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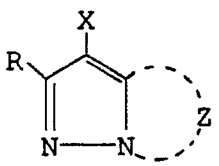
(54) Light-sensitive silver halide color photographic material.

(57) A light-sensitive silver halide color photographic material is disclosed. The photographic material contains a magenta coupler of the formula M-I and a yellow coupler, and the content of calcium atoms in the photographic layers is not more than 15 mg/m^2.

M-I



wherein Z represents a group of nonmetal atoms necessary to form a nitrogen-containing heterocycle, which 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; and R represents a hydrogen atom or a substituent.

BACKGROUND 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 plate making and printing process.

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 plate making and printing 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 correction can be made by simply laying four color film sheets (original colors of the subtractive color mixing 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 and 97140/1984 other methods to prepare a color proof.

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 monolayers 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 selected from subtractive full-color photographic light-sensitive materials 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, a color proof prepared by this method has a defect that the change in color tone becomes larger as the size of a dot becomes smaller. Japanese Patent O.P.I. Publication No. 306569/1988 describes a method to correct the defect by incorporating a magenta coupler and yellow coupler in the same light-sensitive layer, but it still involves problems to be solved and cannot be used practically. That is, when two or more couplers different in spectral absorption are contained in the same light-sensitive layer, a change in manufacturing conditions, such as change in standing time of a coating emulsion, causes the color tone to vary, and storing of the light-sensitive material also brings about a change in photographic properties such as sensitivity.

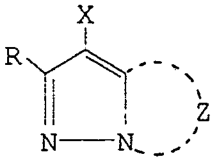
SUMMARY OF THE INVENTION

An object of the present invention is to provide a silver halide color photographic light-sensitive material, which is used to prepare a color proof from plural black-and-white dot images obtained by color separation and dot image conversion, and capable of giving stably a nearly equal color tone to both of large dots and small dots of said color proof.

Another object of the present invention is to provide a silver halide color photographic light-sensitive material for color proof which is stable in sensitivity against variation in storing conditions.

A light-sensitive silver halide color photographic material of the invention has a support and photographic layers at least one of which is a silver halide emulsion layer, wherein at least one silver halide emulsion layer having the same spectral sensitivity contains at least one of the compounds represented by the following Formula M-I and at least one yellow coupler, and the content of calcium atoms in the photographic layers is not more than 15 mg/m^2.

M-I



wherein Z represents a group of nonmetal atoms necessary to form a nitrogen-containing heterocycle, which 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; and R represents a hydrogen atom or a substituent.

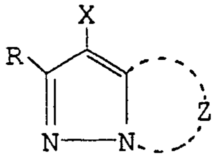
The invention will be hereafter described in detail.

In the invention, the silver halide emulsion layer having the same spectral sensitivity may be a single emulsion layer or may consist of two or more silver halide emulsion layers. When it consists of two or more emulsion layers, these layers are in a combination of silver halide emulsion layers in which the difference among wavelengths at their maximum spectral sensitivities is not more than 30 nm.

In the invention, the expression that at least one silver halide emulsion layer having the same spectral sensitivity contains at least one of the compounds represented by the above Formula M-I and at least one yellow coupler means that when said silver halide emulsion layer is a single layer, at least one of the compounds of Formula M-I and at least one of yellow couplers are contained in said silver halide emulsion layer. When said silver halide emulsion layer consists of plural layers, the compound represented by Formula M-I may be contained in any of said silver halide emulsion layers, the yellow coupler may also be contained in any of said plural layers. In a preferred embodiment of the invention, the compound of Formula M-I and a yellow coupler may be contained in a single emulsion layer. In another preferred embodiment, one of the two silver halide emulsion layers having the same spectral sensitivity contains the compound of Formula M-I, and the other layer contains a yellow coupler.

In the silver halide color photographic light-sensitive material of the invention, the compound represented by the following Formula M-I is contained.

M-I



In Formula M-I, Z represents a group of nonmetal atoms necessary to form a nitrogen-containing heterocycle, 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 subsituent represented by R is not particularly limited, but typical examples thereof include alkyl, aryl, anilino, acylamino, sulfonamide, alkylthio, arylthio, alkenyl and cycloalkyl groups. Other usable examples are halogen atoms; cycloalkenyl, alkynyl, heterocyclic, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imide, ureide, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl 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 ureide group include alkylureide and arylureide 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-furil, 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-tetrahydropyranyl-2-oxy and 1-phenyltetrazole-5-oxy 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.

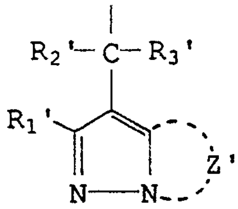
Examples of the siloxy group include trimethylsiloxy, triethylsiloxy and dimethylbutylsiloxy groups.

Examples of the imido group include succinimide, 3-heptadecyl succinimide, phthalimide and glutarimide 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[3,3,1,1^{3,7}]-ecane-1-yl and 7,7-dimethyl-bicyclo[2,2,1]heptane-1-yl.

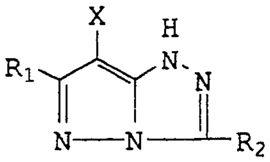
Examples of the group that is represented by X and is capable of being split off upon reaction with an oxidation product of a color developing agent include halogen atoms (e.g., chlorine, bromine and fluorine atoms); alkoxy, aryloxy, heterocyclic oxy, acyloxy, sulfonyloxy, alkoxycarbonyloxy, aryloxycarbonyl,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



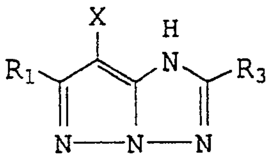
(where R_1' is the same as the above R, Z' is the same as the above Z; and R_2' and R_3' are independently a hydrogen atom, or an aryl, alkyl or heterocyclic group). Among these examples, the preferred is a halogen atom, especially a chlorine atom. Examples of the nitrogen-containing heterocycle formed 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 Formuras M-II to M-VII:

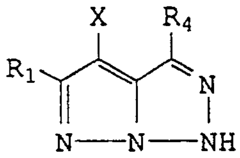
Formula M-II



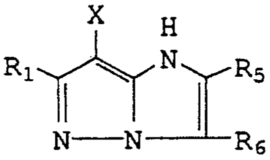
Formula M-III



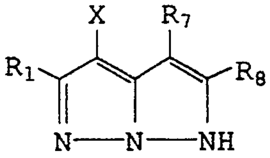
Formula M-IV



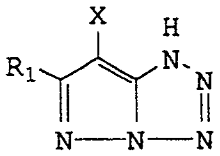
Formula M-V



Formula M-VI



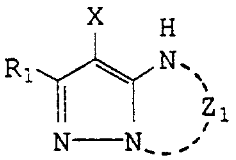
Formula M-VII



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.

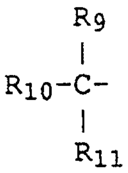
Among the magenta couplers represented by Formulas M-II to M-VII, the particularly preferred are those represented by Formula M-II.

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 2; and the most preferred is that they meet the following requisites 1, 2 and 3.

Requisite 1: The root atom bonding with the heterocycle is a carbon atom.
Requisite 2: Only a single or no hydrogen atom bonds with said carbon atom.
Requisite 3: 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

M-IX



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

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 (e.g., cycloalkane, cycloalkene or heterocycle); and said 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.

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

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.

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 root atom bonding with the heterocycle is a carbon atom.
Requisite 2: At least two hydrogen atoms bond with said carbon atom.

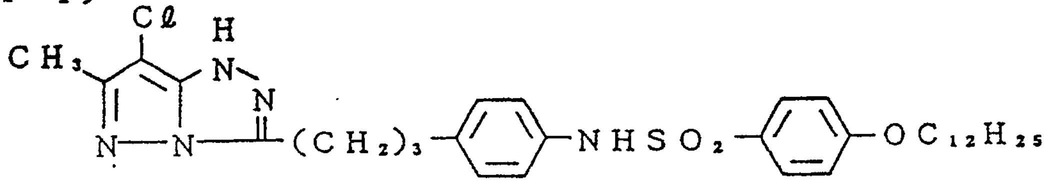
As the substituents R and R_1 which meet the above requisite, those represented by the following

Formula M-XI are particularly preferred.

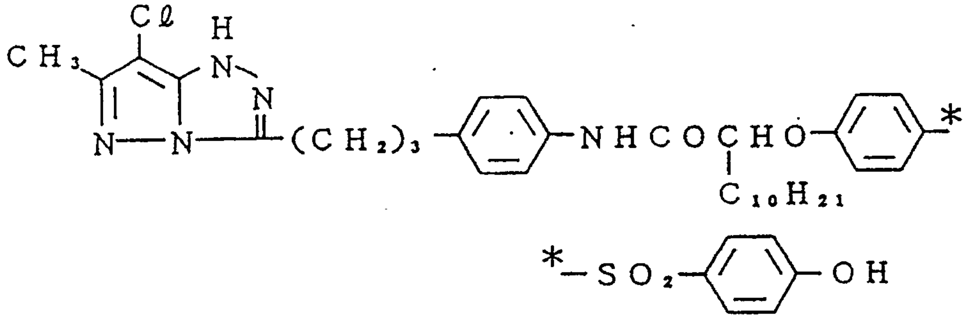
Formula M-XI R_{12} - CH_2 -

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:

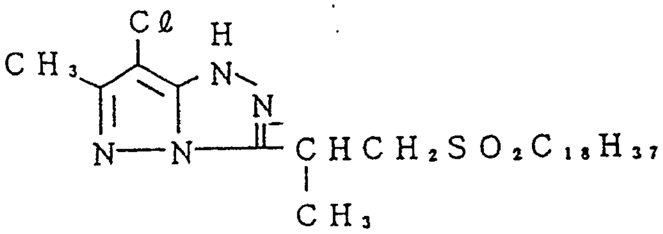
(M－1)



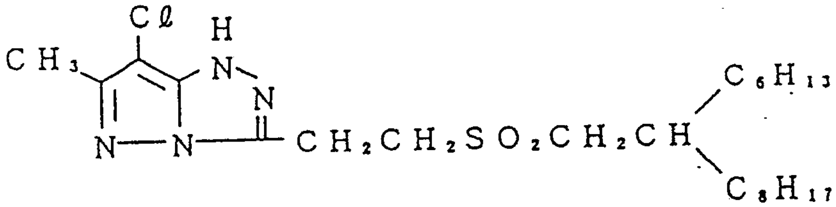
(M－2)



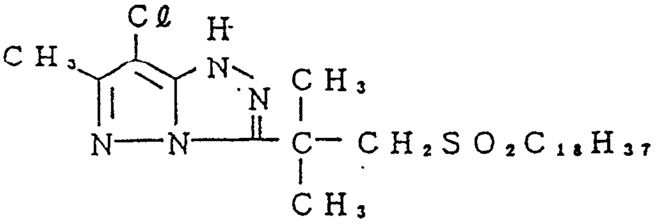
(M－3)



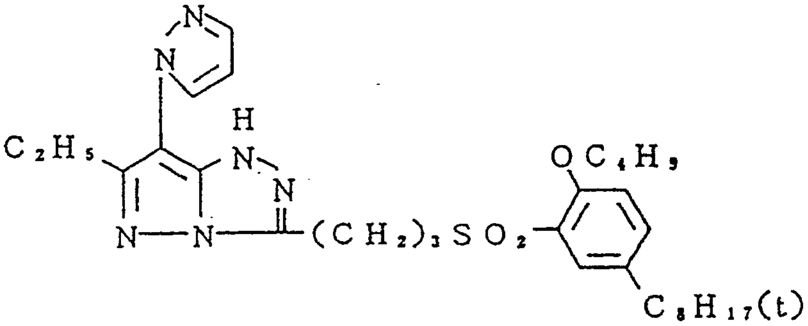
(M－4)



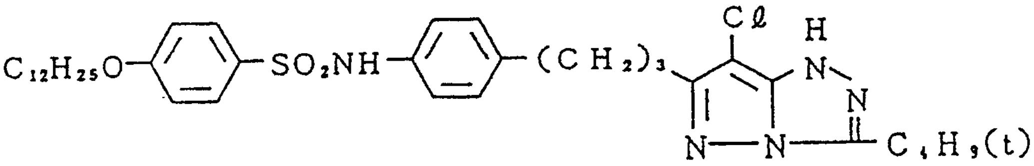
(M－5)



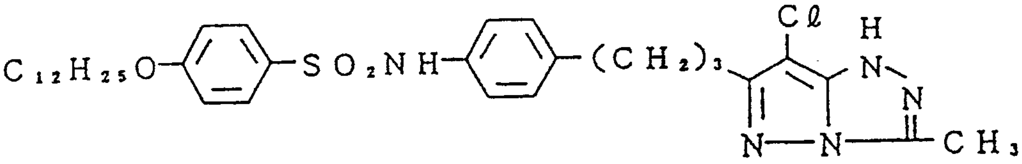
(M－6)



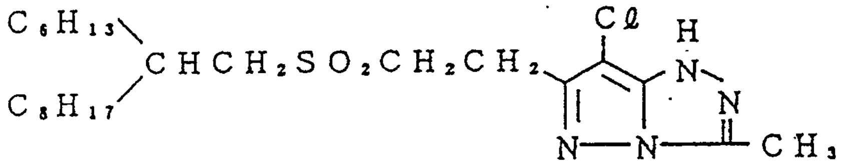
(M－7)



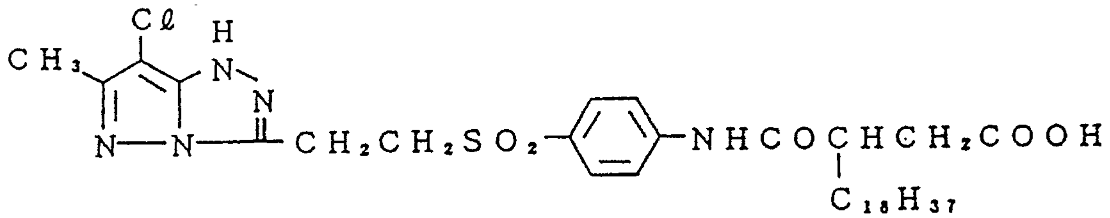
(M－8)



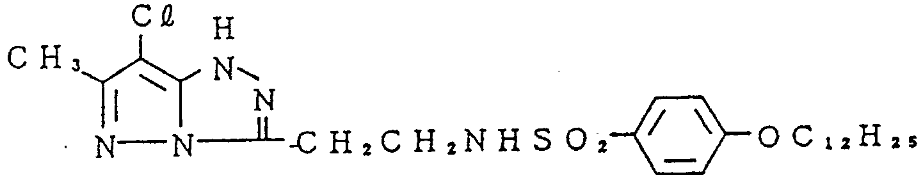
(M－9)



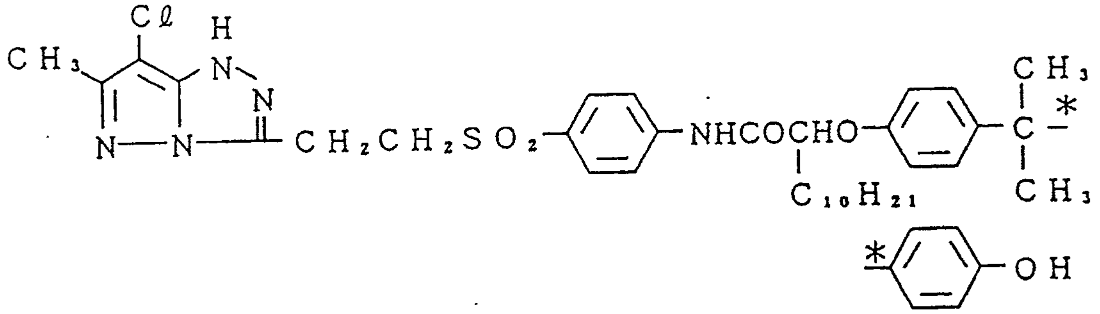
(M－10)



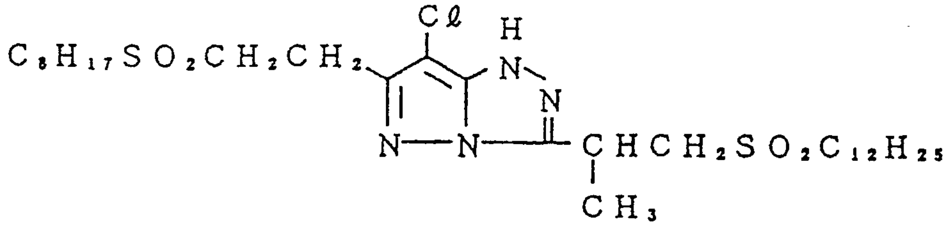
(M－11)



(M－12)



(M−13)



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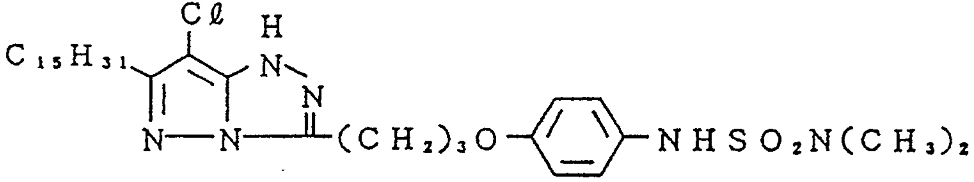
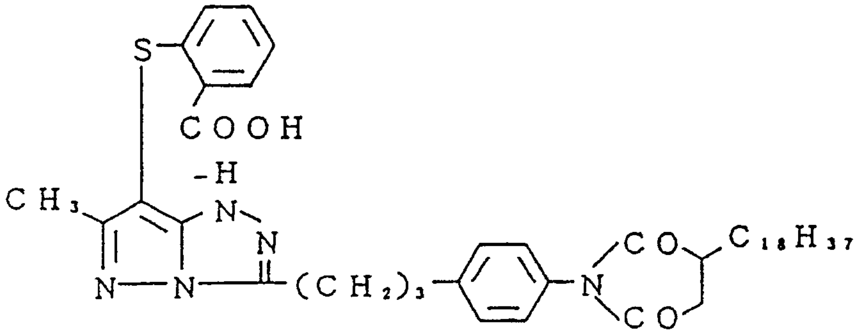
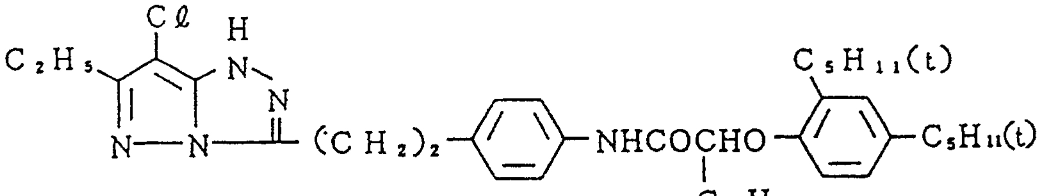


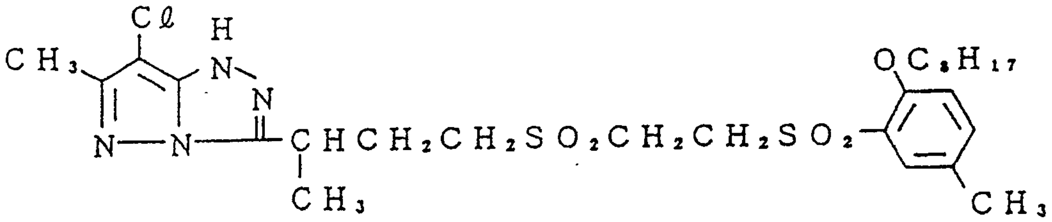
(M−15)



(M−16)



(M－17)



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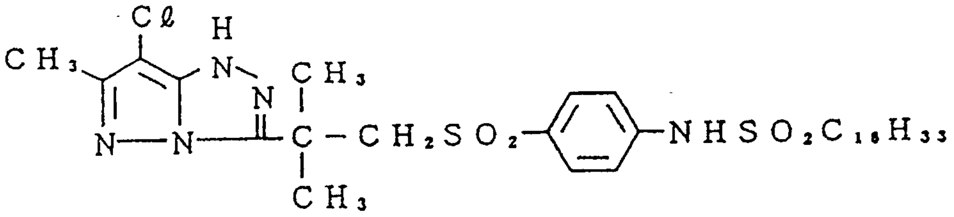
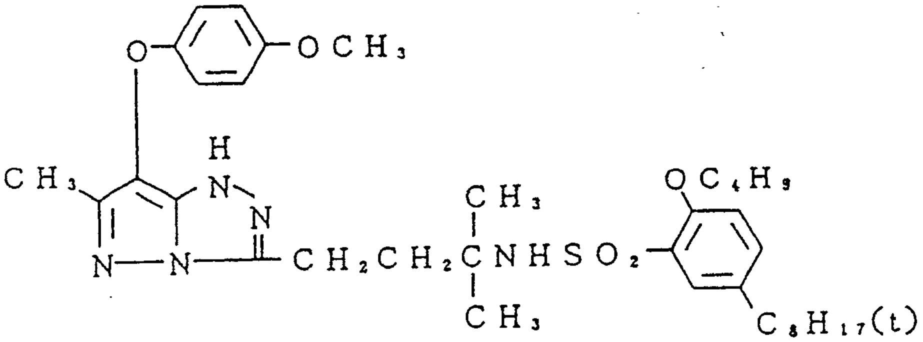


(M－19)



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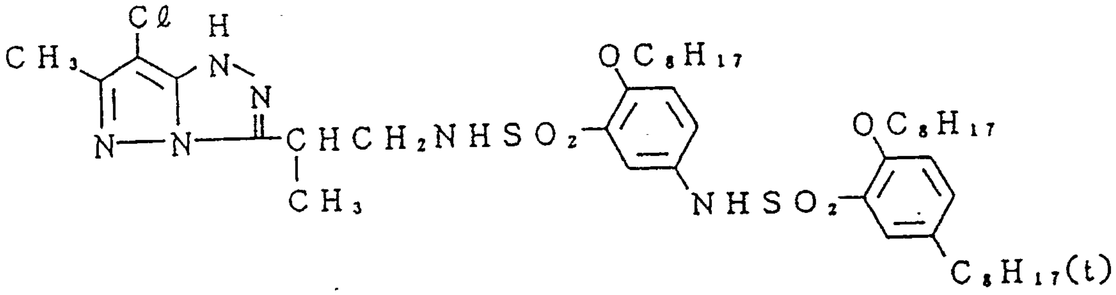

