⑲ Europäisches Patentamt
European Patent Office
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⑪ Publication number: **0 573 048 A2**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **93108959.3**

㉒ Date of filing: **03.06.93**

㉚ Priority: **05.06.92 JP 145849/92**

㊸ Date of publication of application:
08.12.93 Bulletin 93/49

(84) Designated Contracting States:
DE FR GB

(51) Int. Cl.⁵: **G03C 8/40**

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(54) A method of image formation.

(57) A method of image formation is provided, wherein a recording material is subjected to imagewise heating substantially in the absence of water and a base or precursor thereof, wherein the recording material comprises a support having coated thereon a 1,3-sulfur-nitrogen-containing compound capable of being cleaved in the presence of a silver ion or silver complex ion, an organic silver salt and a thermal solvent, and wherein the 1,3-sulfur-nitrogen-containing compound is represented by the following formula.

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(3.10/3.6/3.3.1)

FIELD OF THE INVENTION

The present invention relates to a thermal recording material or heat developable light-sensitive material. The invention also relates to a method of image formation using a thermal recording material or heat developable light-sensitive material.

BACKGROUND OF THE INVENTION

Traditionally, various means have been used to obtain visible images, including ink jets, electrophotography, thermal recording materials and silver halide light-sensitive materials.

Of these means, thermal recording materials have advantages, such as easy operation and maintenance, feasibility for reduction in equipment size and cost and low running cost. Particularly, thermal transfer printing has recently been the subject of many research and development activities as can satisfy the requirements for both image quality and cost, in which a thermal transfer ribbon, comprising a support and a layer of dispersion of dye or pigment in binder coated thereon, and recording paper are superposed and heat according to the image information is applied to the back face of the thermal transfer ribbon via a thermal head to record images. The thermal imaging method using a laser beam has also recently been investigated, which is described in an special issue "Imaging Part 2, - Current Hard Copy Printer Technology" of "Shashin Kogyo", pp. 63-113 (published by Shashin Kogyo Shuppansha on July 20, 1988), for instance. However, much remains unsatisfactory as to image properties, and further improvements are desired.

On the other hand, silver halide photographic light-sensitive materials have a handling problem of the necessity for use of liquids such as a developer, though they surpass other image recording materials with respect to image quality. As a means of solving this problem, what is called the heat development method has been developed, in which exposure is followed by heat development to form images. Details of such a heat development method are given in the proceedings of the 17th symposium of the Society of Photographic Science and Technology of Japan titled "Discussion on Heat Developable Silver Salt Recording System" (May 1987) . In these heat development methods, silver or dye images are formed by heat treatment and, if necessary, pressure treatment, after imagewise exposure of a heat developable light-sensitive material having a light-sensitive silver halide, a binder and a reducing agent on the support. Particularly in thermal transfer type heat developable recording materials, clearer dye images can be obtained by transferring the formed dye image to an image receiving material. Although heat developable light-sensitive materials offer high image quality similarly to silver halide light-sensitive materials, the image quality level is lower than that obtained with conventional liquid processable light-sensitive materials. With this background, further improvements are desired, and development of positive-type heat developable light-sensitive materials is desired.

1,3-sulfur-nitrogen-containing compounds are known to undergo cleavage reaction by the action of silver ion. Attempts have been made to utilize this reaction for imagewise release of reagents in photographic processing. For example, Japanese Patent Examined Publication No. 7576/1980 describes a technology in which a 1,3-sulfur-nitrogen-containing compound is cleaved according to the imagewise distribution of silver ion to release a photographically useful group (hereinafter referred to as PUG), with mention of its applicability to so-called instant photographic materials. Such photographically useful groups include image forming dyes, their intermediates, antifogging agents and gelatin hardeners. On the other hand, silver ions are supplied in the form of a soluble silver complex ions by the action of a silver halide solvent. An imagewise distribution of silver ions occurs in the unexposed portion.

Japanese Patent O.P.I. Publication No. 180548/1984 discloses a method by which a mobile dye is imagewise formed by heating a 1,3-sulfur-nitrogen-containing compound as a dye donator for heat developing type light-sensitive material preferably in the presence of base.

In Examples thereof, however, it was merely shown that images are obtained by transferring image dyes produceded by heat development to image-receiving materials in the presence of water.

In addition, the presence of base or base precursor to the light-sensitive material results in local formation of mobile dye during storage, which in turn poses a problem of image quality deterioration such as increased fogging.

Also, the heat developing type light-sensitive material containing a base or base precursor has a drawback of tendency toward maximum density reduction, though it permits fogging reduction in the desired dye image by acceleration of silver development.

Particularly recording materials incorporating a hydrophilic binder are normally used after being subjected to aging at a given temperature for a given period to increase the degree of hardening. This aging is carried out at temperatures of normally 25 to 50 °C, preferably 30 to 45 °C for periods of normally 12 hours to 1 month, preferably 1 day to 2 weeks. In the light-sensitive material containing a 1,3-sulfur-nitrogen-containing compound and a base or base precursor, a mobile dye forming reaction can take place even during this storage for improvement in the degree of hardening, which leads to a considerable tendency toward image quality deterioration such as increased fogging.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a new thermal recording material or new heat-developable light-sensitive material which works on the basis of chemical reaction of silver ion and 1,3-sulfur-nitrogen-containing compound.

It is another object of the present invention to provide a thermal recording material or heat developable light-sensitive material which offers improved image quality, particularly improvement in image discrimination.

It is still another object of the present invention to provide a new positive-type heat-developable light-sensitive material.

It is yet another object of the present invention to provide a heat-sensitive recording material or heat developing type light-sensitive material which undergoes little deterioration in image quality during long-term storage.

The present inventors found that reaction takes place between an organic silver salt and a 1,3-sulfur-nitrogen-containing compound in the presence of a thermal solvent, and substantially in the absence of water and base, and that the use of this reaction makes it possible to obtain a recording material accomplishing the objects described above.

Accordingly, the objects described above have been accomplished by a recording material wherein at least a 1,3-sulfur-nitrogen-containing compound capable of being cleaved in the presence of silver ions or water-soluble silver complex salt, an organic silver salt and a thermal solvent are coated on a support.

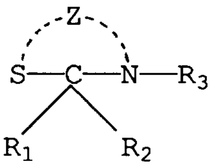
The recording material is capable of forming visible images upon imagewise heating substantially in the absence of water and base. This recording material is embodied as a heat developable light-sensitive material by adding a light-sensitive silver halide. When the recording material is embodied as a heat developable light-sensitive material, images can be formed by subjecting it to imagewise exposure, after which or simultaneously with which it is subjected to heating substantially in the absence of water and base.

The present invention is hereinafter described in detail.

DETAILED DESCRIPTION OF THE INVENTION

The 1,3-sulfur-nitrogen-containing compound of the present invention is preferably represented by the following formula 1.

Formula 1



wherein R_1 and R_2 independently represent a hydrogen atom, aliphatic group, aromatic group or heterocyclic group. R_3 represents a hydrogen atom, aliphatic group, aromatic group, heterocyclic group or acyl group. Z represents a group of non-metallic atoms necessary to form the ring, which ring may have a substituent thereon. Z may cooperate with S-C-N to form a condensed ring. At least one of R_1, R_2, R_3 and the substituent on the ring formed by Z is a photographically useful group (PUG) or precursor thereof released upon reaction of the compound of Formula 1 with a silver ion or silver complex ion under heating. Either of R_1 and R_2 is preferably other than a hydrogen atom, and R_3 is preferably other than a hydrogen atom.

It is therefore possible to release the desired compound by choosing an appropriate substituent in the compound of Formula 1 and heating in the presence of an organic silver salt. Also, the immobility (diffusion resistance) and solubility of the compound of Formula 1 can be regulated by choosing an appropriate substituent.

Typical examples of the substituent include carboxyl, sulfo, nitro, hydroxy, halogens such as chlorine, bromine and cyanogen, and hydrocarbon residues including aliphatic, alicyclic and aromatic groups as well as those exemplified for Formulas 1 above. This substituent may have an ethylenic or acetylenic group, and its carbon chain may be interrupted by a hetero atom or hetero atom-containing group such as S, O, N, SO or NH. This substituent may also contain a substituent such as phenylalkyl, alkyl ether, aryl ether, carboalkoxy, carboxyl, hydroxy, sulfo, halogen, cyano, nitro or alkylamino.

Other appropriate groups include substituted or unsubstituted alkyl groups such as methyl, ethyl, octyl and dodecyl, substituted or unsubstituted cycloalkyl groups such as cyclohexyl, cyclopentyl and cyclooctyl, substituted or unsubstituted alkenyl groups such as vinyl, allyl, butenyl, decenyl, octadienyl and hexatrienyl, substituted or unsubstituted cycloalkenyl groups such as cyclopentenyl, cycloheptenyl and cyclohexadienyl, substituted or unsubstituted alkinyl groups such as ethynyl, hexynyl and octynyl, substituted or unsubstituted aryl groups such as phenyl, tolyl, benzyl and naphthyl, substituted or unsubstituted heterocyclic groups such as those having a 4-, 5-, or 6-membered ring and O, N or S and derivatives thereof such as pyrrole, pyrazole, oxazole, thiazole, imidazole, pyrimidine, piperidine, piperazine, thiophene, pyrrolidine and azetidine.

1,3-sulfur-nitrogen-containing compounds which are used in image recording materials are preferably cyclic sulfur-nitrogen-containing compounds having S and N atoms in their ring, specifically thiazolidine and benzothiazolidine. These compounds undergo cleavage reaction at a given rate upon heating in the presence of an organic silver to release a PUG, particularly a dye.

These compounds can be used under alkaline to acidic conditions and preferably under neutral to acidic conditions.

