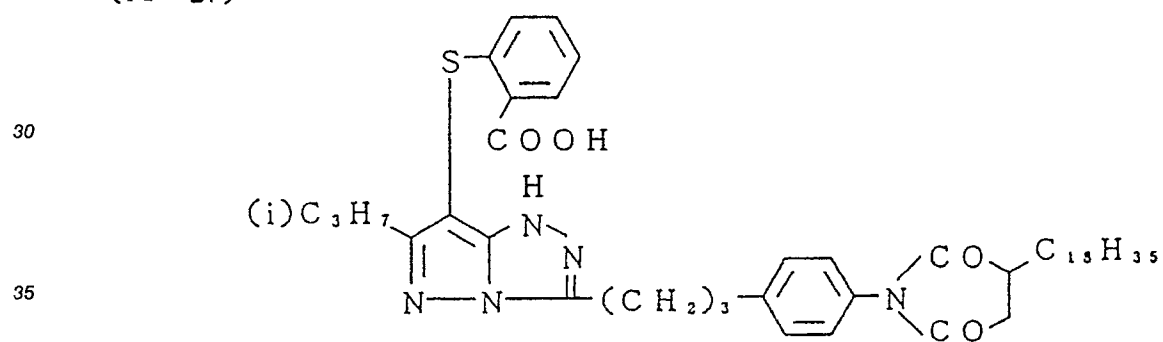
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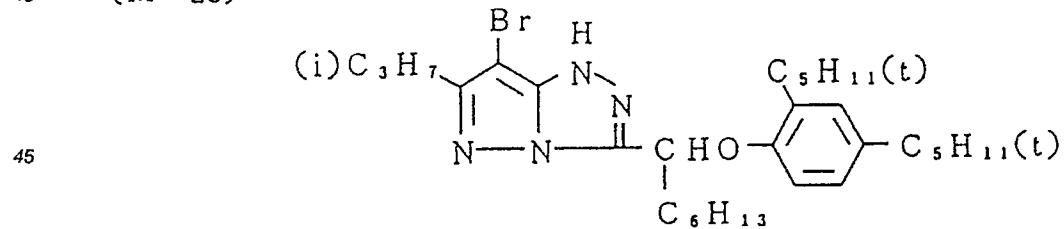
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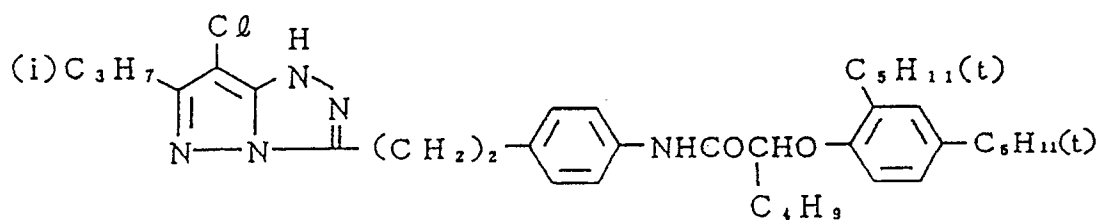
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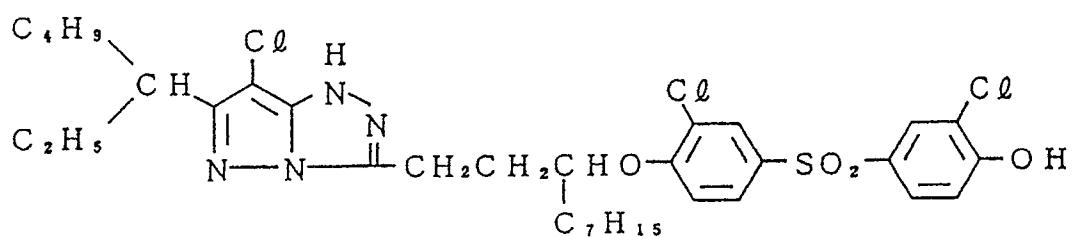
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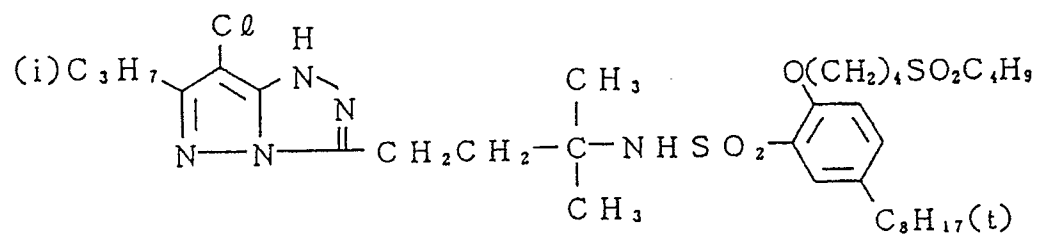
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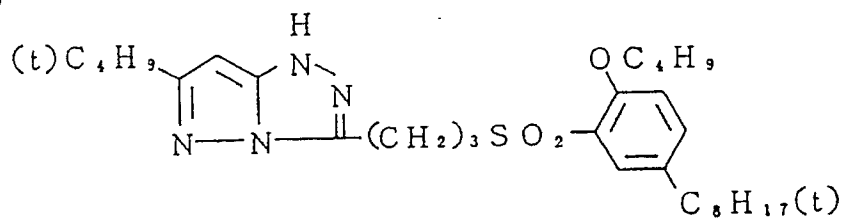
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(M-31)



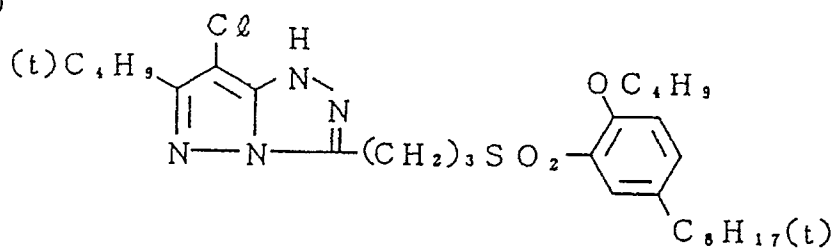
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(M-33)

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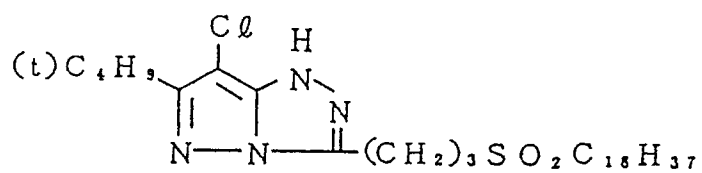
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(M-34)

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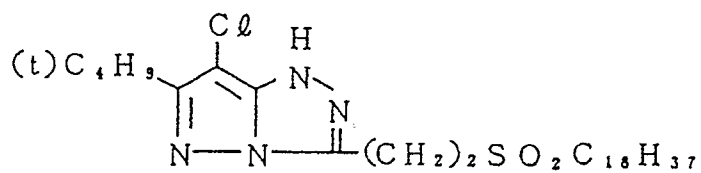
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(M-35)

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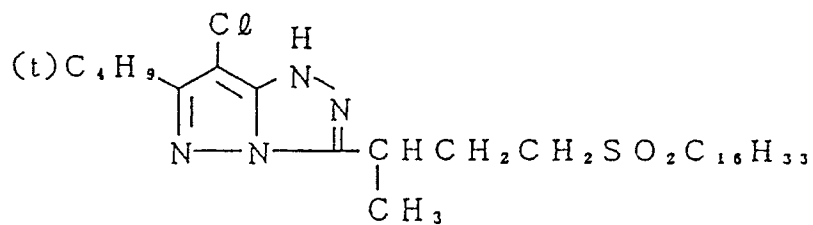
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(M-36)

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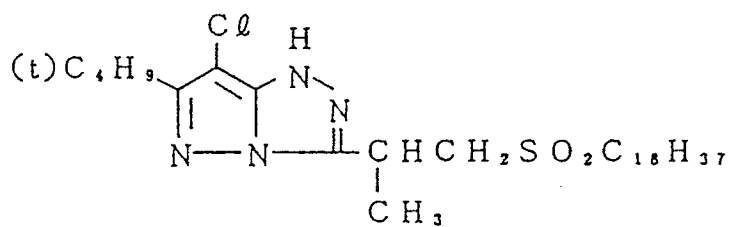
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(M-37)

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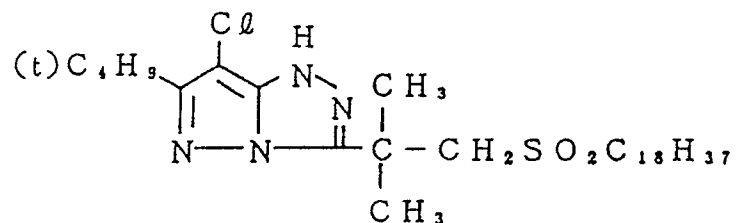


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(M-38)

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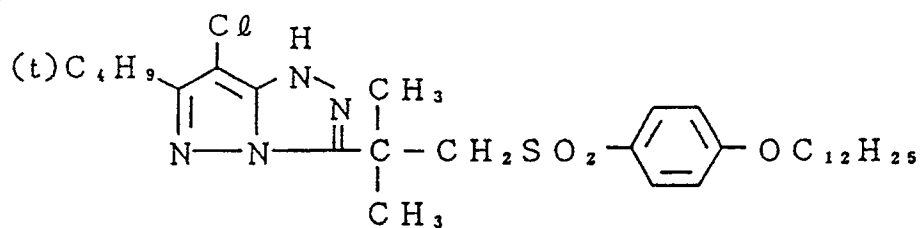
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(M-39)

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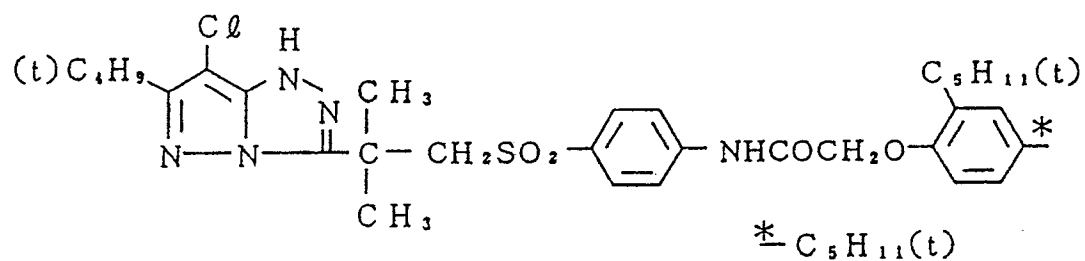
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(M-40)

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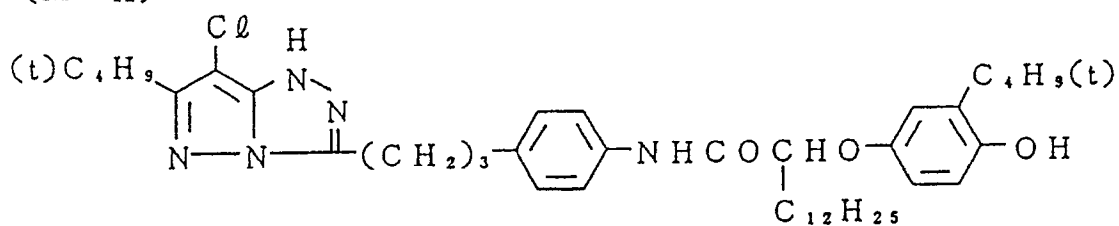
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(M-41)

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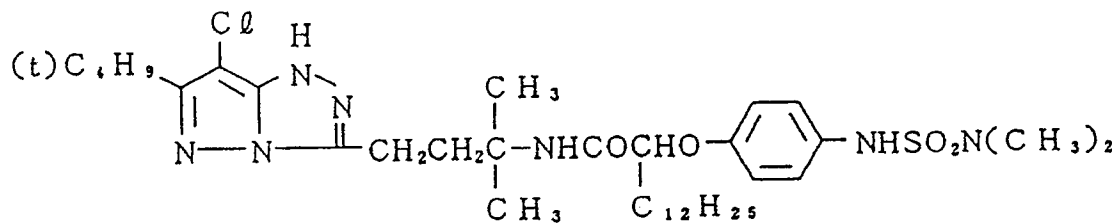


(M-42)

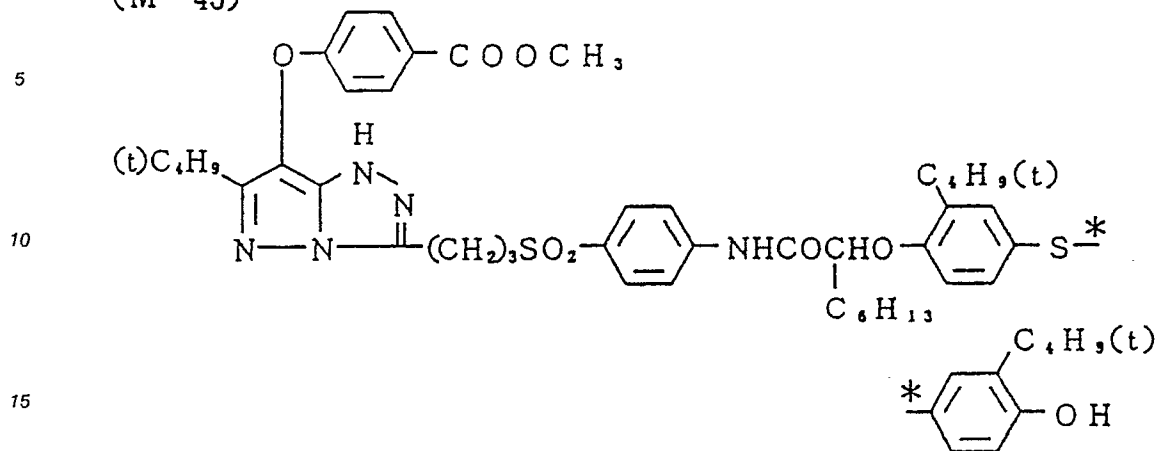
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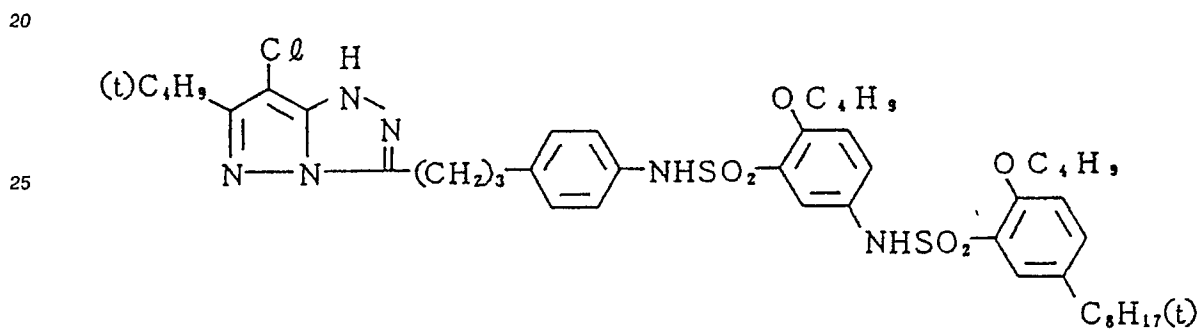
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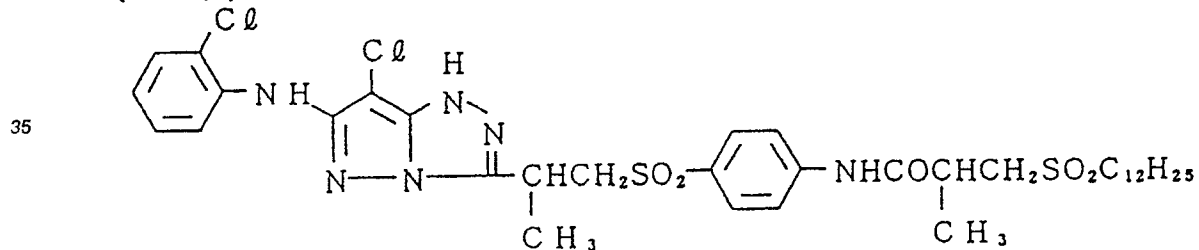
(M-43)



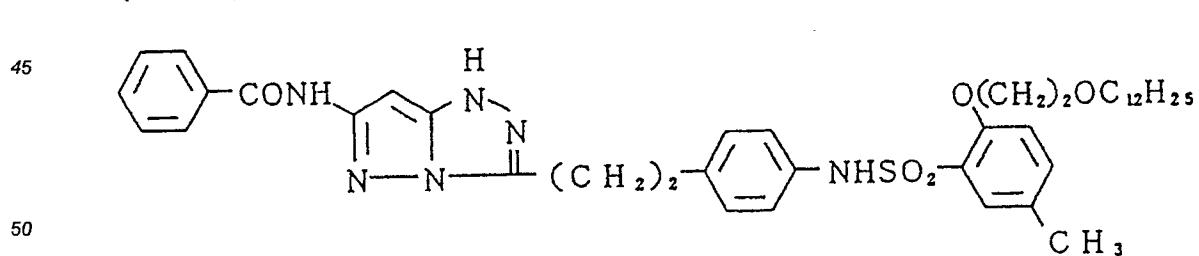
(M-44)



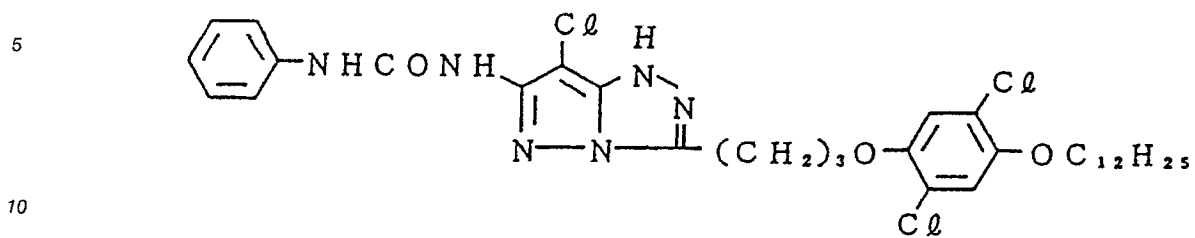
(M-45)



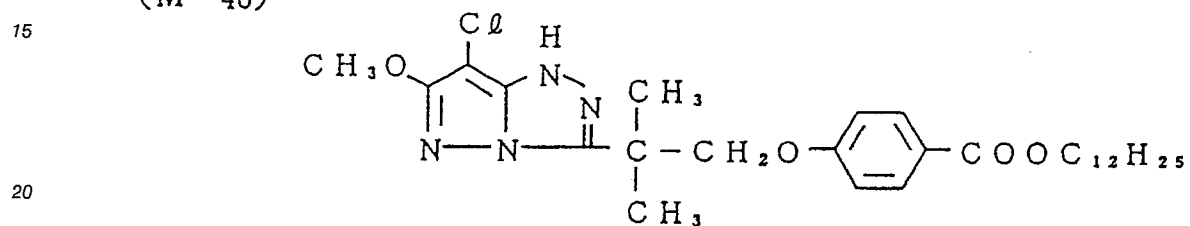
(M-46)



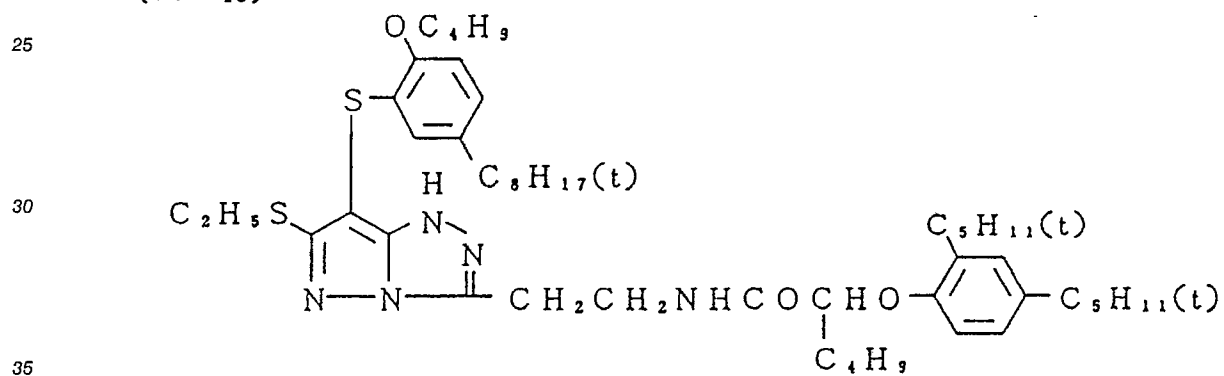
(M-47)



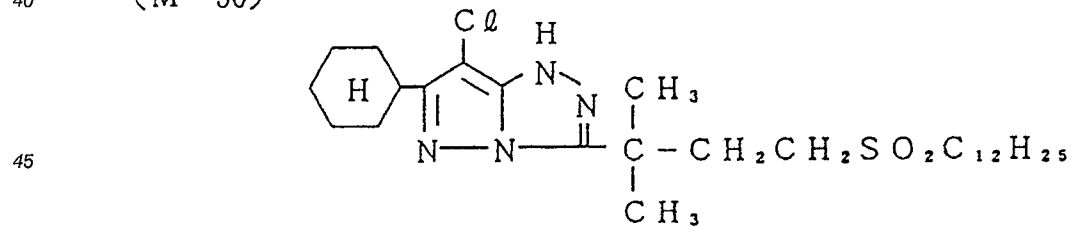
(M-48)



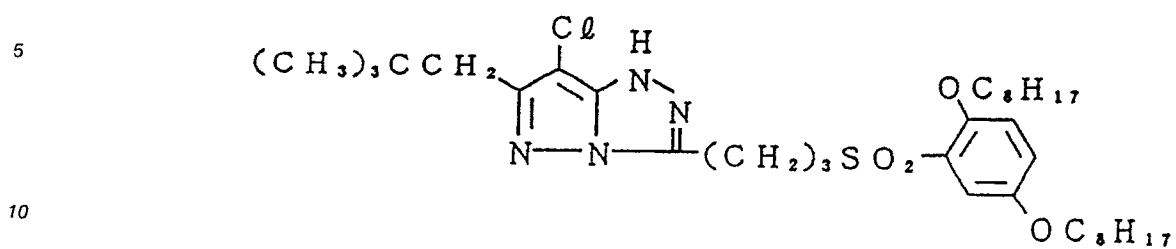
(M-49)



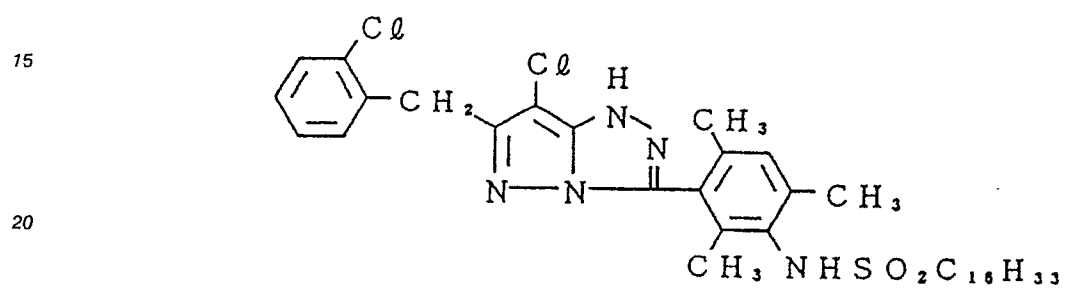
(M-50)