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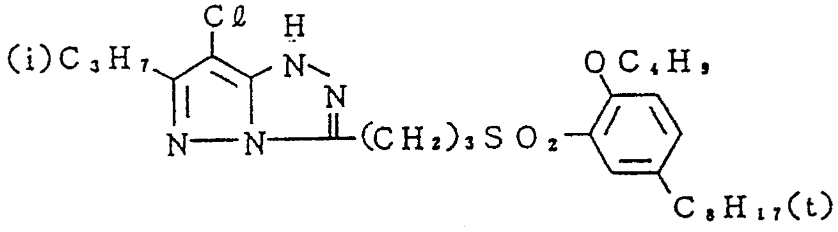
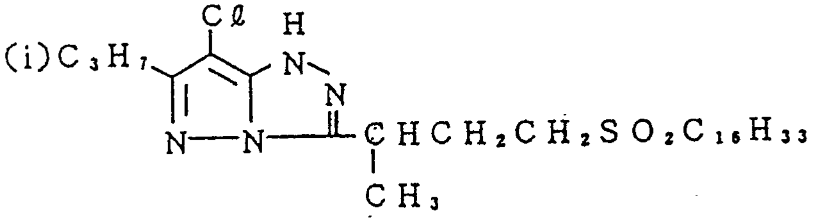
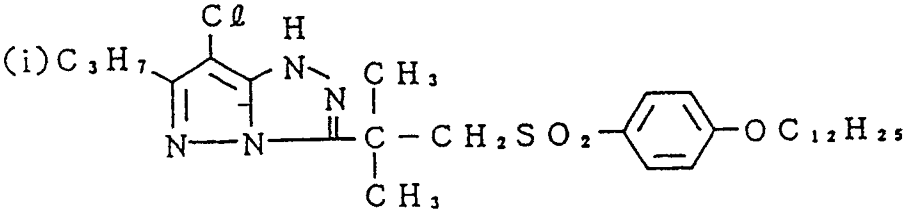


(M-22)



(M-23)



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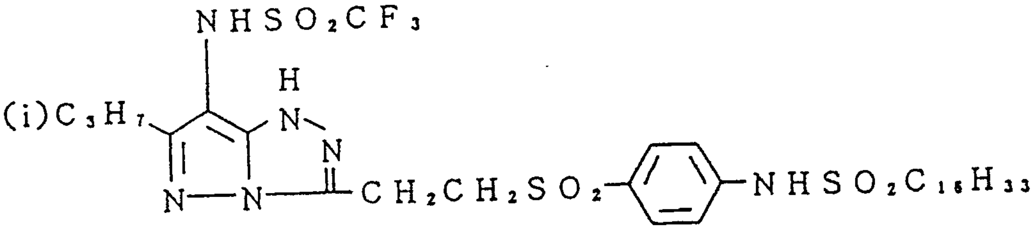
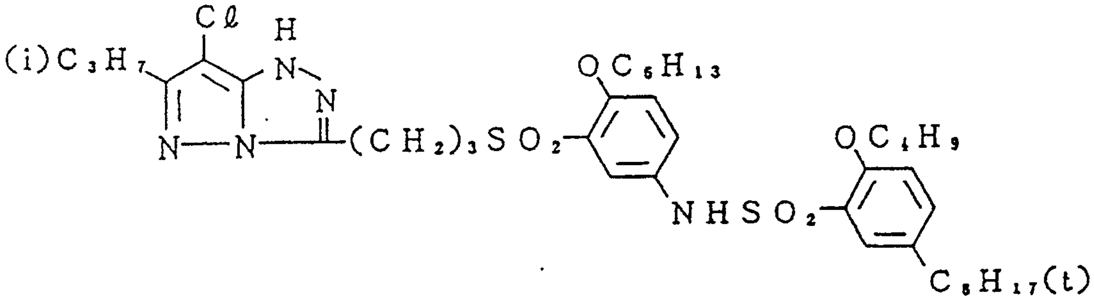


(M－25)



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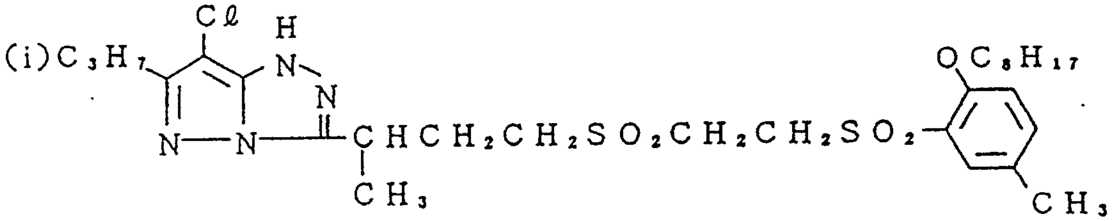
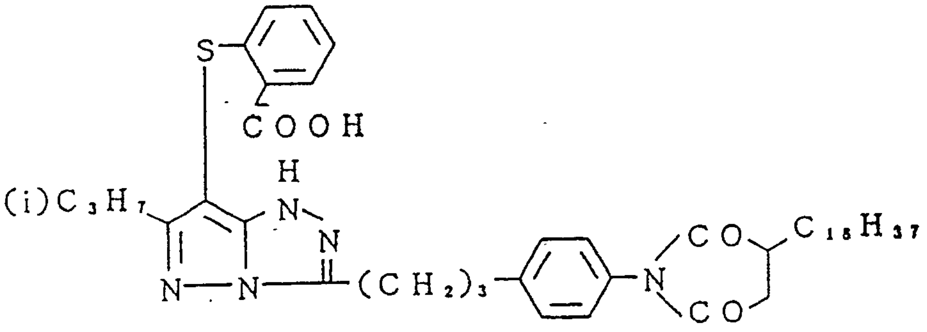


(M－27)



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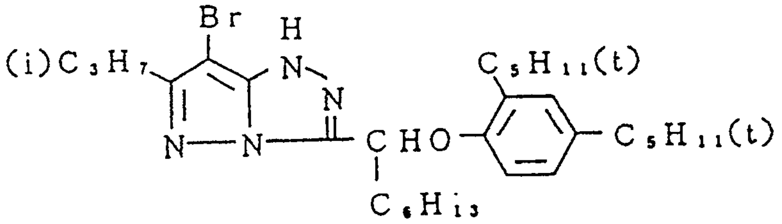
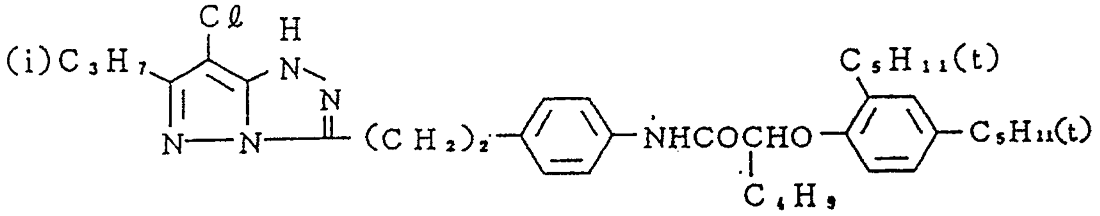
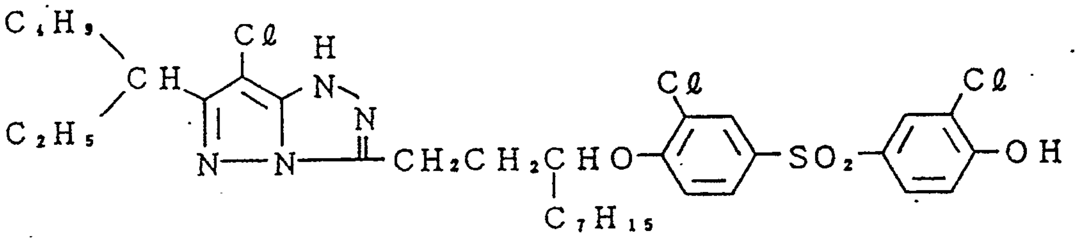


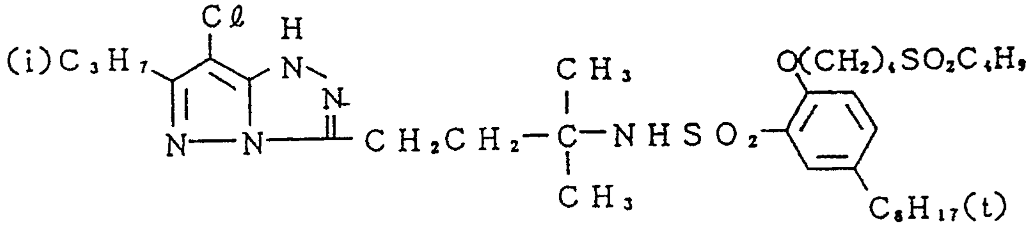
(M−29)



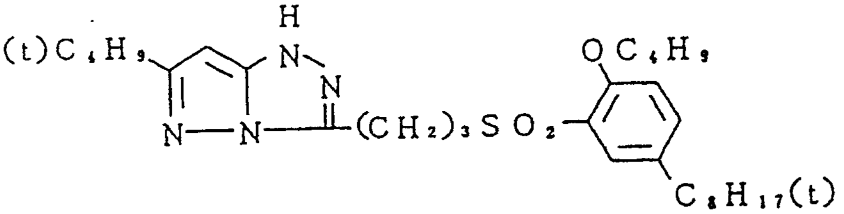
(M−30)



(M−31)



(M−32)



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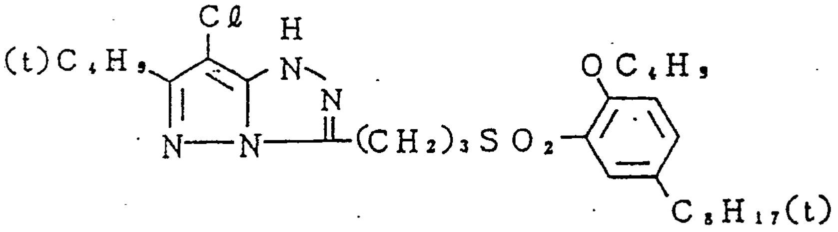

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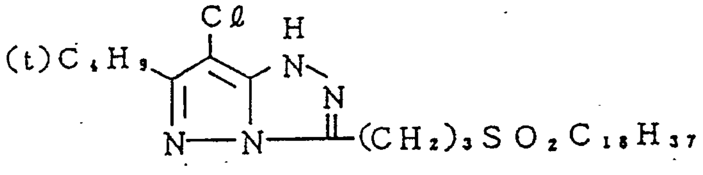

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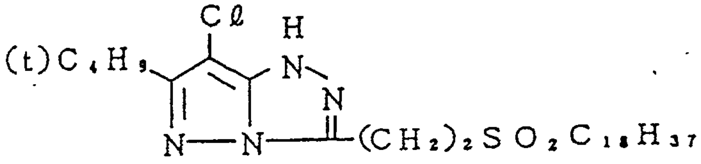
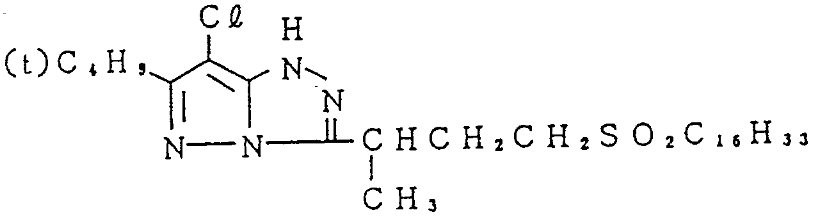
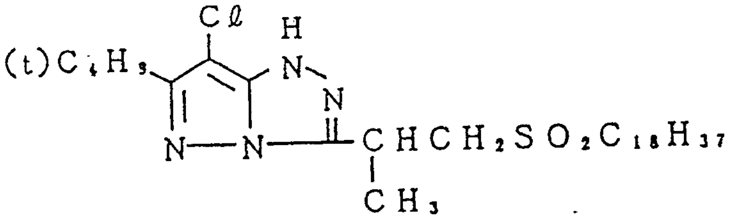


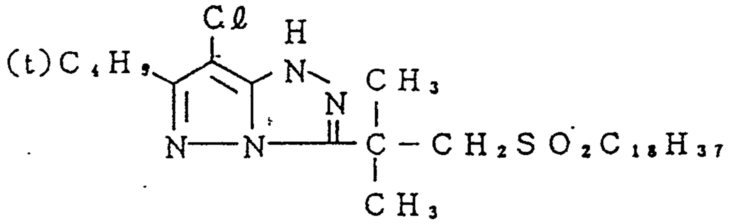
(M－36)



(M－37)



(M-38)



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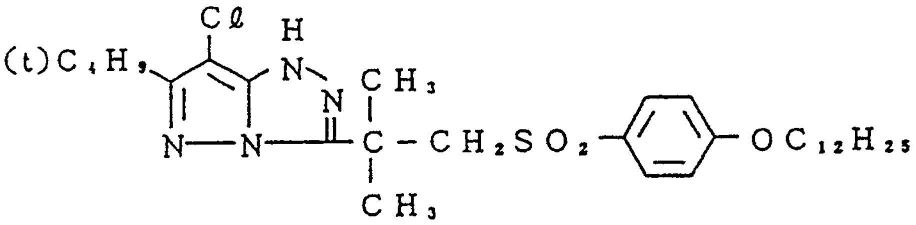
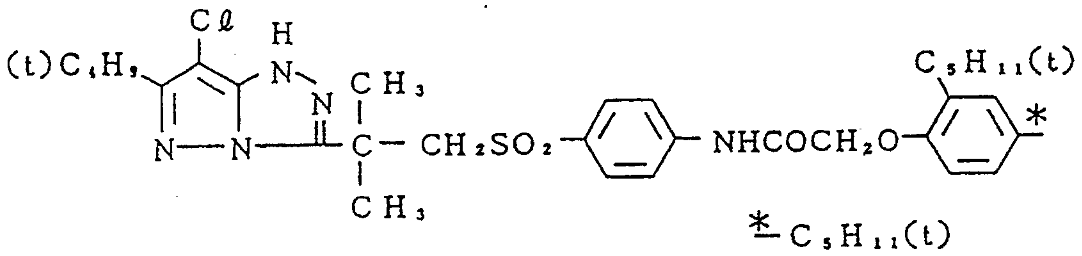
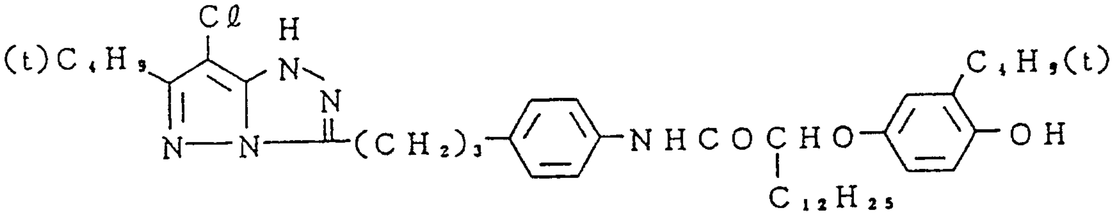


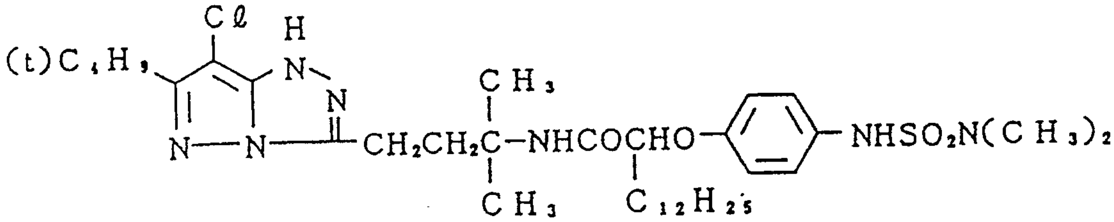
(M-40)



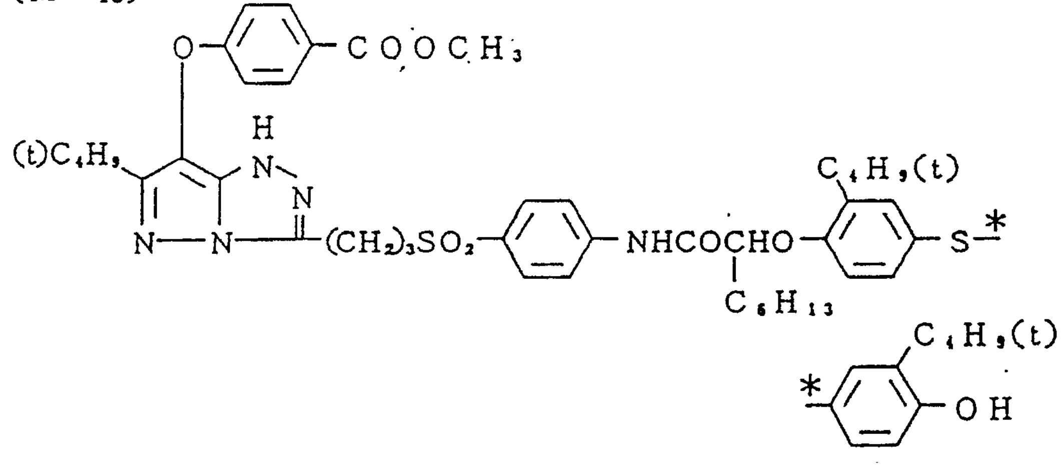
(M-41)



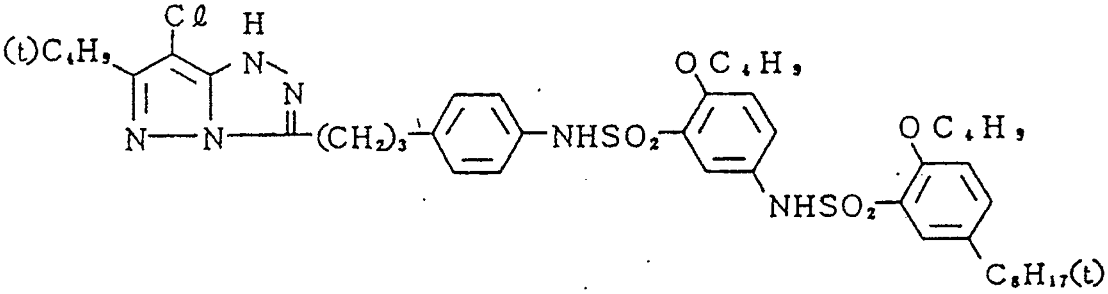
(M-42)



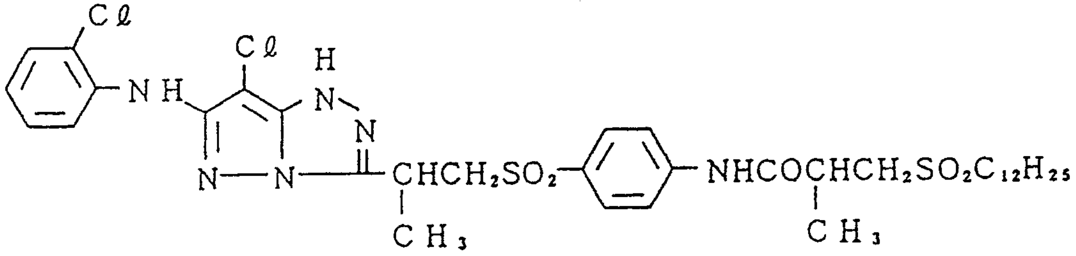
(M－43)



(M－44)



(M－45)



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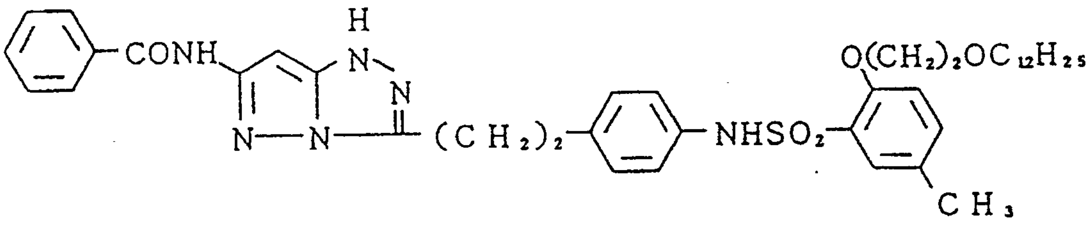
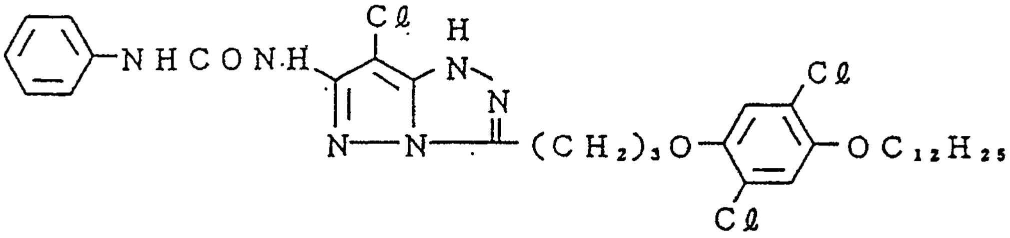


(M－47)



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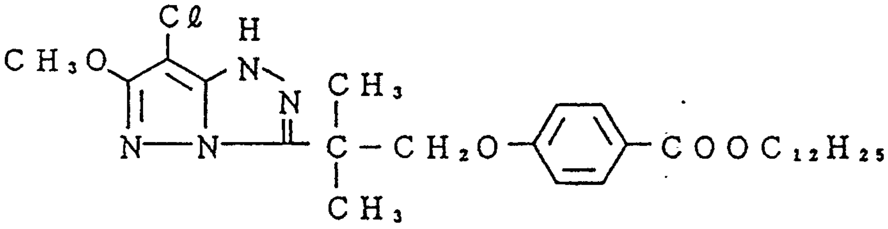
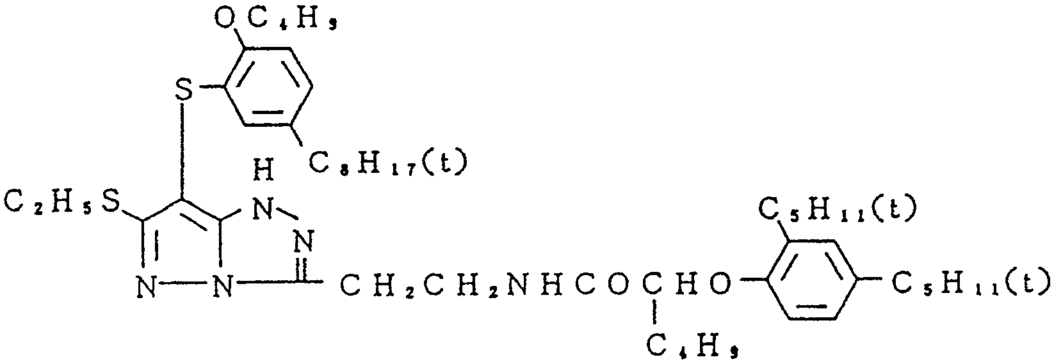