With respect to the 1,3-sulfur-nitrogen-containing compound of the present invention, the photographically useful group (PUG) or precursor thereof is preferably substituted on the carbon atom bound to the sulfur and nitrogen atoms. In other words, one of R_1 and R_2 or both in the compound of Formula 1 are preferably PUG. Examples of PUG include dyes, developing inhibitors, developing accelerators, fogging agents, developing agents, hardeners, couplers, toning agents and brightening agents.

In the present invention, the substances preferably used as PUG are dyes, developing inhibitors and developing accelerators, with preference given to dyes.

When the dye moiety substituted as R_1 or R_2 in the compound of Formula 1 is a transferable dye, R_3 and one or more groups substituted on the ring Z are preferably ballast groups which substantially immobilize the compound of Formula 1.

The balast groups include ordinarily those having at least 8 carbon atoms and preferably substituted or unsubstituted alkyl groups having 8 to 40 carbon atoms.

Here, the balast group may be a polymer residual group. In this case, the average molecular weight of the compound represented by Formula 1 is preferably not less than 10,000.

Among the compounds represented by formula 1, preferable compounds are thiazolidine derivatives or benzothiazolidine derivatives and especially preferable ones are thiazolidine derivatives.

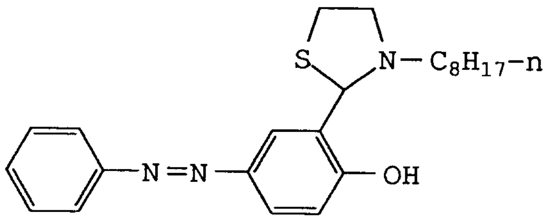
As the transferable dye released from the compounds represented by Formula 1, any conventional dyes known by those skilled in the art including azo, azomethine, indoaniline, oxonol, cyanine, thiazole, anthraquinone, ditriphenylmethane and triphenylmethane dyes can be used.

It is possible to cause releasing dye precursors in place of dyes.

"Dye precursor" is a compound producing dye molecules by reacting with other molecules or ions, or by heating, after being released.

Examples of the dye-releasing compound of the present invention are given below, but these are not to be construed as limitative.

(1)



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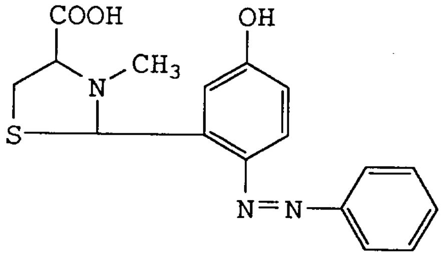

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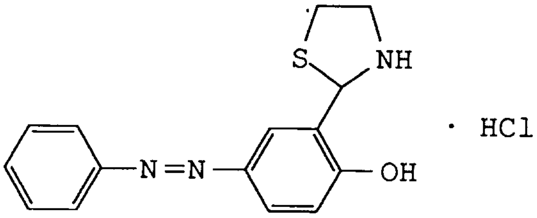

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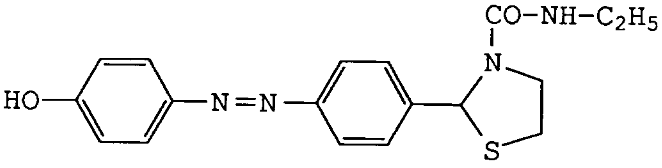

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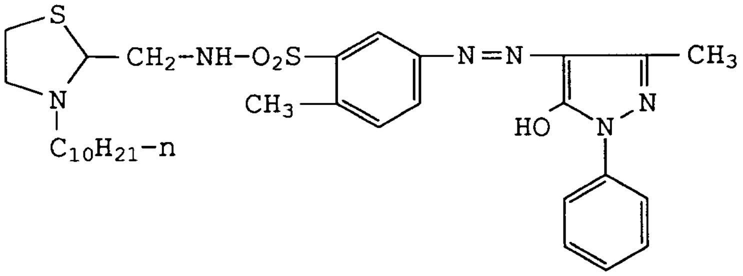

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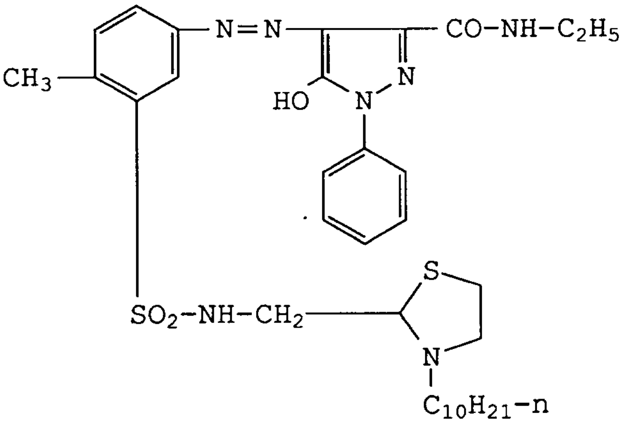

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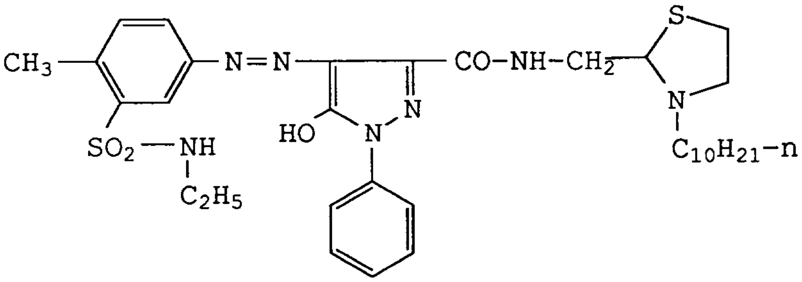

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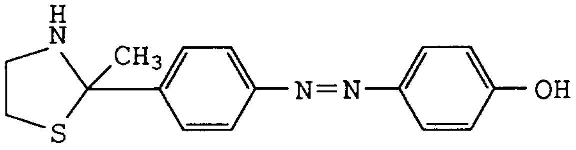

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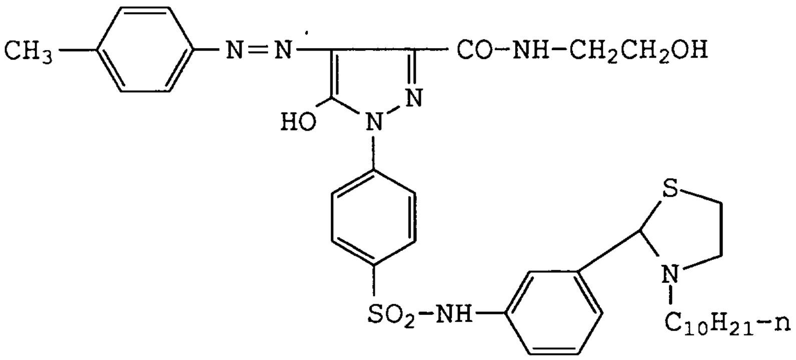

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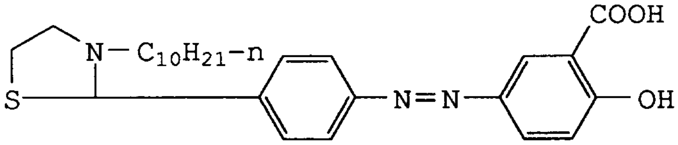

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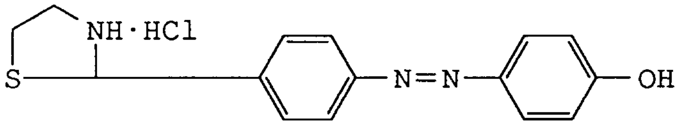

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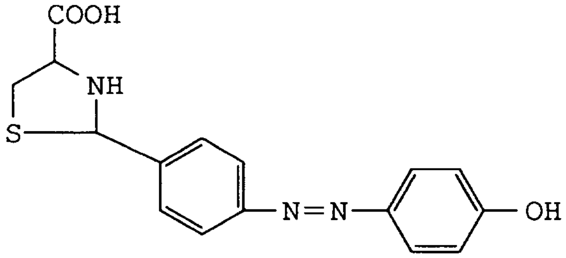

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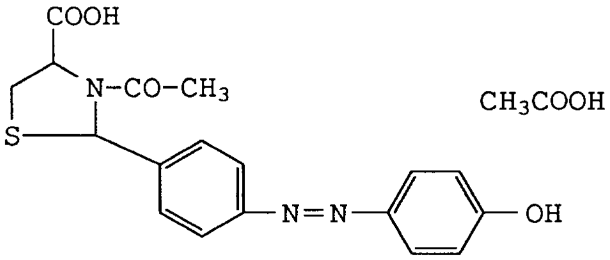
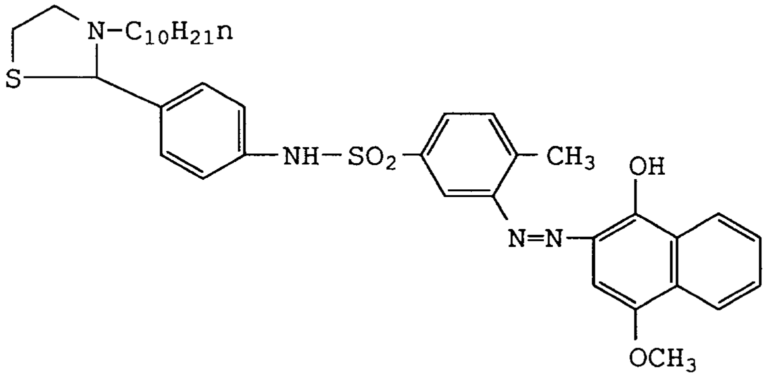
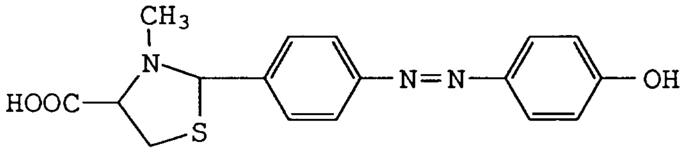