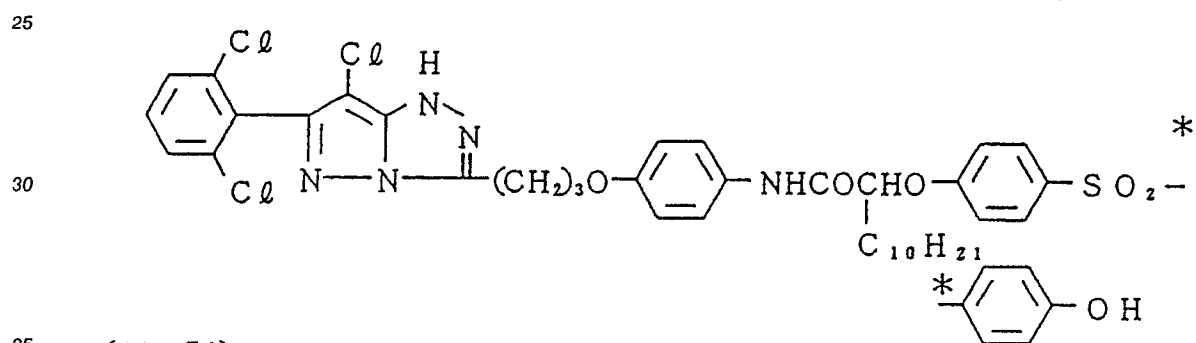
(M-51)



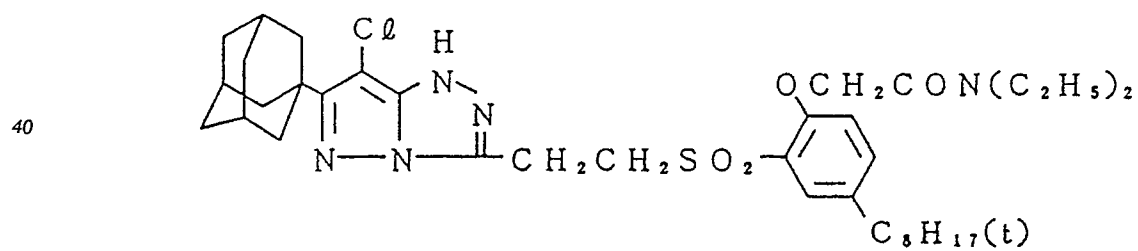
(M-52)



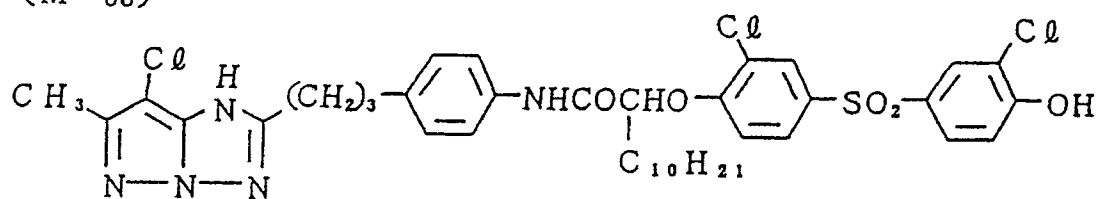
(M-53)



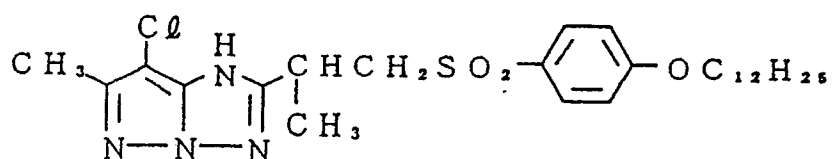
(M-54)



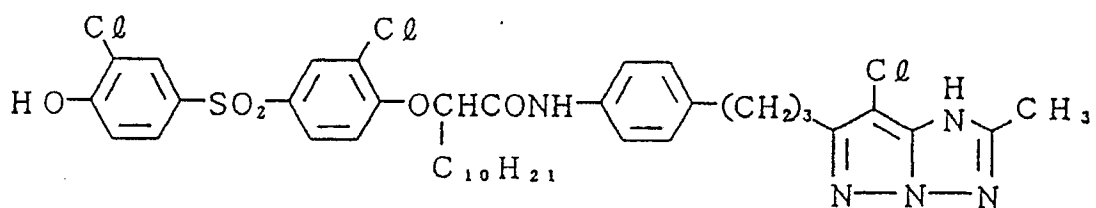
(M-55)



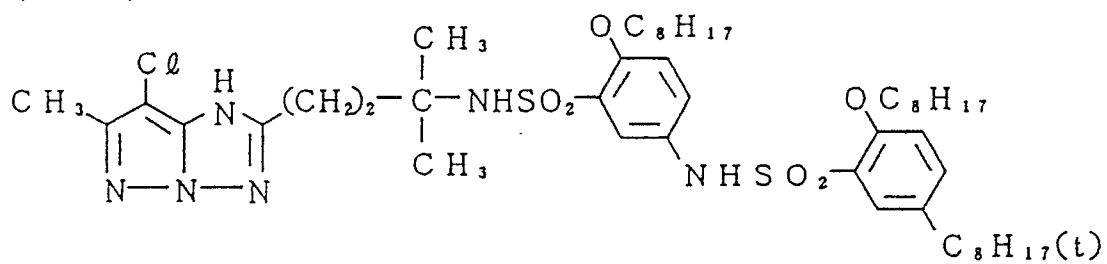
(M-56)



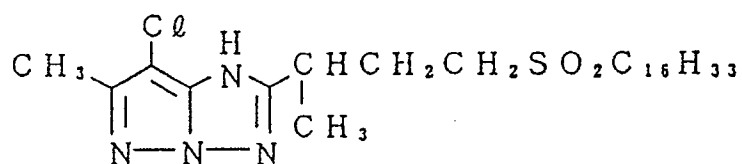
(M-57)



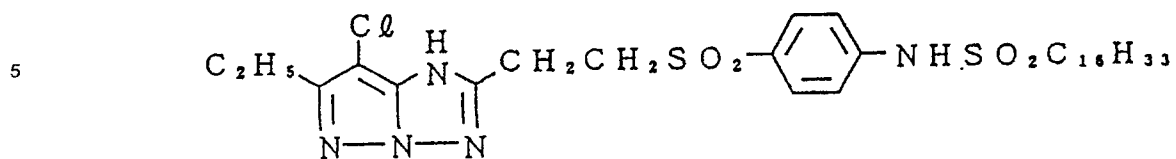
(M-58)



(M-59)

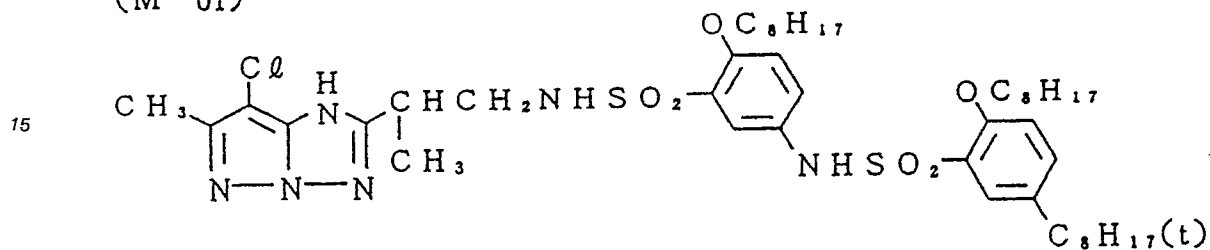


(M-60)



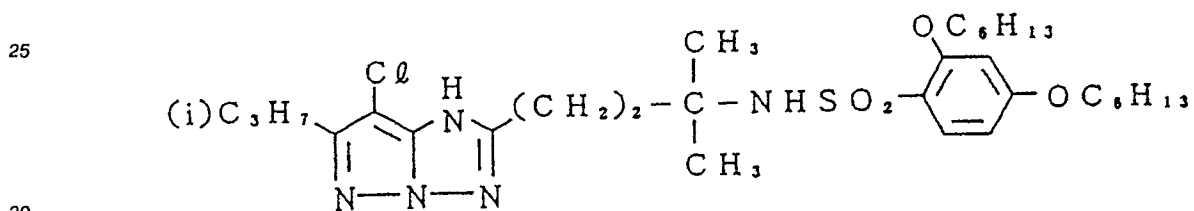
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(M-61)



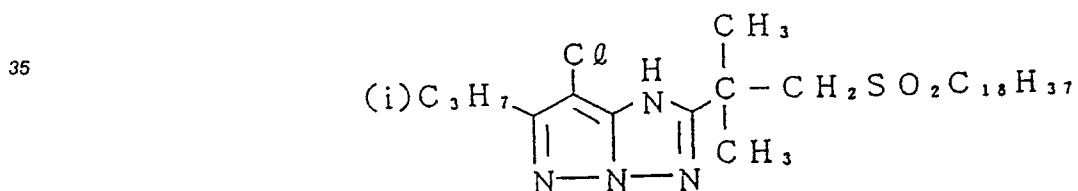
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(M-62)



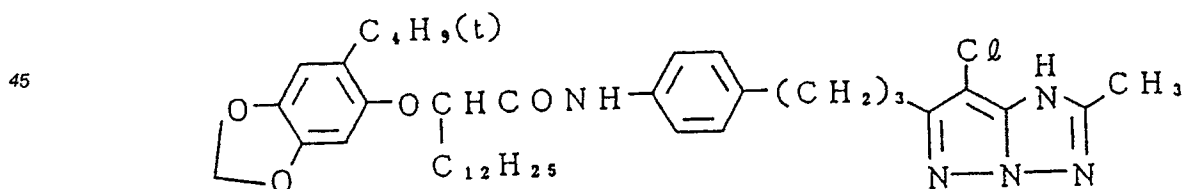
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(M-63)



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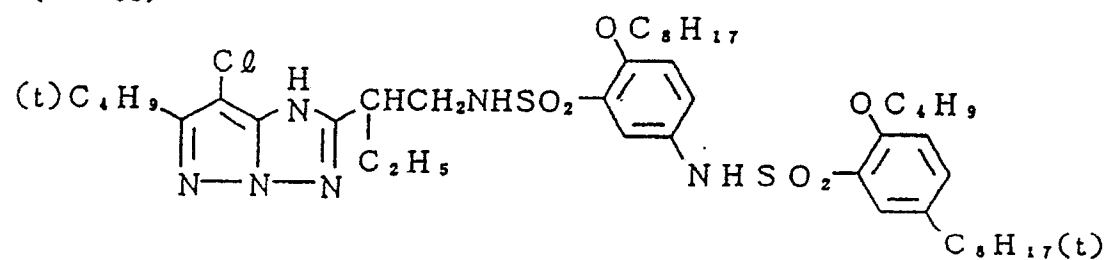
(M-64)



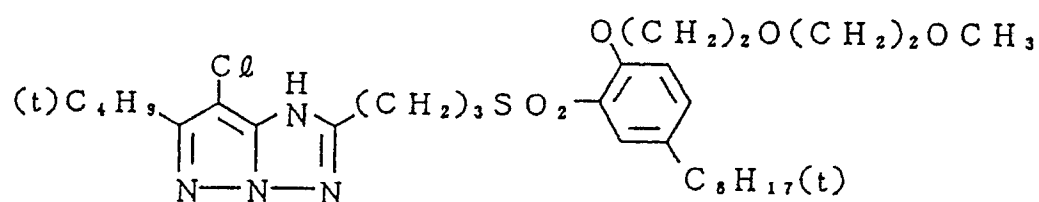
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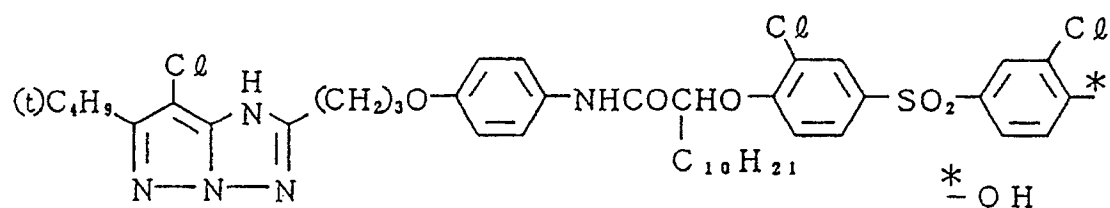
(M-65)



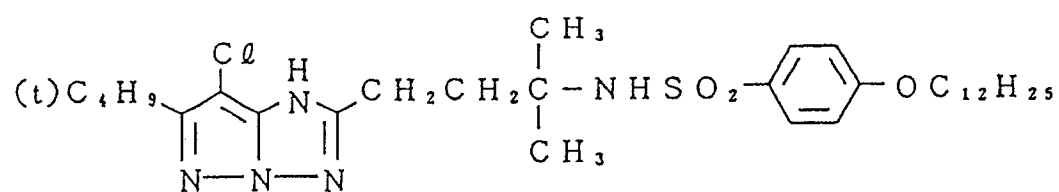
(M-66)



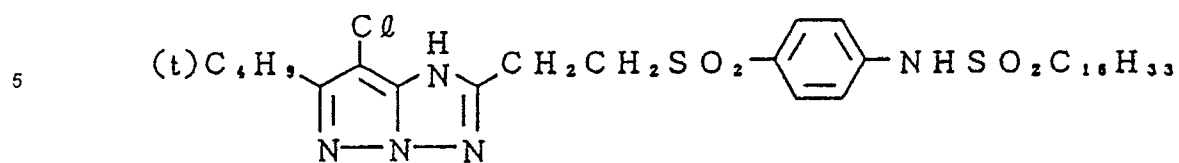
(M-67)



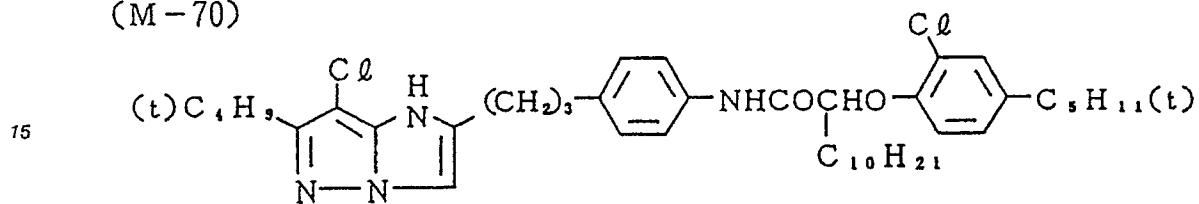
(M-68)



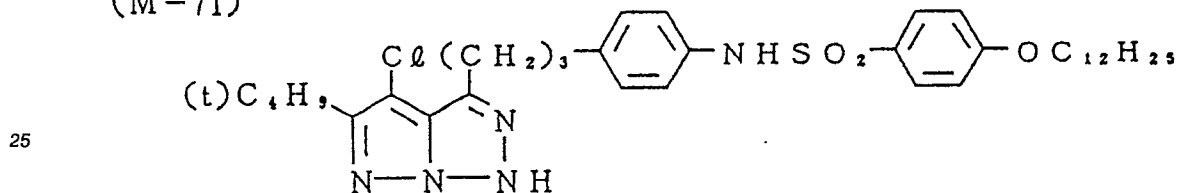
(M-69)



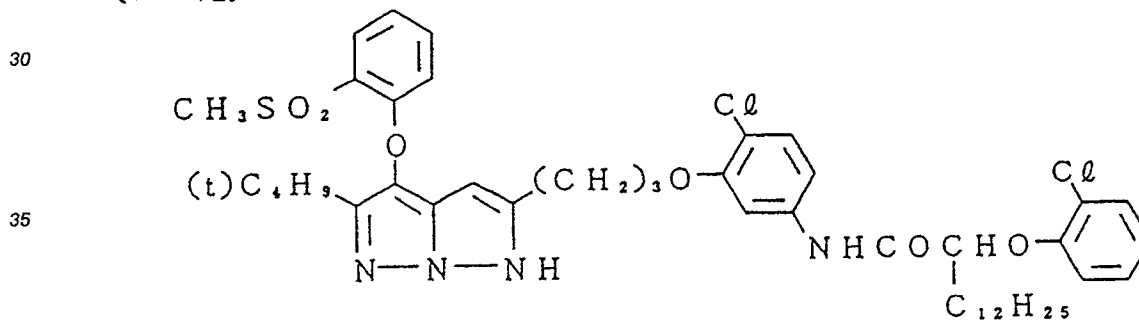
(M-70)



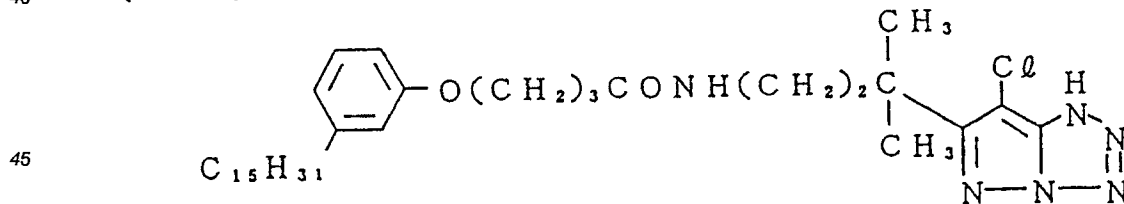
(M-71)



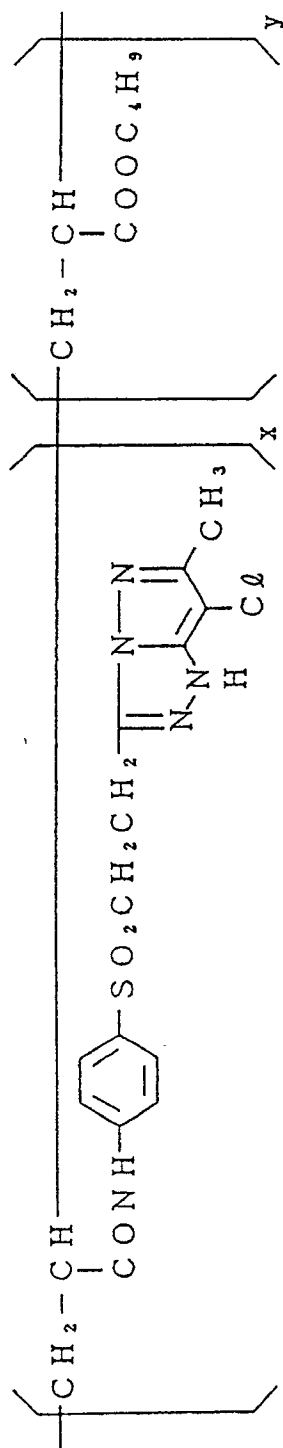
(M-72)



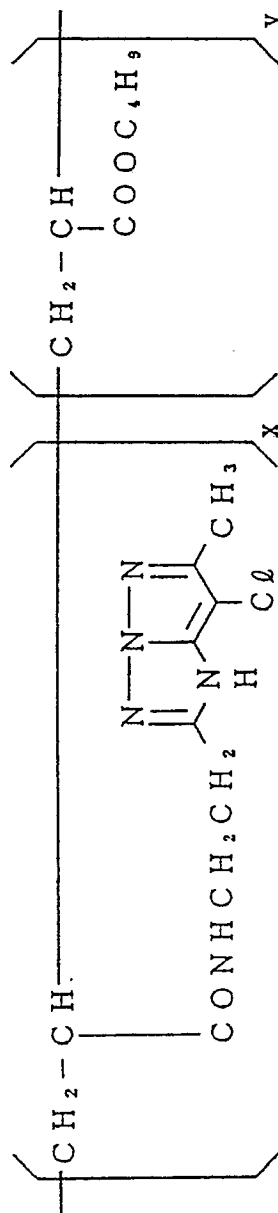
(M-73)

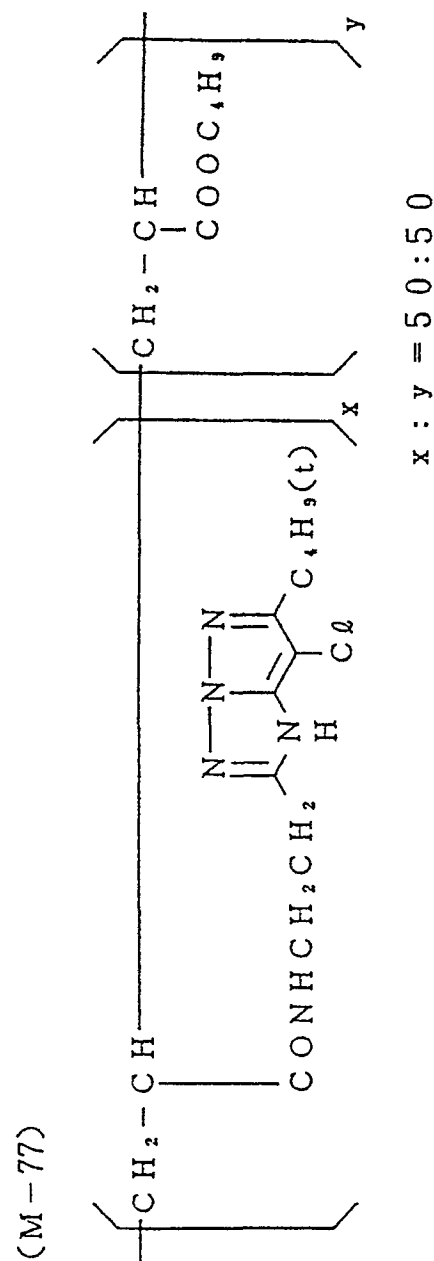
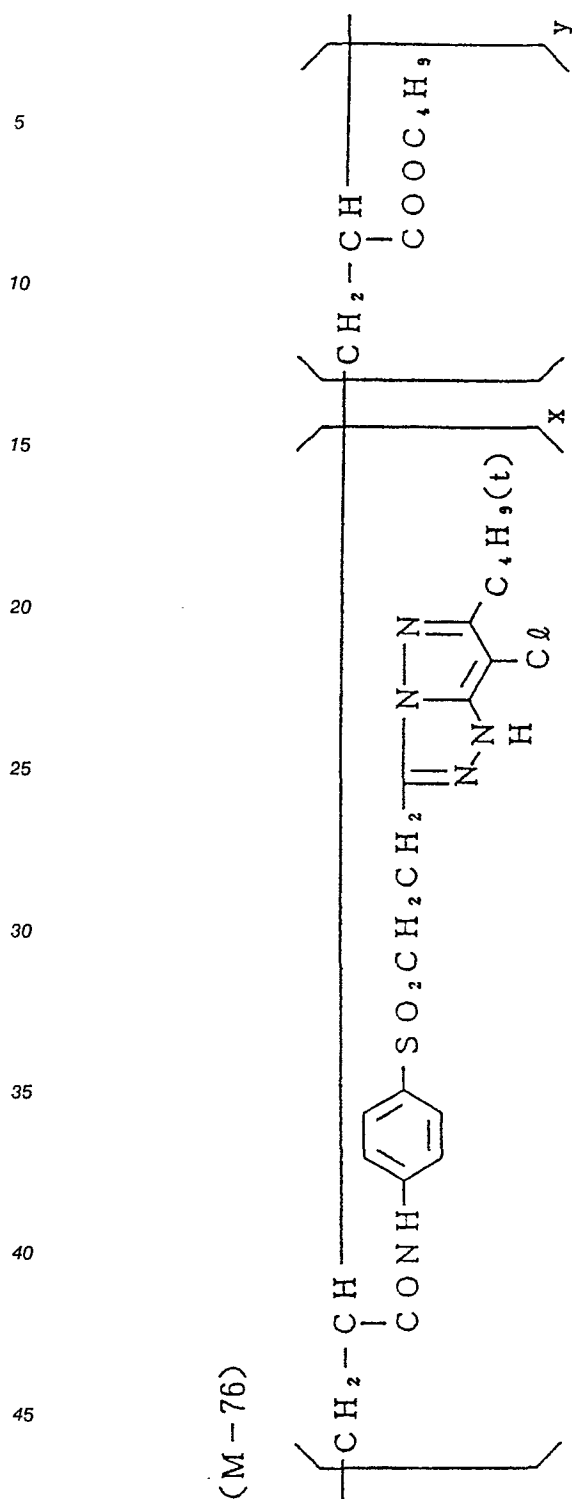


(M-74)

 $x : y = 50 : 50$

(M-75)

 $x : y = 50 : 50$



In addition to the above typical examples, there can be used other compounds shown by Nos. 1 to 4, 6, 8 to 17, 19 to 24, 26 to 43, 45 to 59, 61 to 104, 106 to 121, 123 to 162 and 164 to 223 among those exemplified on pages 66-122 of the specification of Japanese Patent O.P.I. Publication No. 166339/1987.