(M－49)



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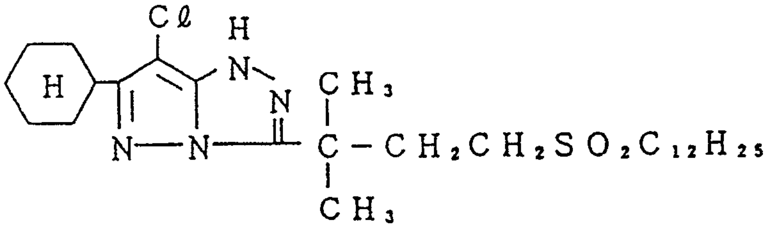
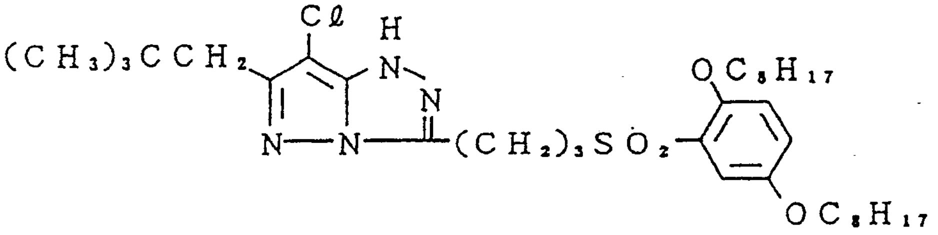


(M－51)



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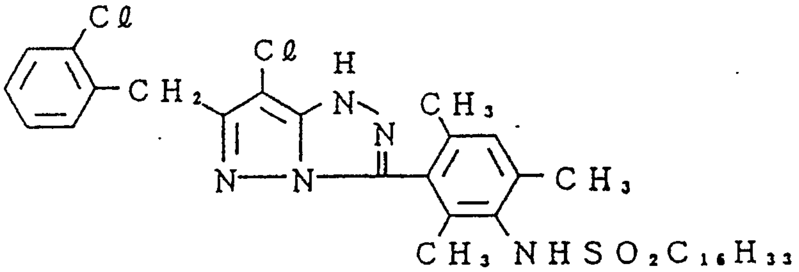

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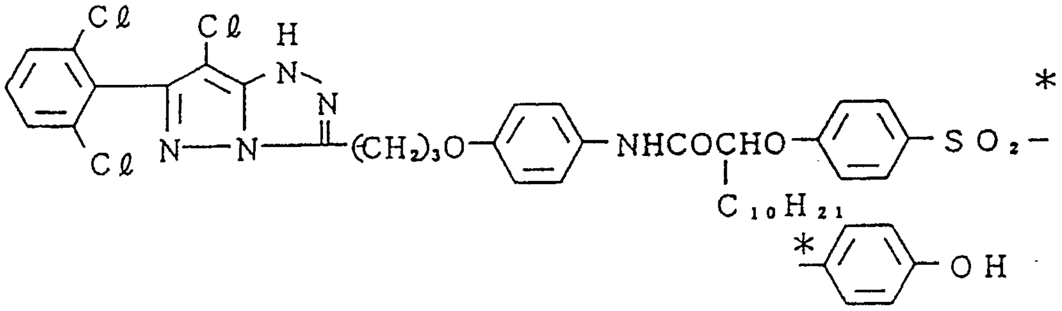

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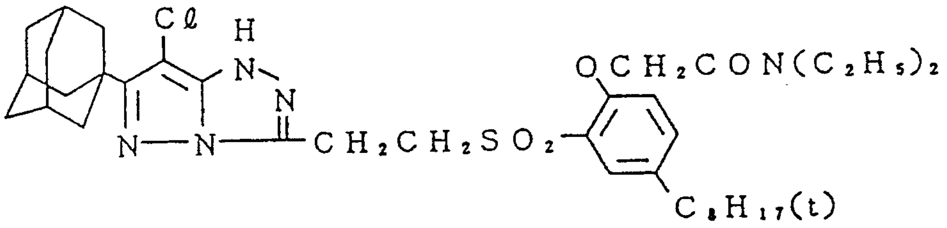

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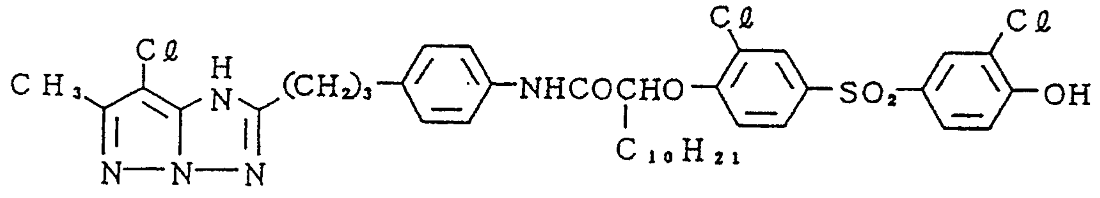

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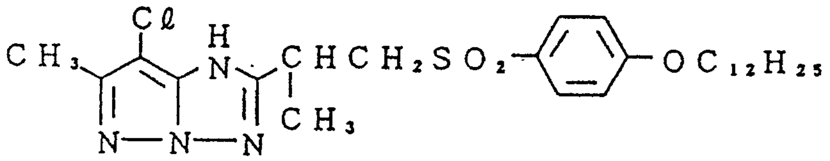

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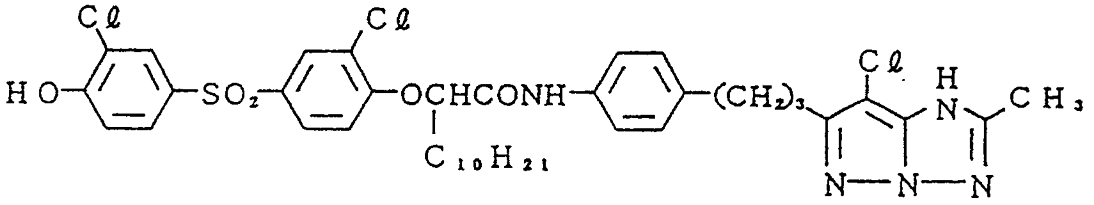

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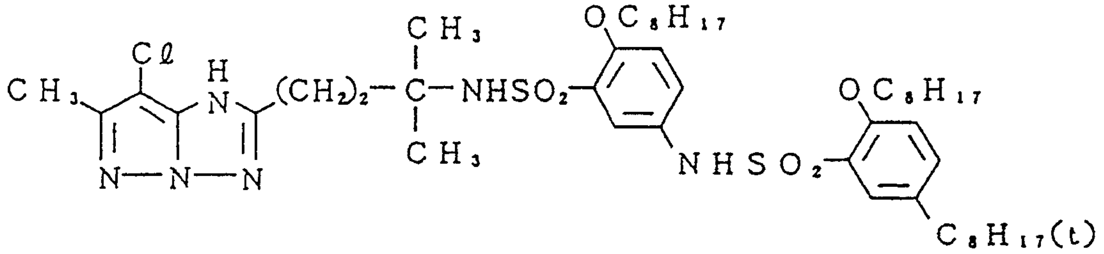

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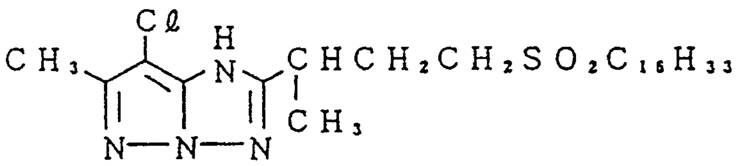

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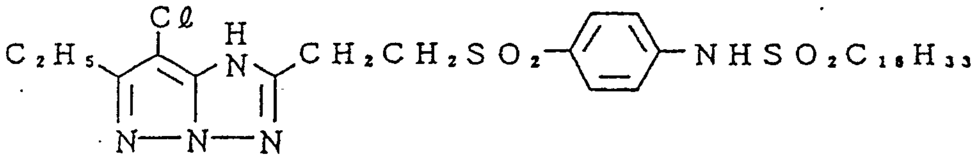
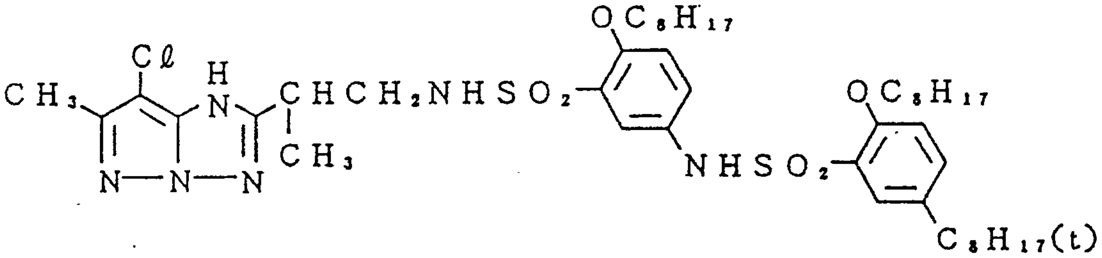
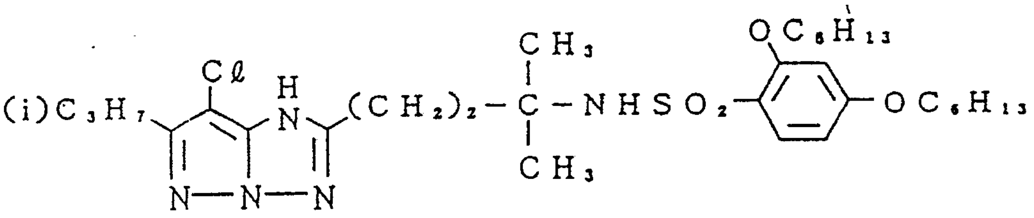


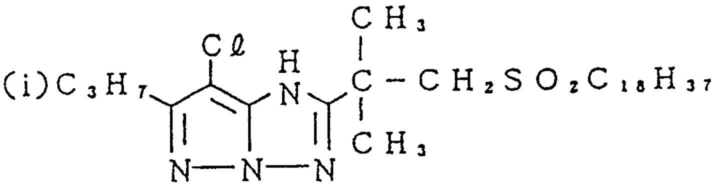
(M－61)



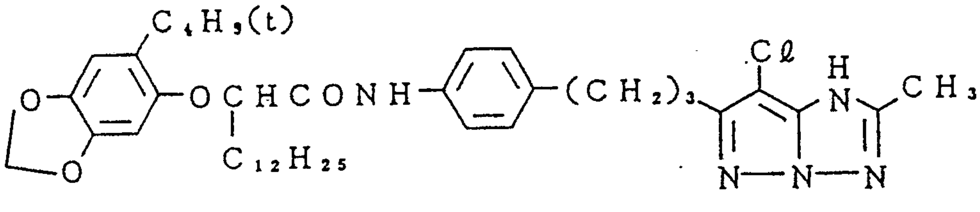
(M－62)



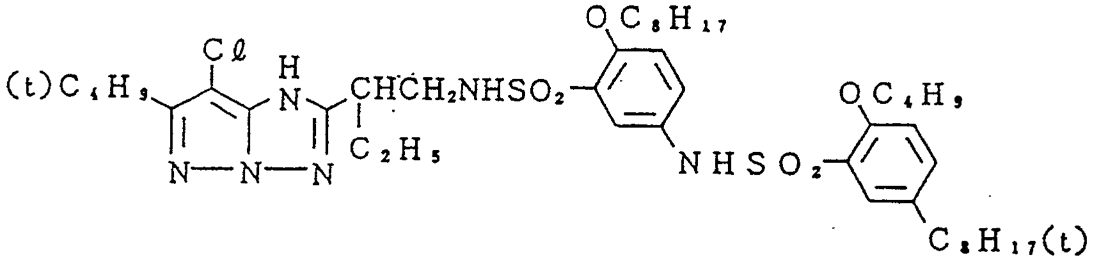
(M－63)



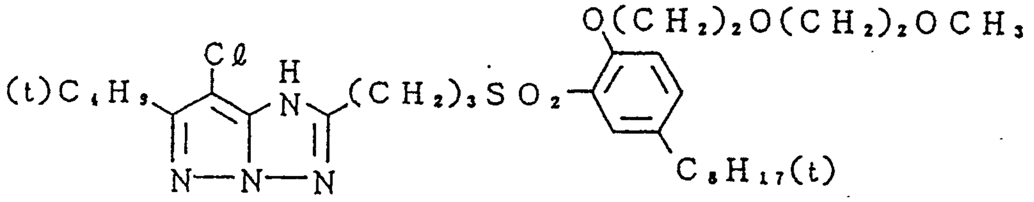
(M－64)



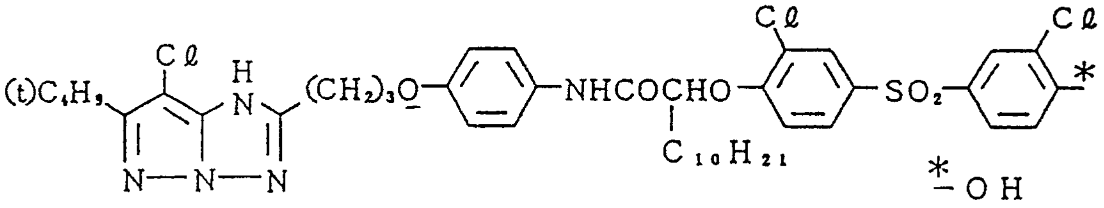
(M-65)



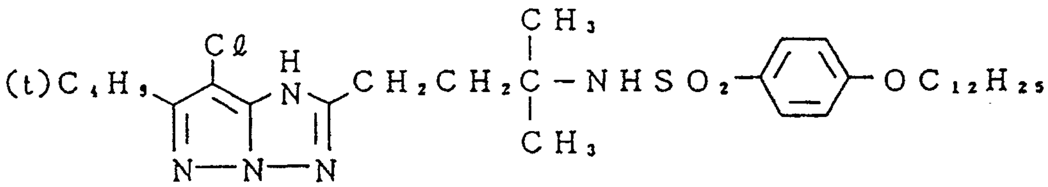
(M-66)



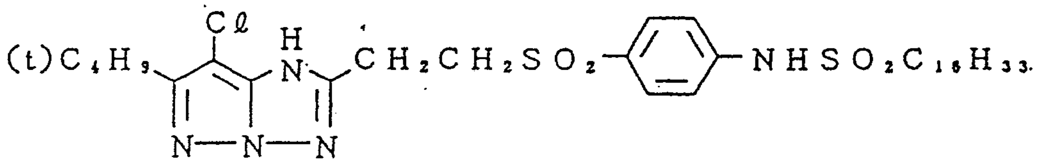
(M-67)



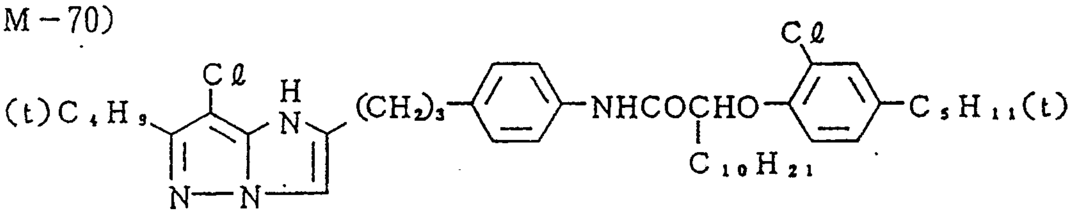
(M-68)



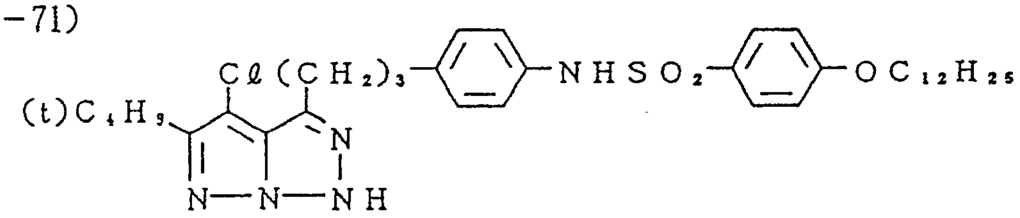
(M－69)



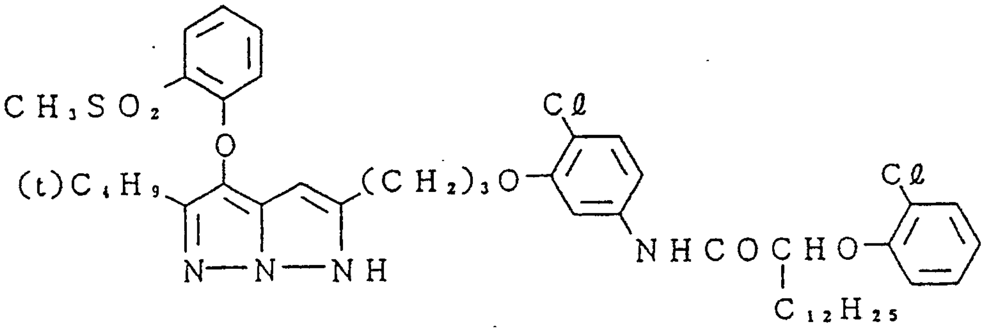
(M－70)



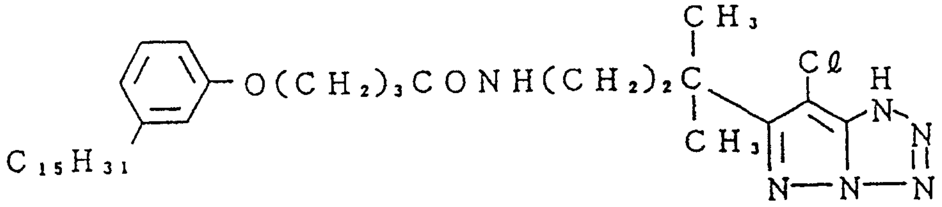
(M－71)



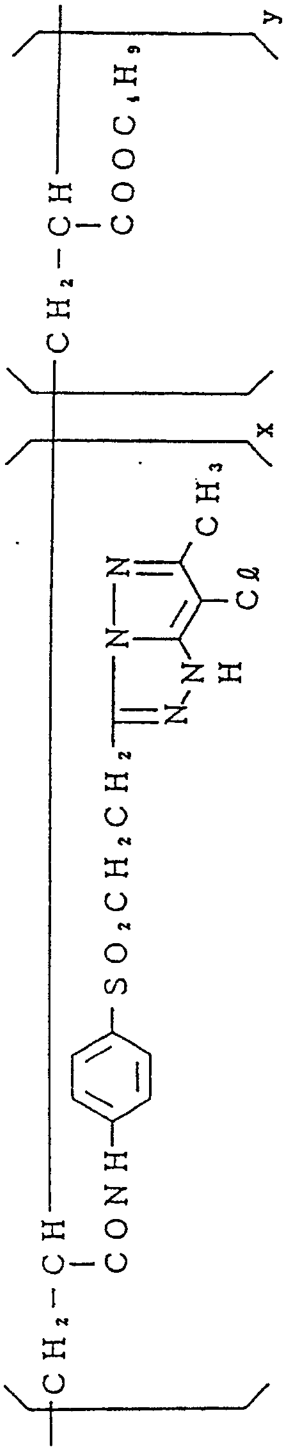
(M－72)



(M－73)

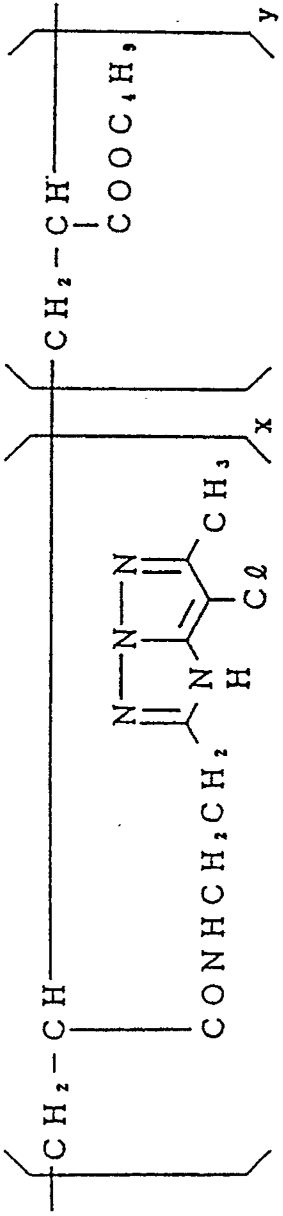


(M−74)



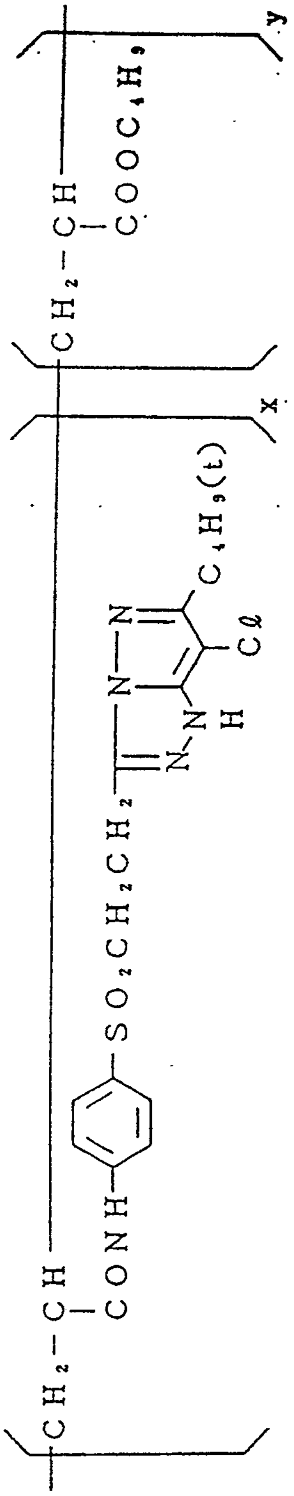
x : y = 50 : 50

(M−75)



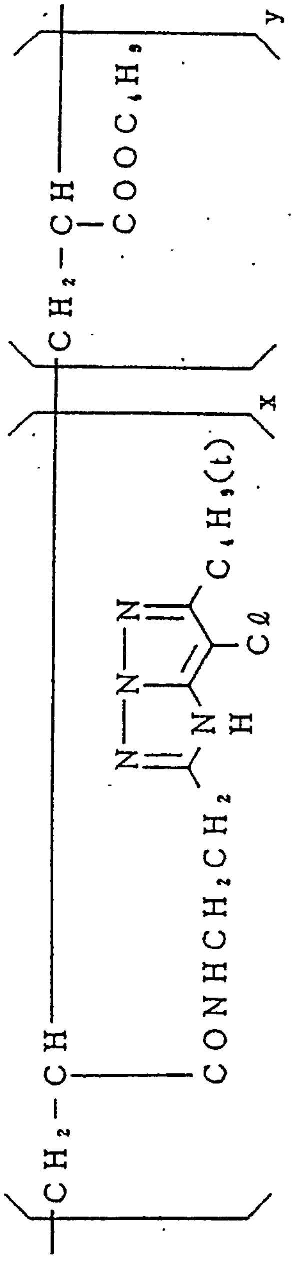
x : y = 50 : 50

(M-76)



x : y = 50 : 50

(M-77)



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 Application No. 9791/1986.