COOH
N-CO-CH3
S
CH3COOH
N=N
OH

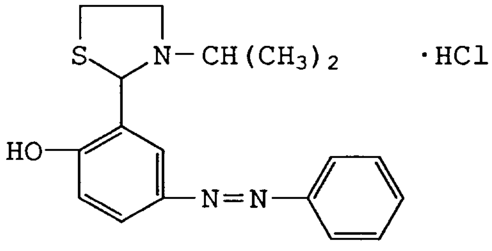
(14)


N-C10H21n
S
NH-SO2
CH3
OH
N=N
OCH3

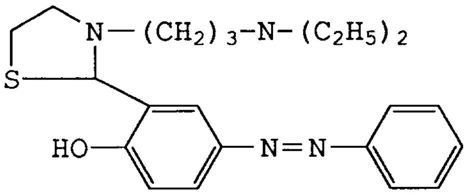
(15)


CH3
N
HOOC
S
N=N
OH

(16)


S
N-CH(CH3)2
·HCl
HO
N=N

(17)



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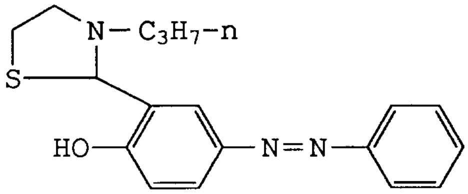

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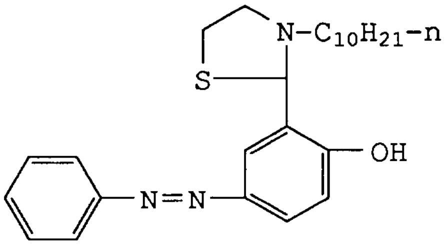

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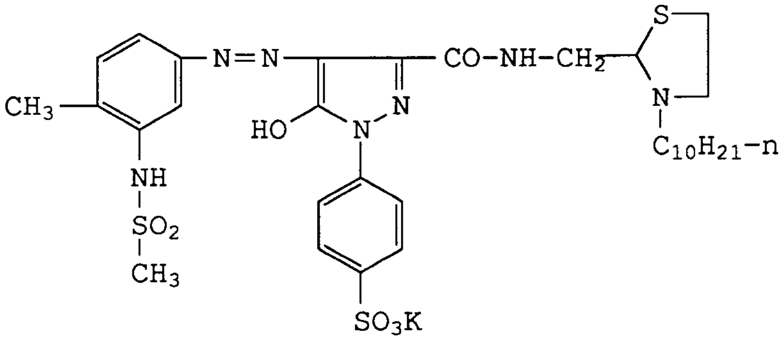

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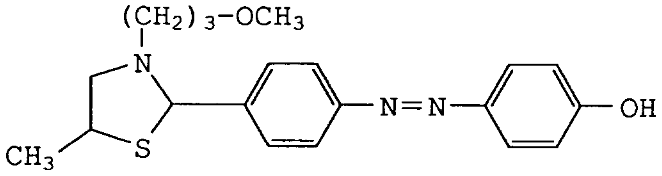

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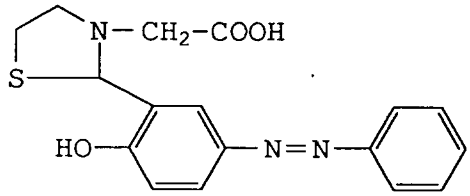

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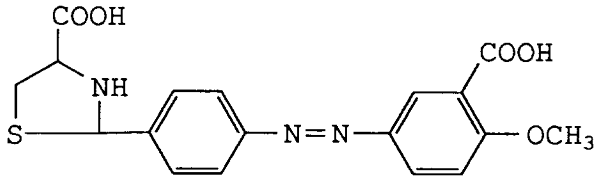

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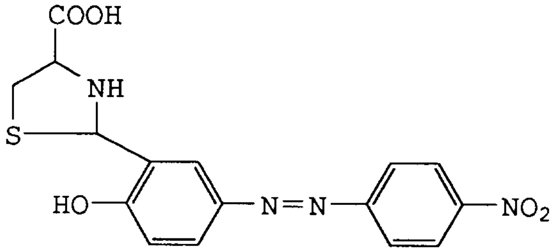

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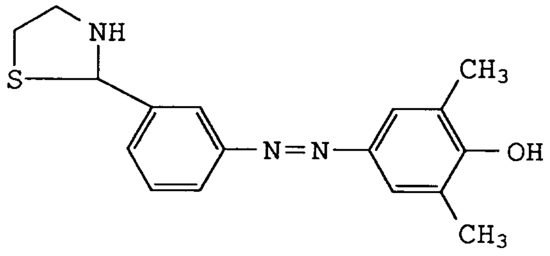

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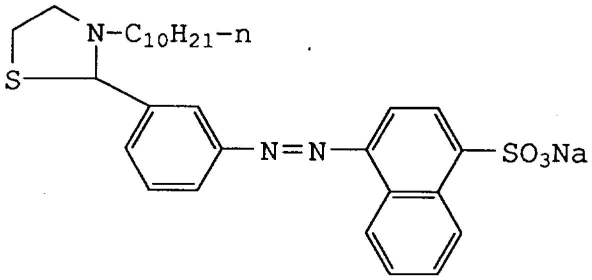

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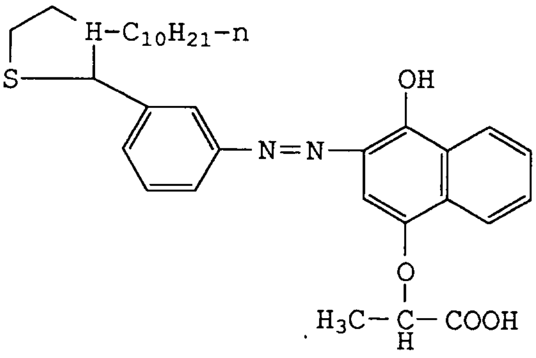

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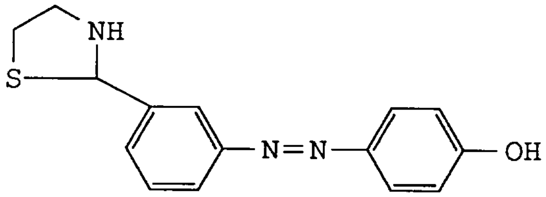

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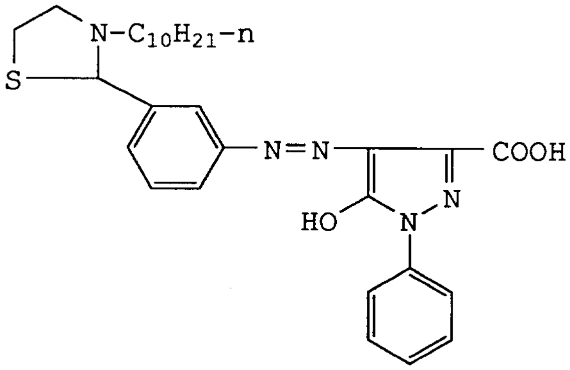

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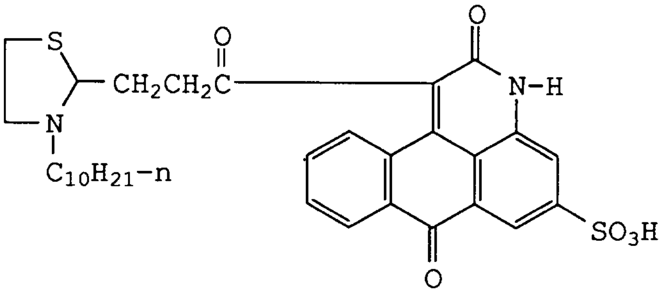

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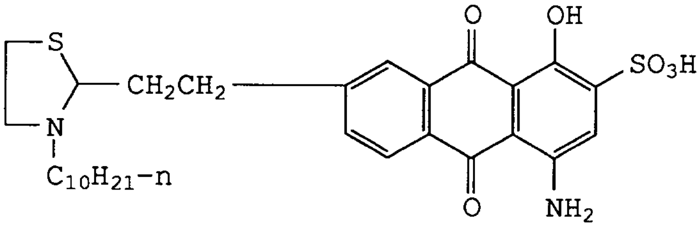

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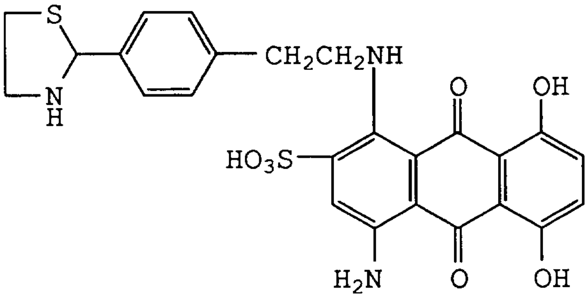

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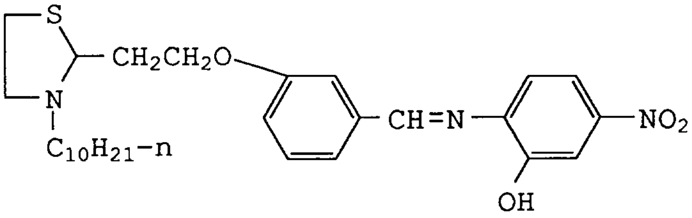