These couplers can be synthesized by referring to Journal of the Chemical Society, Perkin I (1977), pp. 2047-2052; U.S. Patent No. 3,725,067; and Japanese Patent O.P.I. Publication Nos. 99437/1984, 42045/1983, 162548/1984, 171956/1984, 33552/1985, 43659/1985, 172982/1985 and 190779/1985.

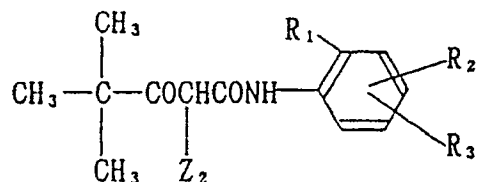
The couplers of the invention are normally used in an amount of 1×10^{-3} mol to 1 mol, preferably 1×10^{-2} mol to 8×10^{-1} mol, per mol of silver halide.

The above couplers may be used in combination with other types of magenta couplers.

In the invention, preferred yellow couplers, which is to be contained in the silver halide emulsion layer together with the magenta coupler are those couplers represented by the following Formula Y-I.

Particularly preferred yellow couplers among those represented by Formula Y-I are yellow couplers having a pKa value at most 3 lower than the pKa value of said magenta coupler.

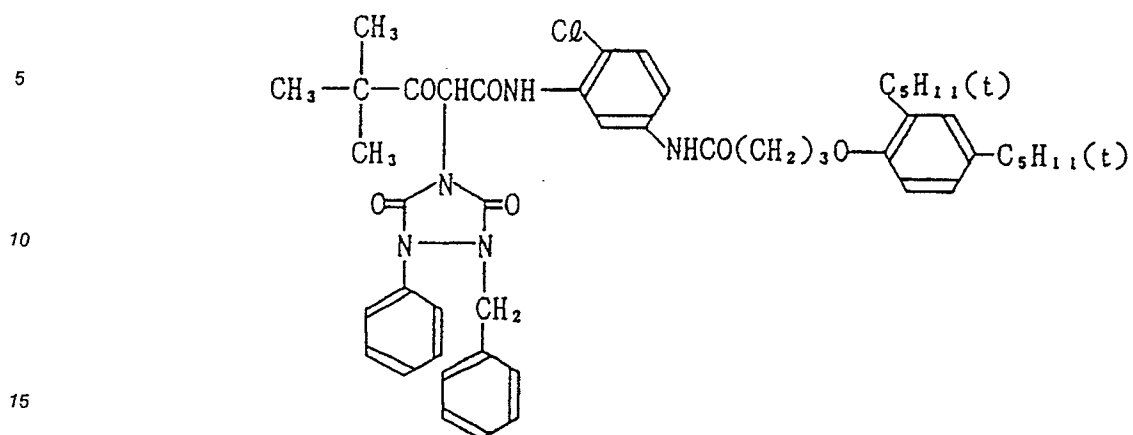
Formula Y-I



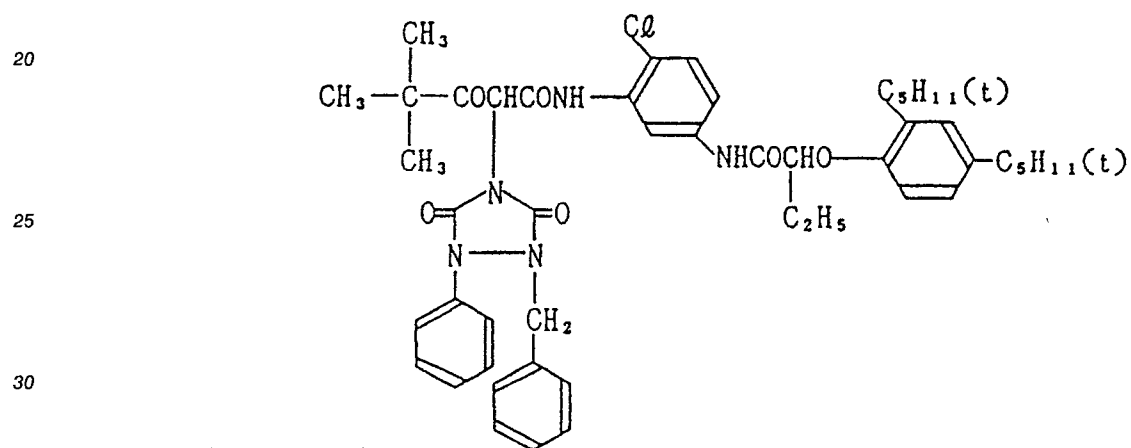
In Formula Y-I, R_1 represents a halogen atom or an alkoxy group; R_2 represents a hydrogen or halogen atom, or an alkoxy group which may have a substituent; R_3 represents an acylamino, alkoxycarbonyl, alkylsulfamoyl, arylsulfamoyl, arylsulfonamido, alkylureido, arylureido, succinimido, alkoxy or aryloxy group, each of which may have a substituent; and Z_2 represents a hydrogen atom, or a monovalent organic group or halogen atom each capable of being split off upon reaction with an oxidation product of a color developing agent.

Examples of the yellow coupler used in the invention are as follows:

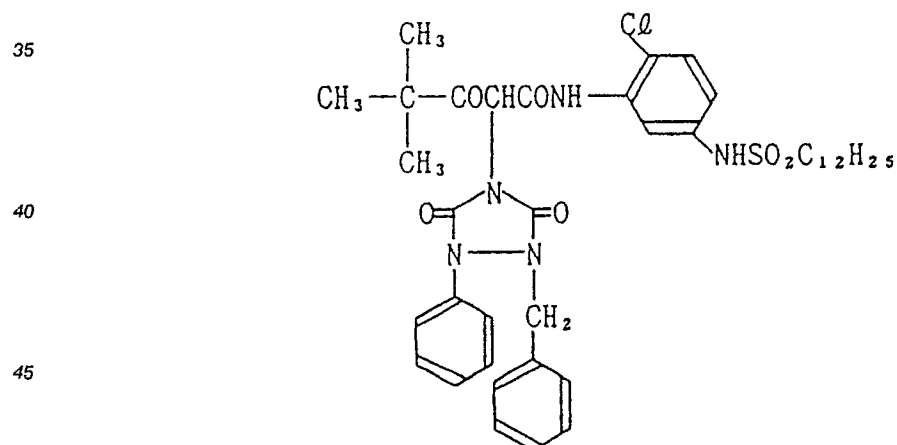
(Y - 1)



(Y - 2)



(Y - 3)



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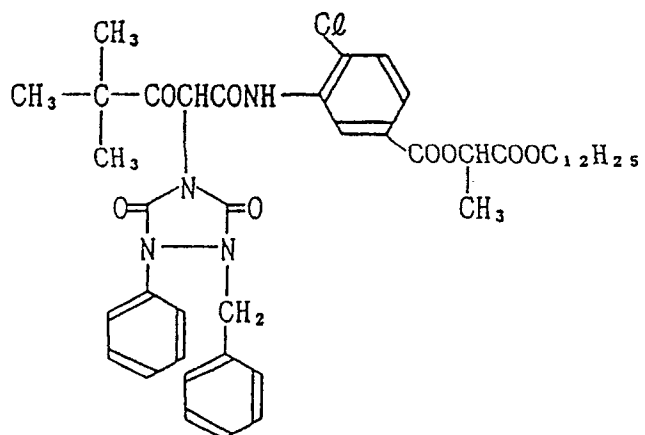
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(Y - 4)

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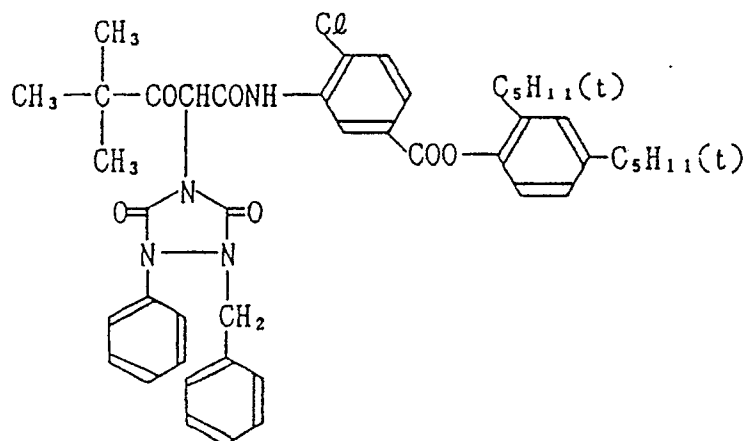
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(Y - 5)

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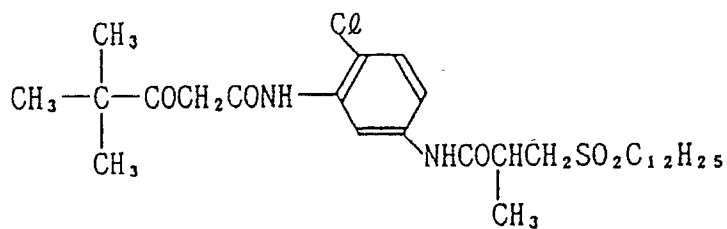
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(Y - 6)

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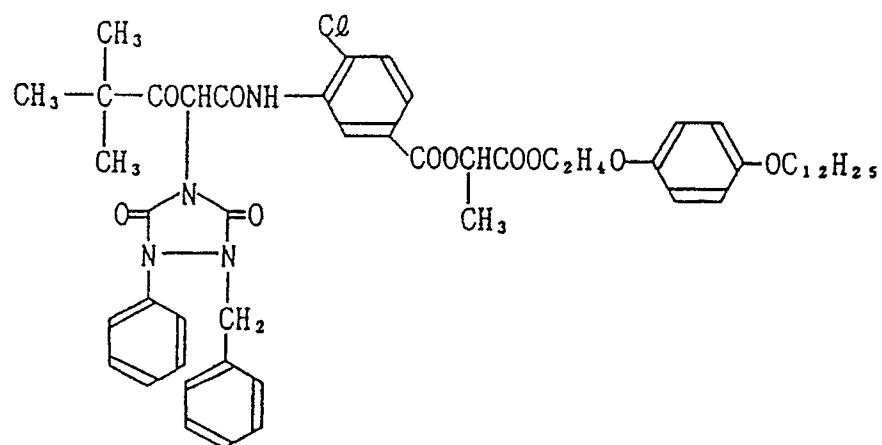


(Y - 7)

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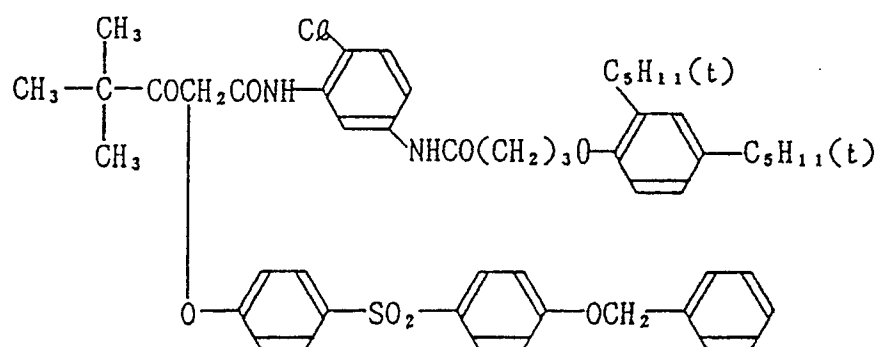


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(Y - 8)

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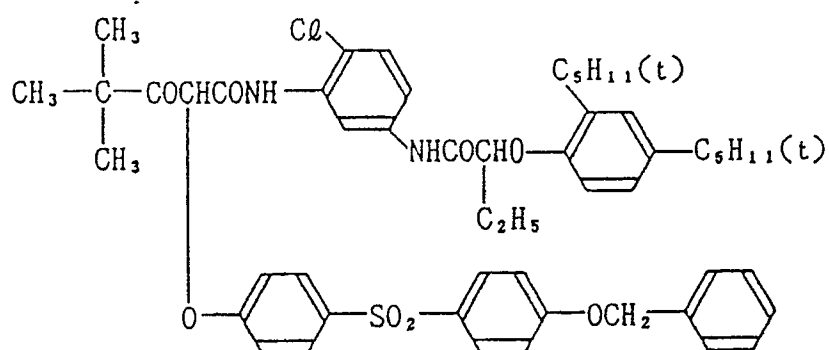
(Y - 9)

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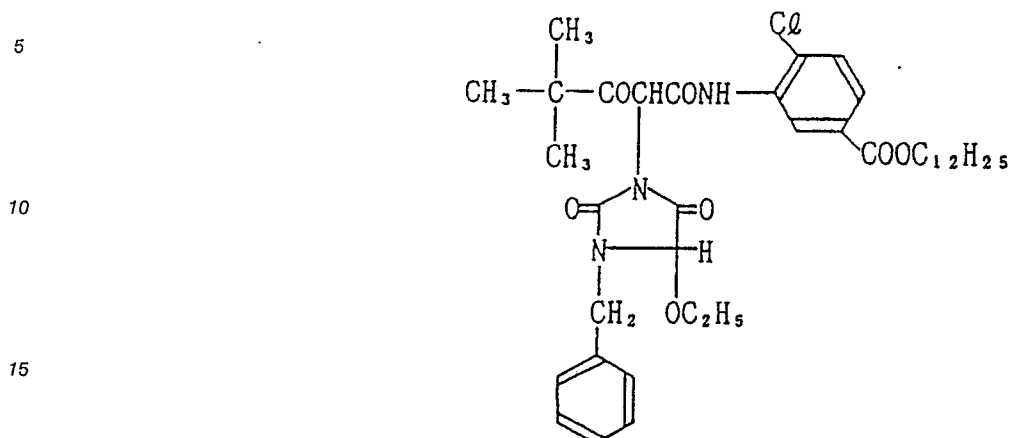
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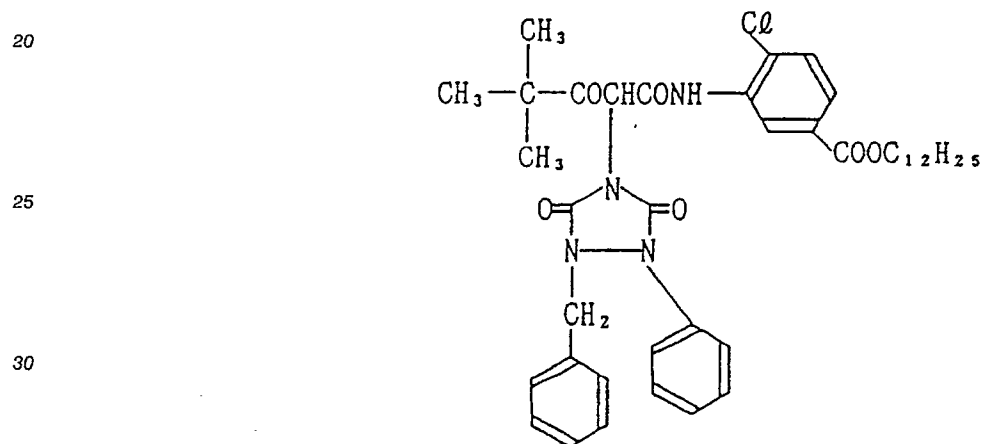
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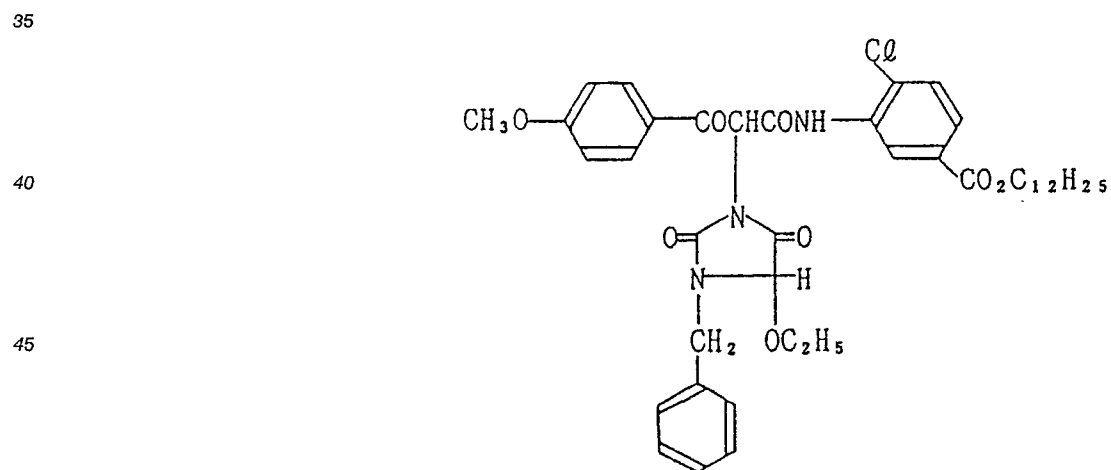
(Y - 10)



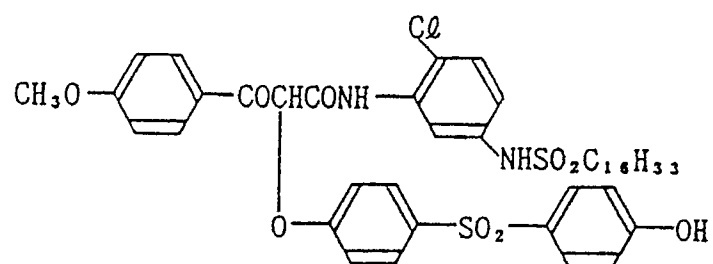
(Y - 11)



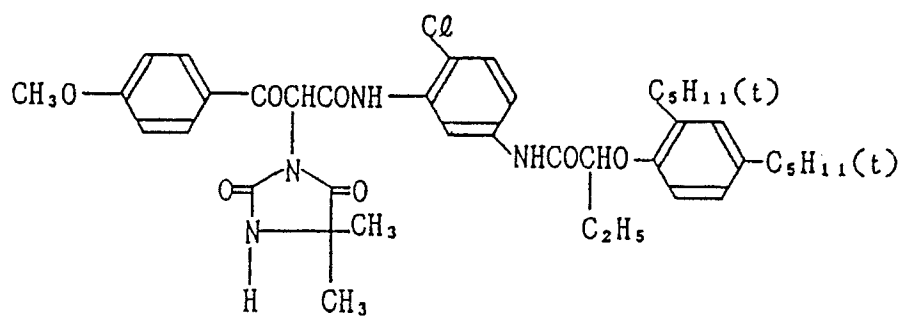
(Y - 12)



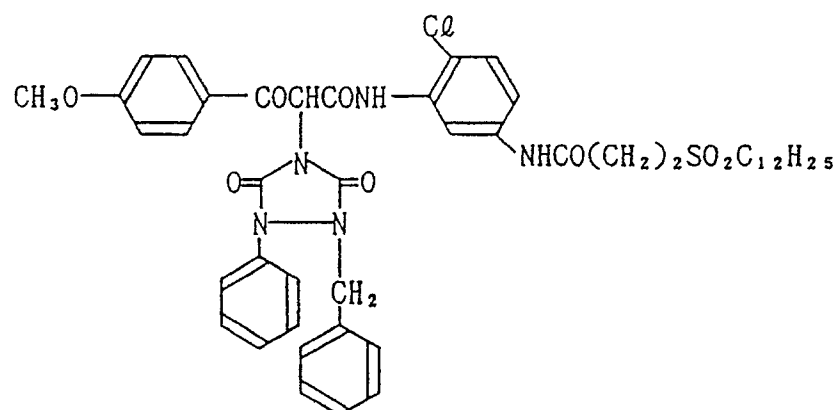
(Y - 13)



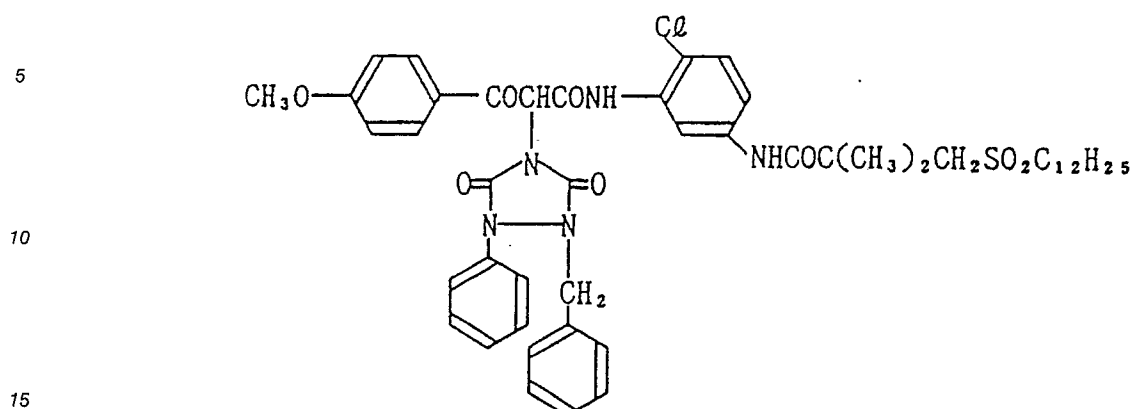
(Y - 14)