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.

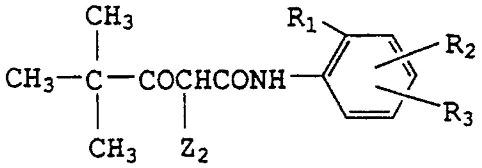
The couplers of the invention are normally used in an amount of 1 X 10^{-3} mol to 1 mol, preferably 1 X 10^{-2} mol to 8 X 10^{-1} mol, per mol of silver halide.

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

In the invention, preferred yellow couplers contained in the silver halide emulsion layer having the same spectral sensitivity, in which the compounds of Formula M-I are contained, are those represented by the following Formula Y-I.

When combined with a magenta coupler represented by Formula M-I, particularly preferred yellow couplers among those represented by Formula Y-I are those having a pKa value at most 3 lower than the pKa value of said magenta coupler.

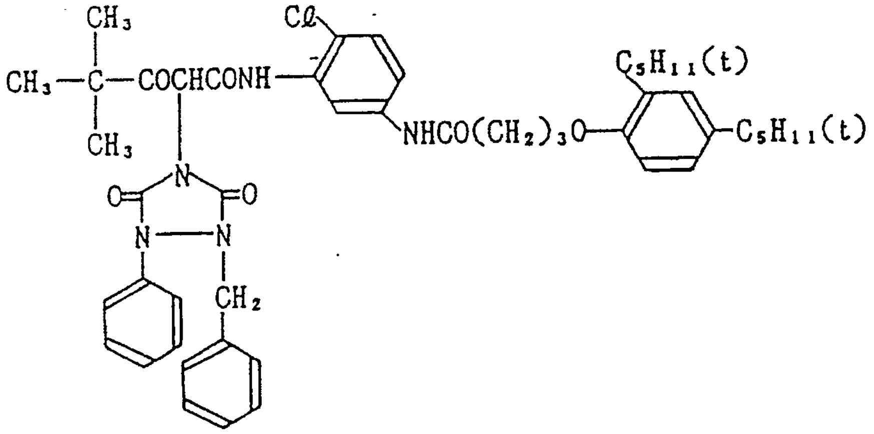
Y-I



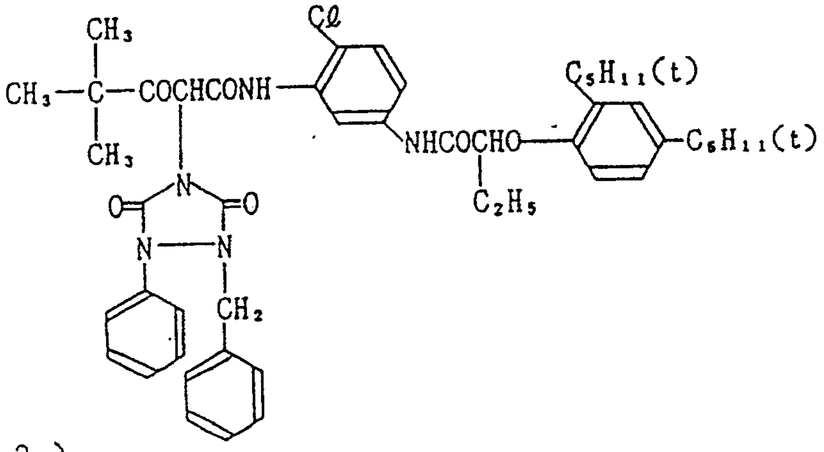
In Formula Y-I, R_1 represents a halogen atom or an alkoxy group; R_2 represents a hydrogen or halogen atom, or an alkoxy group which may have a substituent; R_3 represents an acylamino, alkoxycarbonyl, alkylsulfamoyl, arylsulfamoyl, arylsulfonamide, alkylureide, arylureide, succinimide, alkoxy or aryloxy 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:

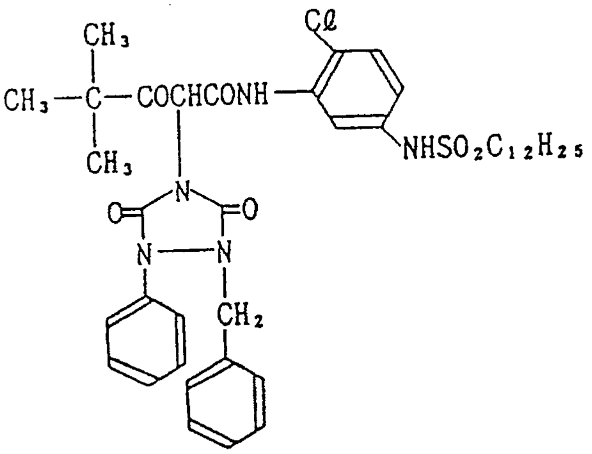
(Y－1)



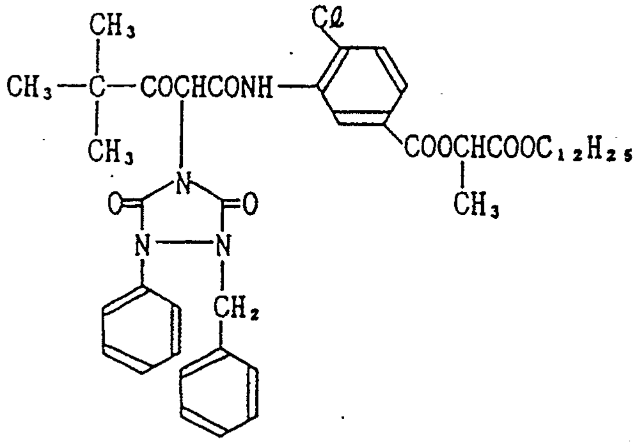
(Y－2)



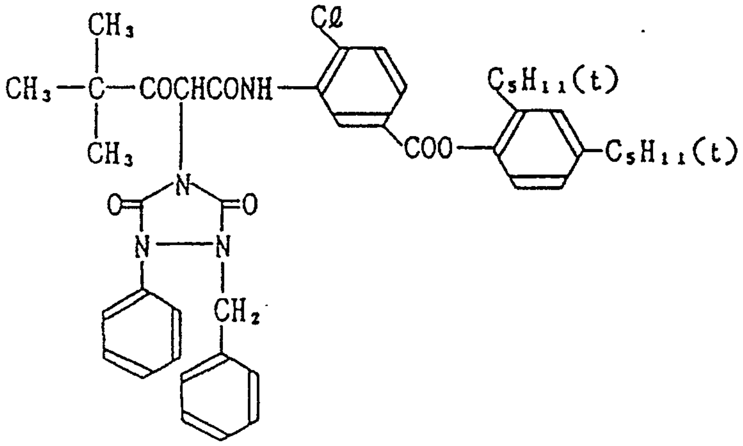
(Y－3)



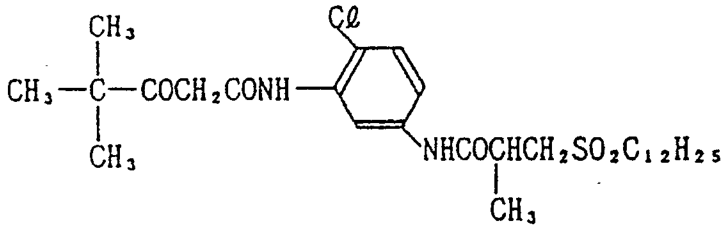
(Y－4)



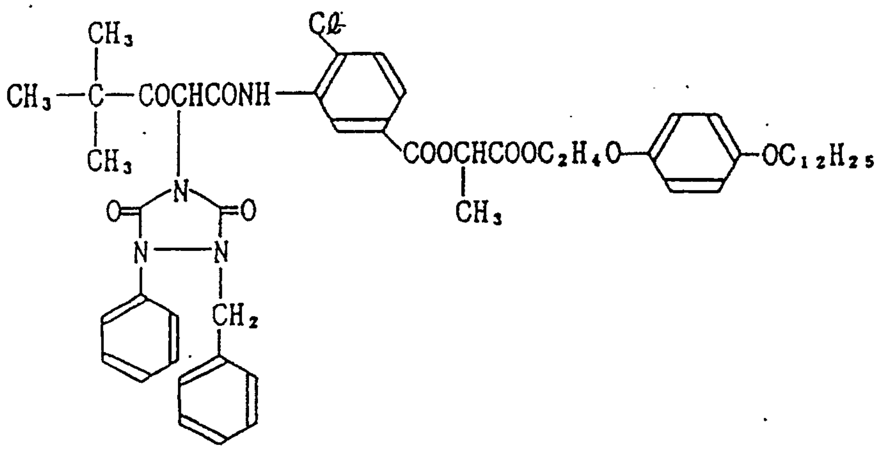
(Y－5)



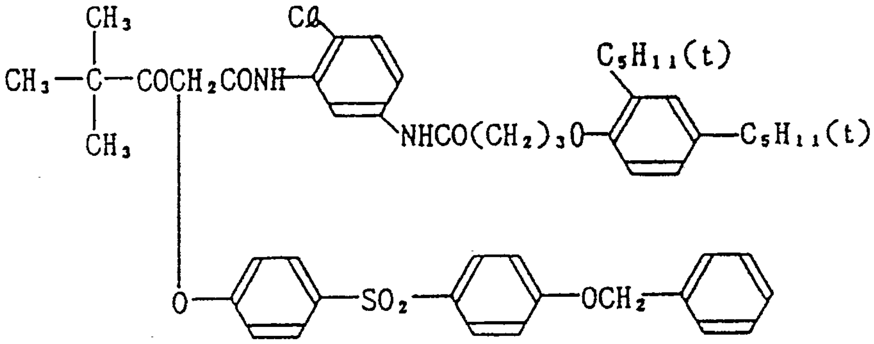
(Y－6)



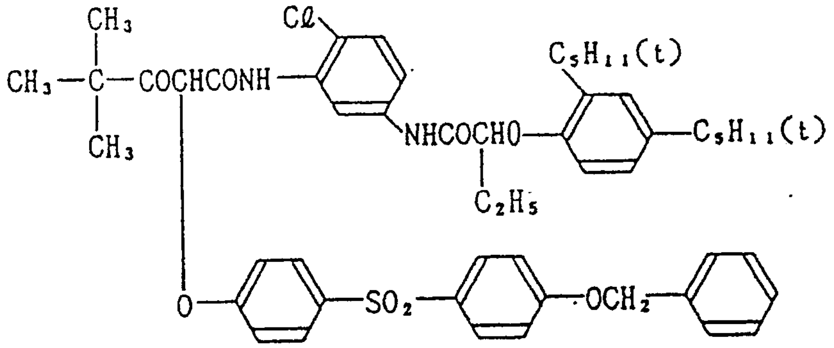
(Y－7)



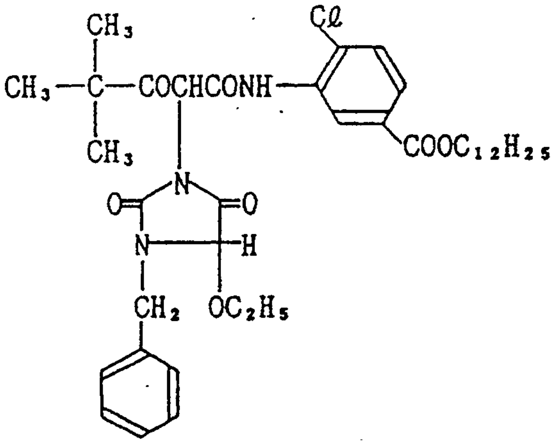
(Y－8)



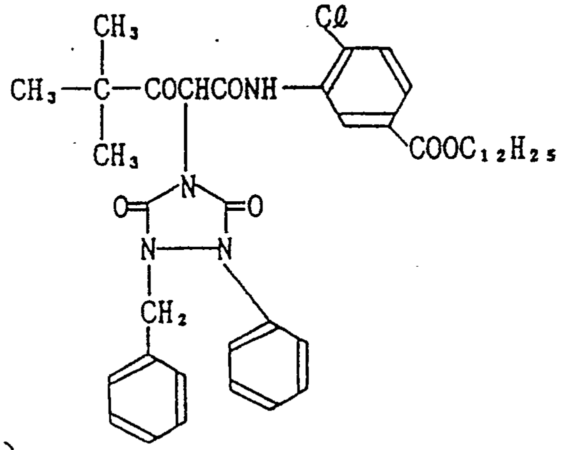
(Y－9)



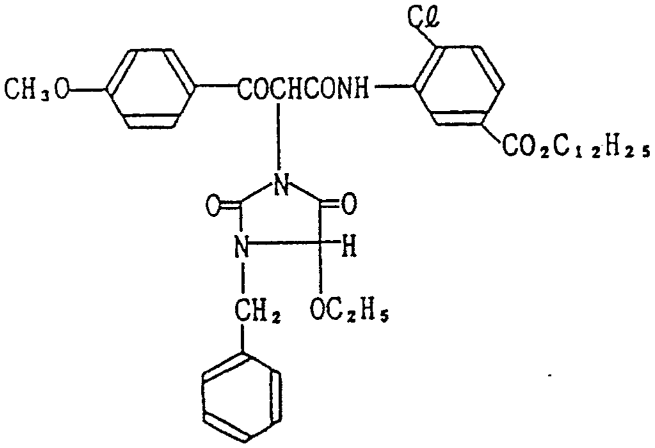
(Y－10)



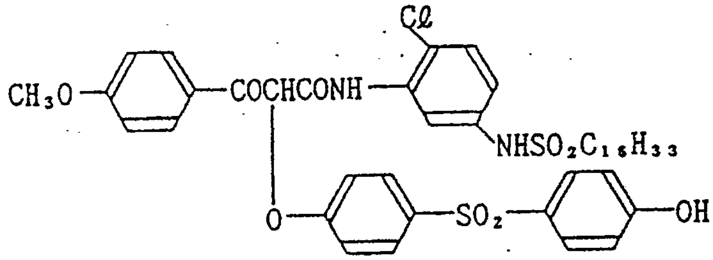
(Y－11)



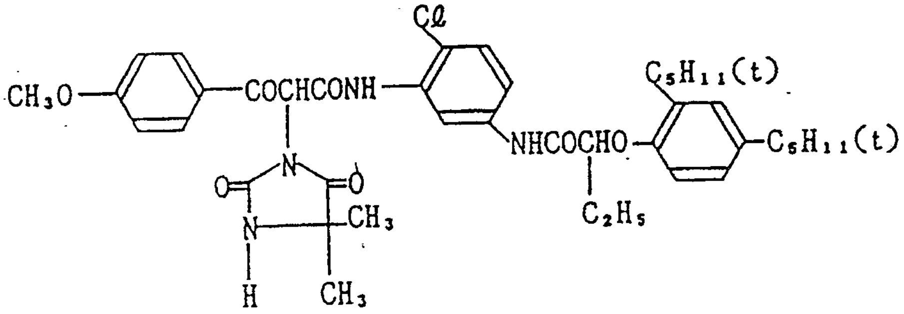
(Y－12)



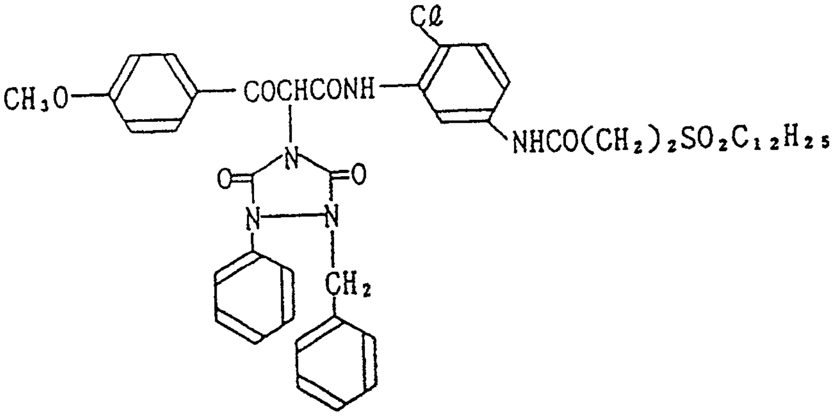
（Y－13）



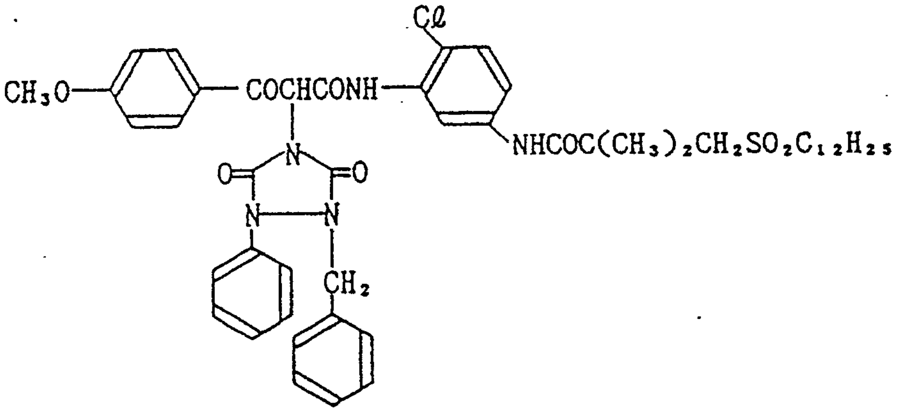
（Y－14）



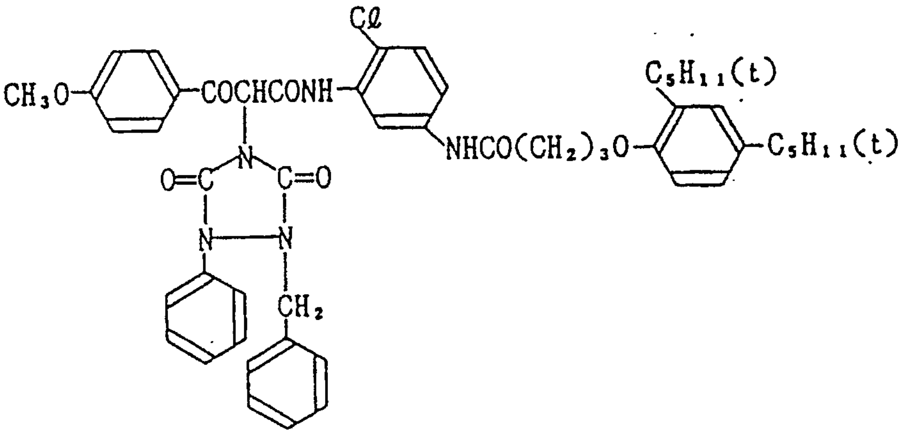
（Y－15）



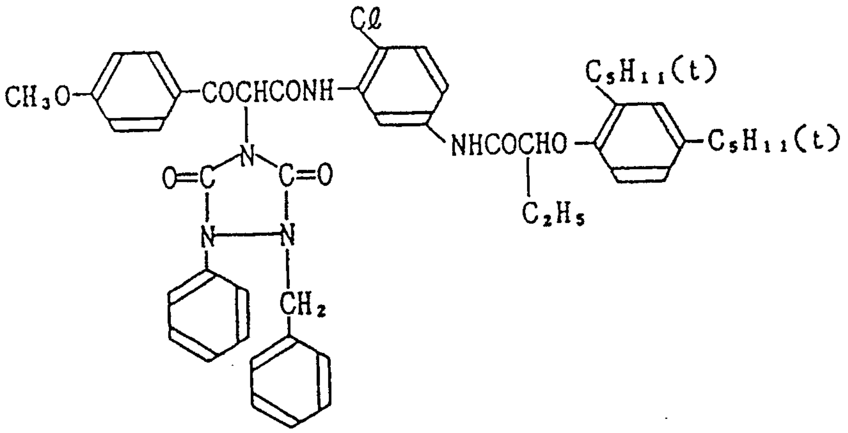
(Y－16)


CH₃O
COCHCONH
Cl
NHCOC(CH₃)₂CH₂SO₂C₁₂H₂₅
N
O
O
N
N
CH₂

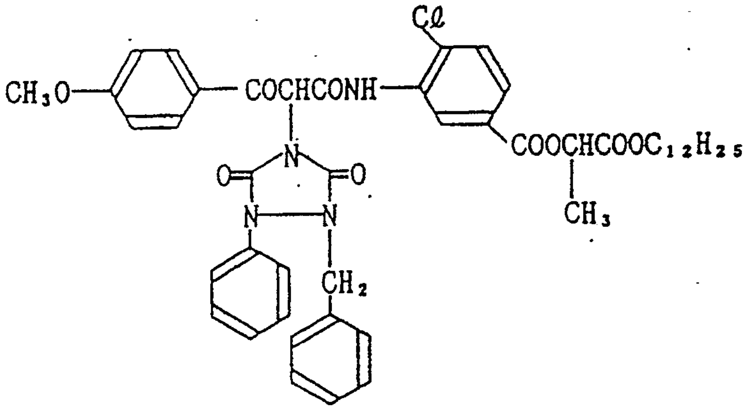
(Y－17)