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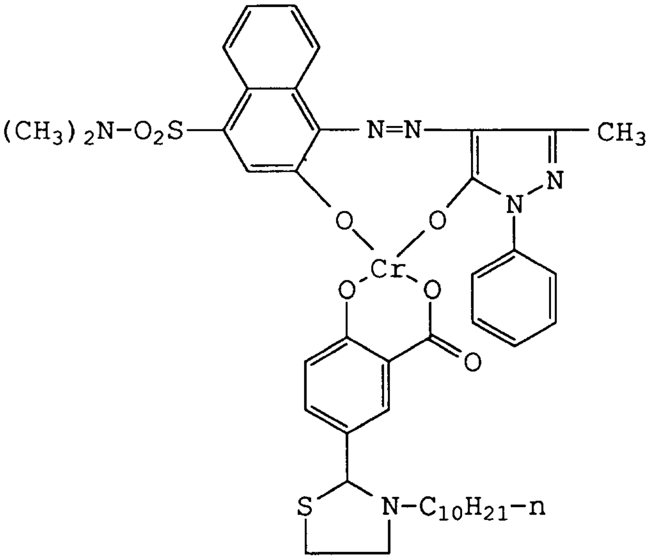

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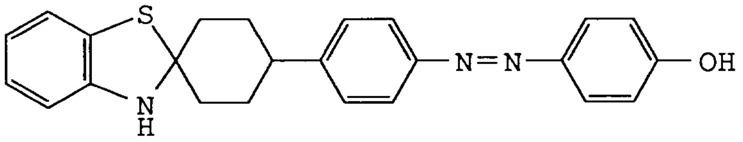
S
N
H
N=N
OH

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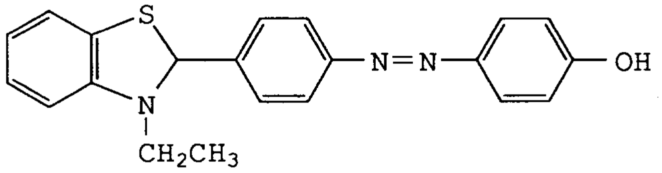
S
N
CH2CH3
N=N
OH

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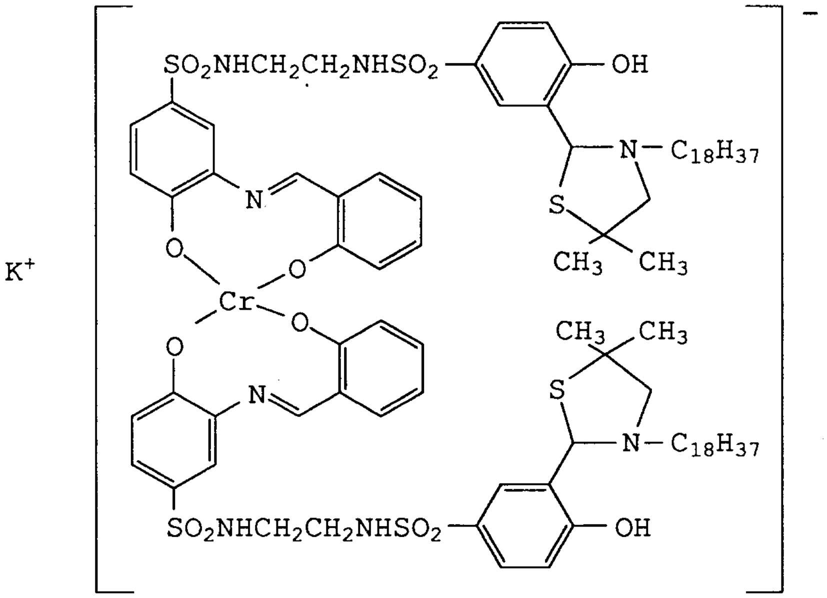
K+
SO2NHCH2CH2NHSO2
OH
N
C18H37
S
CH3
CH3
O
Cr
O
N
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OH

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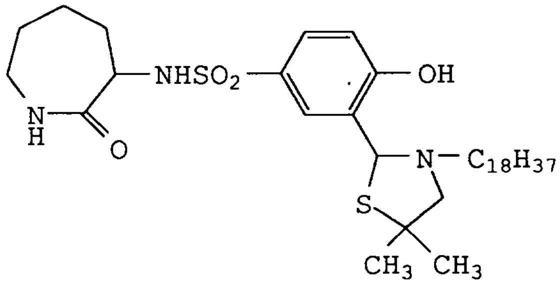

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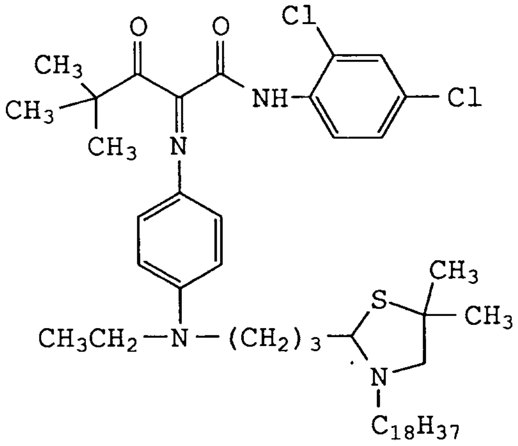

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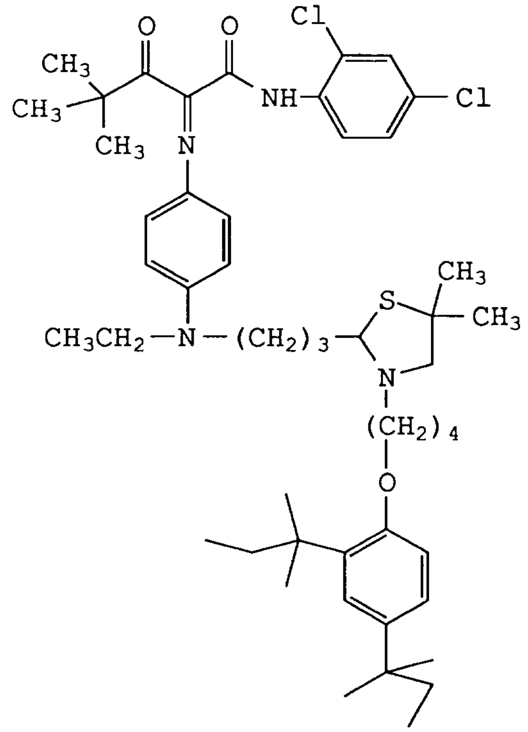

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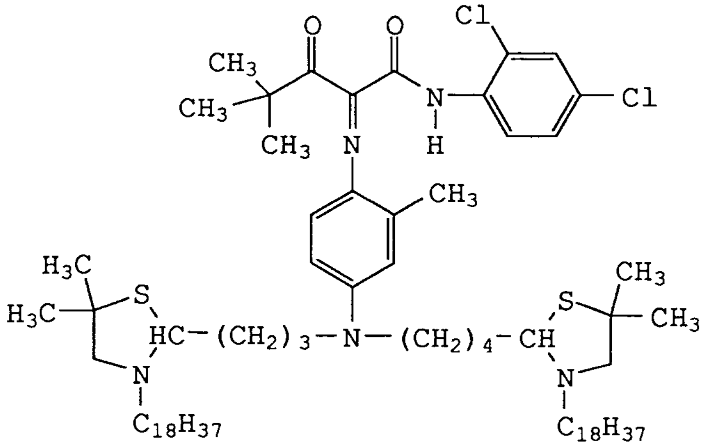

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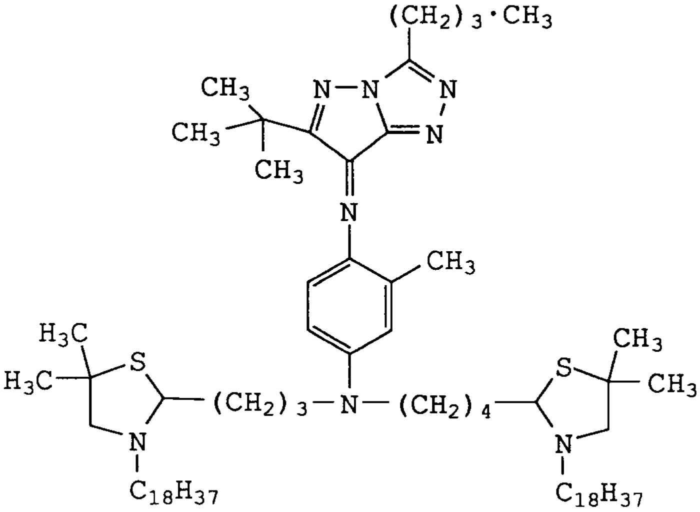

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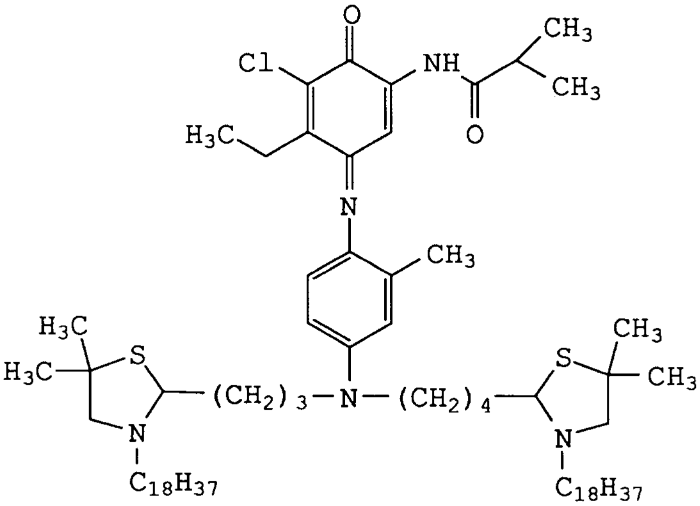