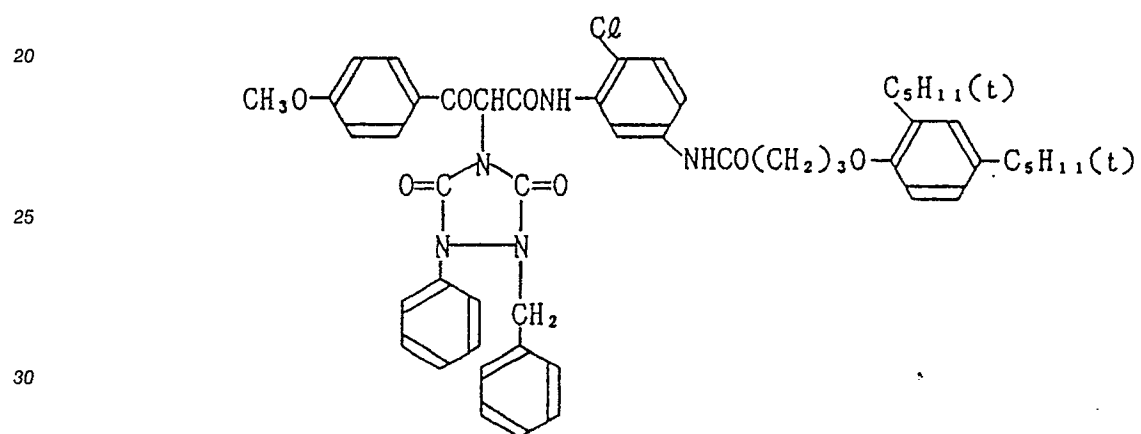
(Y - 15)



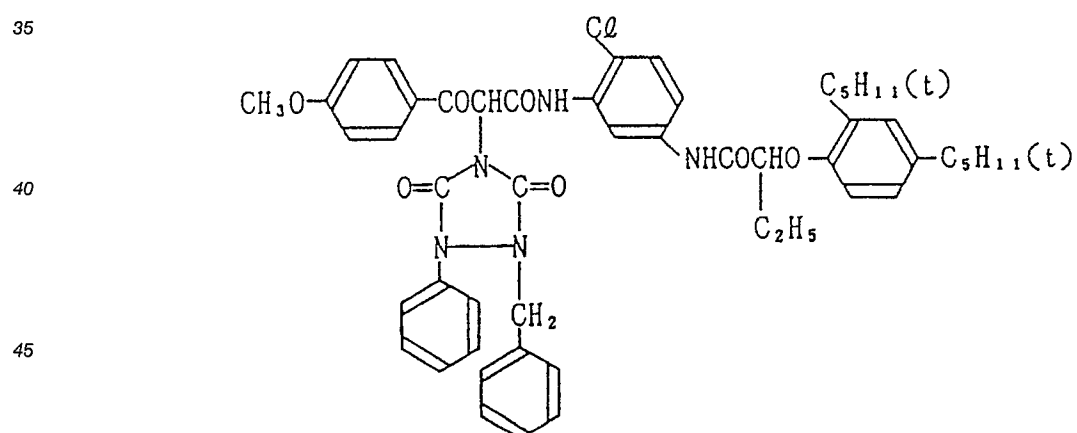
(Y - 16)



(Y - 17)



(Y - 18)

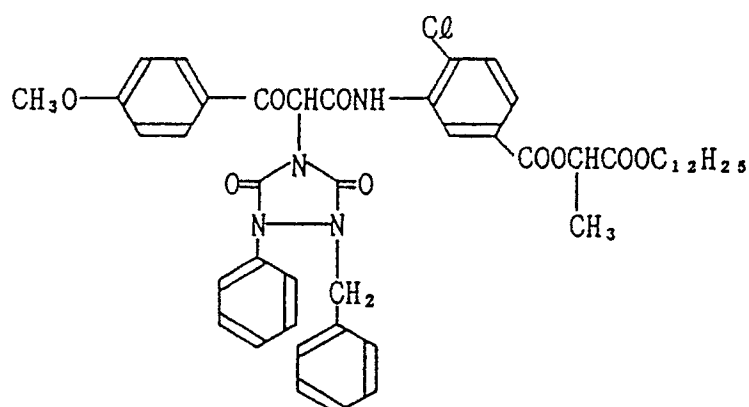


(Y - 19)

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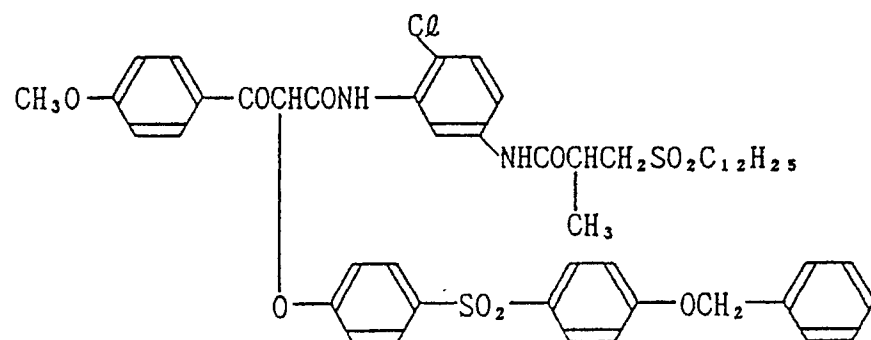


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(Y - 20)

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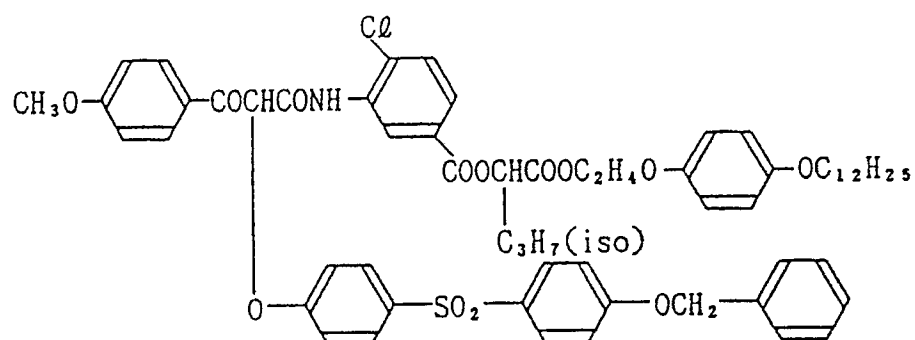


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(Y - 21)

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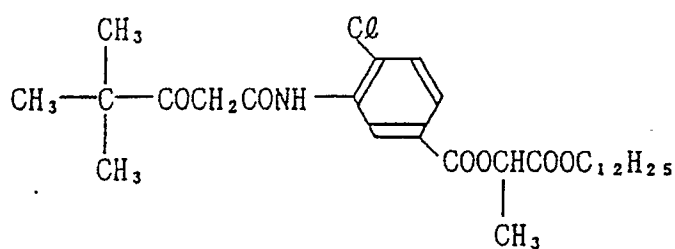
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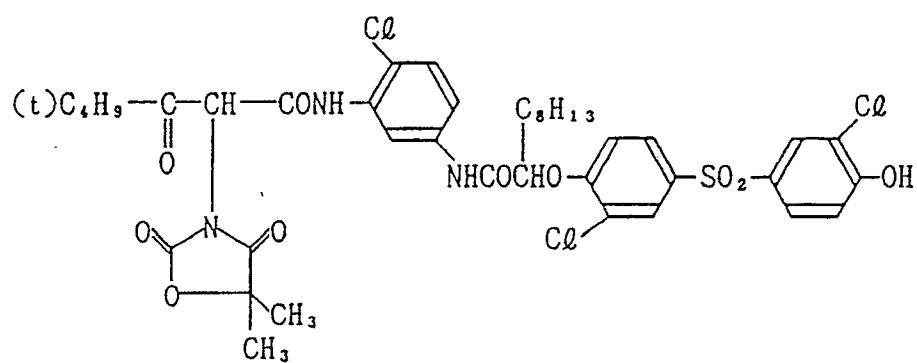
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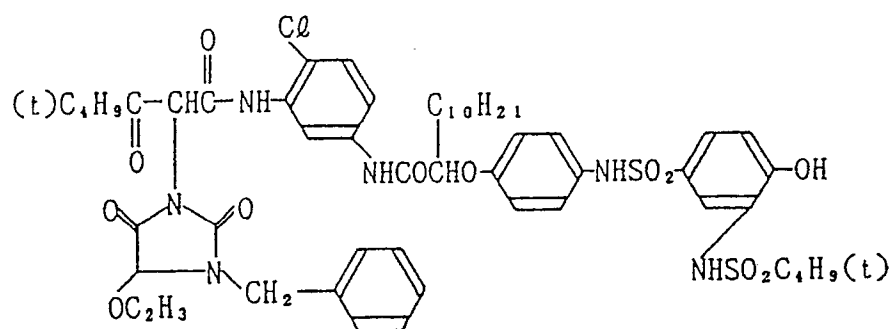
(Y - 22)



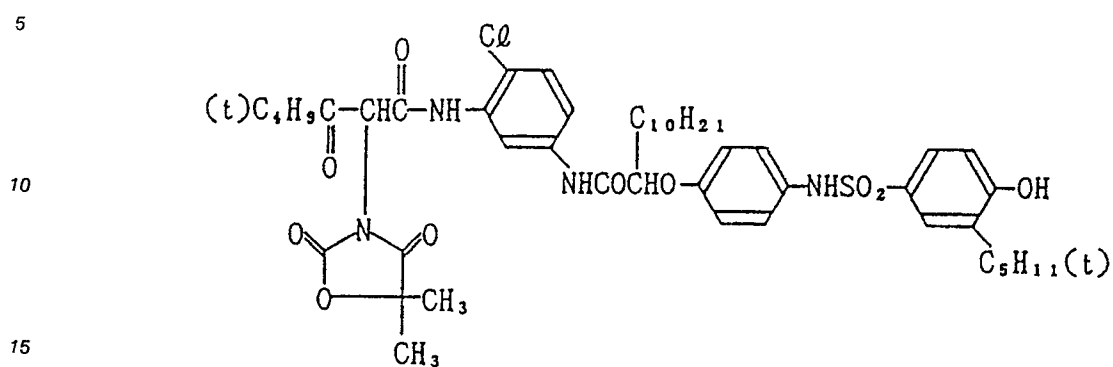
(Y - 23)



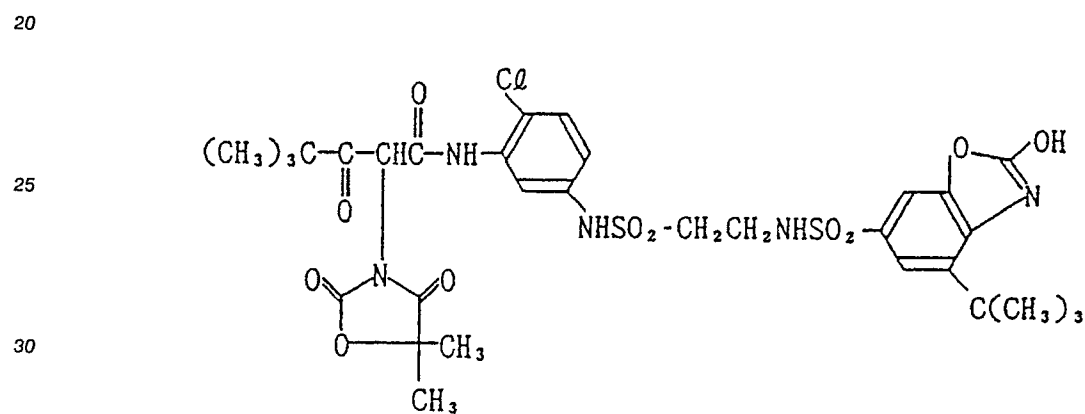
(Y - 24)



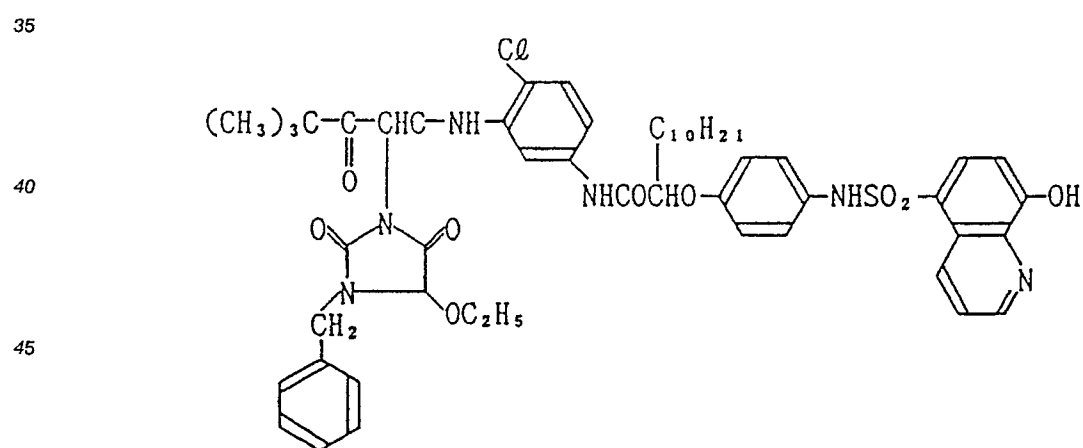
(Y - 25)



(Y - 26)



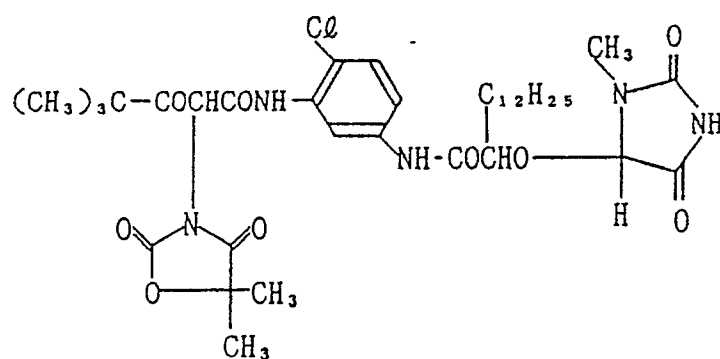
(Y - 27)



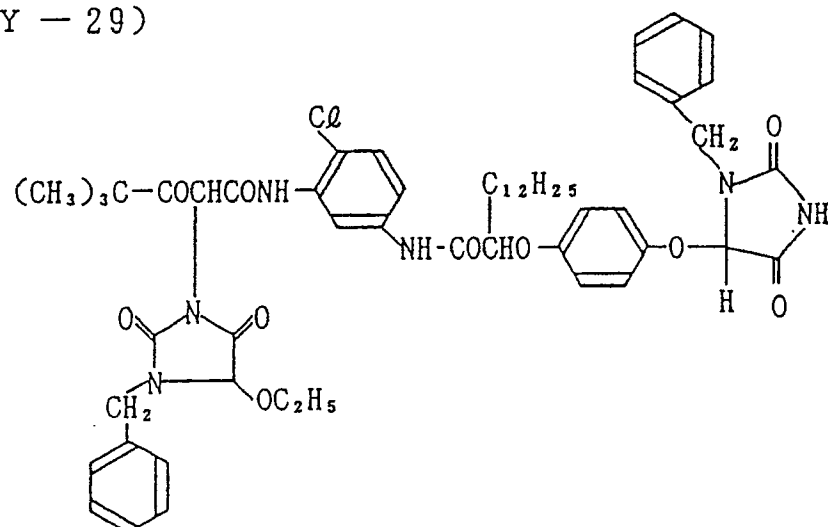
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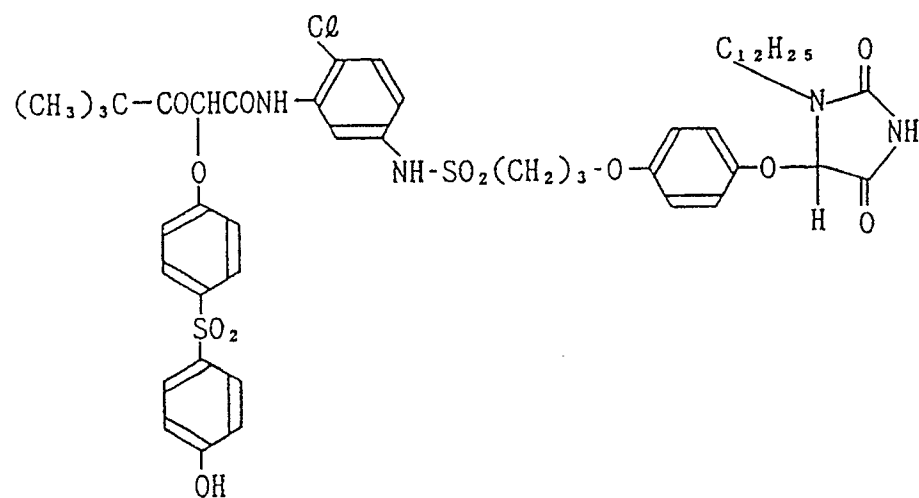
(Y - 28)



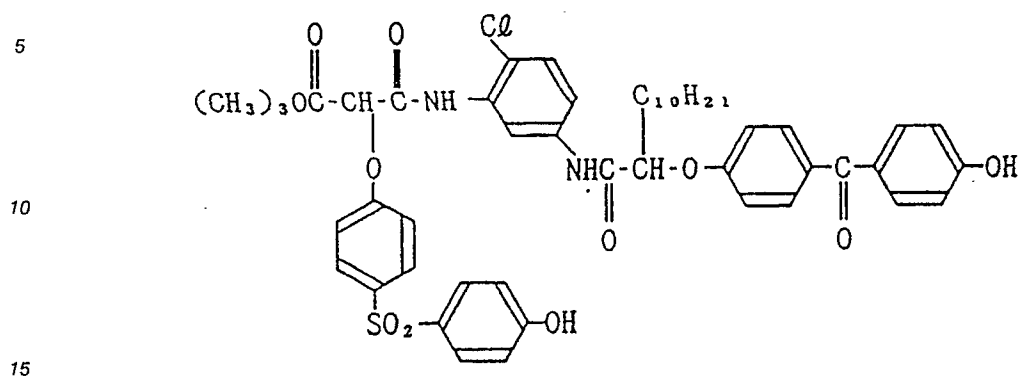
(Y - 29)



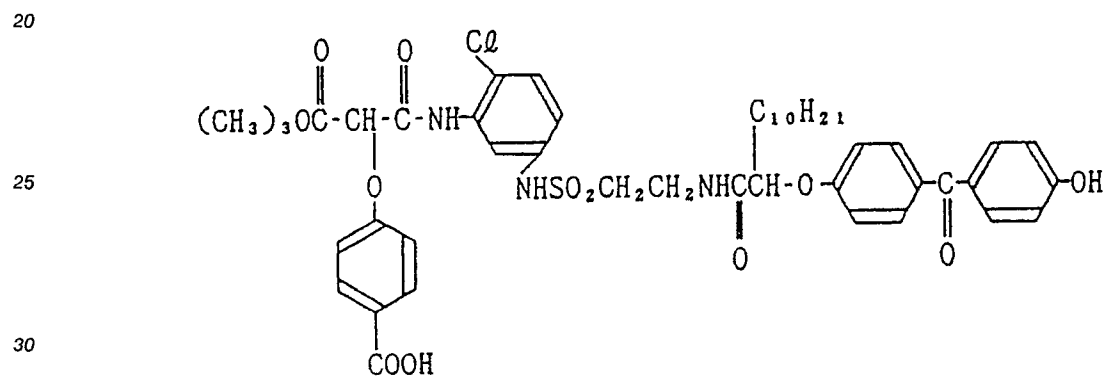
(Y - 30)



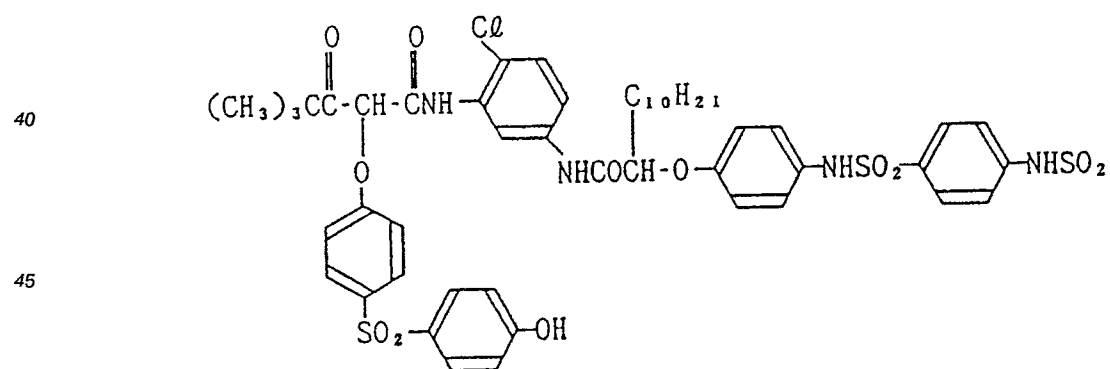
(Y - 31)



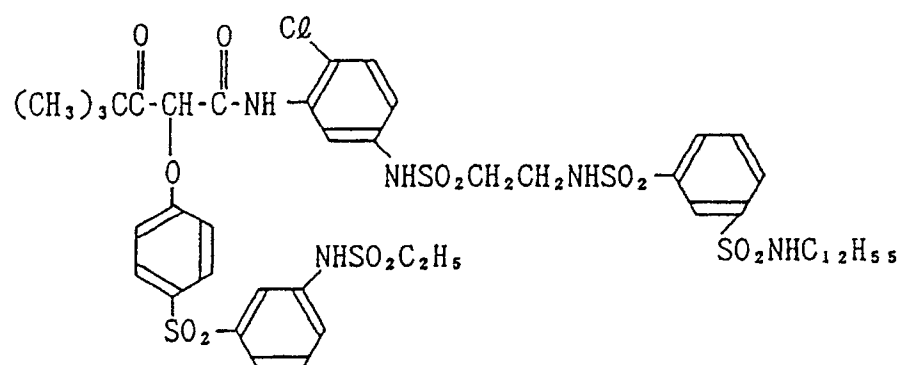
(Y - 32)



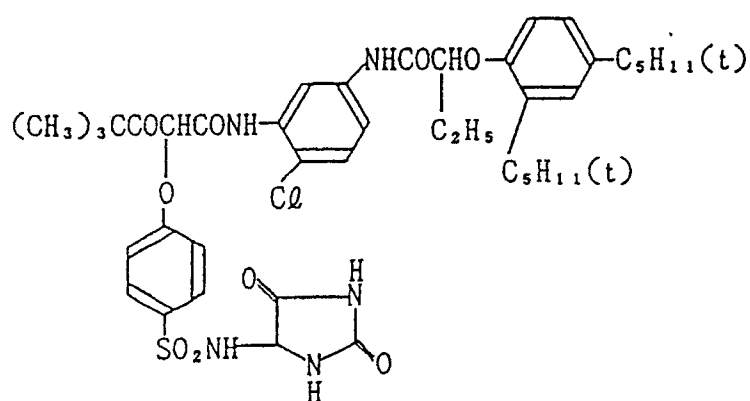
(Y - 33)