CH₃O
COCHCONH
Cl
NHCO(CH₂)₃O
C₅H₁₁(t)
C₅H₁₁(t)
N
O=C
C=O
N
N
CH₂

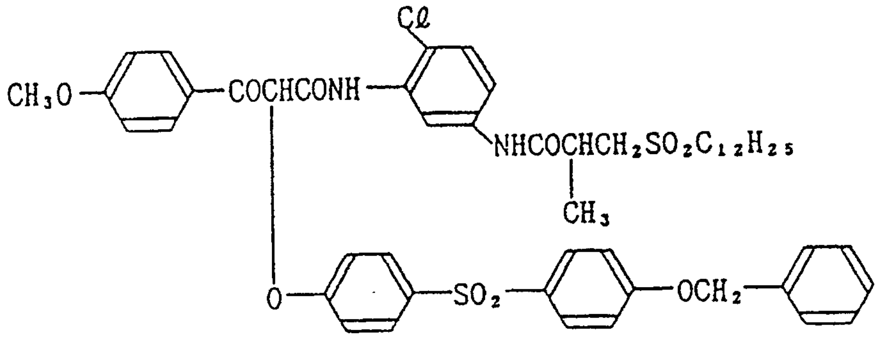
(Y－18)


CH₃O
COCHCONH
Cl
NHCOCHO
C₂H₅
C₅H₁₁(t)
C₅H₁₁(t)
N
O=C
C=O
N
N
CH₂

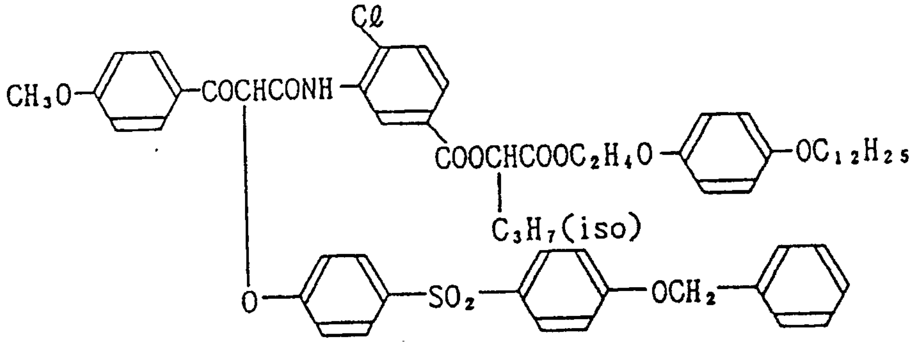
(Y－19)



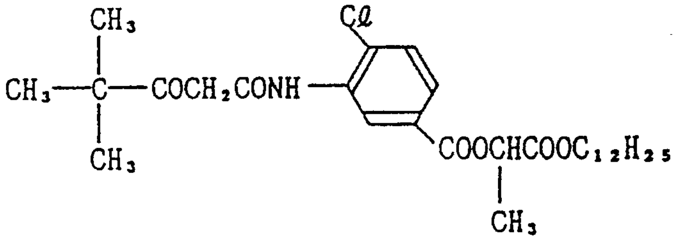
(Y－20)



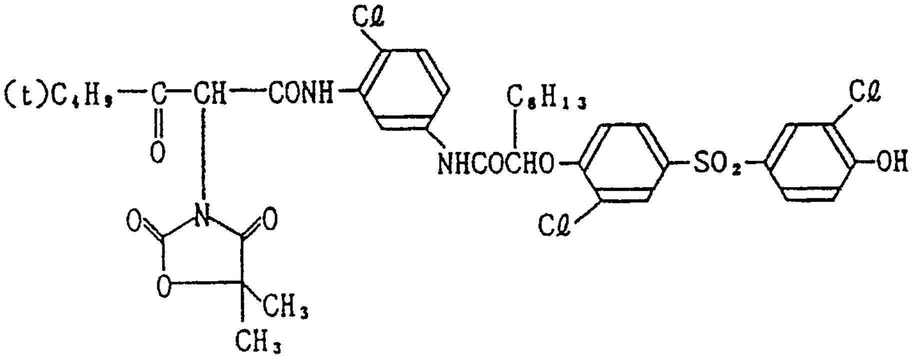
(Y－21)



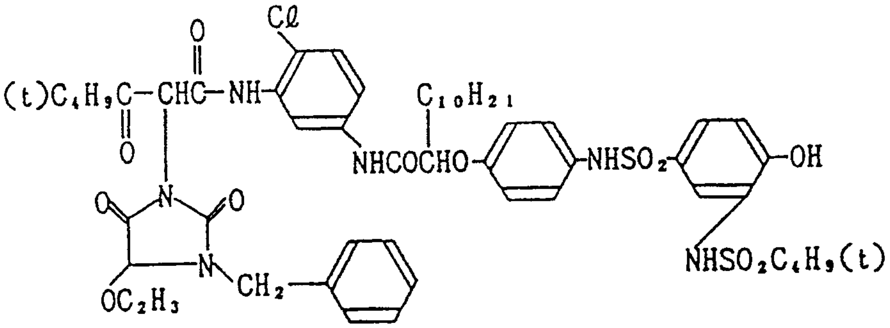
(Y－22)



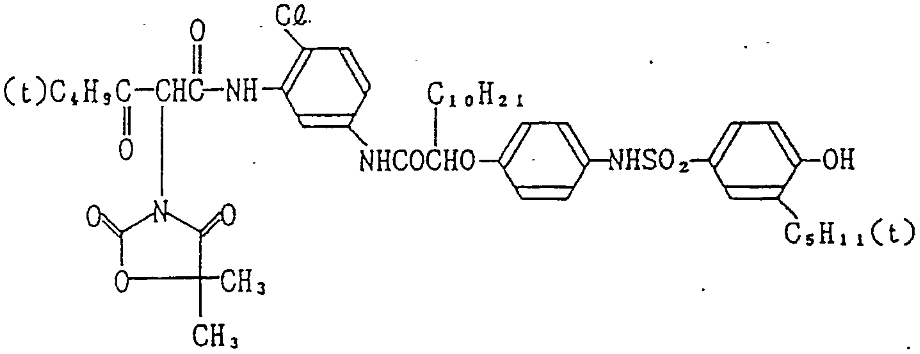
(Y－23)



(Y－24)

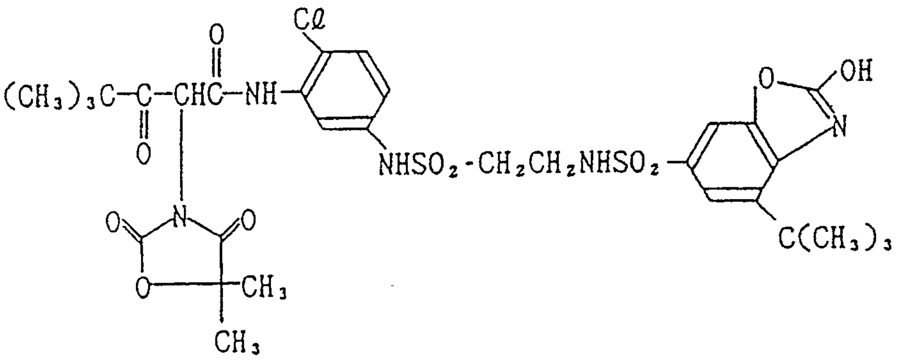


(Y − 25)



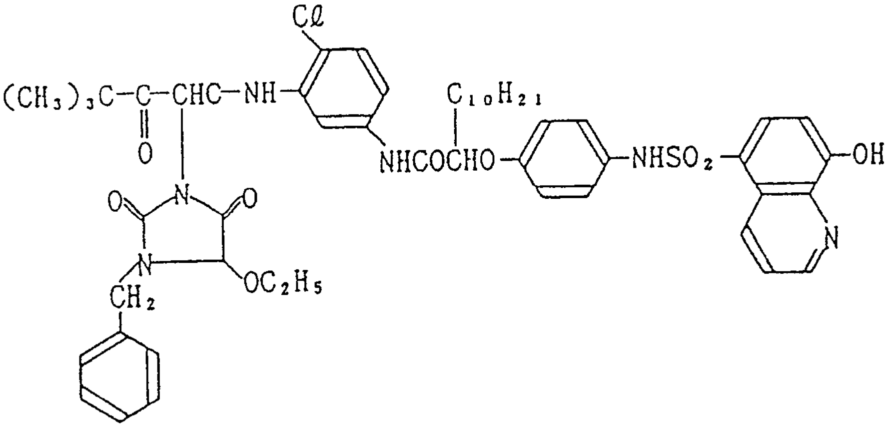
Cℓ
(t)C₄H₉C−CHC−NH
O
O
C₁₀H₂₁
NHCOCHO
NHSO₂
OH
C₅H₁₁(t)
N
O
CH₃
CH₃

(Y − 26)



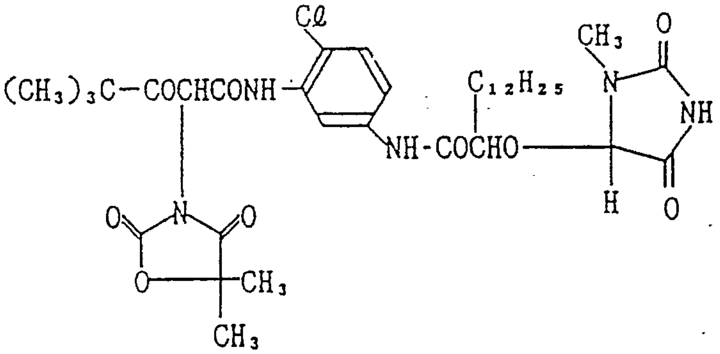
Cℓ
(CH₃)₃C−C−CHC−NH
O
O
NHSO₂-CH₂CH₂NHSO₂
OH
N
C(CH₃)₃
CH₃
CH₃

(Y − 27)

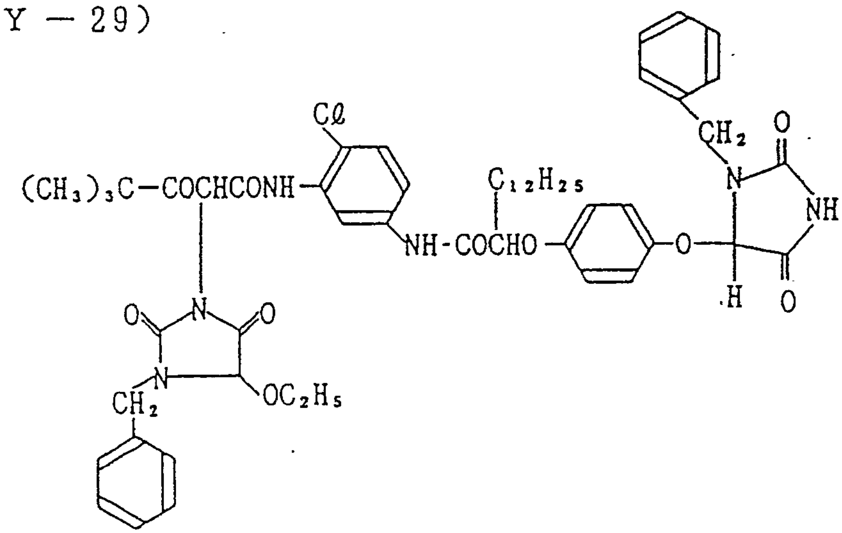


Cℓ
(CH₃)₃C−C−CHC−NH
O
C₁₀H₂₁
NHCOCHO
NHSO₂
OH
N
OC₂H₅
CH₂

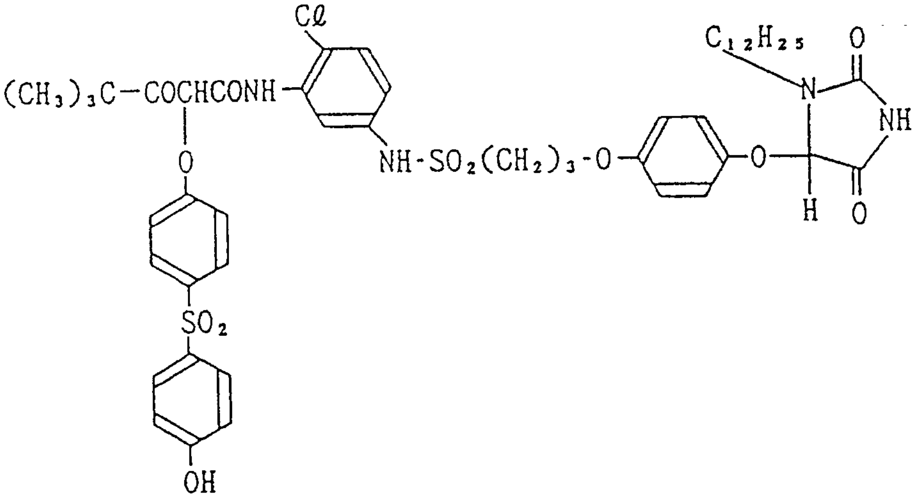
(Y − 28)


Cℓ
(CH₃)₃C−COCHCONH
C₁₂H₂₅
CH₃
NH
NH-COCHO
H
O
CH₃
CH₃

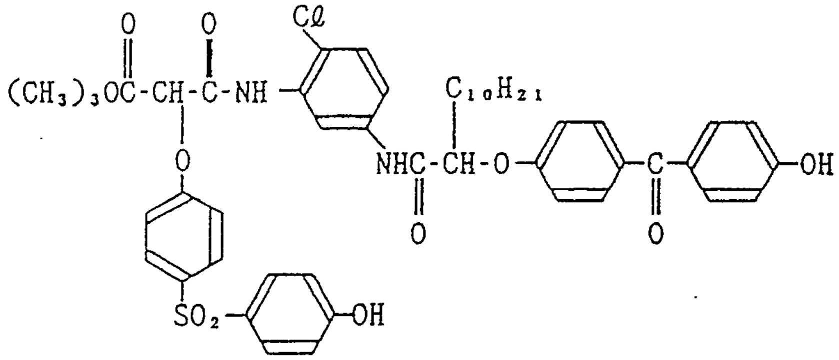
(Y − 29)


Cℓ
(CH₃)₃C−COCHCONH
C₁₂H₂₅
CH₂
NH
NH-COCHO
H
OC₂H₅
CH₂

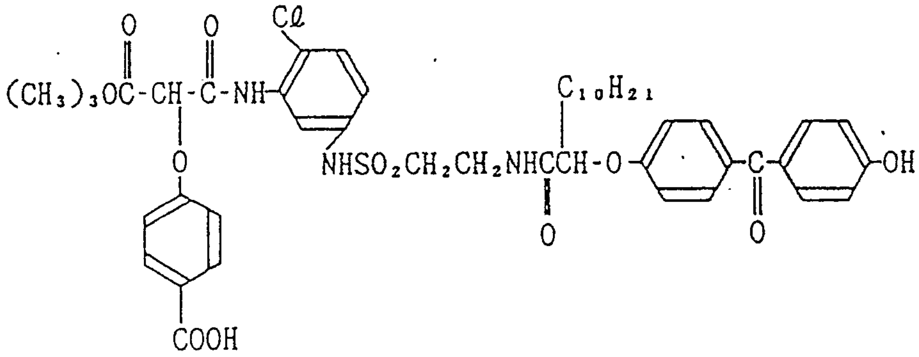
(Y − 30)


Cℓ
(CH₃)₃C−COCHCONH
C₁₂H₂₅
NH
NH-SO₂(CH₂)₃-O
H
SO₂
OH

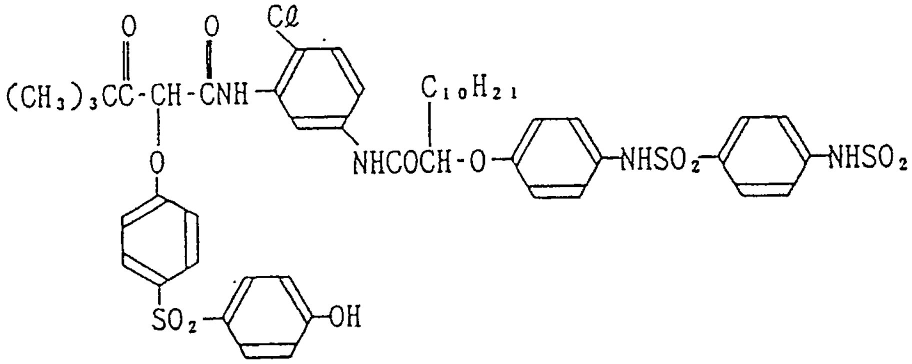
(Y－31)



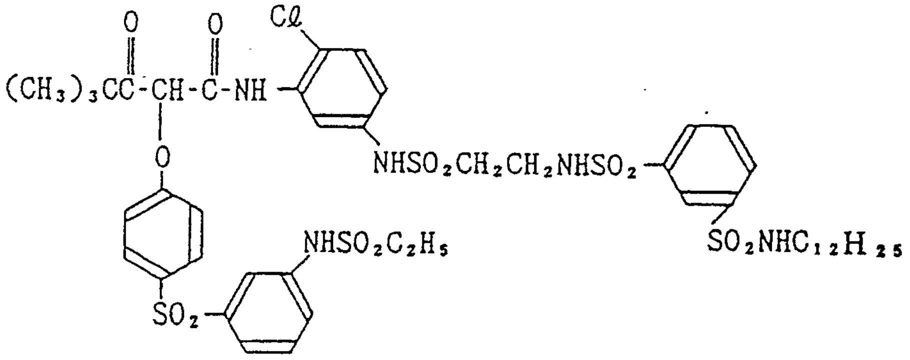
(Y－32)



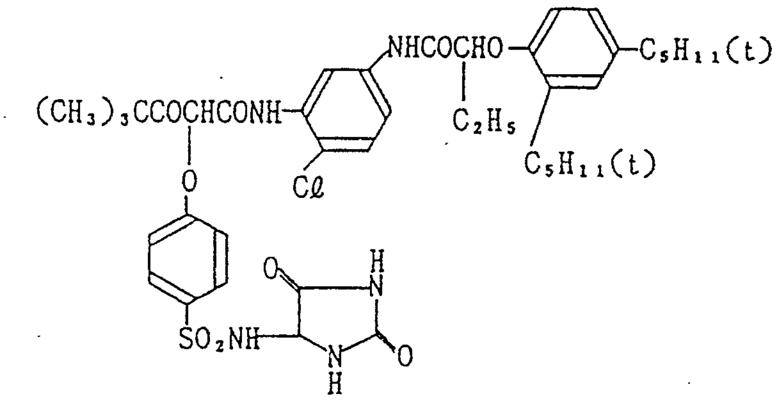
(Y－33)



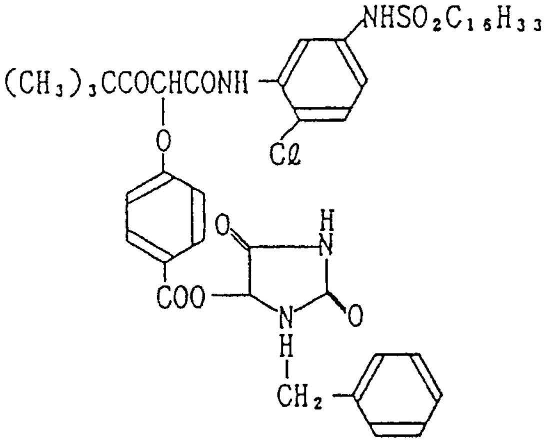
(Y－34)


(CH₃)₃CC-CH-C-NH
O
O
Cℓ
NHSO₂CH₂CH₂NHSO₂
SO₂NHC₁₂H₂₅
NHSO₂C₂H₅
SO₂

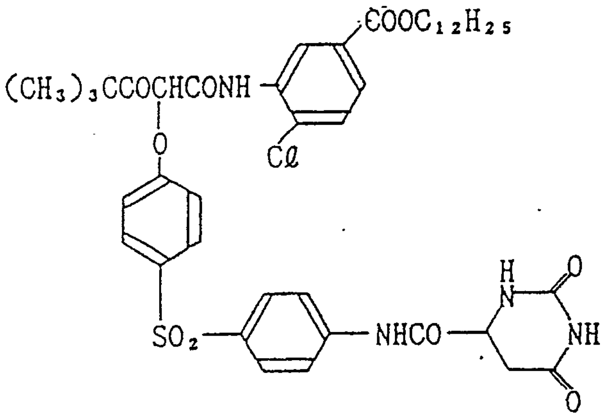
(Y－35)


(CH₃)₃CCOCHCONH
NHCOCHO
C₂H₅
C₅H₁₁(t)
C₅H₁₁(t)
Cℓ
O
SO₂NH
H
N
O
N
H
O

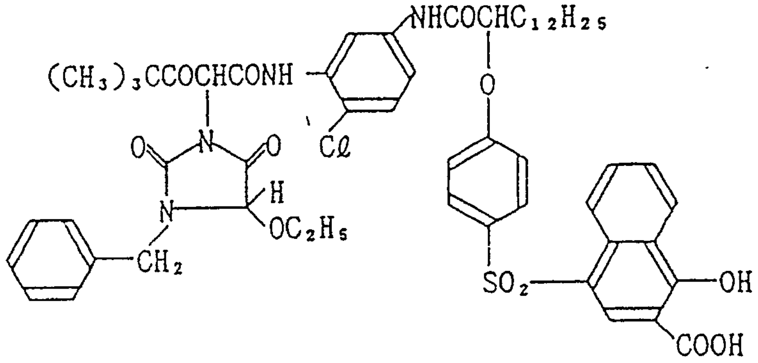
(Y－36)


(CH₃)₃CCOCHCONH
NHSO₂C₁₆H₃₃
Cℓ
O
COO
O
H
N
N
O
H
CH₂

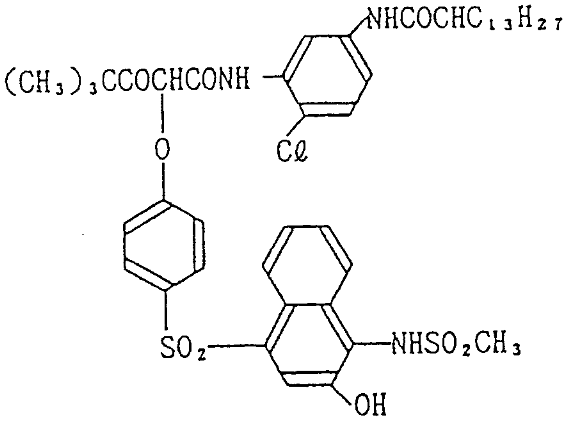
(Y－37)