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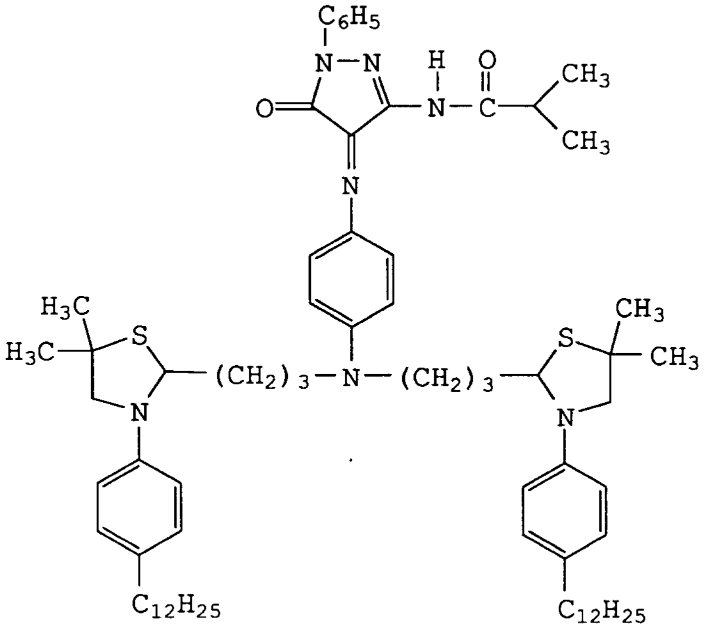

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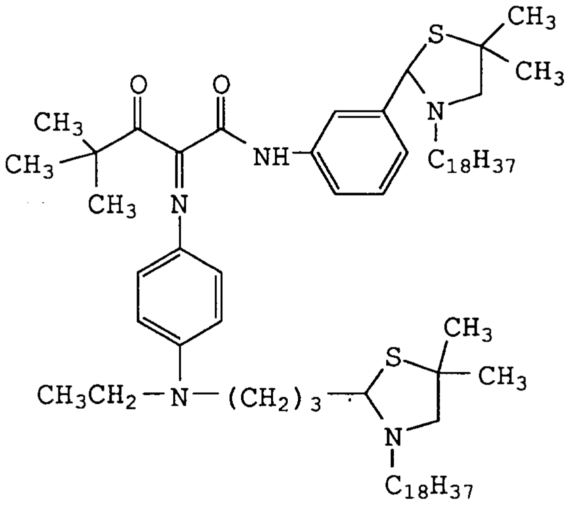

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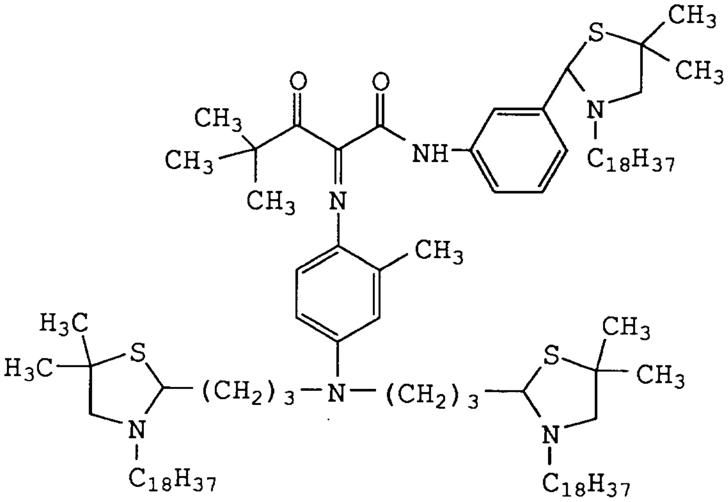

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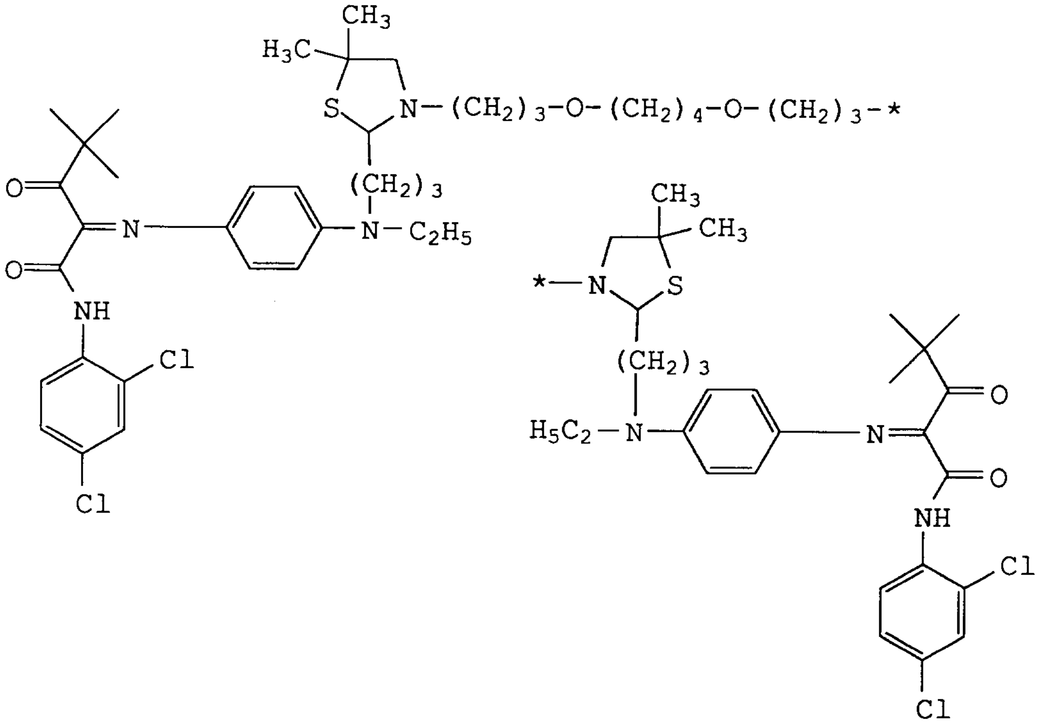

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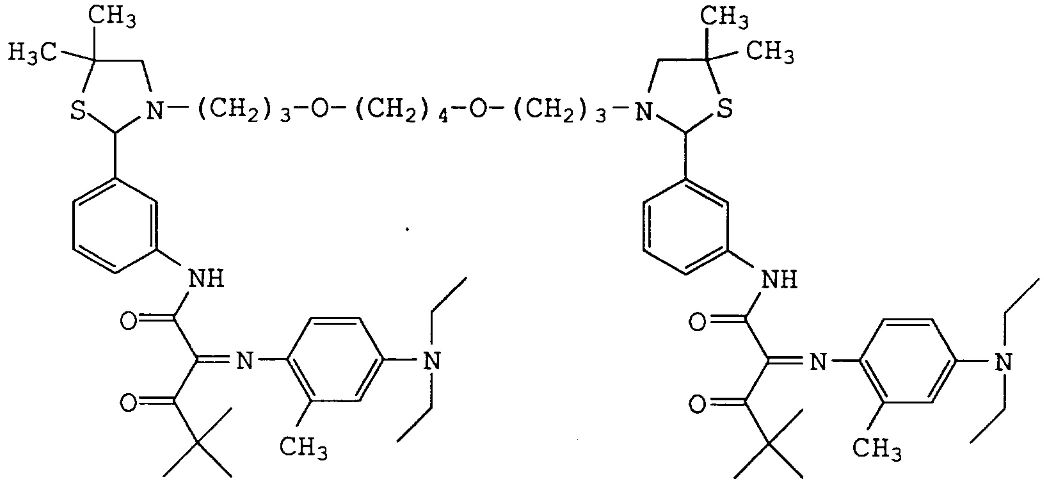

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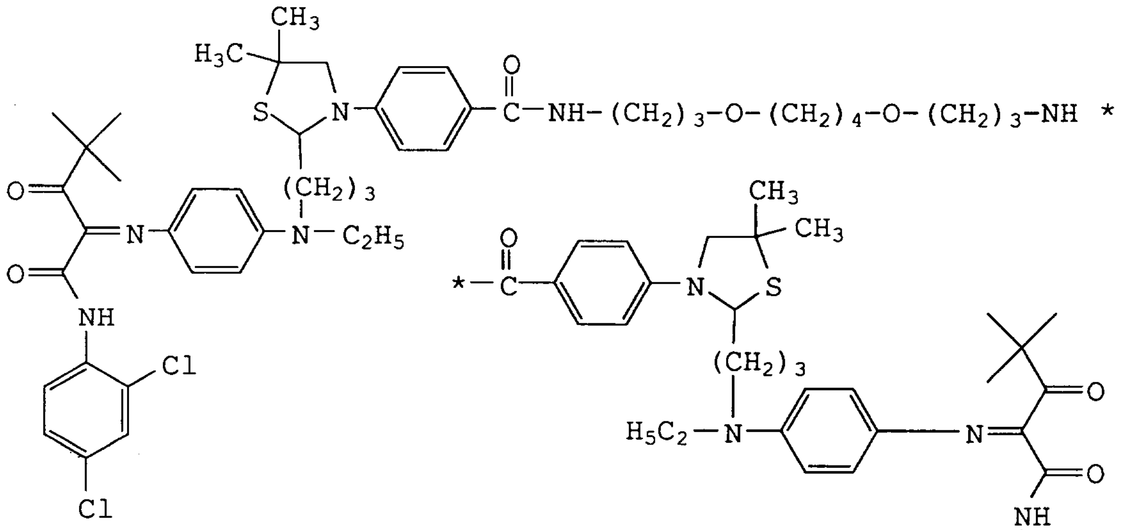