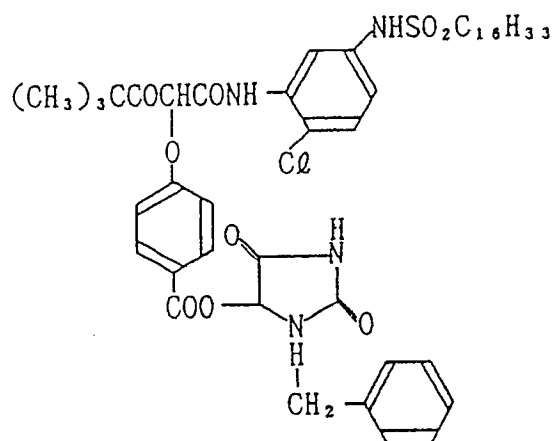
(Y - 34)



(Y - 35)



(Y - 36)

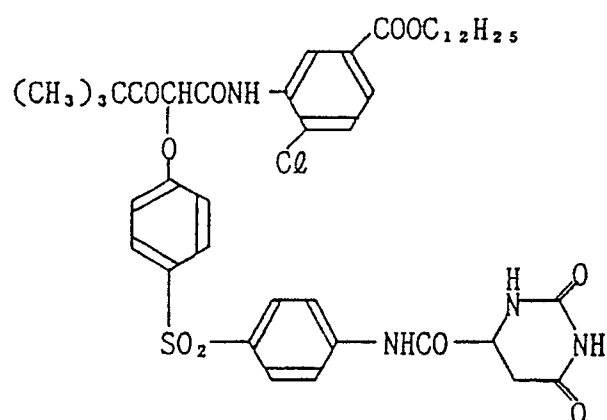


(Y - 37)

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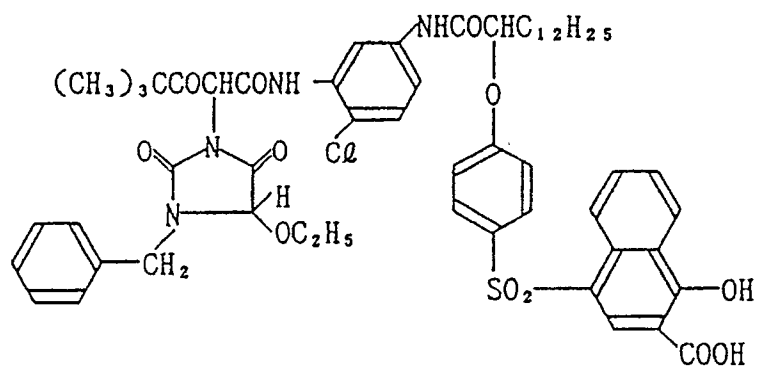


(Y - 38)

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(Y - 39)

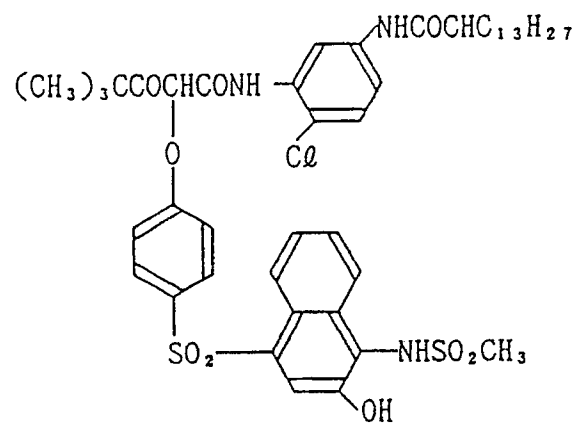
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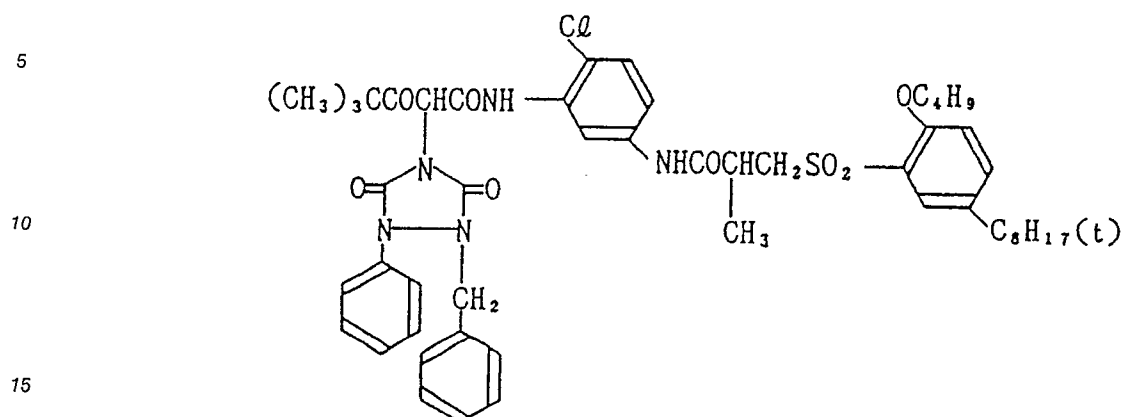
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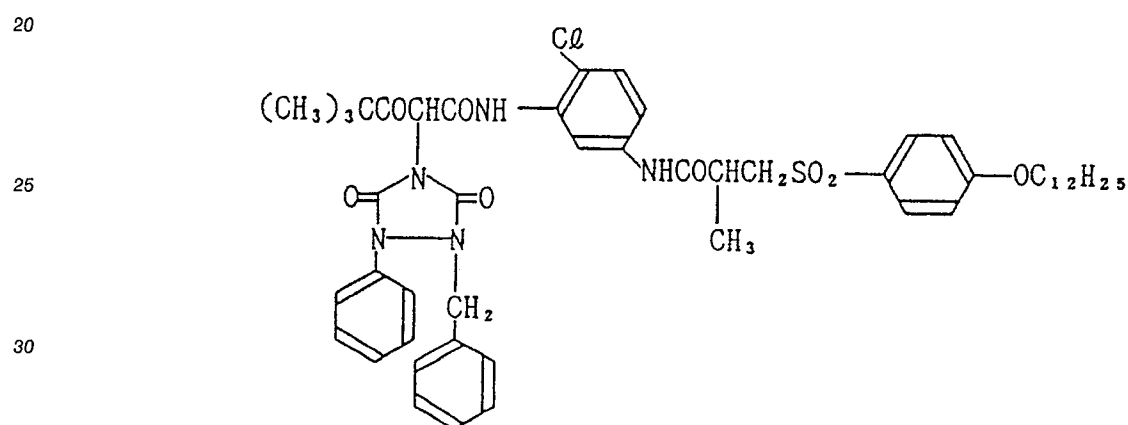
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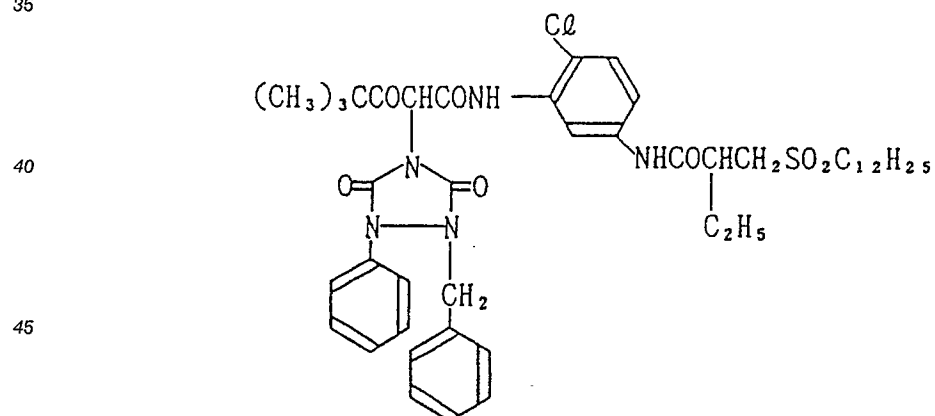
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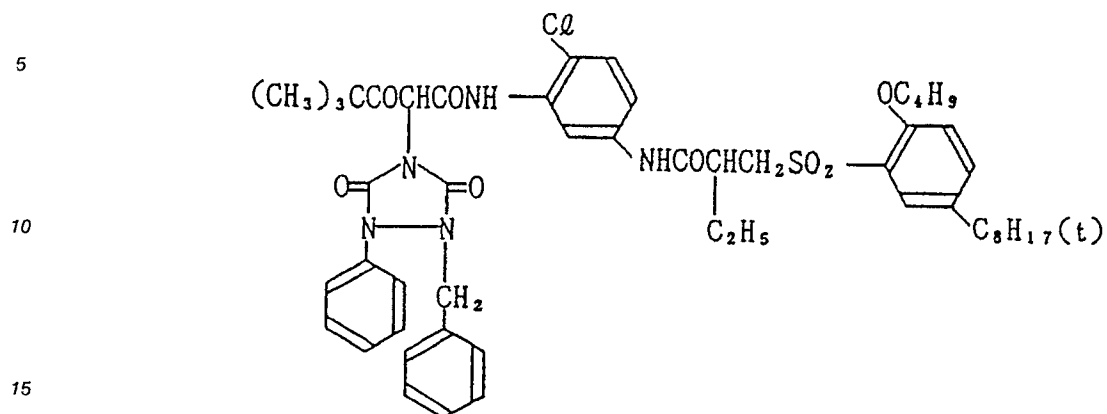
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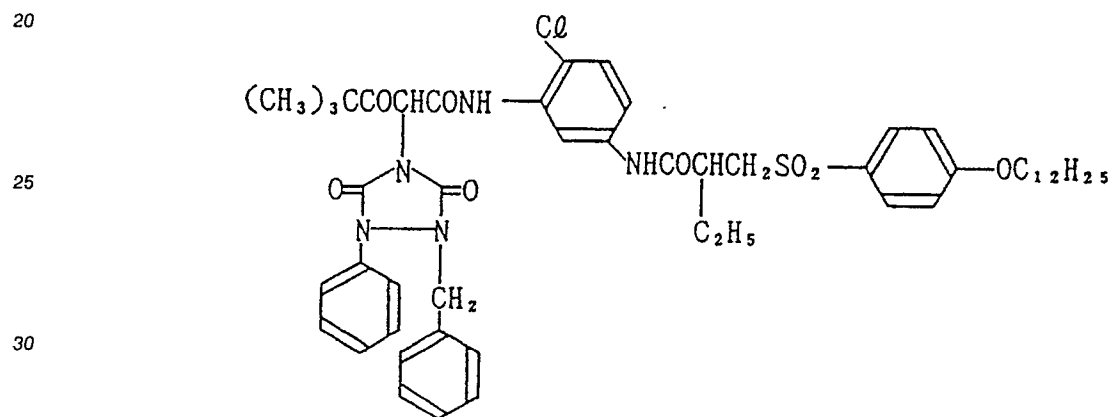
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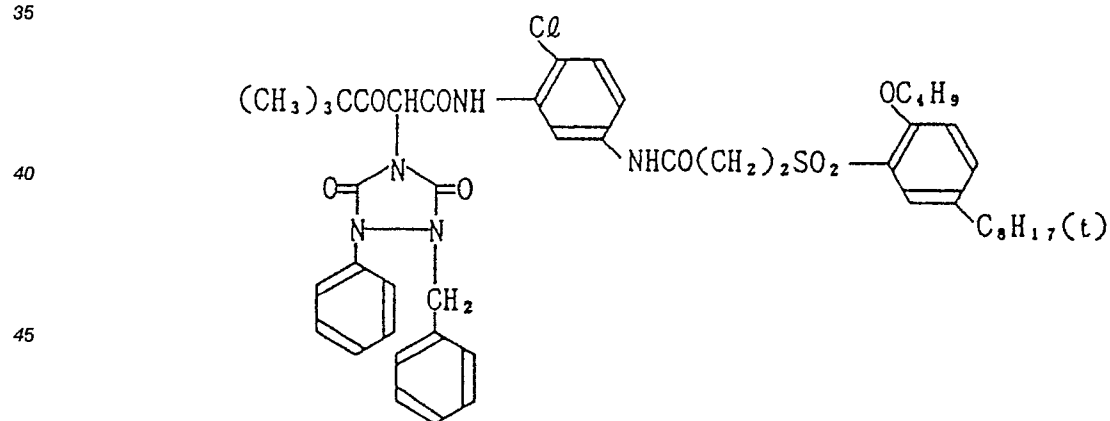
(Y - 43)



(Y - 44)



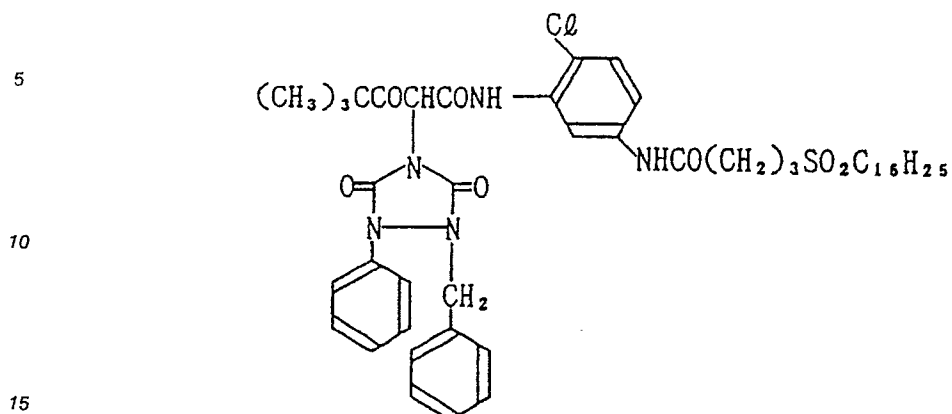
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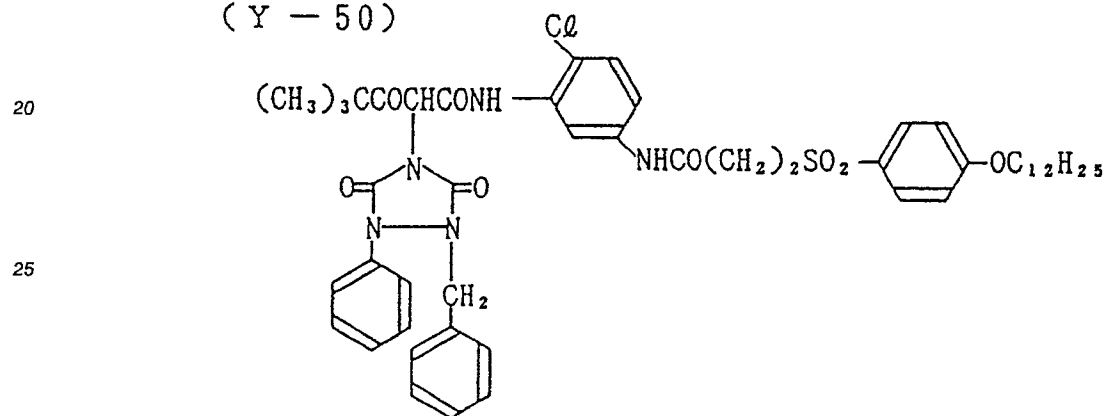
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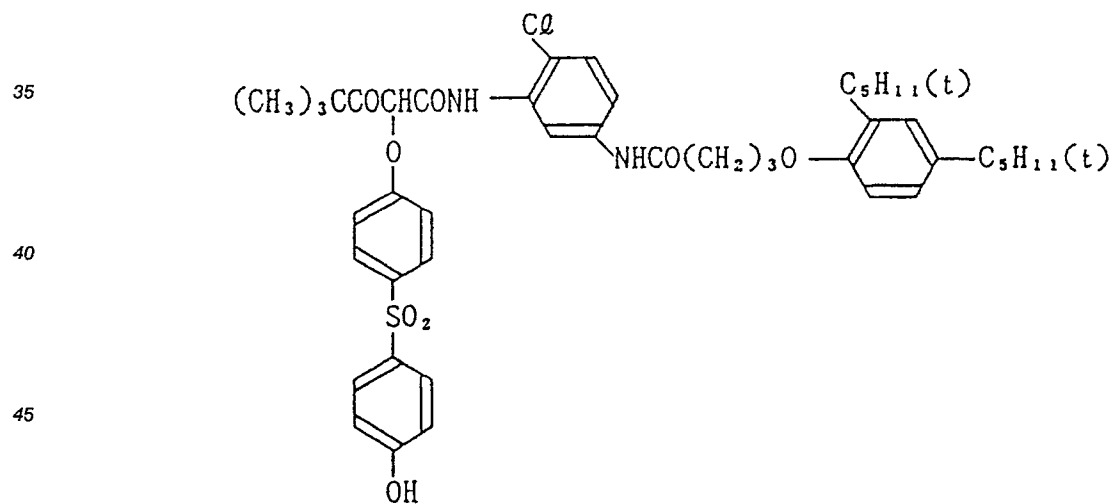
(Y - 49)



(Y - 50)



(Y - 51)

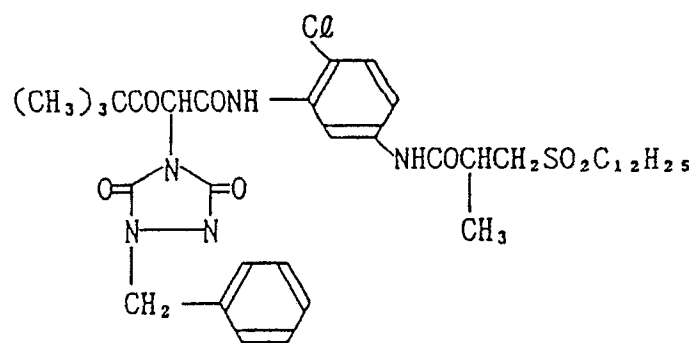


(Y - 52)

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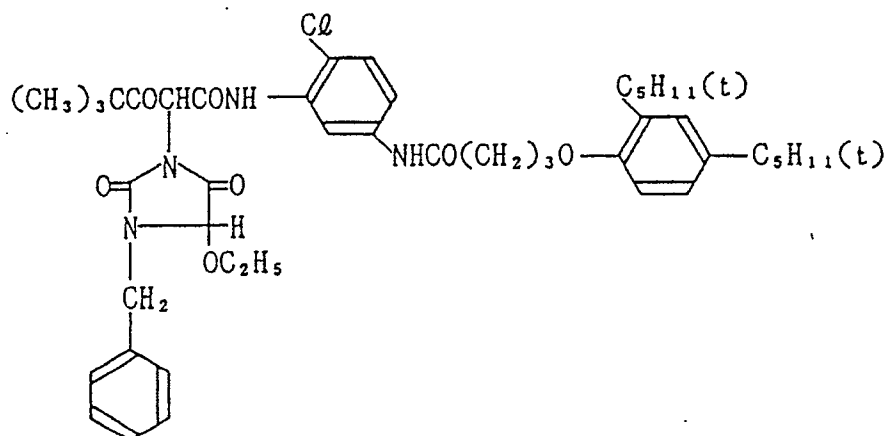


(Y - 53)

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(Y - 54)

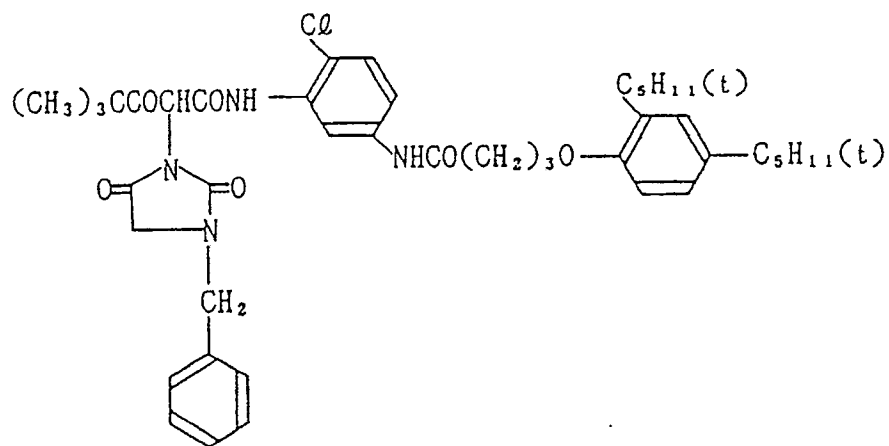
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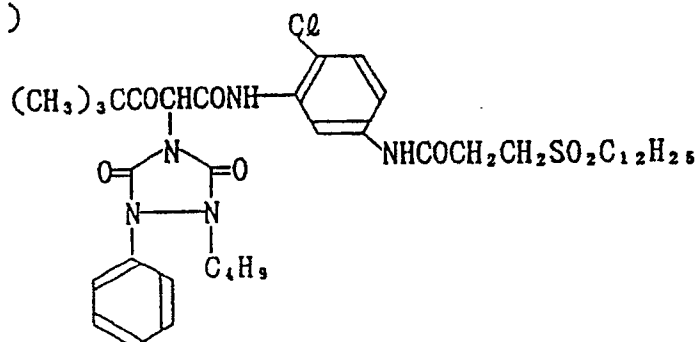
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(Y - 55)

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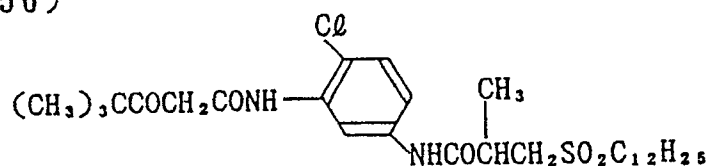
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(Y - 56)

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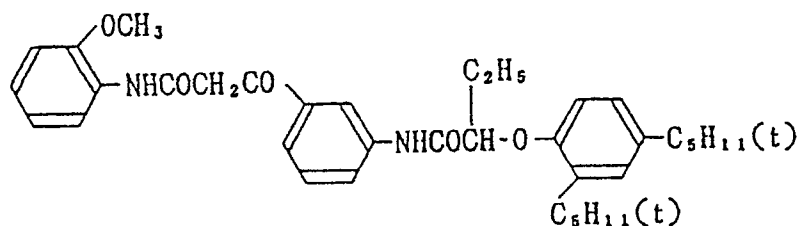
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(Y - 57)

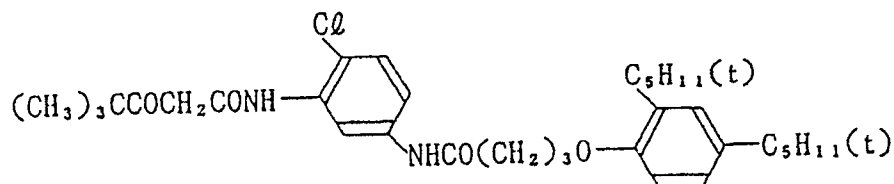
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(Y - 58)

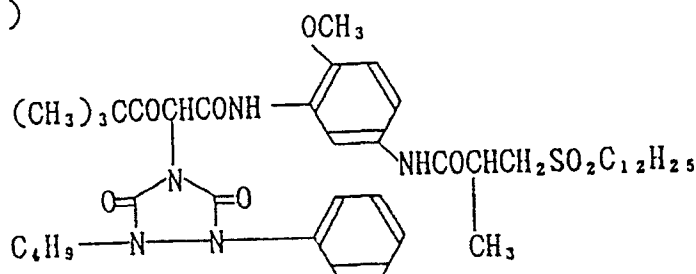
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(Y - 59)

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In a magenta image forming layer of the silver halide color photographic light-sensitive material of the invention, the ratio of the content of the magenta coupler to that of the yellow coupler may be determined so as to have the spectral absorption of color images obtained by color developing of said magenta image forming layer approximate to the spectral absorption of printed images of a magenta printing ink. In concrete terms, an appropriate value of the ratio is normally within a range of 0.02 mol to 0.5 mol of the yellow coupler per 1 mol of the magenta coupler.