COOC₁₂H₂₅
(CH₃)₃CCOCHCONH
O
Cl
SO₂
NHCO
H
N
O
NH
O

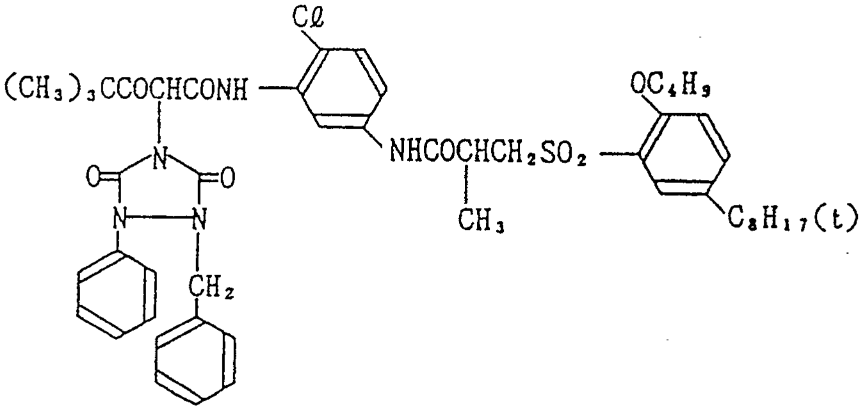
(Y－38)


NHCOCHC₁₂H₂₅
(CH₃)₃CCOCHCONH
O
N
O
O
Cl
H
N
OC₂H₅
CH₂
SO₂
OH
COOH

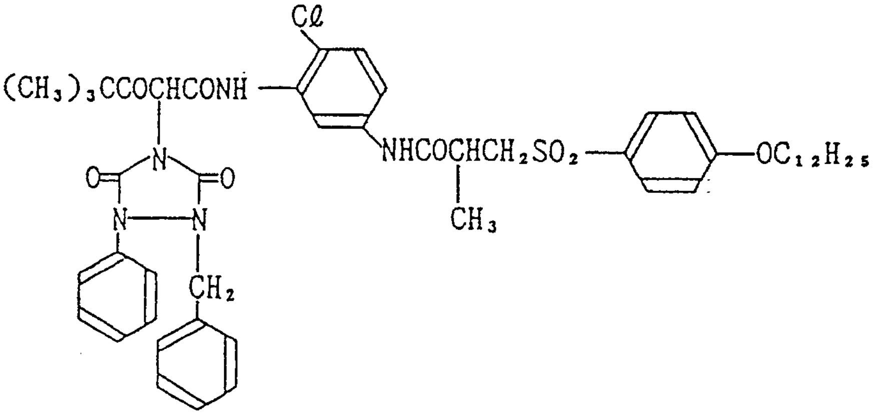
(Y－39)


NHCOCHC₁₃H₂₇
(CH₃)₃CCOCHCONH
O
Cl
SO₂
NHSO₂CH₃
OH

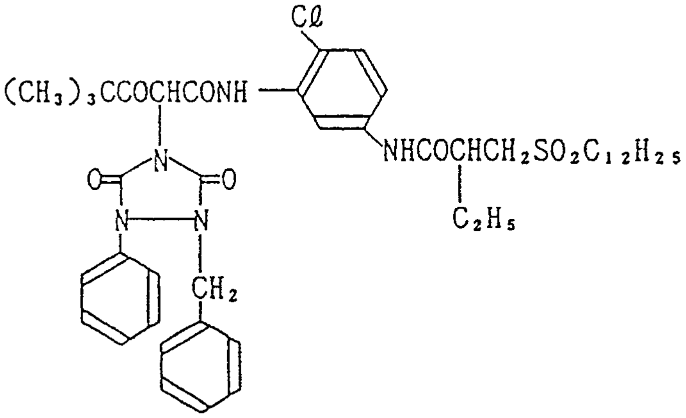
（Y − 40）


Cℓ
(CH₃)₃CCOCHCONH
N
O
N
N
O
CH₂
NHCOCHCH₂SO₂
CH₃
OC₄H₉
C₈H₁₇(t)

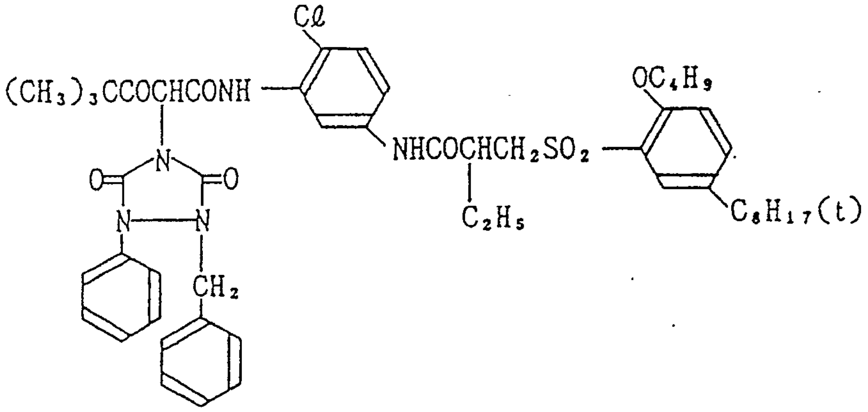
（Y − 41）


Cℓ
(CH₃)₃CCOCHCONH
N
O
N
N
O
CH₂
NHCOCHCH₂SO₂
CH₃
OC₁₂H₂₅

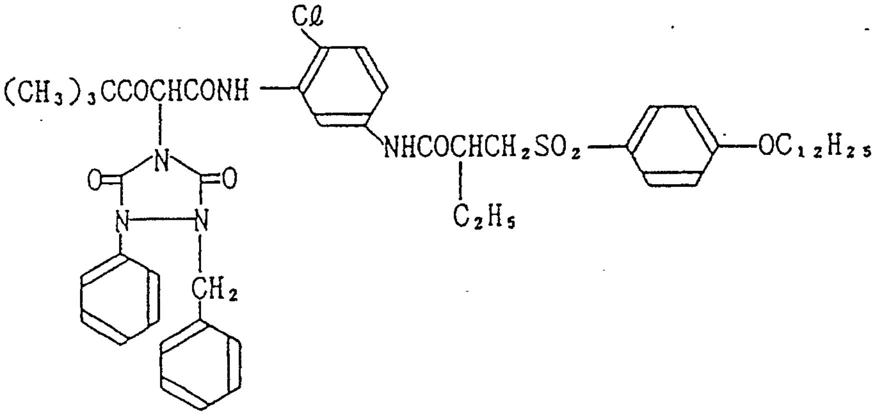
（Y − 42）


Cℓ
(CH₃)₃CCOCHCONH
N
O
N
N
O
CH₂
NHCOCHCH₂SO₂C₁₂H₂₅
C₂H₅

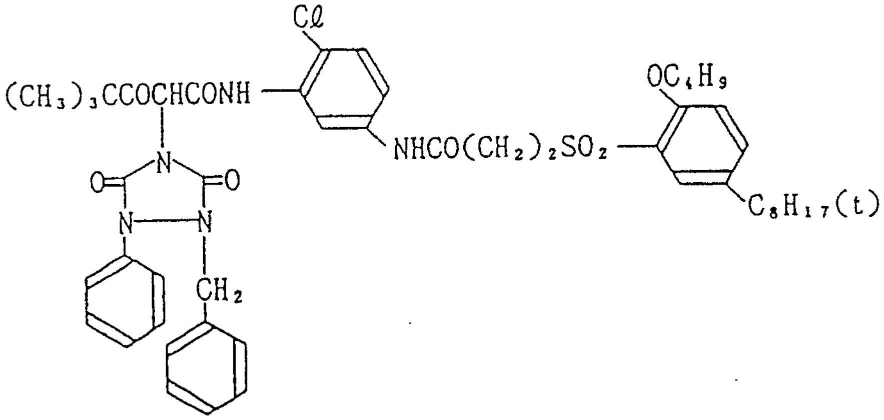
(Y－43)


Cl
(CH₃)₃CCOCHCONH
NHCOCHCH₂SO₂
C₂H₅
OC₄H₉
C₈H₁₇(t)
N
O
N
CH₂

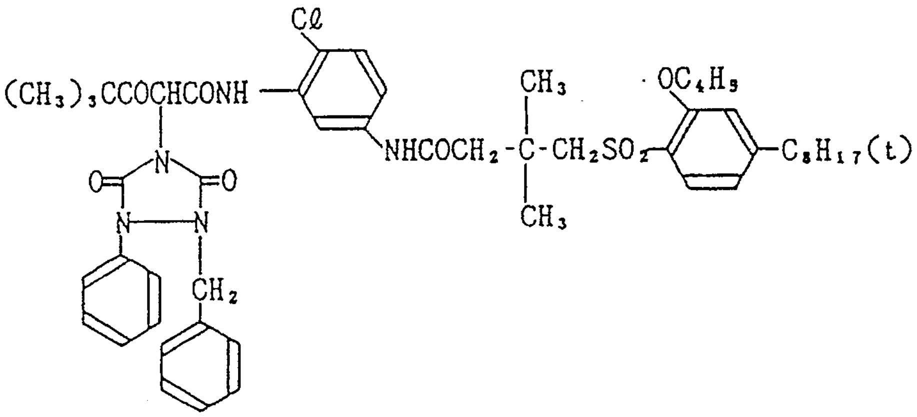
(Y－44)


Cl
(CH₃)₃CCOCHCONH
NHCOCHCH₂SO₂
C₂H₅
OC₁₂H₂₅
N
O
N
CH₂

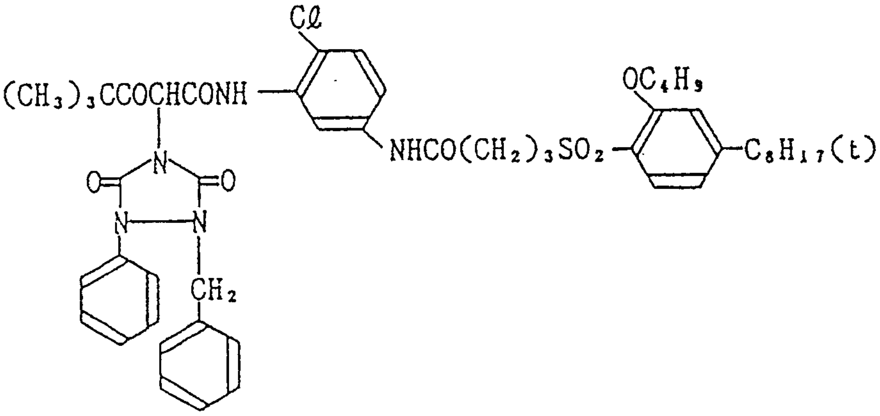
(Y－45)


Cl
(CH₃)₃CCOCHCONH
NHCO(CH₂)₂SO₂
OC₄H₉
C₈H₁₇(t)
N
O
N
CH₂

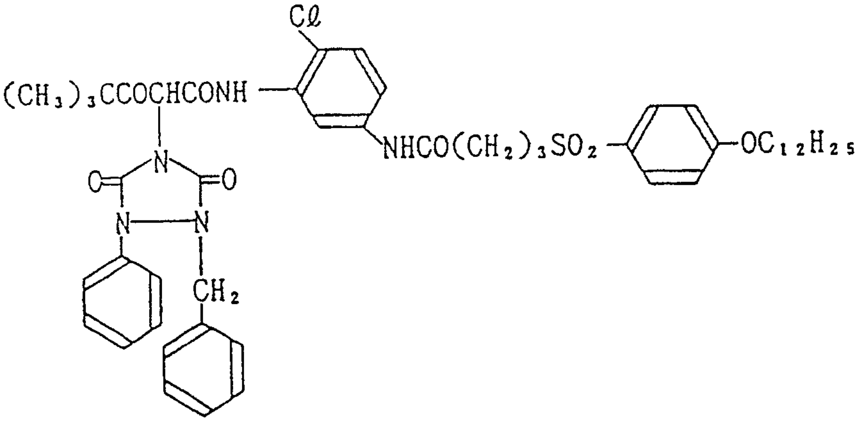
(Y－46)


Cl
(CH₃)₃CCOCHCONH
CH₃
OC₄H₉
NHCOCH₂-C-CH₂SO₂
C₈H₁₇(t)
CH₃
N
O
O
N
N
CH₂

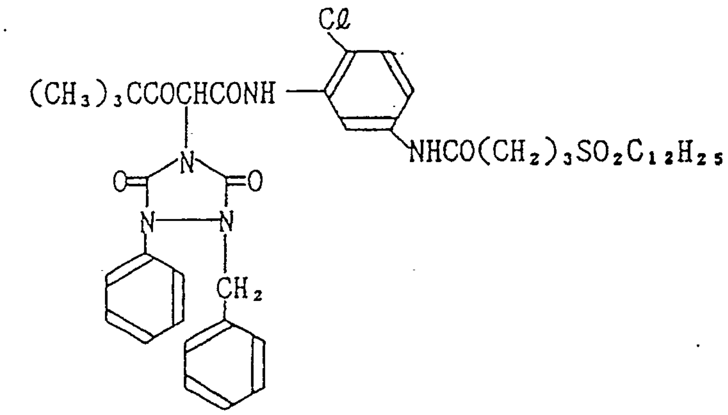
(Y－47)


Cl
(CH₃)₃CCOCHCONH
OC₄H₉
NHCO(CH₂)₃SO₂
C₈H₁₇(t)
N
O
O
N
N
CH₂

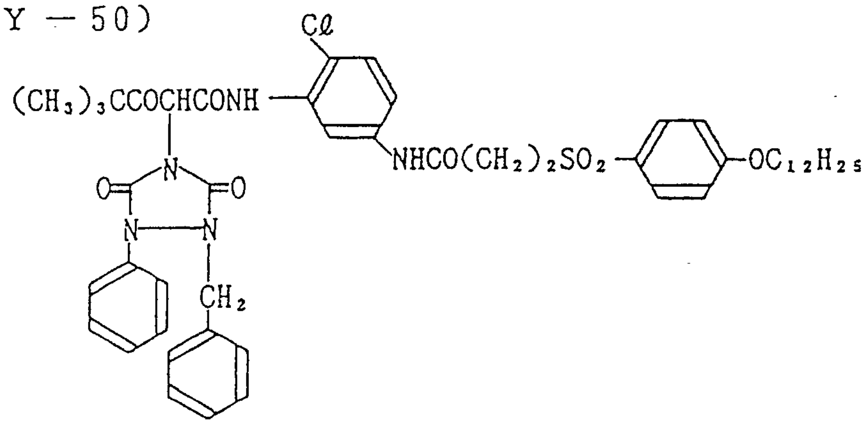
(Y－48)


Cl
(CH₃)₃CCOCHCONH
NHCO(CH₂)₃SO₂
OC₁₂H₂₅
N
O
O
N
N
CH₂

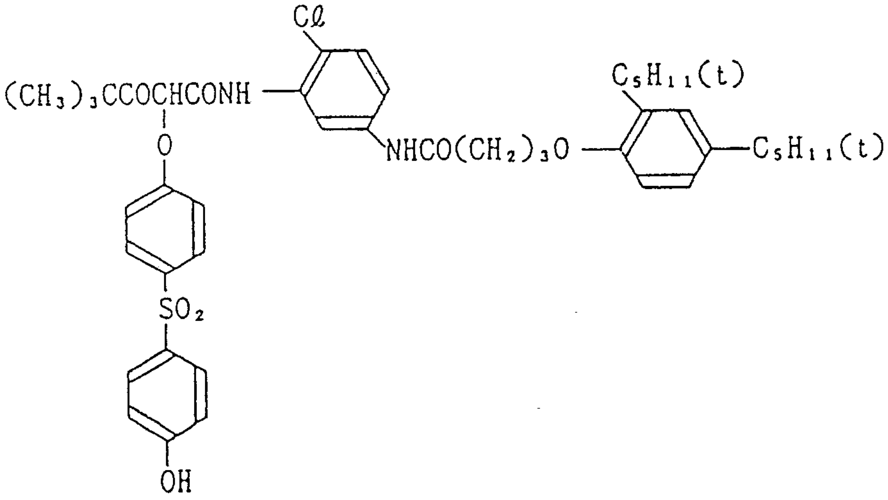
(Y－49)


Cl
(CH₃)₃CCOCHCONH
NHCO(CH₂)₃SO₂C₁₂H₂₅
N
O
O
N
N
CH₂

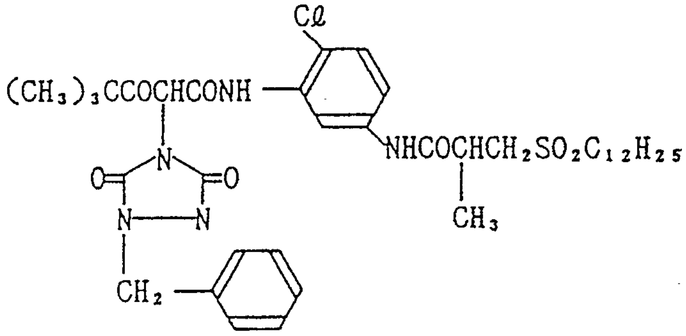
(Y－50)


Cl
(CH₃)₃CCOCHCONH
NHCO(CH₂)₂SO₂
OC₁₂H₂₅
N
O
O
N
N
CH₂

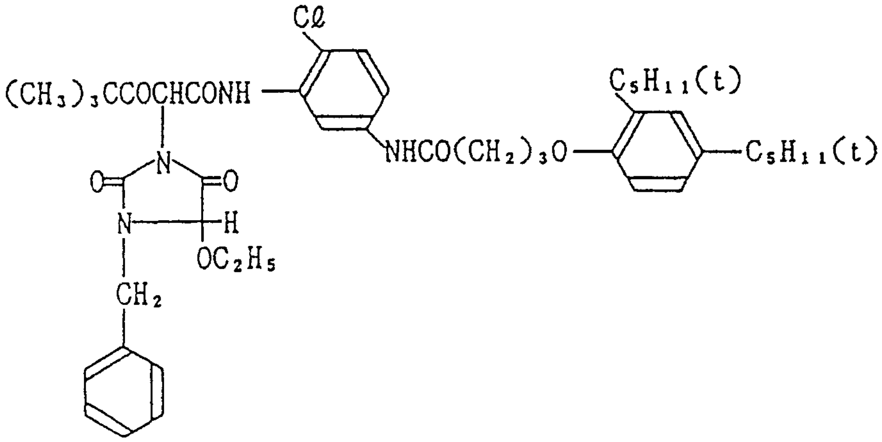
(Y－51)


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

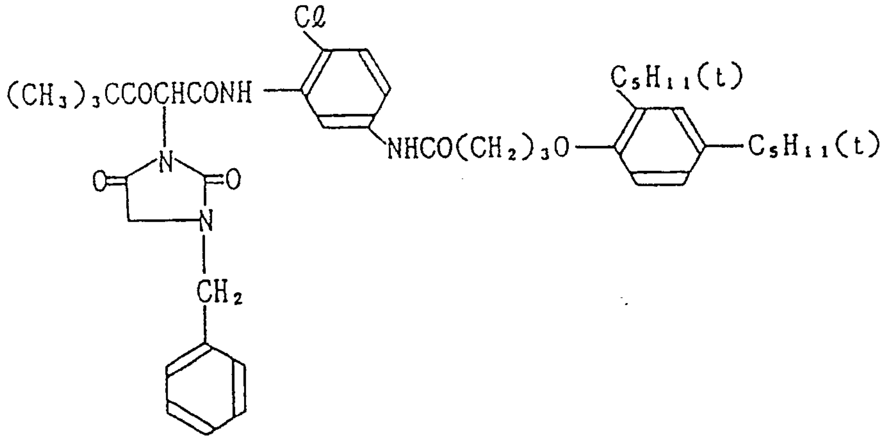
(Y — 52)


Cl
(CH₃)₃CCOCHCONH
NHCOCHCH₂SO₂C₁₂H₂₅
CH₃
N
O
O
N
N
CH₂

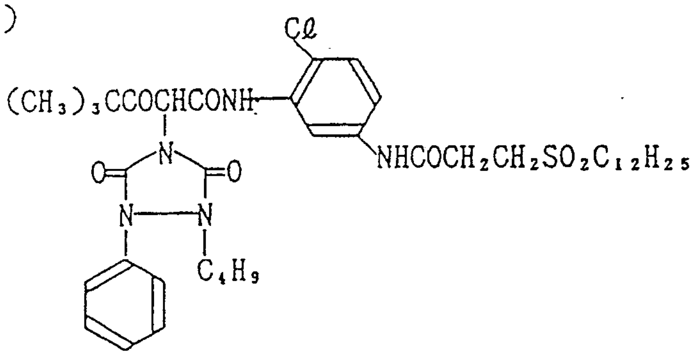
(Y — 53)


Cl
(CH₃)₃CCOCHCONH
NHCO(CH₂)₃O
C₅H₁₁(t)
C₅H₁₁(t)
N
O
O
N
H
OC₂H₅
CH₂

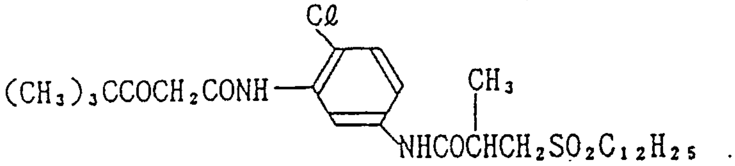
(Y — 54)


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

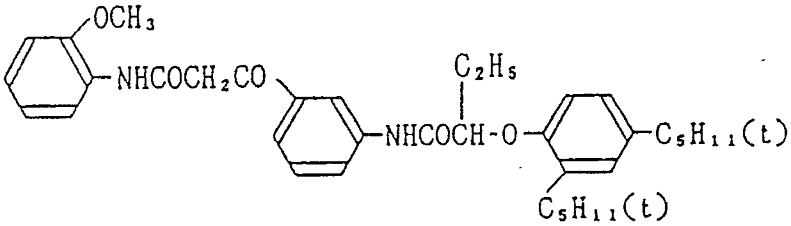
(Y－55)



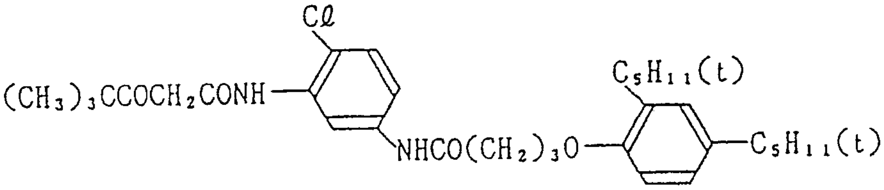
(Y－56)



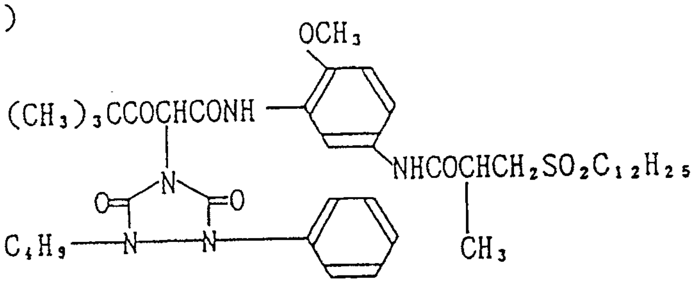
(Y－57)



(Y－58)



(Y－59)



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.