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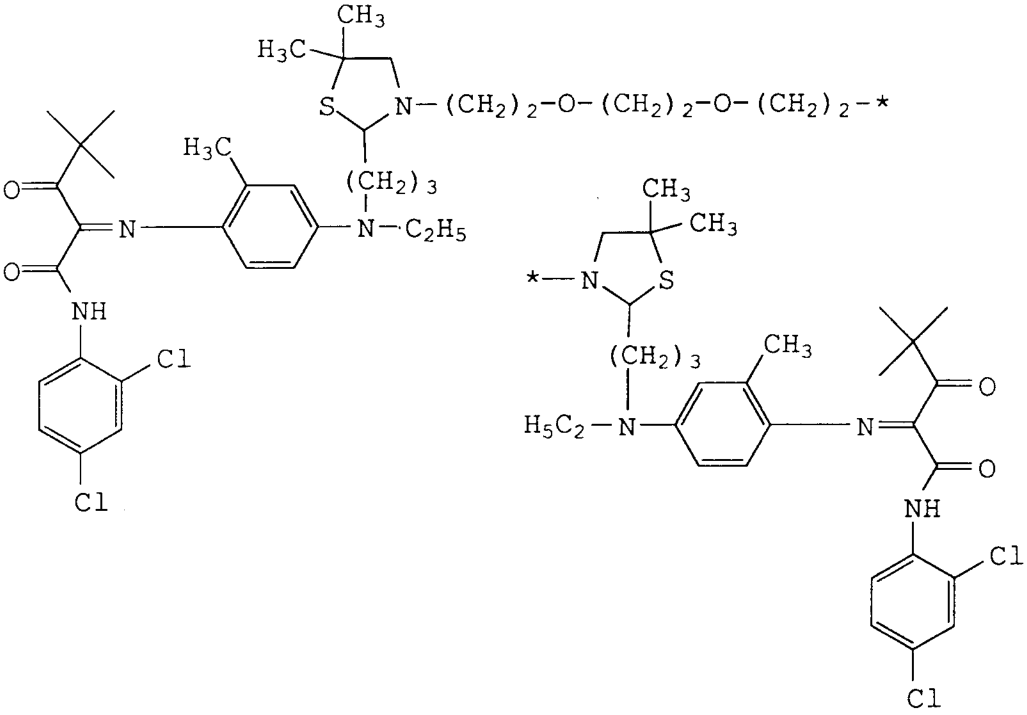

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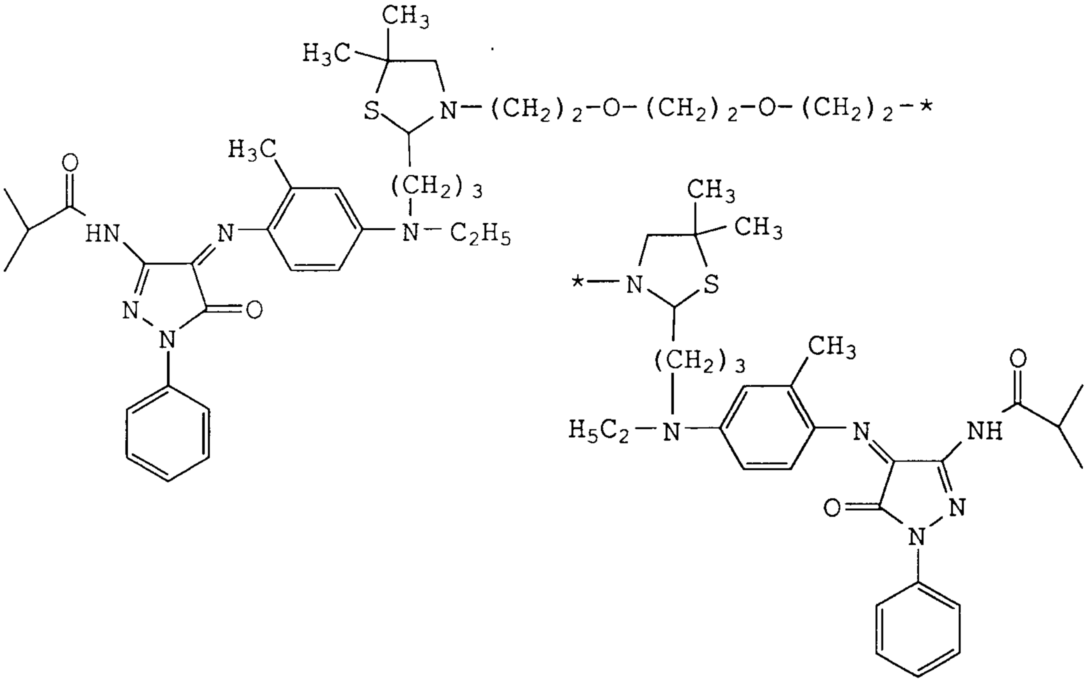

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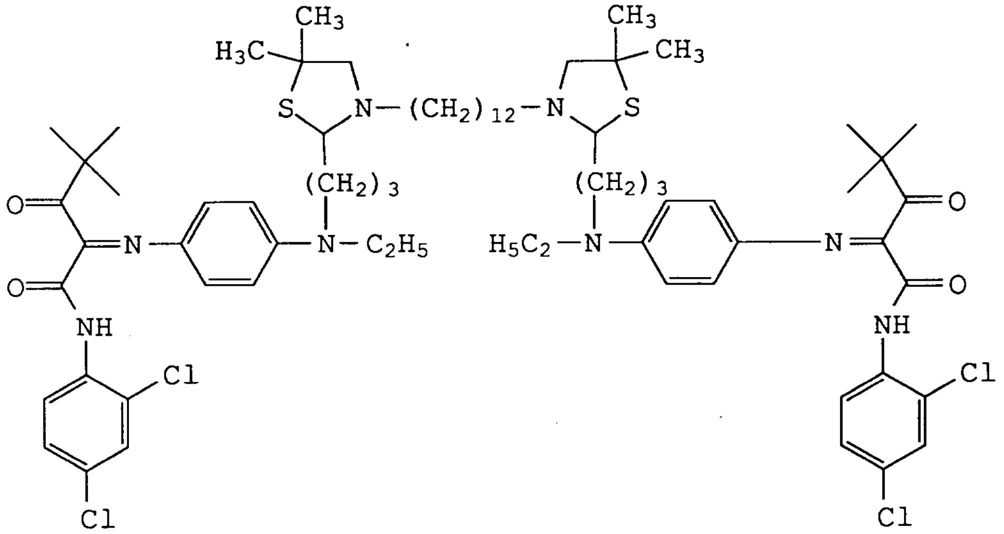
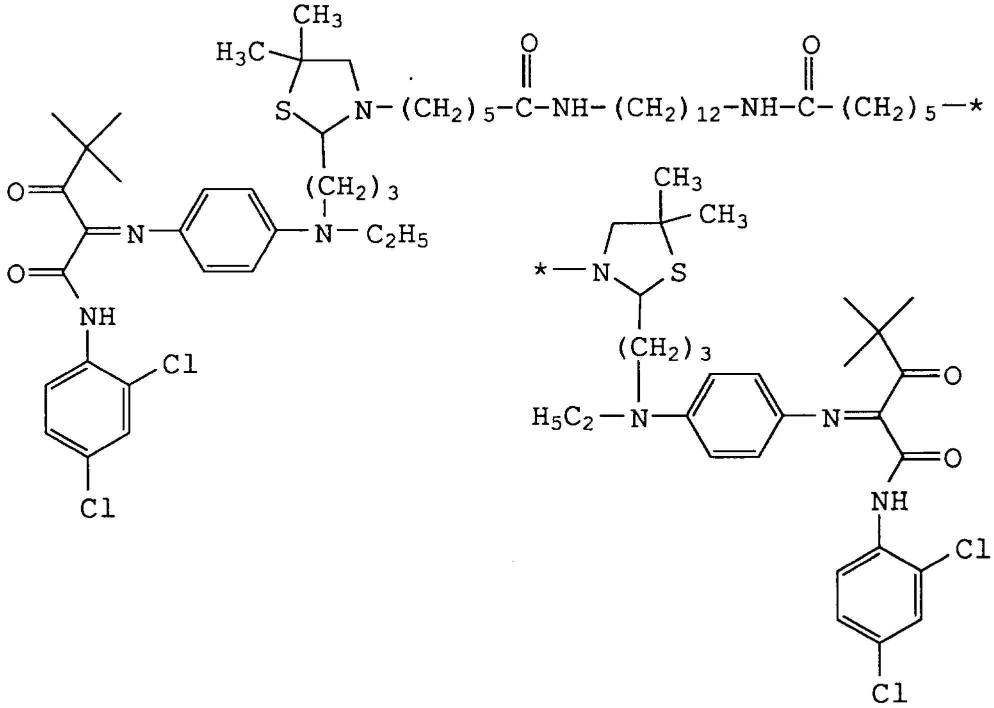
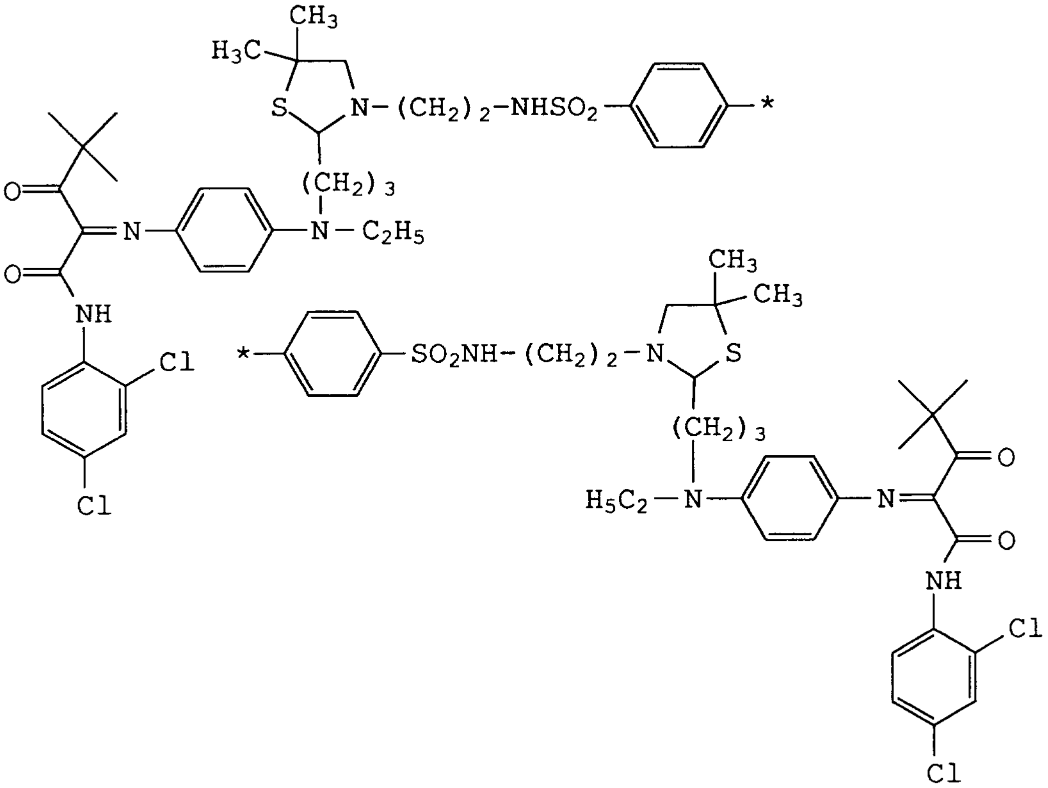