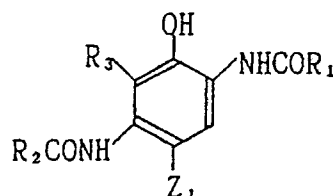
As the yellow coupler contained in a yellow image forming layer of the silver halide color photographic light-sensitive material of the invention, the yellow coupler represented by the above Formula Y-I is also

preferably used.

In the invention, there are used cyan dye image forming couplers of phenol type or naphthol type as a coupler to be contained in a cyan image forming layer.

Among them, couplers represented by the following Formula C-I or C-II are preferred.

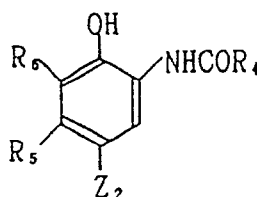
Formula C-I



In Formula C-I, R_1 represents an aryl, cycloalkyl or heterocyclic group. R_2 represents an alkyl or phenyl group each of which may have a substituent. R_3 represents a hydrogen atom, halogen atom, alkyl group or alkoxy group which may have a substituent.

Z_1 represents a hydrogen atom or a group capable of being split off upon reaction with an oxidized product of an aromatic primary amine color developing agent.

Formula C-II



In Formula C-II, R_4 represents an alkyl group such as methyl, ethyl, propyl, butyl, nonyl. R_5 represents an alkyl group such as methyl, ethyl. R_6 represents a hydrogen atom, halogen atom such as fluorine, chlorine, bromine or alkyl group such as methyl, ethyl. Z_2 represents a hydrogen atom or a group capable of being split off upon reaction with an oxidized product of an aromatic primary amine color developing agent.

These cyan couplers are described in U.S. Patent Nos. 2,306,410, 2,356,475, 2,362,596, 2,367,531, 2,369,929, 2,423,730, 2,474,293, 2,476,008, 2,498,466, 2,545,687, 2,728,660, 2,772,162, 2,895,826, 2,976,146, 3,002,836, 3,419,390, 3,446,622, 3,476,563, 3,737,316, 3,758,308, 3,839,044; British Patent Nos. 478,991, 945,542, 1,084,480, 1,377,233, 1,388,024, 1,543,040; and Japanese Patent O.P.I. Publication Nos. 37425/1972, 10135/1975, 25228/1975, 112038/1975, 117422/1975, 130441/1975, 6551/1976, 37647/1976, 52828/1976, 108841/1976, 109630/1978, 48237/1979, 66129/1979, 131931/1979, 32071/1980, 146050/1984, 31953/1984, 117249/1985.

The coupler used in the invention may be used normally in each silver halide emulsion layer in an amount of 1×10^{-3} mol to 1 mol, preferably 1×10^{-2} mol to 8×10^{-1} mol, per mol of silver halide.

In incorporating the above coupler in an emulsion layer, usually, the coupler is dissolved in a high boiling organic solvent having a boiling point of 150°C or more, jointly using a low boiling or water-soluble organic solvent when necessary, after dispersing the solution in a hydrophilic binder such as gelatin aqueous solution with an aid of surfactants, and then the dispersion is added to an objective hydrophilic colloidal layer. A process to remove the low boiling organic solvent may be provided after or concurrently with dispersing process.

In the invention, the ratio of the high boiling organic solvent to the low boiling organic solvent is normally 1:0.1 to 1:50, and preferably 1:1 to 1:20.

The high boiling solvent used in the invention may be any of compounds having a dielectric constant of 6.0 or less. The lower limit of the dielectric constant is not particularly provided, but it is preferably 1.9 or more. Preferable solvents are esters such as phthalates and phosphates, organic acid amides, ketones and hydrocarbons, each of which have a dielectric constant of 6.0 or less. Of these compounds, phthalates and phosphates are particularly preferred.

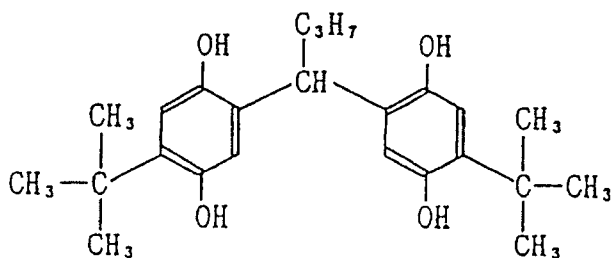
Next, the compounds of Formula I will be described.

In Formula I, R^1 and R^2 independently represent a hydrogen atom, or a group having 8 or less carbon atoms such as alkyl group such as methyl, ethyl, t-butyl, sec-hexyl, t-octyl, alkoxy group such as methoxy, ethoxy, butoxy, 2-ethylhexyloxy, alkylthio group such as methylthio, butylthio, octylthio and alkylamido group such as methaneamido, propaneamido, 2-ethylpentanoylamido; and R^3 represents a hydrogen atom or alkyl group having carbon atoms of 11 or less such as methyl, n-propyl, iso-propyl, heptyl, undecyl, 1-ethylpentyl. The total number of carbon atoms in R^1 , R^2 and R^3 is 8 to 22.

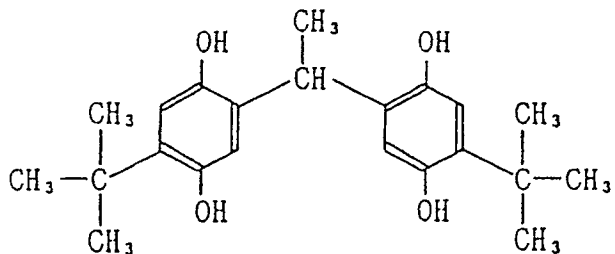
R^1 and R^2 are preferably an alkyl group having 6 or less carbon atoms, respectively. R^3 is preferably an alkyl group having 7 or less carbon atoms. The total number of carbon atoms in R^1 , R^2 and R^3 is 8 to 17.

Typical examples of the compound represented by Formula I are as follows.

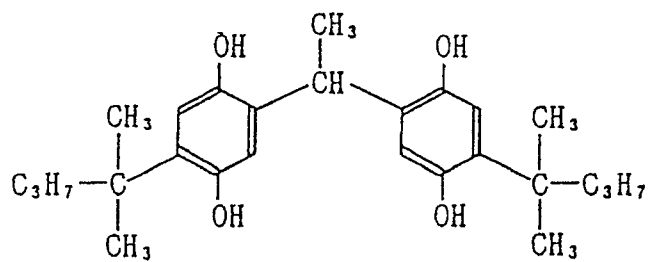
I - (1)



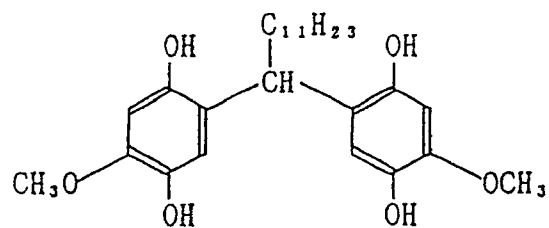
I - (2)



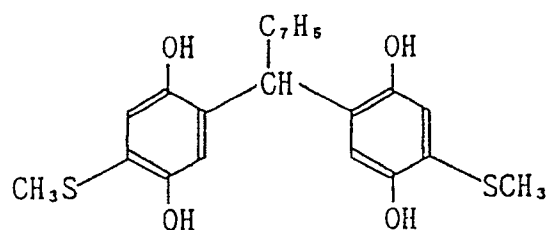
I - (3)



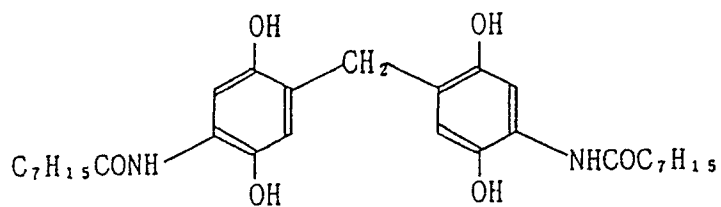
I - (4)



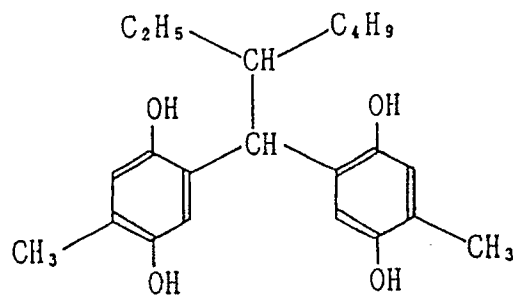
I - (5)



I - (6)



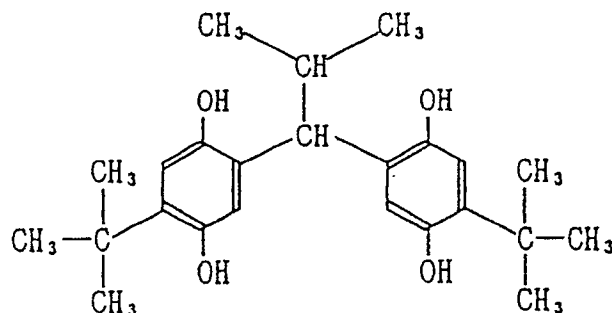
I - (7)



I - (8)

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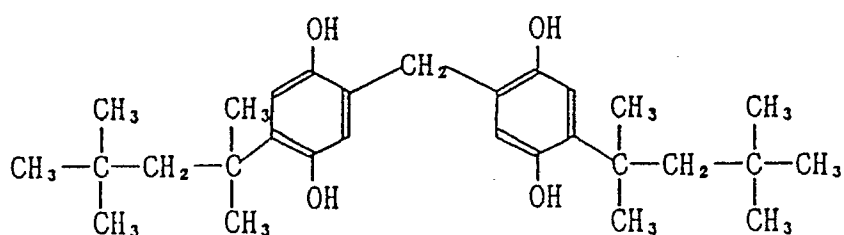
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I - (9)

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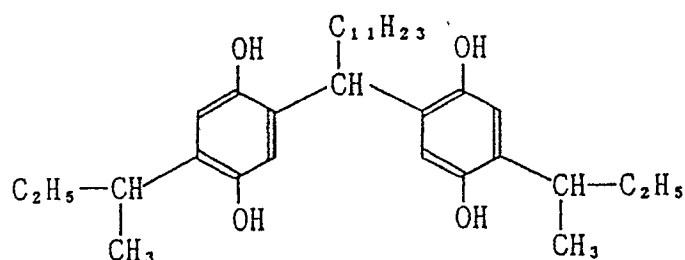
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I - (10)

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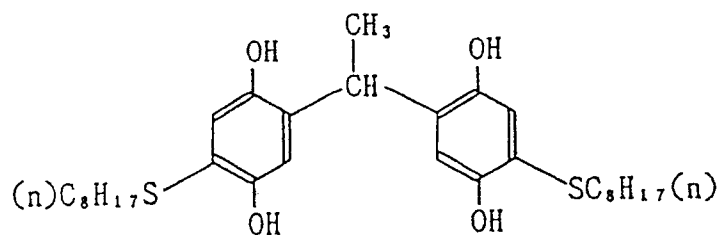
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I - (11)

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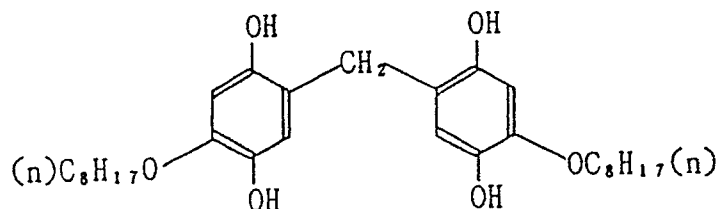
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I - (12)

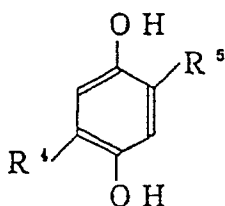
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The addition amount of the compound represented by Formula [I] is 1×10^{-8} mol/m² to 1×10^{-2} mol/m², preferably 1×10^{-7} mol/m² to 1×10^{-3} mol/m², more preferably 1×10^{-6} mol/m² to 1×10^{-4} mol/m². The compound is preferably added in an emulsion layer and/or a layer adjacent thereto.

The compounds of Formula I may be used in combination with those of the same kind, or with the following compound.



wherein R⁴ and R⁵ independently represent a hydrogen atom, or an alkyl, alkoxy, alkylthio or alkylamide group, each of which have 8 or less carbon atoms.

Next, the silver halide emulsion used in a light-sensitive layer of the silver halide color light-sensitive material of the invention will be described.

The silver halide emulsion used in the invention may employ any of silver halides used in ordinary silver halide emulsions, such as silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide and silver chloride.

The construction of silver halide grains may be uniform from inner part to outer part of the grains, or the construction may be different from outer part to inner part. Further, when the composition of the grains are different from outer part to inner part, the composition may change either continuously or discontinuously.

The grain size of silver halide grains is not particularly limited. But in view of rapid processability, sensitivity and other photographic properties, it is preferably 0.2 to 1.6 μm , more preferably 0.25 to 1.2 μm .

The grain size distribution of silver halide grains may be of either monodisperse system or polydisperse system.

The silver halide emulsion used in the invention may be prepared by any of the acid method, neutral method and ammonical method. Said grains may be grown in one step, or may be grown from seed grains prepared beforehand. The method of preparing seed grains may be the same with, or different from, the method of growing seed grains.

Further, in reacting a soluble silver salt with a soluble halogen salt, there may be employed any of the single jet method, reverse jet method, double jet method and combination thereof. Moreover, there may also be used the pAg-controlled double jet method described in Japanese Patent O.P.I. Publication No. 48521/1979 as a version of the double jet method.

If necessary, a halogenated solvent such as thioether may be used.

The silver halide grains used in the invention may be of any form. They may be composed of grains having a uniform form, or may be a mixture of grains different in forms.

In the process of forming and/or growing silver halide grains, there may be contained metal ions in the silver halide emulsion by adding a cadmium salt, zinc salt, lead salt, thallium salt, iridium salt or complex thereof, rhodium salt or complex thereof, or iron salt or complex thereof, so that the metal ions can be included in the inner part and/or outer part of the grains; moreover, there can be provided reduction-sensitized specks in the inner part and/or outer part of the grains by keeping the grains in an appropriate reducing environment.

The silver halide emulsion used in the invention may be subjected to a desalting treatment after completion of silver halide grain formation to remove excessive soluble salts, or such salts may be left unremoved. In removing the excessive salts, the methods described in Research Disclosure No. 17643 are applicable.

The silver halide emulsion used in the invention may be composed of grains in which a latent image is formed mainly on the surface, or of grains in which a latent image is formed mainly at the inner portion.

In the invention, the silver halide emulsion is chemically sensitized by a conventional method. That is, there can be used, singly or in combination, the sulfur sensitization using a sulfur compound reactive to silver ions or an active gelatin, selenium sensitization employing a selenium compound, reduction sensitization using a reducing agent and precious metal sensitization with a compound of gold or other precious metals.

In the invention, the chemical sensitization can be carried out, for example, by a chalcogen sensitizer. "Chalcogen sensitizer" is a general term for a sulfur sensitizer, selenium sensitizer and tellurium sensitizer; of these, a sulfur sensitizer and selenium sensitizer are preferred.

Preferable examples of the sulfur sensitizer include thiosulfate, allylthiocarbazide, thiourea, allylisocyanate, cystine, p-toluene thiosulfonate and rhodanine. Other usable sulfur sensitizers are those described, for example, in U.S. Patent Nos. 1,574,974, 2,410,689, 2,278,947, 2,728,668, 3,501,313, 3,656,955,

West Germany OLS No. 1,422,869 and Japanese Patent O.P.I. Publication Nos. 24937/1981 and 45016/1980.

The addition amount of the sulfur sensitizer greatly varies depending on conditions such as pH, temperature and size of silver halide grains, but it is roughly 10^{-7} to 10^{-1} mol per mol of silver halide.

The selenium sensitization may be used instead of the sulfur sensitization. Preferable examples of the
 5 selenium sensitizer are aliphatic isoselenocyanates such as allylisoselenocyanate; selenoureas; selenoketones; selenoamides; selenocarboxylates, selenophosphates; and selenides such as diethyl selenide and diethyl diselenide. Among these examples, typical ones can be seen in U.S. Patent 1,574,944, 1,602,592 and 1,623,499.

Further, the reduction sensitization may also be performed in conjunction. Usable reducing agents are
 10 not particularly limited in types, but preferable examples are stannous chloride, thiourea dioxide, hydrazine and polyamines.

Precious metal compounds other than gold, such as palladium compounds, may be jointly used.

When a direct positive image forming silver halide emulsion is used as an silver halide emulsion, an
 internal latent image type silver halide emulsion may be used. For example, there may be used the so-
 15 called conversion type silver halide emulsions according to the conversion method described in U.S. Patent No. 3,592,250; silver halide emulsions which contain silver halide grains internally and chemically sensitized as described in U.S. Patent Nos. 3,206,316, 3,317,322 and 3,367,778; silver halide emulsions which have silver halide grains internally containing polyvalent metal ions as described in U.S. Patent Nos. 3,271,157, 3,447,927 and 3,531,291; silver halide emulsions in which the surfaces of doped silver halide grains are
 20 slightly subjected to chemical sensitization as described in U.S. Patent No. 3,761,276; the so-called core shell type silver halide emulsions according to the layer forming methods disclosed in Japanese Patent O.P.I. Publication Nos. 8524/1975, 38525/1975 and 2408/1978; and other silver halide emulsions including those described in Japanese Patent O.P.I. Publication Nos. 156614/1977, 127549/1980 and 79940/1982. Of these internal latent image type silver halide emulsions, the particularly preferred are those consisting of
 25 grains of layered structure.

Such silver halide grains can be prepared in the same manner as with grains of ordinary layered structure. As is described in Japanese Patent O.P.I. Publication Nos. 8524/1975, 38525/1975, 60222/1978, 1524/1980 and U.S. Patent 3,206,313, for example, there may be formed a layered structure by a method in which silver chloride grains formed beforehand are converted into silver bromide grains with the addition of
 30 a bromide, and then different layers are successively formed thereon with the further addition of halides and silver nitrate; or a method in which silver iodobromide grains are formed under conditions of less excessive halogen, and then silver chloride and silver bromide are successively deposited in layers.

The internal latent image type silver halide emulsion used in the invention may contain a conventional stabilizer such as an azaindene-ring-containing compound or mercapto-group-containing heterocyclic com-
 35 pound, in order to control reverse side sensitivity as low as possible and to give a lower minimum density and stable photographic characteristics.

A preferable example of the azaindene-ring-containing compound is 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

Preferable nitrogen-containing heterocyclic compound in the mercapto-group-containing heterocyclic
 40 compound are ones having pyrazole ring, 1,2,4-triazole ring, 1,2,3-triazole ring, 1,3,4-thiadiazole ring, 1,2,3-thiadiazole ring, 1,2,4-thiadiazole ring, 1,2,5-thiadiazole ring, 1,2,3,4-tetrazole ring, pyridazine ring, 1,2,3-triazine ring, 1,2,4-triazine ring and 1,3,5-triazine ring. Further, there may also be used the compound having condensation products of two or three of these heterocycles such as triazolotriazole ring, diazaindene ring, triazaindene ring, tetrazaindene ring, pentazaindene ring; phthalazinone ring; and imidazole ring. Among
 45 them, 1-phenyl-5-mercaptotetrazole is particularly preferred.

In the silver halide color photographic light-sensitive material, the following sensitizing dyes are used to have at least three silver halide emulsion layers different in spectral sensitivities from one another.

Useful examples of the sensitizing dye employed in a blue-sensitive silver halide emulsion layer include those described in West Germany Patent No. 929,080, U.S. Patent Nos. 2,231,658, 2,493,748, 2,503,776,
 50 2,519,001, 2,912,329, 3,656,959, 3,672,897, 3,694,317, 4,025,349, 4,046,572, British Patent No. 1,242,588 and Japanese Patent Examined Publication 14030/1969 and 24844/1977. Typical examples of the sensitizing dye useful for a green-sensitive silver halide emulsion layer are those cyanine dyes, merocyanine dyes and complex cyanine dyes which are described in U.S. Patent Nos. 1,939,201, 2,072,098, 2,739,149, 2,945,763, British Patent No. 505,979. Typical examples of the sensitizing dye used in a red-sensitive emulsion layer
 55 are those cyanine dyes, merocyanine dyes and complex cyanine dyes which are described in U.S. Patent Nos. 2,269,234, 2,270,378, 2,442,710, 2,454,629 and 2,776,280. Further, there may be advantageously used, in a green-sensitive or red-sensitive emulsion layer, cyanine dyes or complex cyanine dyes described in U.S. Patent Nos. 2,213,995, 2,493,748, 2,519,001 and West Germany Patent No. 929,080.

These sensitizing dyes may be used singly or in combination. Combination of sensitizing dyes is often practiced for the purpose of supersensitization. Typical examples thereof can be seen in Japanese Patent Examined Publication Nos. 4932/1968, 4933/1968, 4936/1968, 32753/1969, 25831/1970, 26474/1970, 11627/1971, 18107/1971, 8741/1972, 11114/1972, 25379/1972, 37443/1972, 28293/1973, 38406/1973, 38407/1973, 38408/1973, 41204/1973, 6207/1974, 40662/1975, 12375/1978, 34535/1979, 1569/1980, Japanese Patent O.P.I. Publication Nos. 33220/1975, 33828/1975, 38526/1975, 107127/1976, 115820/1976, 135528/1976, 151527/1976, 23931/1977, 51932/1977, 104916/1977, 104917/1977, 109925/1977, 110618/1977, 80118/1979, 25728/1981, 1483/1982, 10753/1983, 91445/1983, 153926/1983, 114533/1984, 11645/1984, 116647/1984 and U.S. Patent 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,917,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, 4,026,707.