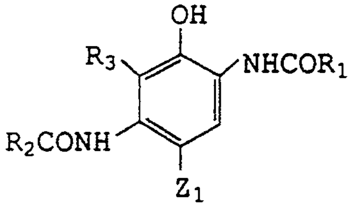
As the yellow coupler contained in the magenta image forming layer of the silver halide color photographic light-sensitive material of the invention, the yellow coupler represented by the above Formula

Y-I is 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.

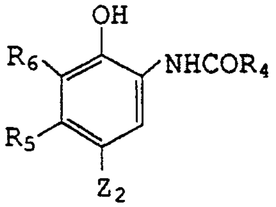
C-I



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

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 (e.g., methyl, ethyl, propyl, butyl, nonyl). R_5 represents an alkyl group (e.g., methyl, ethyl). R_6 represents a hydrogen atom, halogen atom (e.g., fluorine, chlorine, bromine) or alkyl group (e.g., 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 photographic material of the invention may comprises a light sensitive silver halide emulsion layer containing a yellow coupler, which layer is different from that containing a magenta coupler and a yellow coupler. The same yellow couplers may be used in this emulsion layer as those illustrated for the use in the magenta dye forming layer.

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.

In the invention, the amount of calcium (in terms of calcium atom) contained in the silver halide photographic light-sensitive material depends mainly upon the amount of calcium contained in the gelatin used as a binder in said silver halide photographic light-sensitive material.

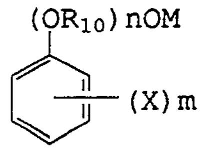
If a treatment to remove calcium is not carried out, there is normally contained more than 16 mg/m^2 of calcium.

The invention allows use of any gelatin, as long as it gives a silver halide photographic light-sensitive material having a calcium content of not more than 15 mg/m^2. But in practice, it is preferable to prepare the silver halide photographic light-sensitive material using solely or partly an ion-exchange-resin-treated or dialyzed gelatin containing less calcium. The term "gelatin containing less calcium" means a gelatin whose calcium content is not more than 100 ppm.

In the invention, the allowable calcium content of the silver halide photographic light-sensitive material is 15 mg/m^2 or less, but the preferred content is 10 mg/m^2 or less.

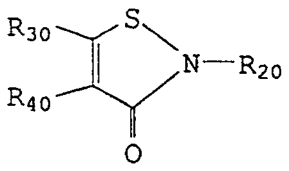
In the invention, it is preferable that the silver halide photographic light-sensitive material contain at least one of the compounds represented by the following Formula I, II, III, or IV.

Formula I



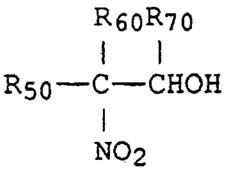
In the formula, R_{10} represents a lower alkylene group, and M represents a hydrogen atom, alkali metal or alkyl group. X represents a halogen atom, or an alkyl, cycloalkyl, aryl, carboxyl, amino, sulfo, nitro or alkoxycarbonyl group. n represents 0 or 1, and m represents an integer from 1 to 5.

Formula [II]



In the formula, R_{20} represents a hydrogen atom, or an alkyl, cycloalkyl, alkenyl, aralkyl, aryl, alkoxy, -CONHR (R is an alkyl, aryl, alkylthio, arylthio, alkylsulfonyl or arylsulfonyl group) or heterocyclic group. R_{30} and R_{40} each represent a hydrogen or halogen atom, or an alkyl, cycloalkyl, aryl, heterocyclic, cyano, alkylthio, arylthio, alkylsulfoxide, alkylsulfonyl or alkylsulfinyl group; R_{30} and R_{40} may link with each other to form a benzene ring which may have a substituent.

III

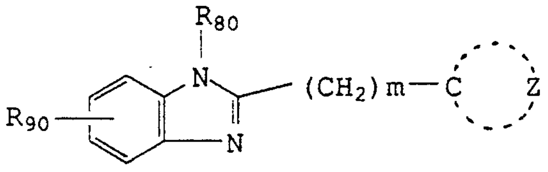


$$R_{50}-\overset{\displaystyle R_{60}}{\underset{\displaystyle NO_2}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle R_{70}}{\overset{|}{C}}HOH$$

In the formula, R_{50} and R_{60} each represent a hydrogen or halogen atom, or a lower alkyl group having

1 to 5 carbon atoms or an hydroxymethyl group. R_{70} represents a hydrogen atom or lower alkyl group having 1 to 5 carbon atoms.

IV



In the formula, R_{80} represents a hydrogen atom, alkyl group or aryl group. R_{90} represents a hydrogen or halogen atom, or an alkyl, aryl, nitro, carboxyl, sulfo, sulfamoyl, hydroxy, alkoxy or thiazolyl group. m represents 0 or 1. Z represents a group of atoms which constitute a thiazolyl ring.

In Formula I, examples of the lower alkylene group represented by R_{10} include a methylene, ethylene and propylene group. The halogen atom represented by M is a chlorine, bromine or iodine atom. The alkyl group is preferably a straight or branced alkyl group having 1 to 8 carbon atoms. The cycloalkyl group is preferably one having 4 to 8 carbon atoms. As the aryl group, phenyl and naphthyl groups are preferred. The number of carbon atoms in the alkoxycarbonyl group is preferably 1 to 5.

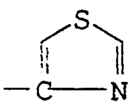
Each of the above groups may be substituted by an alkyl group having 1 to 4 carbon atoms, a halogen atom, or a hydroxyl, sulfo, nitro, amino, cyano, carboxyl or phenyl group.

In Formula II, the number of carbon atoms of the alkyl group or alkenyl group each represented by R_{20} is 1 to 36, preferably 1 to 18. The cycloalkyl group has 3 to 12, preferably 3 to 6 carbon atoms. Each of these alkyl, alkenyl, cycloalkyl, aralkyl, aryl and heterocyclic groups may have a substituent selected from halogen atoms and nitro, cyano, thiocyano, aryl, alkoxy, aryloxy, carboxy, sulfoxy, alkoxycarbonyl, arylcarbonyl, alkoxycarbonyl, aryloxycarbonyl, sulfo, acyloxy, sulfamoyl, carbamoyl, acylamino, diacylamino, ureide, thioureide, urethane, thiourethane, sulfonamide, heterocyclic, arylsulfonyloxy, alkylsulfonyloxy, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylsulfinyl, arylsulfinyl, alkylamino, dialkylamino, anilino, N-alkylanilino, N-arylanilino, N-acylamino, hydroxy and mercapto groups.

The number of carbon atoms contained in the alkyl group represented by R_{30} or R_{40} is 1 to 18, preferably 1 to 9. The number of carbon atoms in the equally represented cycloalkyl group is 3 to 12, preferably 3 to 6. Each of these alkyl, cycloalkyl and aryl groups may have a substituent such as a halogen atom or a nitro, sulfonic, aryl or hydroxy group. When R_{30} and R_{40} jointly form a benzene ring, said benzene ring may have a substituent such as a hydrogen, halogen atom or an alkyl, alkoxy, cyano or nitro group.

In Formula III, the lower alkyl group of 1 to 5 carbon atoms represented by R_{50}, R_{60} or R_{70} and the hydroxylmethyl group represented by R_{70} may have a substituent.

In Formula IV, R_{80} is preferably a hydrogen atom. R_{90} is preferably a hydrogen or halogen atom, an alkyl group having 1 to 3 carbon atoms, or an amino, nitro, sulfo or hydroxy group. m is preferably 1. The thiazolyl ring represented by Z is preferably



Some of the compounds represented by Formula I, II, III or IV are known as a preservative for a hydrophilic colloid used in a silver halide photographic light-sensitive material.

Some of the compounds represented by Formula I are described in Japanese Patent O.P.I. Publication Nos. 22847/1984 and 257747/1988. Some of the compounds represented by Formula II are described in Japanese Patent O.P.I. Publication Nos. 27424/1979, 131929/1984, 142543/1984, 166343/1983 and 2263453/1984. Some of the compounds represented by Formula III are described in Japanese Patent O.P.I. Publication Nos. 119547/1985 and 231936/1987. Some of the compounds represented by Formula IV are described in Japanese Patent O.P.I. Publication Nos. 274944/1988 and 263938/1985.

However, no description is found in any of the above specifications on the preservability of raw samples.

Typical examples of the compounds represented by Formulas I, II, III and IV are shown hereunder.

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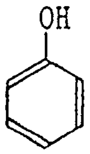

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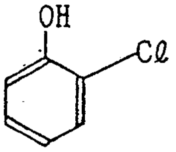

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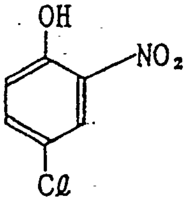

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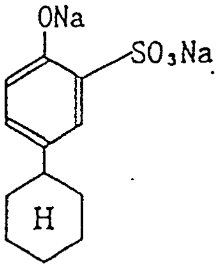

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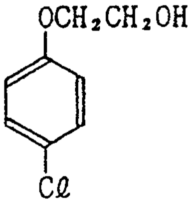

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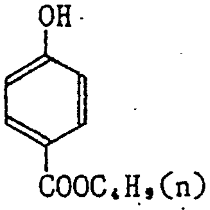

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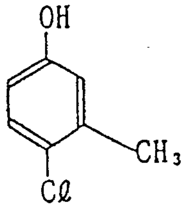

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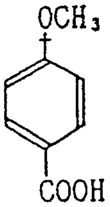

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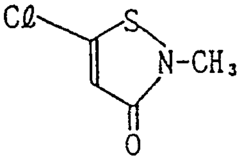

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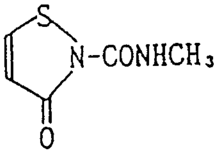

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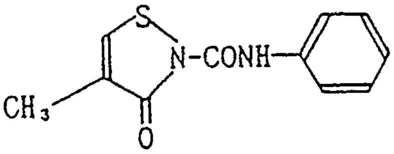

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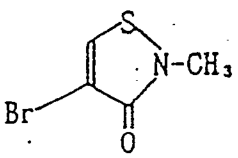

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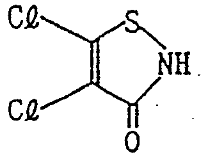

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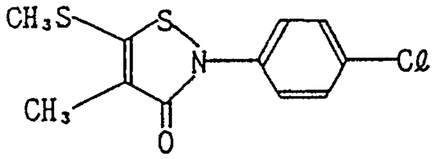

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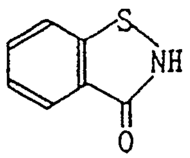

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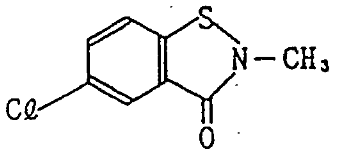

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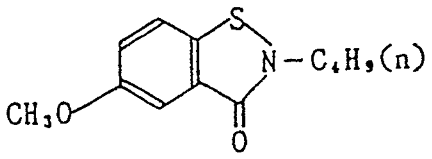

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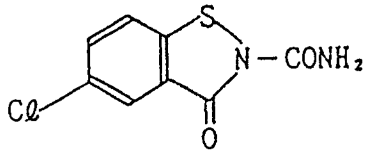

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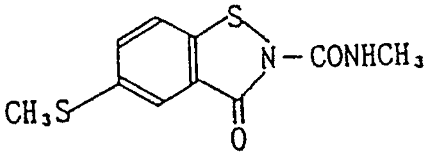

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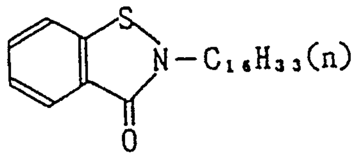

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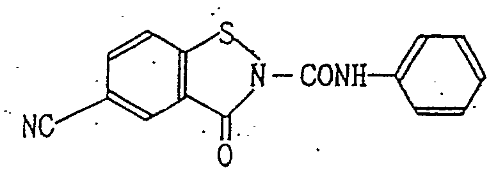

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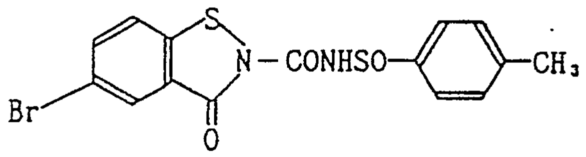

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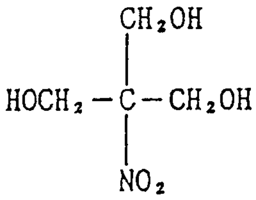
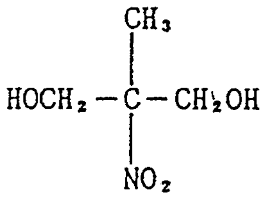


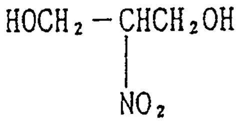
$$\mathrm{HOCH_2-\underset{NO_2}{\underset{|}{\overset{CH_2OH}{\overset{|}{C}}}}-CH_2OH}$$

2 4



$$\mathrm{HOCH_2-\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2OH}$$

2 5



$$\mathrm{HOCH_2-\underset{NO_2}{\underset{|}{C}}HCH_2OH}$$

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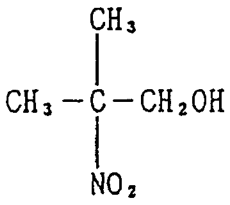
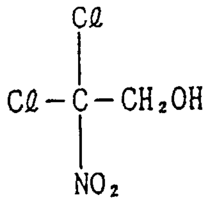


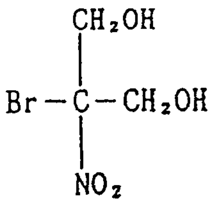
$$\mathrm{CH_3-\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2OH}$$

2 7



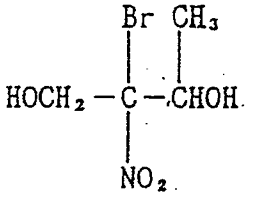
$$\mathrm{C\ell-\underset{NO_2}{\underset{|}{\overset{C\ell}{\overset{|}{C}}}}-CH_2OH}$$

2 8



$$\mathrm{Br-\underset{NO_2}{\underset{|}{\overset{CH_2OH}{\overset{|}{C}}}}-CH_2OH}$$

29



$$HOCH_2-\overset{Br}{\underset{NO_2}{C}}-\overset{CH_3}{C}HOH$$

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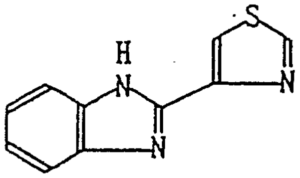

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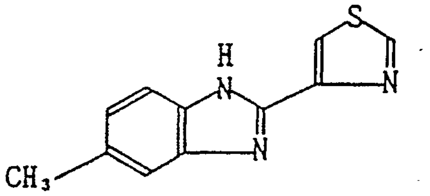

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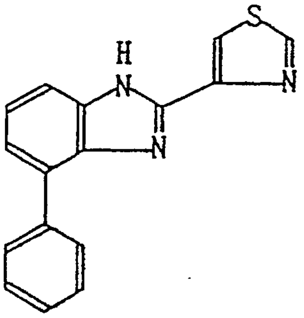

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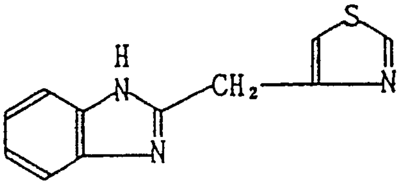

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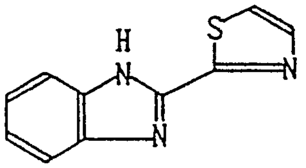

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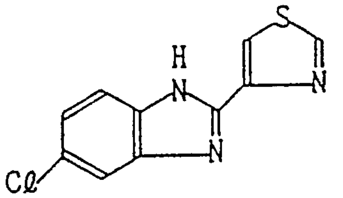

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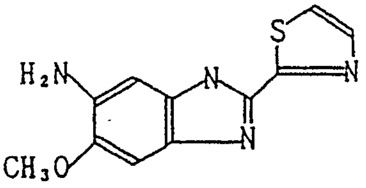


In the invention, one, or two or more compounds can be selected to use from the above exemplified compounds.

In general, these exemplified compounds are well known and marketed by I.C.I. Japan, Dainippon Ink & Chemicals, Rohm & Haas Japan, Sanai Sekiyu, etc.

The addition amount of the compounds represented by Formulas I, II, III and V is not limited, but preferably 1 X 10^{-4} to 1 X 10^{-2} g/m^2. These may be added in either a silver halide emulsion layer or a non-emulsion layer; there is no specific limitation on the method of addition.

Next, 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 ammonia 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 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 not particularly limited in types, but preferable examples are stannous chloride, thiourea dixide, 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-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 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 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 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 compound, 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 compound are 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 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 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, 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 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 (e.g., those described in U.S. Patent No. 3,473,510), cadmium salts, azaindene compounds and amino still compounds substituted with a nitrogen-containing heterocycle (e.g., 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, 120, 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, esterified gelatin, etc.

In addition to gelatin, the silver halide color photographic 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 silver halide color photographic 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, when the image forming layer consists of an internal latent image type silver halide color photographic light-sensitive material, 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.

For the silver halide color photographic light-sensitive material of the invention, it is preferable to have a layer configuration in which one of the at least three light-sensitive layers different in spectral sensitivities from one another is made into a blue-sensitive silver halide emulsion layer, another is made into a green-sensitive silver halide emulsion layer having a maximum sensitivity to green light with a sensitizing dye, and the other is made into a red-sensitive silver halide emulsion layer having a maximum sensitivity to red light with a sensitizing dye. Consequently, said light-sensitive material can have a spectral sensitivity which causes less color mixing when exposed to rays different in spectral distribution from plural black-and-white dot images. The following are examples of the preferable layer configuration including combinations of the above three layers' spectral sensitivities and image hues.

λmax in spectral sensitivity of yellow-coupler-containing layer	λmax in spectral sensitivity of magenta-coupler-containing layer	λmax in spectral sensitivity of cyan-coupler-containing layer
470 nm	550 nm	650 nm
470 nm	550 nm	700 nm
450 nm	550 nm	700 nm
470 nm	590 nm	700 nm
550 nm	470 nm	660 nm
660 nm	470 nm	550 nm
470 nm	650 nm	800 nm

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.

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 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 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, N-ethyl-N-β-hydroxyethyl aminoaniline, 4-amino-3-methyl-N,N-diethylaniline and 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluene sulfonate.

In a color developer for processing silver halide photographic 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 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 generally within the range from 20 to 60 seconds, preferably within the range from 30 to 50 seconds.

The silver halide photographic 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 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 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 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 case of the overall uniform exposure, it is preferable that an imagewise-exposed internal latent image type silver halide photographic light-sensitive material be dipped in or wetted with a developer solution or another aqueous solution and then subjected to exposure. Any of light sources can be used as long as the light is in a wavelength region to which the internal latent image type silver halide photographic light-sensitive material is sensitive. Further, there may be used a short time irradiation of a high illuminance beams such as flash beams, or a long time irradiation of a weak light. Time for the overall uniform exposure can be widely changed in consideration of kinds of internal latent image type silver halide photographic light-sensitive material, developing conditions and types of light source used, in order to obtain a positive image of the highest quality. In case a fogging agent is used, an appropriate fogging agent can be selected from many kinds of compounds, and fogging can be performed by having a fogging agent exist in the course of development. That is, such a fogging agent may be contained in an internal latent image type silver halide photographic light-sensitive material (in a silver halide emulsion layer, for example) or a developer, or in a treating solution for a process preceding development. Of these, addition in a silver halide emulsion layer is preferred. The addition amount can be changed in a wide range according to a specific requirement. In adding a fogging agent in a silver halide emulsion layer, the addition amount is 1 to 1,500 mg, preferably 10 to 1,000 mg per mol of silver halide. When added in a treating solution such as developer, the addition amount is 0.01 to 5 g/ℓ, preferably 0.08 to 0.15 g/ℓ. Examples of such a fogging agent include hydrazine compounds described in U.S. Patent Nos. 2,563,785 and 2,588,982; hydrazides and hydrazone compounds described in U.S. Patent Nos. 3,227,552; heterocyclic quaternary nitrogen compounds described in U.S. Patent Nos. 3,615, 615, 3,718,470, 3,719,494, 3,734,738 and 3,759,901; and acylhydrazinophenylthiourea described in U.S. Patent No. 4,030,925. These fogging agents may be used in combination. For example, a combination of a non-adsorbent fogging agent and an adsorbent fogging agent is described in Research Disclosure No. 15162; this can be applied to the invention.

Typical examples of useful fogging agents are hydrazine compounds such as hydrazine hydrochloride, phenylhydrazine hydrochloride, 1-formyl-2-(4-methylphenyl)hydrazine, 4-methylphenylhydrazine hydrochloride, 1-acetyl-2-phenylhydrazine, 1-acethyl-2-(4-acetamidophenyl)hydrazine, 1-methylsulfonyl-2-phenylhydrazine, 1-benzoyl-2-phenylhydrazine, 1-methylsulfonyl-2-(3-phenylsulfonamidophenyl)hydrazine and formaldehydephenylhydrazine.

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.

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.

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.

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.

Examples of typical additives include developing agents such as 1-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 excessive surface developing inhibitors containing traces of iodides and mercapto compounds.

After developing, the silver halide photographic 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 ion (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.

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.

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.

The invention may be applied to the silver dye bleaching method. This can be easily practiced in the same manner as with the silver halide photographic light-sensitive material to which the above color developing method is applied, since the difference in spectral characteristics between a yellow dye used in the silver dye bleaching method and a color of a printing ink is similar to the difference in spectral characteristics between a dye formed from a yellow coupler by color developing and a color of a printing ink.

EXAMPLES

Typical examples of the invention are described hereunder.

Example 1

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 bronide 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-1 was prepared.

Preparation of blue-sensitive emulsion EM-B

After sensitizing EM-1 with sensitizing dye D-5, 600 mg/mol AgX of T-1 was added thereto, and then 8×10^{-5} mol/mol AgX of FA-1 and 5×10^{-4} mol/mol AgX of FA-2 were added, so that blue-sensitive emulsion EM-B was prepared.

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.

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.