CH3
H3C
S
N
(CH2)12
N
S
CH3
CH3
(CH2)3
(CH2)3
O
O
N
N
C2H5
H5C2
N
N
O
O
NH
NH
Cl
Cl
Cl
Cl

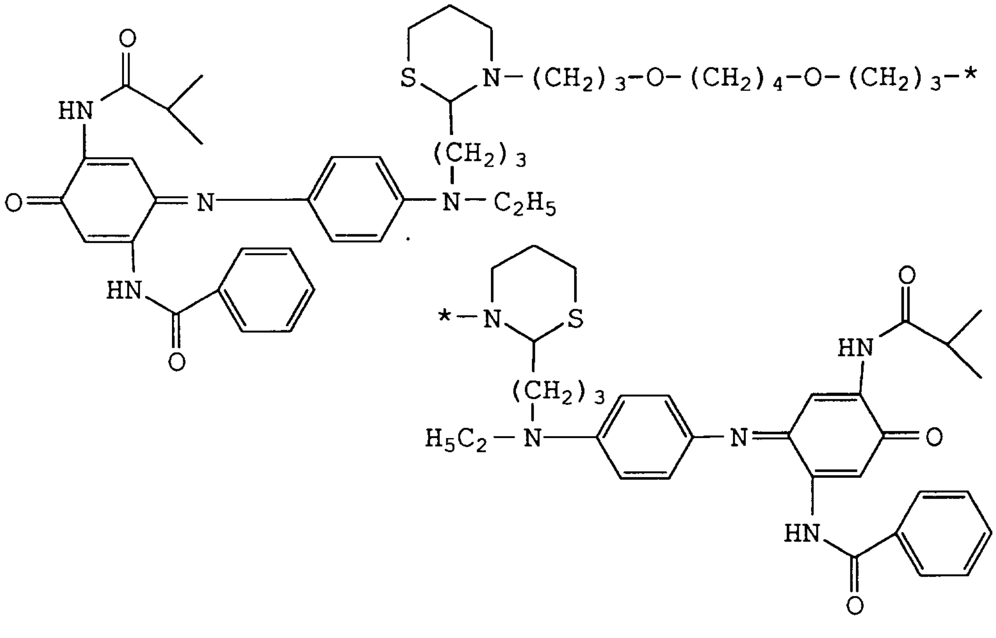
(53)


CH3
H3C
S
N
(CH2)5
C
NH
(CH2)12
NH
C
(CH2)5
O
O
*
(CH2)3
N
C2H5
O
O
N
NH
Cl
Cl
CH3
CH3
*
N
S
(CH2)3
H5C2
N
N
O
O
NH
Cl
Cl

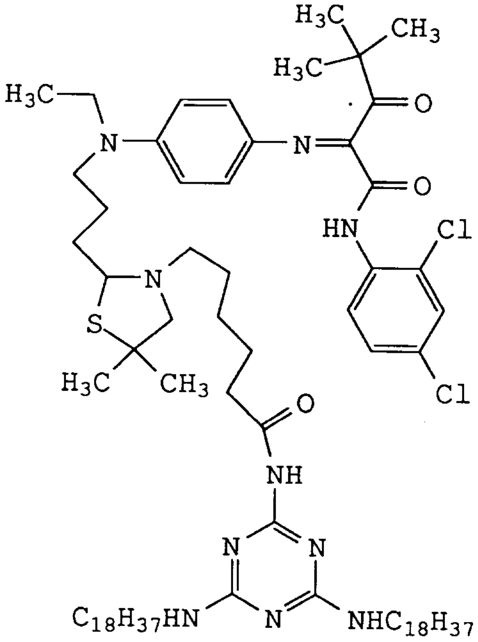
(54)


CH3
H3C
S
N-(CH2)2-NHSO2
*
(CH2)3
O
N
N-C2H5
O
NH
Cl
Cl
CH3
CH3
*
SO2NH-(CH2)2-N
S
(CH2)3
O
H5C2-N
N
O
NH
Cl
Cl

(55)


O
HN
S
N-(CH2)3-O-(CH2)4-O-(CH2)3-*
(CH2)3
O
N
N-C2H5
HN
O
*-N
S
O
HN
(CH2)3
H5C2-N
N
O
HN
O

(56)


H3C
CH3
H3C
O
H3C
N
N
O
HN
Cl
N
S
H3C
CH3
Cl
O
NH
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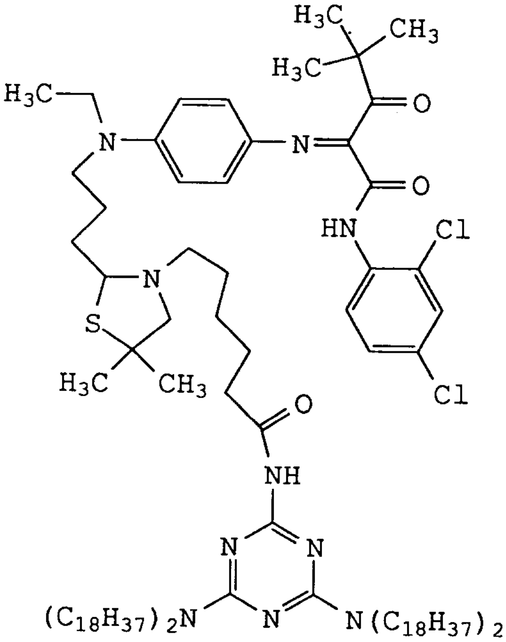
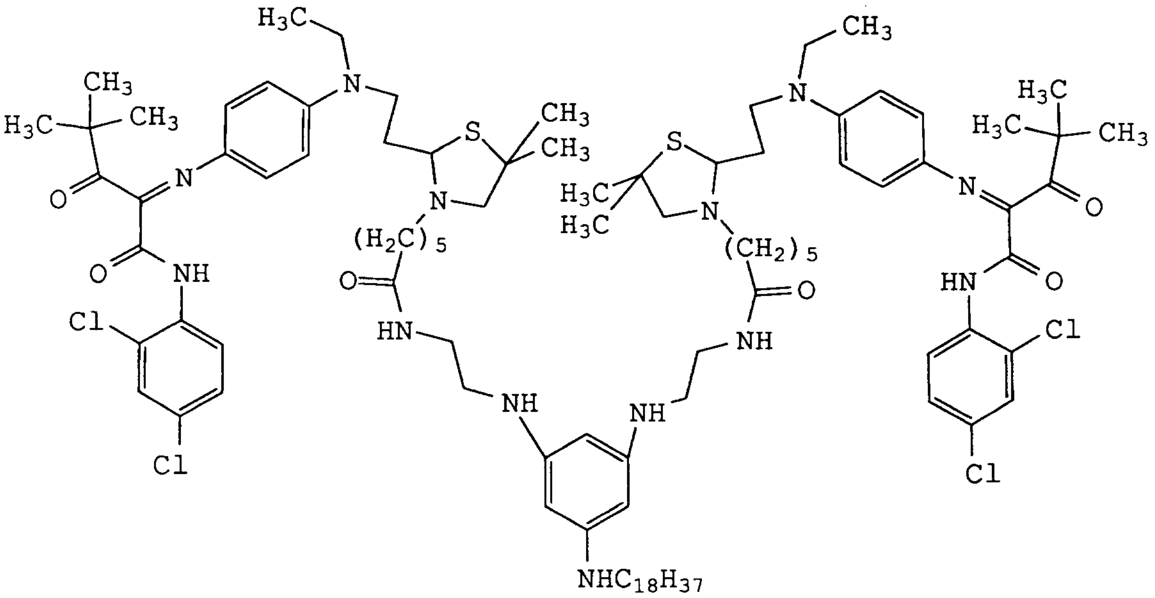
N
NHC18H37