There are used, together with the above sensitizing dye, dyes having no spectral sensitizing effect by themselves, or compounds absorbing no visible light substantially and having a supersensitizing effect. Examples thereof include aromatic acid formaldehyde condensates such as those described in U.S. Patent No. 3,473,510, cadmium salts, azaindene compounds and aminostilbene compounds substituted with a nitrogen-containing heterocycle such as those described in U.S. Patent Nos. 2,933,390 and 3,635,721. The particularly useful are combinations described in U.S. Patent Nos. 3,615,613, 3,615,641, 3,617,295 and 3,635,721.

In addition to the above compounds, the silver halide color photographic light-sensitive material of the invention may use other conventional additives.

As a wetting agent, dihydroxyalkane, for example, may be used. To improve physical properties of the layer, there may be added an aqueous dispersion of fine particle polymeric substance prepared by emulsion polymerization, such as copolymer of alkyl acrylate or alkyl methacrylate and acrylic acid or methacrylic acid, styrene-maleic acid copolymer or styrene-maleic anhydride half alkyl ester copolymer. Examples of the coating aid include saponin, polyethylene glycol and lauryl ether. Other photographic additives which may be optionally used in the invention are gelatin plasticizers, surfactants, ultraviolet absorbents, pH regulators, antioxidants, antistatic agents, thickeners, graininess improvers, dyes, mordants, brightening agents, development control agents, matting agents and anti-irradiation dyes.

To prevent color fading in dye images attributable to high frequency active rays, there may be used ultraviolet absorbents such as thiazolidone type, benzotriazole type, acrylonitrile type and benzophenone type compounds. The particularly advantageous is to use Tinuvin PS, I20, 320, 326, 327 or 328, products of Ciba-Geigy AG, singly or in combination.

The image forming layer of the invention may contain gelatin including oxidized gelatin or derivatives thereof appropriate to a specific requirement. Preferable examples of the gelatin derivative are acylated gelatin, guanidinated gelatin, carbamylated gelatin, cyanoethylated gelatin, estrified gelatin, etc.

In addition to gelatin, the color light-sensitive material of the invention may contain other hydrophilic binders in its hydrophilic colloid layers.

Such other hydrophilic binders may be added, according to specific requirements, in photographic structural layers such as emulsion layer, intermediate layer, filter layer and subbing layer. Further, these hydrophilic binders may use a plasticizer, lubricant, etc., depending on required photographic properties.

Further, the color light-sensitive material of the invention may have, according to specific requirements, various photographic structural layers such as filter layer, intermediate layer, protective layer, subbing layer, backing layer and anti-halation layer, in addition to the emulsion layer that constitutes a layer that carries images on a support. In coating of these layers, there can be used various methods including dip coating, air doctor coating, extrusion coating, slide hopper coating and curtain flow coating.

In the invention, typical examples of the support, though any type of support is applicable, are polyethylene terephthalate film which may be subbed when necessary, polycarbonate film, polystyrene film, polypropylene film and cellulose acetate film, baryta paper, paper laminated with polyolefin such as polyethylene, and polyethylene terephthalate film in which a white pigment is compounded.

The light-sensitive material of the invention can be exposed with electromagnetic waves having a spectral region to which the emulsion layer of said light-sensitive material is sensitive. As a light source, there can be used any of the known light sources such as natural light (sunlight); tungsten lamp; fluorescent lamp; mercury lamp; xenon arc lamp; carbon arc lamp; xenon flash tube; cathode ray tube flying spot; various laser beams; light emitting diode beams; and beams emitted from a luminescent body excited by electron beams, X-rays, γ -rays or α -rays.

The silver halide color photographic light-sensitive material of the invention can be made into a structure of ordinary color paper having color sensitive layers of blue-sensitivity, green-sensitivity and red-sensitivity. In this case, three-color separation filters, such as Wratten Nos. 25, 29, 58, 61, 47B, can be used as an optical filter.

Exposure can be completed within an exposure time as short as less than 1 millisecond, not to mention the exposure time for ordinary printers which ranges from 1 millisecond to 10 seconds. For example, an exposure of 100 microseconds to 1 millisecond can be practiced with a cathode ray tube or xenon flash tube. On the contrary, an exposure time longer than 10 seconds is also applicable.

5 Said exposure may be made continuously or intermittently.

In the invention, the color developing agent used in a color developer includes conventional ones widely used in various color photographic processes. The developer contains an aminophenol derivative and p-phenylenediamine derivative. These compounds are more stable when dissociated; therefore, they are generally used in the form of salt such as hydrochloride or sulfate. These compounds are generally used in
10 an amount of approx. 0.1 to approx. 30 g per liter of color developer, preferably in an amount of approx. 1 to approx. 15 g per liter of color developer.

Useful examples of the aminophenol type developing agent include o-aminophenol, p-aminophenol, 5-amino-2-oxytoluene, 2-amino-3-oxytoluene and 2-oxy-3-amino-1,4-dimethylbenzene.

Preferable examples of the aromatic primary amine color developing agent are N,N-dialkyl-p-phenylenediamine compounds, of which alkyl and phenyl groups may be substituted or unsubstituted. Of
15 them, the particularly preferred are N,N-diethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine hydrochloride, N,N-dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)toluene, N-ethyl-N- β -methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, 4-amino-N-ethyl-N-(β -hydroxyethyl)aniline sulfate, 4-amino-3-methyl-N,N-diethylaniline and 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline p-toluene sulfonate; and the most preferred is 4-amino-N-ethyl-N-(β -hydroxyethyl)aniline sulfate.
20

In a color developer for processing light-sensitive material of the invention, there may be optionally added, besides the above aromatic primary amine color developing agent, conventional developer component compounds such as alkali agents including sodium hydroxide, sodium carbonate and potassium
25 carbonate; alkali metal bisulfites; alkali metal thiocyanates; alkali metal halides; benzyl alcohol; water-softening agents; and thickeners.

The pH value of the color developer is normally more than 7, typically approx. 10 to approx. 13.

The developing temperature is normally higher than 15°C, typically within the range from 20°C to 50°C. For rapid processing, a temperature not less than 30°C is preferred. The color developing time is
30 generally within the range from 20 to 60 seconds, preferably within the range from 30 to 50 seconds.

The light-sensitive material according to the invention contains, in the hydrophilic colloid, the above color developing agents in their original forms, or as precursors thereof to be treated in an alkaline activating bath. The precursor of a color developing agent, which is capable of forming a color developing agent under alkaline conditions, falls into various types; namely, a Schiff's base precursor obtained by
35 condensation with an aromatic aldehyde, polyvalent metal ion complex precursor, phthalimide derivative precursor, phosphorimide derivative precursor, sugar amine reactant precursor and urethane precursor. These precursors of aromatic primary amine color developing agents are described, for example, in U.S. Patent Nos. 3,342,599, 2,507,114, 2,695,234, 3,719,492, British Patent No. 808,783, Japanese Patent O.P.I. Publication Nos. 185628/1978, 79035/1979 and Research Disclosure Nos. 15159, 12146, 13924.

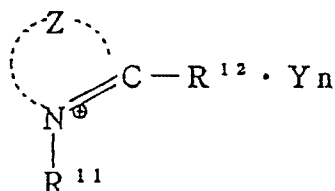
It is necessary that the addition amount of these aromatic primary amine color developing agents or precursors thereof be large enough to give activated products sufficient for proper color developing. The addition amount is roughly 0.1 to 5 mols, preferable 0.5 to 3 mols per mol of silver halide, though it greatly varies depending on types of light-sensitive material. These color developing agents or precursors thereof
40 may be used singly or in combination. When contained in a light-sensitive material, they can be added therein in the form of solution in a suitable solvent such as water, methanol, ethanol or acetone, or in the form of dispersion in a high boiling organic solvent such as dibutyl phthalate, dioctyl phthalate or tricresyl phosphate, or may be added using a latex polymer impregnated with them as described in Research Disclosure No. 14850.

In case of forming a positive image directly with a light-sensitive material of the invention having an
50 internal latent image type silver halide emulsion layer as an image forming layer, the principal process is to subject an internal latent image type light-sensitive material which is not fogged beforehand to imagewise exposing, and then to subject it to surface developing after a fogging treatment or while fogging it. Such a fogging treatment can be performed by giving an overall uniform exposure to the light-sensitive material or using a fogging agent. In this case, use of a fogging agent is preferred. Usable fogging agents range over
55 various chemical types, and fogging can be performed by simply having a fogging agent exist in the developing system. That is, it may be contained, for example, in a silver halide emulsion layer of an internal latent image type silver halide photographic light-sensitive material or in a developer, or it may be contained in treating solution used in a process that proceeds developing. But addition in an internal latent image type

silver halide photographic light-sensitive material is preferred, particularly addition in a silver halide emulsion is preferred.

Typical examples of the preferred fogging agent are those represented by the following Formula FA-I or FA-II.

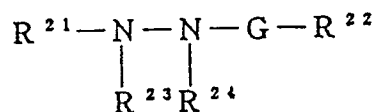
FA-I



In Formula FA-I, Z represents a group of atoms necessary to form a five- or six-membered heterocycle; R¹¹ is an aliphatic group; and R¹² represents a hydrogen atom, or an aliphatic or aromatic group. Each of Z, R¹¹ and R¹² may be substituted; R¹² may form a ring by bonding with the heterocyclic group which is completed by Z; provided that at least one of groups respectively represented by R¹¹, R¹² and Z contain a alkynyl, acyl, hydrazine or hydrazone group, or R¹¹ and R¹² jointly form a six-membered ring, namely, a dihydropyridinium skeleton.

Y is a counter ions for balancing electric charge. n is an integer of 0 or 1.

FA-II



In Formula FA-II, R²¹ represents an aliphatic, aromatic or heterocyclic group; R²² represents a hydrogen atom, or an alkyl, aralkyl, aryl, alkoxy, aryloxy or amino group; G represents a carbonyl, sulfonyl, sulfoxy, phosphoryl or iminomethylene group, HN=C<; R²³ and R²⁴ are both hydrogen atoms, or one of them is a hydrogen atom and the other is an alkylsulfonyl, arylsulfonyl or acyl group; and a hydrazone structure, >N-N=C<, may be formed in conjunction of G, R²², R²⁴ and the hydrazine nitrogen. The above groups may be substituted if possible.

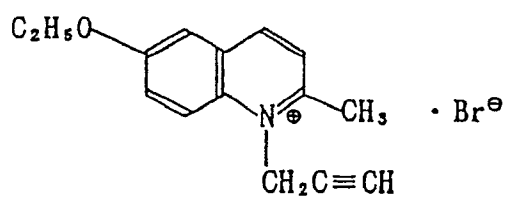
The compounds of Formula FA-I and manufacturing methods thereof are described, for example, in Research Disclosure No.22,534 (published in January, 1983, pp. 50-54), Japanese Patent O.P.I. Publication Nos. 138742/1980, 11837/1985, 90154/1990 and U.S. Patent Nos. 4,306,016, 4,471,044.

The following are typical examples of the compound represented by Formula FA-I.

FA - I - 1

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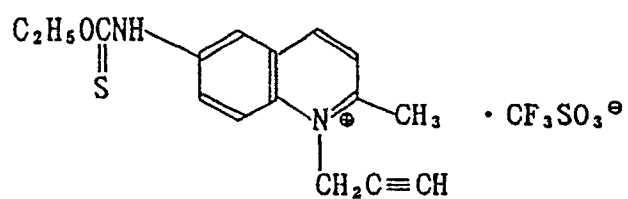
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FA - I - 2

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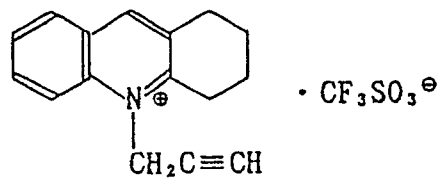
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FA - I - 3

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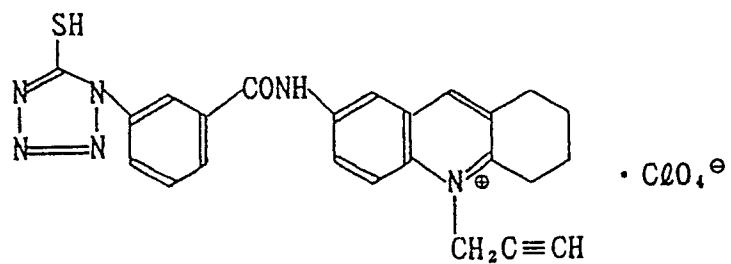


FA - I - 4

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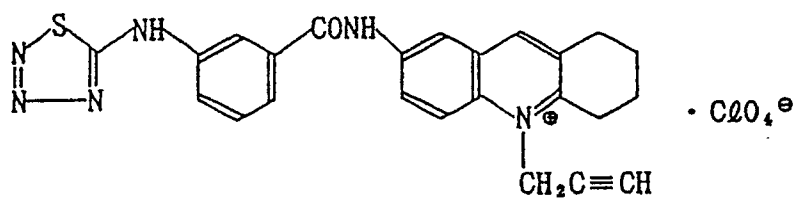
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FA - I - 5

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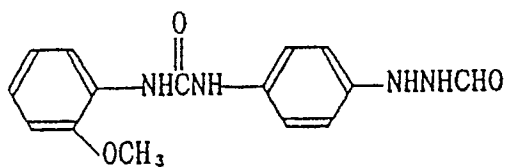
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The synthesis methods of the compounds represented by Formula FA-II are described, for example, in U.S. Patent Nos. 4,030,925, 4,080,207, 4,276,364, 4,459,347, 4,560,632, 4,560,638, 4,478,928, British Patent No. 2,011,391B, and Japanese Patent O.P.I. Publication Nos. 163533/1980, 86829/1982, 179734/1985. In recent literature, description of the compound can be seen in Japanese Patent O.P.I. Publication No. 90154/1990.

Typical examples of the compound represented by Formula FA-II are as follows.

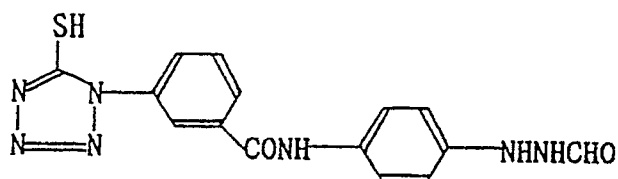
FA-II-1



F A - II - 2

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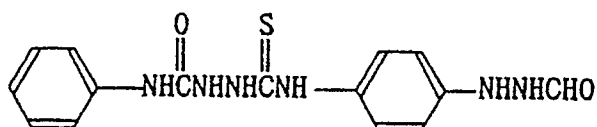
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F A - II - 3

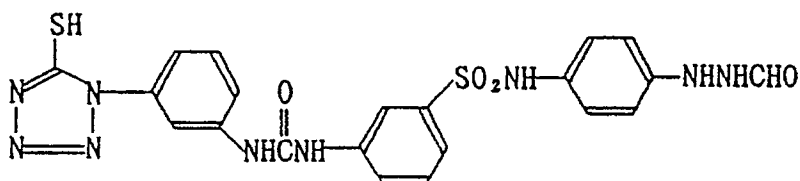
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F A - II - 4

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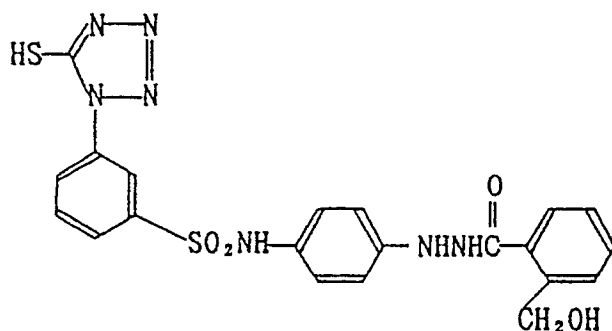


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F A - II - 5

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45 In incorporating the compounds represented by Formula FA-I or FA-II in the photographic light-sensitive material of the invention, these are dissolved in water-miscible organic solvents such as alcohols, such as methanol, ethanol, esters such as ethyl acetate or ketones such as acetone, or in water when these are water-soluble, and then added to a hydrophilic colloid solution.

50 In case the compounds are added in a photographic emulsion, the addition may be made any time in a period between start of chemical ripening and before coating, but the addition after chemical ripening is preferred.

In the invention, the fogging agent represented by Formula FA-I or FA-II may be contained in a hydrophilic colloid layer adjacent to a silver halide emulsion layer, but it is preferably contained in a silver halide emulsion layer.

55 The addition amount of the compound varies over a wide range, since it depends on many factors such as characteristics of the silver halide emulsion, chemical structure of the fogging agent and developing conditions. But it is practically in a range from 1×10^{-8} to 1×10^{-2} mol per mol of silver halide, preferably from 1×10^{-7} to 1×10^{-2} mol per mol of silver halide.

The preferred fogging agents used in the invention are those having the structure of Formula FA-I.

Among them, those in which R^{12} forms a ring in conjunction with the heterocycle completed by Z are particularly preferred.

In the invention, there may be used a speck formation accelerator in order to enhance the function of the fogging agent.

5 Preferable speck forming accelerators include tetrazaindenes, triazaindenes and pentazaindenes, each having at least one mercapto group which may be substituted by an alkali metal atom or ammonium group, as well as the compounds described in the specification of Japanese Patent O.P.I. Publication No. 106656/1988 (pp.6-16).

10 The speck forming accelerator may be incorporated in a light-sensitive material or treating solution, but it is preferable to incorporate it in an internal latent image type silver halide emulsion layer or other hydrophilic colloid layers, e.g., as intermediate layer and protective layer, of a light-sensitive material. The particularly preferable is to incorporate it in a silver halide emulsion layer or a layer adjacent thereto.

15 When the light-sensitive material of the invention is embodied in the form of internal latent image type silver halide photographic light-sensitive material, positive images are directly formed by imagewise exposing followed by overall exposing or developing in the presence of the fogging agent. Though developing of said light-sensitive material may be performed by any of developing methods, the surface developing method is preferred. The surface developing method means a treatment with a developer substantially devoid of a silver halide solvent.

20 In the invention, positive images corresponding to original images are formed by subjecting an exposed silver halide color photographic light-sensitive material to development and then to treatment with a treating solution having a fixing capability.

25 Besides color development, the above development includes combination of black-and-white development used in reverse color processing and color development. Further, there are also included overall exposure and development in the presence of the fogging agent, which are used in processing of the internal latent image type silver halide photographic light-sensitive material.

30 A black-and-white developer used in the development is equivalent to a conventional developer called black-and-white first developer, which is used in processing of a color photographic light-sensitive material, or to a conventional developer for a black-and-white photographic light-sensitive material. This black-and-white developer can contain various additives used in conventional black-and-white developers.

35 Examples of typical additives include developing agents such as l-phenyl-3-pyrazolidone, metol and hydroquinone; preservatives such as sulfites; alkaline accelerators such as sodium hydroxide, sodium carbonate and potassium carbonate; inorganic and organic inhibitors such as potassium bromide, 2-methylbenzimidazole and methylbenzothiazole; water softeners such as polyphosphates; and inhibitors against excessive surface developing containing traces of iodides and mercapto compounds.

40 After developing, the light-sensitive material of the invention is subjected to bleaching and fixing. Bleaching may be carried out concurrently with fixing. Among many compounds usable as a bleaching agent, the preferred are polyvalent metal compounds such as compounds of iron (III), cobalt (III) and copper (II). The especially preferred are their complex salts with organic acids such as aminopolycarboxylic acids including ethylenediamine tetracetate, nitrilotriacetic acid, N-hydroxyethyl ethylenediamine diacetate; and malonic acid, tartaric acid, malic acid, diglycolic acid and thioglycolic acid. Other usable bleaching agents are ferricyanates and bichromates. These bleaching agents may be used singly or in combination.

45 As a fixing agent, a soluble complexing agent which solubilizes silver halide as a complex salt is used. Examples of the soluble complexing agent include sodium thiosulfate, ammonium thiosulfate, potassium thiocyanate, thiourea and thioether.

50 Fixing is usually followed by washing. But washing may be replaced by stabilizing or carried out concurrently with stabilizing. In a stabilizer solution, there may be added a pH regulator, chelating agent and mildewproofing agent. Specific conditions on them can be seen in Japanese Patent O.P.I. Publication No. 134636/1983.

50 EXAMPLES

Typical examples of the invention are described hereunder.

Example I.

55

Molar equivalents of a silver nitrate aqueous solution and a potassium bromide aqueous solution were simultaneously added to a gelatin aqueous solution by the double jet method at 50° C over a period of 50 minutes, so that an emulsion consisting of cubic silver bromide grains having an average grain size of 0.3

μm.

There were added to the emulsion 6.5 mg/mol AgX of sodium thiosulfate and 3 mg/mol AgX of potassium chloroaurate, and the emulsion was chemically ripened at 70 ° C for 70 minutes. Then, a silver nitrate aqueous solution and a mixed aqueous solution of sodium chloride and potassium bromide (1:9 molar ratio) were simultaneously added thereto to prepare a cubic core/shell type emulsion which contained grains consisting of the silver bromide core and silver chlorobromide shell and having an average grain size of 0.45 μm. After washing for desalination, there were added 2.0 mg/mol AgX of sodium thiosulfate and 1.0 mg/mol AgX of potassium chloroaurate, and the emulsion was subjected to chemical ripening at 60 ° C for 50 minutes, and thereby a direct positive silver halide emulsion EM-I was prepared.

10

Preparation of blue-sensitive emulsion EM-B

After sensitizing EM-I with sensitizing dye D-5, 600 mg/mol AgX of T-I was added thereto, and then 8×10^{-5} mol/mol AgX of FA-II-2 and 5×10^{-4} mol/mol AgX of FA-I-4 were added, so that blue-sensitive emulsion EM-B was prepared.

15

Preparation of green-sensitive emulsion EM-G

Green-sensitive emulsion EM-G was prepared in the same manner as with the blue-sensitive emulsion, except that sensitizing dye D-6 was used in the optical sensitization.

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Preparation of red-sensitive emulsion EM-R

Red-sensitive emulsion EM-R was prepared in the same manner as with the blue-sensitive emulsion, except that sensitizing dye D-7 was used in the optical sensitization.

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Using EM-B, EM-G and EM-R, silver halide color light-sensitive materials having the constitution of Table I were prepared.