Using EM-B, EM-G and EM-R, silver halide color light-sensitive materials having the constitution of Table 1 were prepared.

Table 1

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

Table 1 (cont'd)

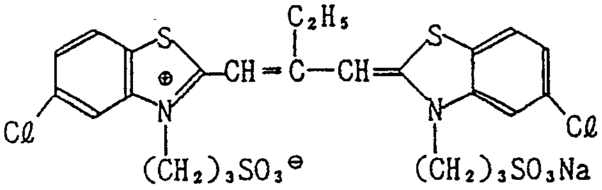
Layer (Sample 1)	Constitution	Coating weight* (mg/dm^2)
	polyvinyl pyrrolidone (PVP)	0.47
6th layer (intermediate layer)	gelatin	5.4
	color-mixing inhibitor (AS-1)	0.55
	solvent (SO-2)	0.72
5th layer (green-sensitive layer)	gelatin	14.3
	green-sensitive emulsion EM-G (amount of Ag coated)	5.0
	magenta coupler	Table 2
	yellow coupler	Table 2
	anti-stain agent (AS-2)	0.19
	solvent (SO-1)	3.1
	anti-irradiation dye (AI-3)	0.35
	inhibitors (ST-1, ST-2, T-1)	
4th layer (intermediate layer)	gelatin	7.5
	color-mixing inhibitor (AS-1)	0.55
	solvent (SO-2)	0.72
3rd layer (red-sensitive layer)	gelatin	13.8
	red-sensitive emulsion EM-R (amount of Ag coated)	3.0
	cyan coupler (CC-3)	4.4
	color adjusting agent (A-1)	2.2
	antistain agent (AS-2)	0.15
	anti-irradiation dye (AI-4)	0.25

Table 1 (cont'd)

Layer (Sample 1)	Constitution	Coating weight* (mg/dm^2)
	inhibitors (ST-1, ST-2, T-1)	
2nd layer (intermediate layer)	gelatin	5.4
	color mixing inhibitor (AS-1)	0.55
	solvent (SO-2)	0.72
1st layer (antihalation layer)	gelatin	6.0
	black colloidal silver	1.0

* Amount of Ag coated is in terms of silver.

(D - 7)



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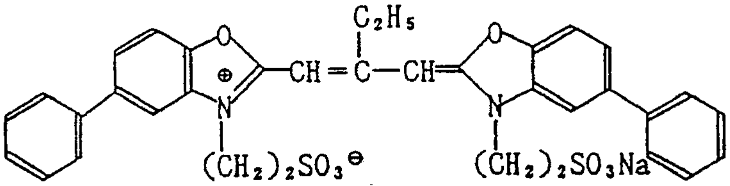

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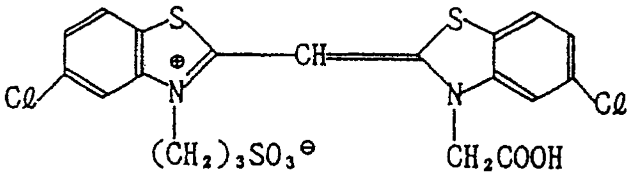

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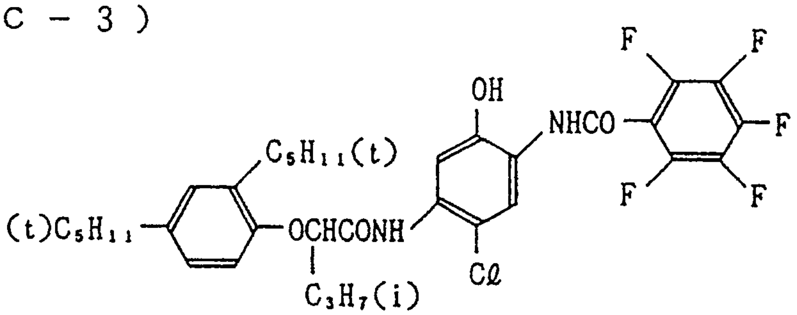

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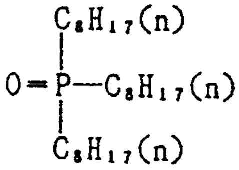

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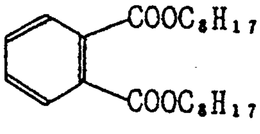

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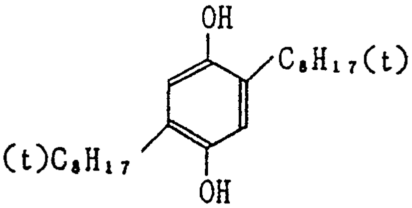

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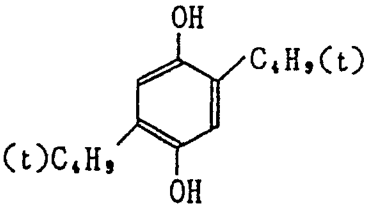

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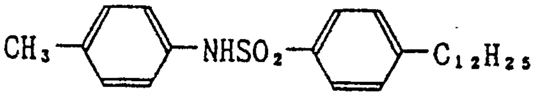

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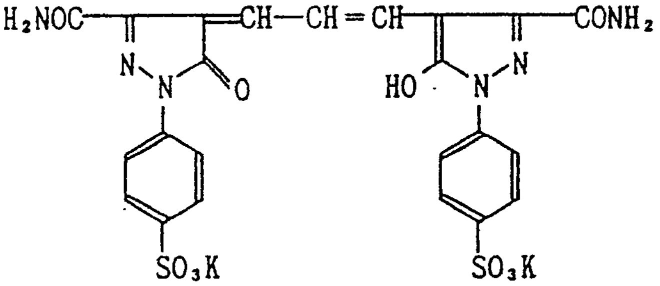

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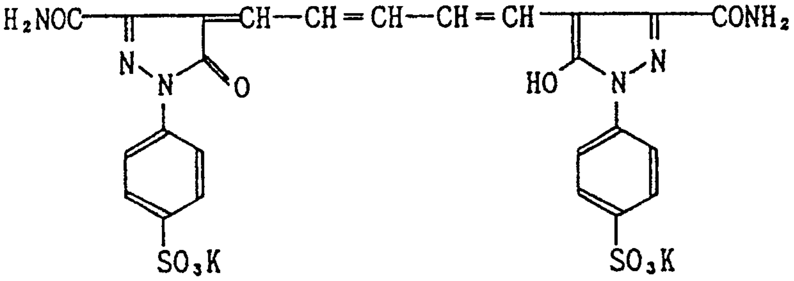

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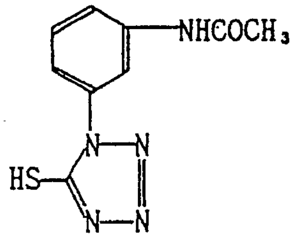

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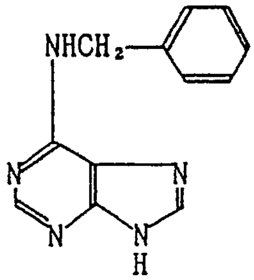

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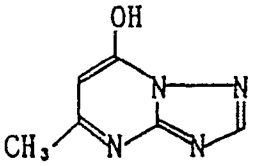

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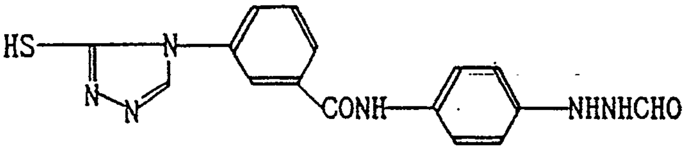

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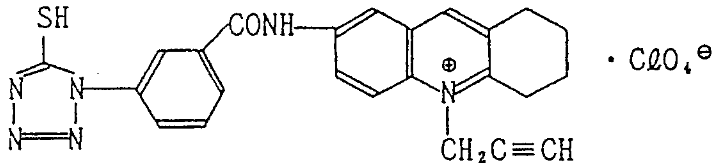

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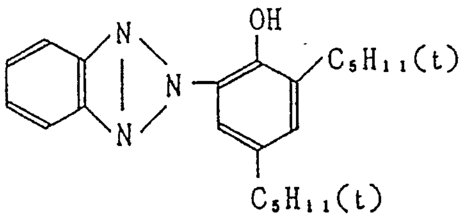

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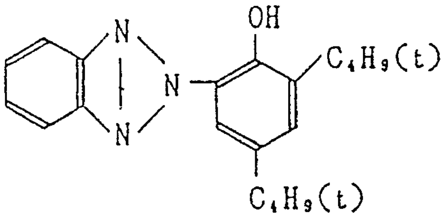
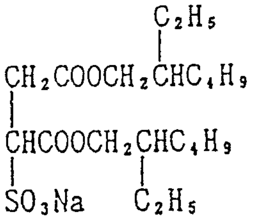


(SA-1)



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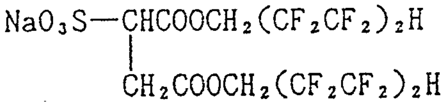
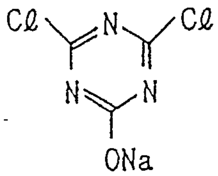


$NaO_3S-CH(COOCH_2(CF_2CF_2)_2H)-CH_2COOCH_2(CF_2CF_2)_2H$

H-1



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

The amount of calcium contained in the light-sensitive material was varied as shown in Table 2 by varying the mixing ratio of a gelating having a calcium content of 3,000 ppm to a gelatin having a calcium content of 100 ppm. In each light-sensitive material sample, a gelatin of the same mixing ratio was used in all the layers from 1st layer through 10th layer.

Further, the coating solution for 5th green-sensitive layer was divided into two portions when prepared; before being coated, one portion was stored at 40° C for 2 hours, and the other portion was stored at 40° C for 10 hours.

Each sample prepared as above was exposed as follows: a blue light obtained through a color separation filter was irradiated allover the sample at an exposure to confine the color formation of the blue-sensitive layer to a minimum, and then a red light obtained through a color separation filter was irradiated allover the sample at an exposure to confine the color formation of the red-sensitive layer to a minimum.

Next, each sample was subjected to the following processes, and then evaluated for the magenta density and yellow density on an image formed by development of the green-sensitive layer.

Table 2

Sample No.	Amount of magenta coupler added (mol/m^2)	Amount of yellow coupler added (mol/m^2)	Calcium content (mg/m^2)	Standing time of coating solution (hr)
1 Comparison	M-3 (4.4×10^{-4})	Y-58 (1.1×10^{-4})	17	2
2 Comparison	M-3 (4.4×10^{-4})	Y-58 (1.1×10^{-4})	17	10
3 Invention	M-3 (4.4×10^{-4})	Y-58 (1.1×10^{-4})	12	2
4 Invention	M-3 (4.4×10^{-4})	Y-58 (1.1×10^{-4})	12	10
5 Comparison	MC-1 (4.4×10^{-4})	Y-58 (1.1×10^{-4})	12	2
6 Comparison	MC-1 (4.4×10^{-4})	Y-58 (1.1×10^{-4})	12	10
7 Invention	M-61 (4.4×10^{-4})	Y-6 (1.1×10^{-4})	13	2
8 Invention	M-61 (4.4×10^{-4})	Y-6 (1.1×10^{-4})	13	10
9 Invention	M-12 (4.4×10^{-4})	Y-4 (1.1×10^{-4})	8	2
10 Invention	M-12 (4.4×10^{-4})	Y-4 (1.1×10^{-4})	8	10
11 Invention	M-22 (4.4×10^{-4})	Y-22 (1.1×10^{-4})	5	2
12 Invention	M-22 (4.4×10^{-4})	Y-22 (1.1×10^{-4})	5	10
13 Invention	M-44 (4.4×10^{-4})	Y-49 (1.1×10^{-4})	8	2
14 Invention	M-44 (4.4×10^{-4})	Y-49 (1.1×10^{-4})	8	10

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

Compositions of treating solutions

(Color developer)

Benzyl alcohol	15 mℓ
Cerium sulfate	0.015 g
Ethylene glycol	8 mℓ
Potassium sulfite	2.5 g
Potassium bromide	0.8 g
Sodium chloride	0.2 g
Potassium carbonate	25.0 g
T-1	0.1 g
Hydroxylamine sulfate	5.0 g
Diethylenetriamine pentacetate	2.0 g
4-Amino-N-ethyl-N-(ß-hydroxyethyl) aniline sulfate	4.5 g
Optical brightener (4,4'-diaminostilbene disulfonate derivative)	1.0 g
Potassium hydroxide	2.0 g
Diethylene glycol	15 mℓ
Potassium phosphate	8.0 g

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

pH was adjusted to 10.50.

(Bleach-fixer)

Ammonium ferric ethylenediamine tetracetate (dihydrate)	60 g
Ethylenediamine tetracetate	3 g

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

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

(Stabilizer)

5-Chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	10 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.5 g
Bismuth chloride	0.2 g
Magnesium chloride	0.1 g
Ammonium hydroxide (28% solution)	2.0 g
Sodium nitrilotriacetate	1.0 g

Water was added to make the total volume 1 liter, and pH was adjusted to 7.0 with ammonium hydroxide or sulfuric acid.

The stabilizing was carried out with a two-tank counter-flow apparatus. The results obtained are shown in Table 3.

Table 3

Sample No.	Change in density balance Y/M by standing (%)
1 Comparison	100%
2 Comparison	85%
3 Invention	100%
4 Invention	96%
5 Comparison	100%
6 Comparison	87%
7 Invention	100%
8 Invention	94%
9 Invention	100%
10 Invention	95%
11 Invention	100%
12 Invention	96%
13 Invention	100%
14 Invention	94%

The therm "change in density balance Y/M by standing (%)" used here means the ratio of the yellow density measured on a sample to the magenta density thereof, namely, (yellow density)/(magenta density). The lower line of each pair in the table shows a value for the 10-hour standing before coating and is expressed in percentage by a value relative to a value for the 2-hour standing which is set at 100%. The table shows that the color change of the green-sensitive layer attributable to standing of the coating solution becomes smaller as the value gets nearer to 100%. As seen in the table, the samples of the invention exhibit higher stabilities against a fluctuation in manufacturing conditions with the values nearer to 100%.

Example 2

Molar equivalents of a silver nitrate aqueous solution and an aqueous solution containing potassium bromide and sodium chloride (KBr:NaCℓ molar ratio was 70:30) were simultaneously added to a gelatin aqueous solution by the double jet method at 50°C over a period of 50 minutes, and thereby an emulsion consisting of cubic silver chlorobromide grains having an average grain size of 0.48 µm was prepared.

To the emulsion were added 6.2 mg/mol AgX of sodium thiosulfate and 3.0 mg/mol AgX of potassium chloroaurate, and the emulsion was subjected to chemical ripening at 70°C for 70 minutes to prepare negative type silver halide emulsion Em-2.

Preparation of blue-sensitive emulsion EM-2B

Blue-sensitive emulsion EM-2B was prepared by subjecting Em-2 to optical sensitization using sensitizing dye D-5.

Preparation of green-sensitive emulsion EM-2G

Green-sensitive emulsion EM-2G was prepared by optically sensitizing Em-2 with sensitizing dye D-6.

Preparation of red-sensitive emulsion EM-2R

Red-sensitive emulsion EM-2R was prepared by optical sensitization of Em-2 with sensitizing dye D-7.

Silver halide color light-sensitive materials having the constitution shown in Table 4 were prepared using EM-2B, EM-2G and EM-2R. In the preparation, the calcium content of the light-sensitive material were varied as shown in Table 5 in the same manner as in Example 1. Also, compounds shown in Table 5 were added in the green-sensitive 3rd layer.

One portion of each sample was stored for 3 days under conditions of 42°C and 50% RH, and then subjected to preservation test for 3 days under conditions of 55°C and 80% RH. After being subjected to wedge exposure, each sample was processed in the same manner as in Example 1 and then evaluated for the relative sensitivity of magenta. The results are shown in Table 6.

Table 4

Layer	Constitution	Coating weight (mg/dm^2)
7th layer (protective layer)	gelatin	7.8
6th layer (UV absorbent layer)	gelatin	7.8
	UV absorbent (UV-2)	0.65
	UV absorbent (UV-1)	1.95
	solvent (SO-2)	1.0
5th layer (red-sensitive layer)	gelatin	13.8
	red-sensitive emulsion EM-2R	3.0
	cyan coupler (CC-3)	4.4
	color adjusting agent (A-1)	2.2
	antistain agent (AS-2)	0.15
	anti-irradiation dye (AI-4)	0.25
	inhibitors (ST-1, ST-2, T-1)	
4th layer (intermediate layer)	gelatin	5.4
	color-mixing inhibitor (AS-1)	0.55
	solvent (SO-2)	0.72
3rd layer (green-sensitive layer)	gelatin	13.0
	green-sensitive emulsion EM-2G	4.0
	magenta coupler (M-61)	3.0
	yellow coupler (Y-47)	0.7
	antistain agent (AS-2)	0.19
	solvent (SO-1)	3.1

Table 4 (cont'd)

Layer	Constitution	Coating weight (mg/dm^2)
anti-irradiation dye (AI-3)		0.35
	inhibitors (ST-1, ST-2, T-1)	
2nd layer (intermediate layer)	gelatin	7.5
	color-mixing inhibitor (AS-1)	0.55
	solvent (SO-2)	0.72
1st layer (blue-sensitive layer)	gelatin	14.3
	blue-sensitive emulsion EM-2B	5.0
	yellow coupler (Y-59)	8.2
	antistain agent (AS-2)	0.25
	solvent (SO-1)	8.2
	inhibitors (ST-1, ST-2, T-1)	

Table 5

Sample No.	Calcium content (mg/m^2)	Compound added* (10 mg/mol AgI)
15	12	-
16	17	-
17	12	Compound 6
18	12	Compound 16
19	12	Compound 24
20	12	Compound 35

* Compounds selected from Formulas I through IV

Table 6

Relative sensitivity / Sample No.	Zero day under 55°C, 81% RH	3 days under 55°C, 80% RH
15	100	87
16	89	79
17	101	94
18	98	94
19	99	93
20	100	95

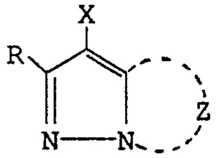
* Relative sensitivities of magenta, which are shown by values relative to the sensitivity of sample 15 preserved under 55°C and 80% RH which is set at 100.

As apparent from Table 6, the samples containing compounds of Formulas I through IV exhibit stable sensitivities against preservation.

Claims

1. A light-sensitive silver halide color photographic material having a support and photographic layers at least one of which is a silver halide emulsion layer, wherein at least one silver halide emulsion layer having the same spectral sensitivity contains at least one of the compounds represented by the following Formula M-I and at least one yellow coupler, and the content of calcium atoms in the photographic layers is not more than 15 mg/m^2.

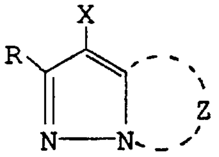
M-I



wherein Z represents a group of nonmetal atoms necessary to form a nitrogen-containing heterocycle, which 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; and R represents a hydrogen atom or a substituent.

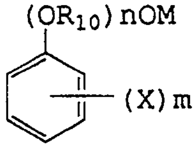
2. A light-sensitive silver halide color photographic material having a support and photographic layers comprising blue, green and red sensitive silver halide emulsion layers, wherein the green sensitive silver halide emulsion layer contains a magenta coupler represented by the following Formula M-I, at least one yellow coupler and at least one of the compounds represented by the following Formula I, II, III, or IV, and the content of calcium atoms in the photographic layers is not more than 15 mg/m^2;

M-I



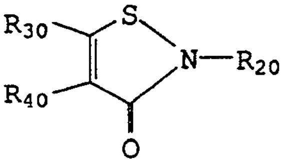
wherein Z represents a group of nonmetal atoms necessary to form a nitrogen-containing heterocycle, which may have a substituent; X represents a hydrogen atom or a group capable of being split off upon reaction with an oxidized product of a color developing agent; and R represents a hydrogen atom or a substituent;

I



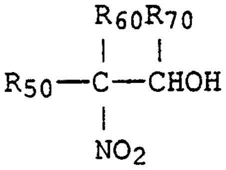
wherein, R_{10} represents a lower alkylene group, and M represents a hydrogen atom, alkali metal or alkyl group. X represents a halogen atom, or an alkyl, cycloalkyl, aryl, carboxyl, amino, sulfo, nitro or alkoxycarbonyl group. n represents 0 or 1, and m represents an integer from 1 to 5;

II



wherein R_{20} represents a hydrogen atom, or an alkyl, cycloalkyl, alkenyl, aralkyl, aryl, alkoxy, -CONHR (R is an alkyl, aryl, alkylthio, arylthio, alkylsulfonyl or arylsulfonyl group) or heterocyclic group, R_{30} and R_{40} each represent a hydrogen or halogen atom, or an alkyl, cycloalkyl, aryl, heterocyclic, cyano, alkylthio, arylthio, alkylsulfoxide, alkylsulfonyl or alkylsulfinyl group; R_{30} and R_{40} may link with each other to form a benzene ring which may have a substituent;

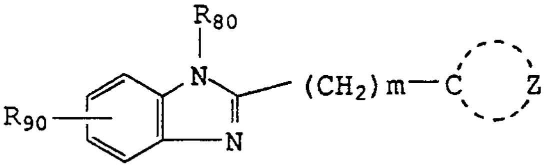
III



$$R_{50}-\overset{R_{60}}{\underset{NO_2}{C}}-\overset{R_{70}}{CHOH}$$

wherein R_{50} and R_{60} each represent a hydrogen or halogen atom, or a lower alkyl group having 1 to 5 carbon atoms or an hydroxymethyl group, R_{70} represents a hydrogen atom or lower alkyl group having 1 to 5 carbon atoms;

IV



wherein R_{80} represents a hydrogen atom, alkyl group or aryl group, R_{90} represents a hydrogen or halogen atom, or an alkyl, aryl, nitro, carboxyl, sulfo, sulfamoyl, hydroxy, alkoxy or thiazolyl group, m represents 0 or 1. Z represents a group of atoms which constitute a thiazolyl ring.

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 8548

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	EP-A-0 330 093 (FUJI) * page 10, line 1 - page 31, line 56 * * page 106 *compound (M-1) * – – –	1,2	G 03 C 7/30 G 03 C 7/392
Y	JP-A-2 124 568 (KONICA) * abstract * * pages 7 - 14 * – – –	1,2	
Y	GB-A-1 474 994 (FUJI) * page 7, lines 26 - 31 * – – –	1,2	
Y	US-A-4 584 266 (HIROSE ET AL.) * column 8, line 61 - column 10, line 61 * – – – – –	1,2	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	01 August 91	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

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