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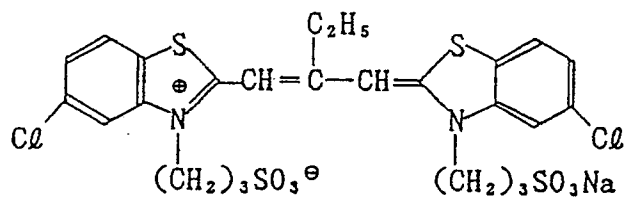
Table 1

Layer (Sample 1)	Constitution	Coating weight* (mg/dm ²)
10th layer (UV absorbent layer)	gelatin UV absorbent (UV-1) UV absorbent (UV-2) solvent (SO-2) colloidal silica	7.8 0.65 1.95 1.0 0.30
9th layer (blue-sensitive layer)	gelatin blue-sensitive emulsion EM-B (amount of Ag coated) yellow coupler (Y-59) antistain agent (AS-2) solvent (SO-1) inhibitors (ST-1, ST-2, T-1)	14.3 5.0 8.2 0.25 8.2
8th layer (intermediate layer)	gelatin antistain agent (AS-1) solvent (SO-2)	5.4 0.55 0.72
7th layer (yellow colloidal silver layer)	gelatin yellow colloidal silver antistain agent (AS-1) solvent (SO-2) polyvinyl pyrrolidone (PVP)	4.2 1.0 0.40 0.49 0.47
6th layer (intermediate layer)	gelatin antistain agent (AS-1) solvent (SO-2)	5.4 0.55 0.72

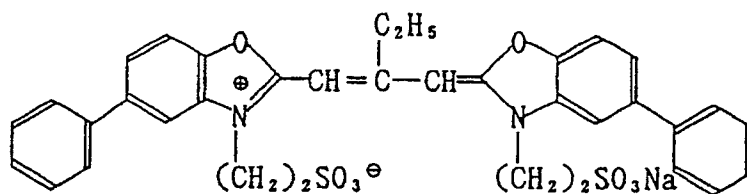
Layer (Sample 1)	Constitution	Coating weight* (mg/dm ²)
5th layer (green-sensitive layer)	gelatin green-sensitive emulsion EM-G (amount of Ag coated) magenta coupler yellow coupler Compound I solvent (SO-1) anti-irradiation dye (AI-3) inhibitors (ST-1, ST-2, T-1)	14.3 4.0 Table 2 Table 2 Table 2 3.1 0.35
4th layer (intermediate layer)	gelatin antistain agent (AS-1) solvent (SO-2)	7.5 0.55 0.72
3rd layer (red-sensitive layer)	gelatin red-sensitive emulsion EM-R (amount of Ag coated) cyan coupler (CC-3) antistain agent (A-1) antistain agent (AS-2) anti-irradiation dye (AI-4) inhibitors (ST-1, ST-2, T-1)	13.5 3.0 4.4 2.2 0.15 0.25
2nd layer (intermediate layer)	gelatin antistain agent (AS-1) solvent (SO-2)	5.4 0.55 0.72
1st layer (anti-halation layer)	gelatin black colloidal silver	6.0 1.0

* Amount of Ag coated is in terms of silver.

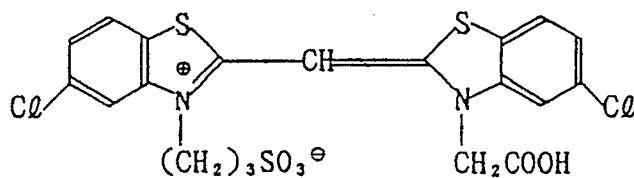
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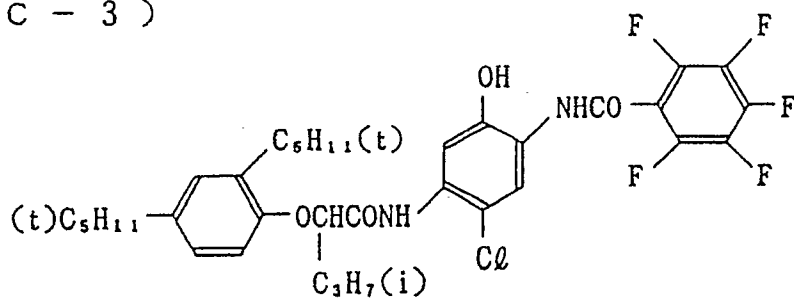
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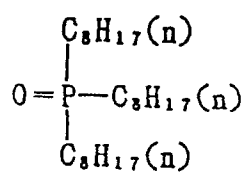


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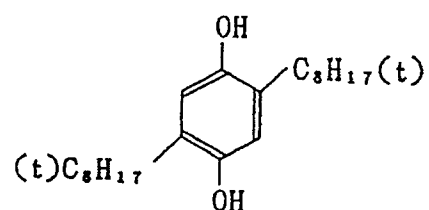
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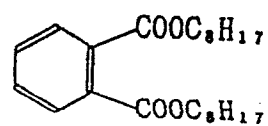
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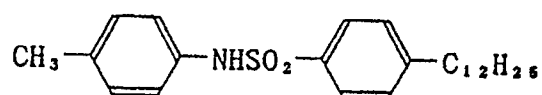
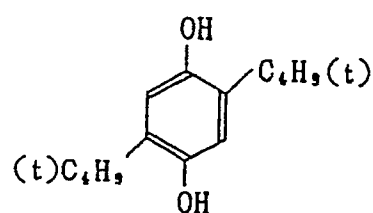
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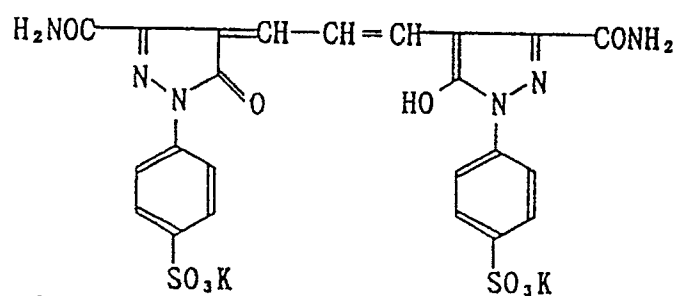
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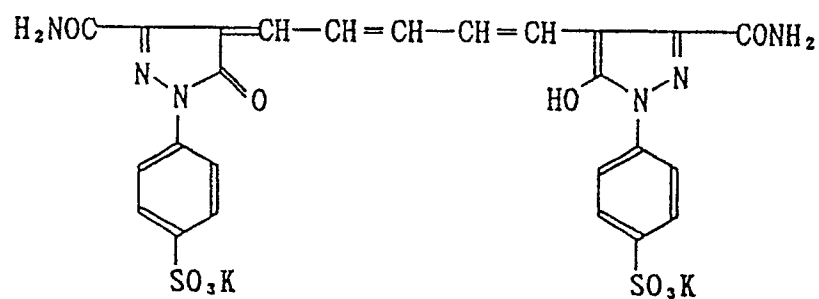
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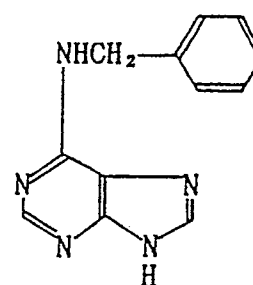
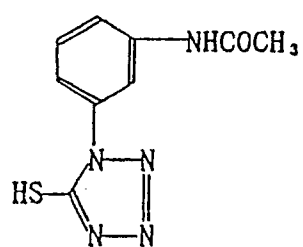
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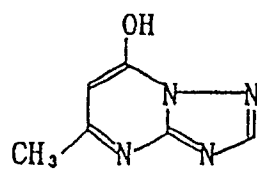
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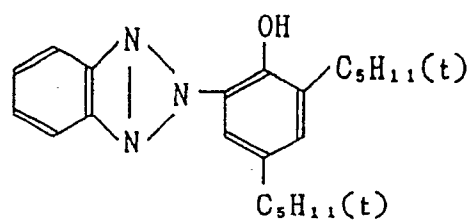
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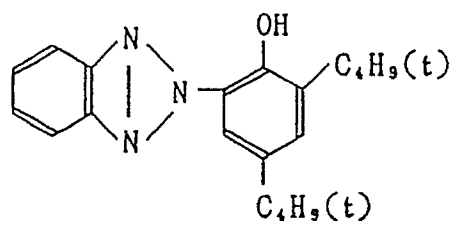
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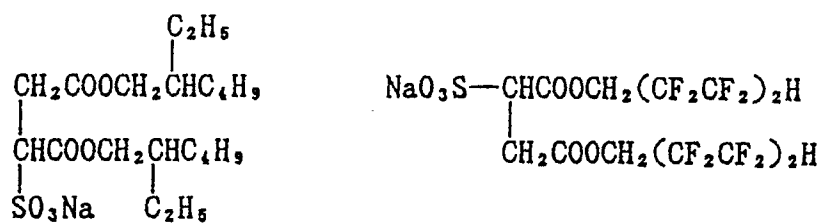


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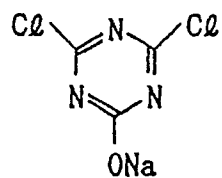
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H - 1

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On a paper support laminated with polyethylene on both sides, there were coated 1st through 10th layers in a constitution shown in Table 2. In coating, SA-1 and SA-2 were used as coating aids, and H-1 as a hardener.

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Table 2

Sample No.	Magenta coupler addition amount (mol/m ²)	Yellow coupler addition amount (mol/m ²)	Coating weight of compound [I] (mg/m ²)
1 Comparison	MC-1 (4.4 x 10 ⁻⁴)	Y-58 (1.1 x 10 ⁻⁴)	-
2 Comparison	MC-1 (4.4 x 10 ⁻⁴)	Y-58 (1.1 x 10 ⁻⁴)	AS-1 (0.19)
3 Comparison	MC-1 (4.4 x 10 ⁻⁴)	Y-58 (1.1 x 10 ⁻⁴)	I-(2)(0.19)
4 Comparison	M-3 (4.4 x 10 ⁻⁴)	Y-58 (1.1 x 10 ⁻⁴)	-
5 Comparison	M-3 (4.4 x 10 ⁻⁴)	Y-58 (1.1 x 10 ⁻⁴)	AS-1 (0.19)
6 Invention	M-3 (4.4 x 10 ⁻⁴)	Y-58 (1.1 x 10 ⁻⁴)	I-(2)(0.19)
7 Invention	M-3 (4.4 x 10 ⁻⁴)	Y-58 (1.1 x 10 ⁻⁴)	I-(9)(0.19)
8 Invention	M-61 (4.4 x 10 ⁻⁴)	Y-6 (1.1 x 10 ⁻⁴)	I-(2)(0.19)
9 Invention	M-12 (4.4 x 10 ⁻⁴)	Y-4 (1.1 x 10 ⁻⁴)	I-(2)(0.19)
10 Invention	M-22 (4.4 x 10 ⁻⁴)	Y-22 (1.1 x 10 ⁻⁴)	I-(2)(0.19)
11 Invention	M-44 (4.4 x 10 ⁻⁴)	Y-49 (1.1 x 10 ⁻⁴)	I-(2)(0.19)

Each sample prepared as above was exposed as follows. A 0.075-step gray scale tablet and a dot positive scale of 150 line/in 1% to 5% were closely contacted with a printer DSF-605F (product of Dainippon Screen Co.) and the sample was exposed to the light passed through a Wratten filter No. 58 (green).

Next, the original film was removed and subjected to exposure first through a Wratten filter No.47B (blue), then through a Wratten filter No.25 (red).

The exposure was carried out in a minimum exposing time in order to hold the color formation at a white portion to a minimum level.

The exposed sample was treated by the following processes to confirm the effect of the invention. The evaluation results are shown in Table 3.

EP 0 459 331 A1

	Process	Temperature	Time
	(1) Color developing	35°C	2 min 30 sec
5	(2) Bleach-fixing	35°C	1 min
	(3) Stabilizing	25 - 30°C	1 min 30 sec
10	(4) Drying	78 - 80°C	1 min

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Compositions of treating solutions

(Color developer)

5	Benzyl alcohol	15 ml
	Cerium sulfate	0.015 g
10	Ethylene glycol	8 ml
	Potassium sulfite	2.5 g
	Potassium bromide	0.8 g
15	Sodium chloride	0.2 g
	Potassium carbonate	25.0 g
20	T-1	0.1 g
	Hydroxylamine sulfate	5.0 g
	Diethylenetriamine pentacetate	2.0 g
25	4-Amino-N-ethyl-N-(β -hydroxyethyl)	
	aniline sulfate	4.5 g
30	Optical brightener	
	(4,4'-diaminostilbene disulfonate derivative)	1.0 g
	Potassium hydroxide	2.0 g
35	Diethylene glycol	15 ml
	Potassium phosphate	8.0 g
40	Water was added to make the total volume 1 liter, and then pH was adjusted to 10.50.	

(Bleach-fixer)

45	Ammonium ferric ethylenediamine tetracetate	
	(dihydrate)	60 g
50	Ethylenediamine tetracetic acid	3 g

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Ammonium thiosulfate (70% solution) 100 ml
Ammonium sulfite (40% solution) 27.5 ml

5

pH was adjusted to 7.1 with potassium carbonate or
glacial acetic acid, then water was added to make the
total volume 1 liter.

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(Stabilizer)

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5-Chloro-2-methyl-4-isothiazoline-3-one 1.0 g

Ethylene glycol 10 g

1-Hydroxyethylidene-1,1-diphosphonic acid 2.5 g

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Bismuth chloride 0.2 g

Magnesium chloride 0.1 g

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Ammonium hydroxide (28% solution) 2.0 g

Sodium nitrilotriacetate 1.0 g

Water was added to make the total volume 1 liter, and

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pH was adjusted to 7.0 with ammonium hydroxide or
sulfuric acid.

35 The stabilizing was carried out with a two-tank counter-flow apparatus.

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Table 3

Sample No.	Color tone of magenta image *1	Relative gamma value at low den- sity area *2	Reproduci- bility of small dots *3	Density of non-image portion *4
1 Comparison	1	100	5.2%	0.15
2 Comparison	2	110	3.5%	0.12
3 Comparison	3	118	2.5%	0.10
4 Comparison	3	111	3.5%	0.13
5 Comparison	5	121	2.3%	0.08
6 Invention	5	126	1.8%	0.06
7 Invention	5	128	1.7%	0.07
8 Invention	5	125	1.9%	0.06
9 Invention	5	123	1.8%	0.07
10 Invention	5	125	1.9%	0.06
11 Invention	5	125	1.9%	0.06

*1: Evaluation of magenta color tone:

The magenta color tone of a sample was compared with that of a printing ink for a fixed density, and the result was rated by a five-grade system. The larger the value is, the better the magenta color tone is.

*2: Evaluation of gamma value at low density area:

Rating was made using the following expression

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$$\left| \frac{0.50 - 0.02}{b - a} \right|$$

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where b is a value of log E for Fog + 0.50, a is a value of log E for Fog + 0.02, and Fog is a fogged density. The results are expressed by values relative to that of sample 1, which is set at 100.

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*3: Evaluation of small dot reproducibility:

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Ten persons observed a 150 line/inch dot image of 1 to 5% dots with a magnifying lens to determine the percentage of the smallest dot reproduced in the image. Mean values of the evaluation results are shown in Table 3.

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*4: White portion density:

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Densitometer PDA-65 (product of Konica Corp.) was used.

Example 2

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Samples 4 and 6 of Example 1 were subjected to dot exposure and then processed in the same manner as in Example 1, except that the following developing agents were used in place of 4-amino-N-ethyl-N-(β -hydroxyethyl)-aniline sulfate.

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- (1) 4-(N-ethyl-N- β -hydroxyethylamino)-2-methylaniline sulfate
 - (2) N-ethyl-N-(β -methanesulfonamideethyl)-3-methyl-4-aminoaniline sulfate
- Test results shown in Table 4 were obtained.

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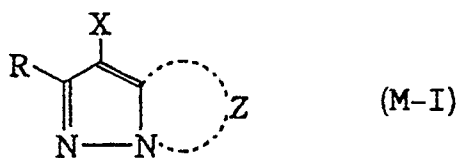
55

Table 4

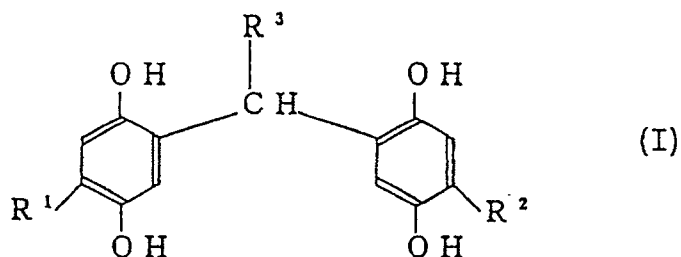
Sample No.	Deve- loping agent	Color tone of magenta image	Relative gamma value at low density area	Reproduci- bility of small dot	Density of non- image portion
4	(1)	2	105	4.5%	0.15
4	(2)	3	109	4.0%	0.14
6	(1)	3	118	2.2%	0.08
6	(2)	4	122	2.0%	0.07

Claims

1. A silver halide color photographic material comprising a support having thereon a silver halide emulsion layer containing a yellow coupler and a magenta coupler represented by the following Formula M-I and said silver halide emulsion layer or a layer adjacent to said emulsion layer contains a compound represented by the following Formula I:



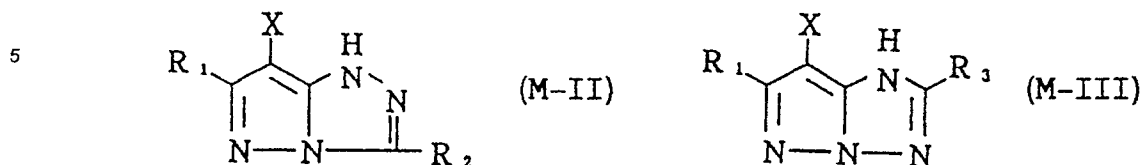
wherein Z is a group of atoms necessary forming a nitrogen-containing heterocyclic ring; X is a hydrogen atom or a substituent capable of being split off upon reaction with the oxidation product of a color developing agent; and R is a hydrogen atom or a substituent:



wherein R¹ and R² each a hydrogen atom, or an alkyl group, an alkoxy group, an alkylthio group or an alkylamido group, said alkyl group, alkoxy group, alkylthio group and alkylamido group each have 1 to 8 carbon atoms; and R³ is a hydrogen atom or a alkyl group having 1 to 11 carbon atoms, provided that the number of carbon atoms contained in said groups represented by R¹, R² and R³ is 8 to 22 in total.

2. The material of claim 1, wherein said magenta coupler is a coupler represented by the following

Formula M-II or Formula M-III;



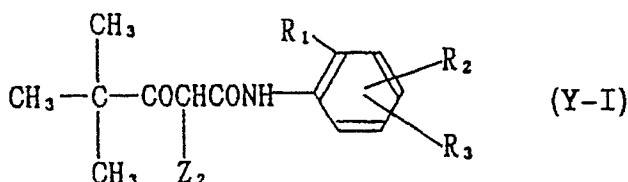
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wherein R_1 , R_2 , and R_3 , and X are the same as R and X defined in Formula M-1, respectively.

3. The material of claim 1, wherein a group represented by said R of Formula M-I satisfies the following requisits;
- 15 (1) the atom directly bonding with the heterocyclic ring is a carbon atom, and (2) the bonds between said carbon atom and the atoms adjacent thereto are single bonds.
4. The material of claim 1, wherein said yellow coupler is a compound represented by the following Formula Y-1:

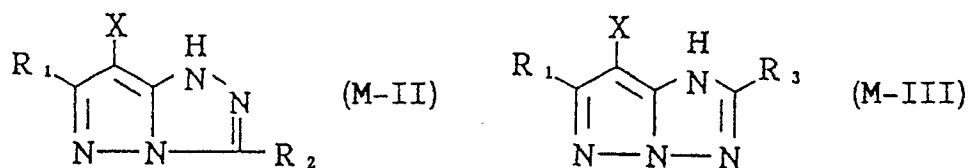
20

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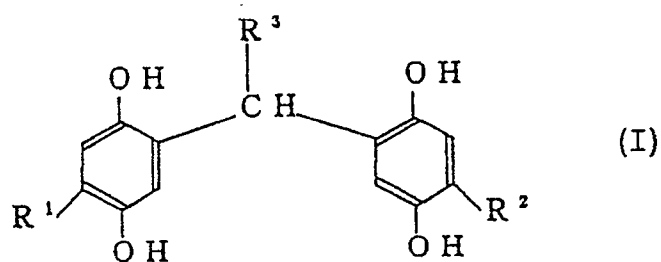


30 wherein R_1 is a halogen atom or an alkoxy group; R_2 is a hydrogen atom, a halogen atom, an acylamino group, an alkoxycarbonyl group, an alkylsulfamoyl group, an arylsulfamoyl group, an arylsulfonamido group, an alkylureido group, an arylureido group, a succinimido group, an alkoxy group or an aryloxy group; and Z_2 is a hydrogen atom or a substituent capable of being split off upon reaction with the oxidation product of a color developing agent.

- 35 5. The material of claim 1, wherein said yellow coupler has a pKa value at most 3 lower than the pKa value of said magenta coupler.
6. The material of claim 1, wherein said silver halide emulsion layer contains said yellow coupler in a ratio of 0.02 mols to 0.5 mols per mol of said magenta coupler.
- 40 7. The material of claim 1, wherein said silver halide emulsion layer or a layer adjacent thereto contains said compound represented by Formula I in an amount of 1×10^{-8} mols/m² to 1×10^{-2} mols/m².
8. The material of claim 7, wherein said silver halide emulsion layer or a layer adjacent thereto contains said compound represented by Formula I in an amount of 1×10^{-7} mols/m² to 1×10^{-3} mols/m².
- 45 9. The material of claim 1, wherein the number of carbon atoms contained in the groups represented by R^1 , R^2 and R^3 in said Formula I is 8 to 17 in total.
- 50 10. A silver halide color photographic material comprising a support having thereon a silver halide emulsion layer containing a yellow coupler and a magenta coupler represented by Formula M-II or Formula M-III and said silver halide emulsion layer or a layer adjacent to said emulsion layer contains a compound represented by Formula I, provided that said yellow coupler has a pKa value at most 3 lower than the pKa value of said magenta coupler and the ratio of said yellow coupler to said magenta coupler is 0.02 mols to 0.5 mols per mol of said magenta coupler:
- 55



10 wherein R_1 , R_2 and R_3 are independently a substituent satisfying the requisites of (1) the atom directly bonding with the heterocyclic ring is a carbon atom, and (2) the bonds between said carbon atoms and the atoms adjacent thereto are single bonds; X is a hydrogen atom or a substituent capable of being split off upon reaction with the oxidation product of a color developing agent:



25 wherein R^1 and R^2 each a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group or an alkylamido group, said alkyl group, alkoxy group, alkylthio group and alkylamido group each have 1 to 6 carbon atoms; and R^3 is a hydrogen atom or a alkyl group having 1 to 11 carbon atoms, provided that the number of carbon atoms contained in said groups represented by R^1 , R^2 and R^3 is 8 to 17 in total.

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European
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EUROPEAN SEARCH REPORT

Application Number

EP 91 10 8545

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	JP-A-2 124 568 (KONICA) * abstract ** pages 7 - 14 * - - -	1-10	G 03 C 7/30
Y	GB-A-1 474 994 (FUJI) * page 4, lines 23 - 51 ** page 7, lines 26 - 31 ** page 13, lines 42 - 46 * - - -	1-10	
Y	EP-A-0 355 818 (FUJI) * page 4, line 1 - page 9, line 45 ** page 26 *compound (III-5) ** page 50 *compound (Y-3) * - - - - -	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 C
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 01 August 91	Examiner MAGRIZOS S.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone</div> <div>Y: particularly relevant if combined with another document of the same category</div> <div>A: technological background</div> <div>O: non-written disclosure</div> <div>P: intermediate document</div> <div>T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date</div> <div>D: document cited in the application</div> <div>L: document cited for other reasons</div> <div>&: member of the same patent family, corresponding document</div>			