(57)


H3C
CH3
H3C
O
H3C
N
N
O
HN
Cl
N
S
H3C
CH3
Cl
O
NH
N
N
(C18H37)2N
N
N(C18H37)2

(58)



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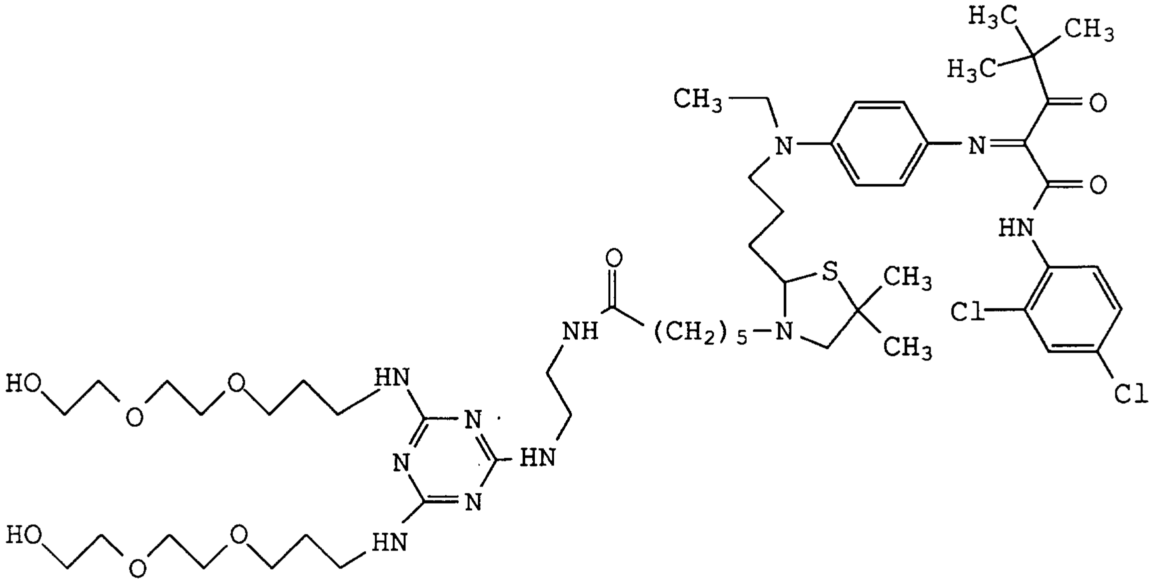

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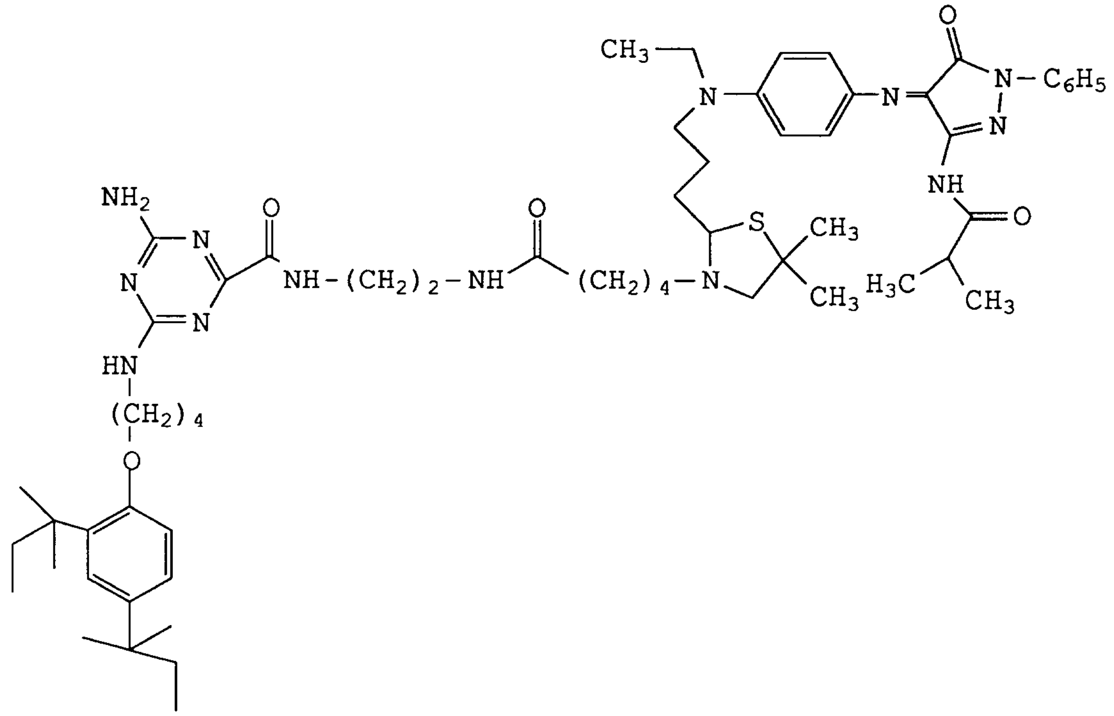
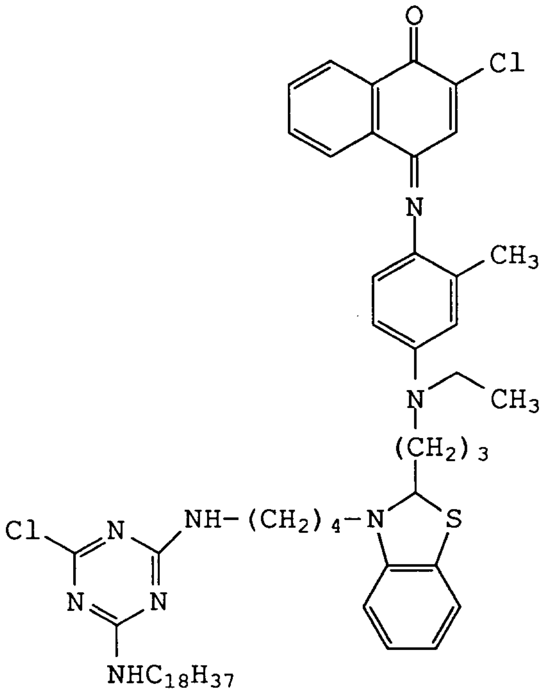
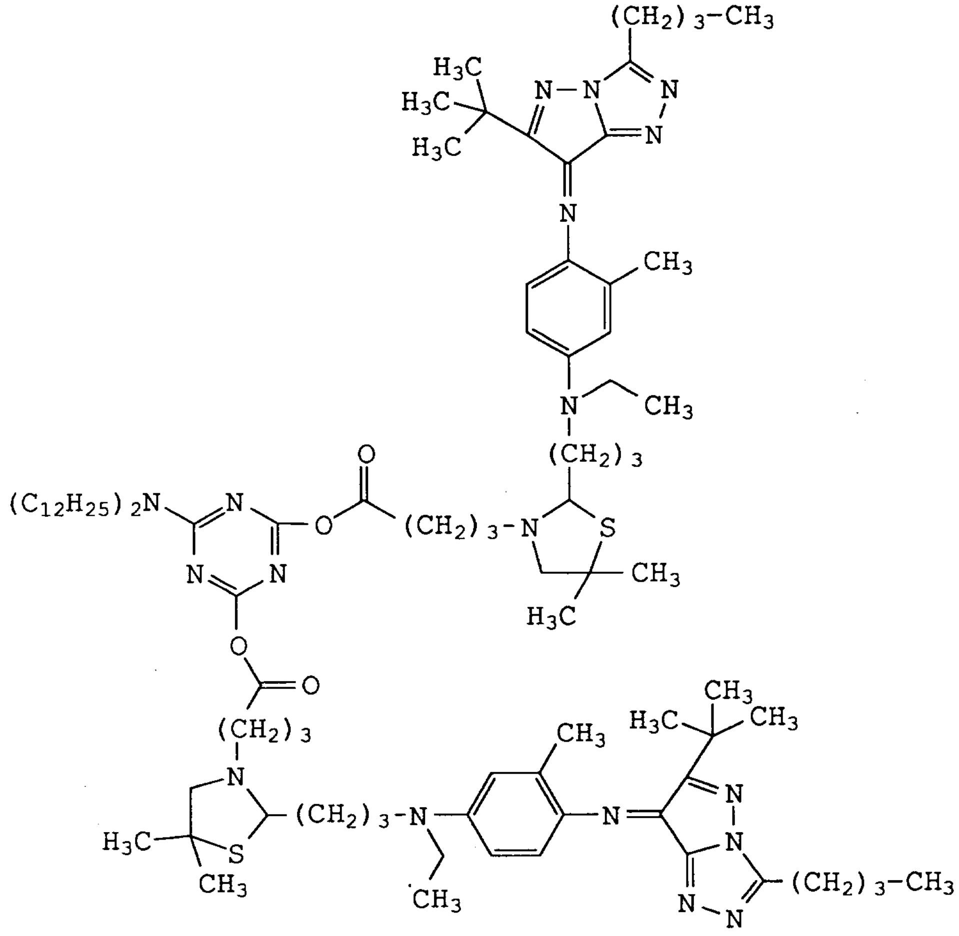

CH3
N
N
O
N
C6H5
N
NH
O
H3C
CH3
NH2
N
N
N
O
NH-(CH2)2-NH
O
(CH2)4
N
S
CH3
CH3
HN
(CH2)4
O

(61)


O
Cl
N
CH3
N
CH3
(CH2)3
Cl
N
NH-(CH2)4-N
S
N
N
NHC18H37

(62)



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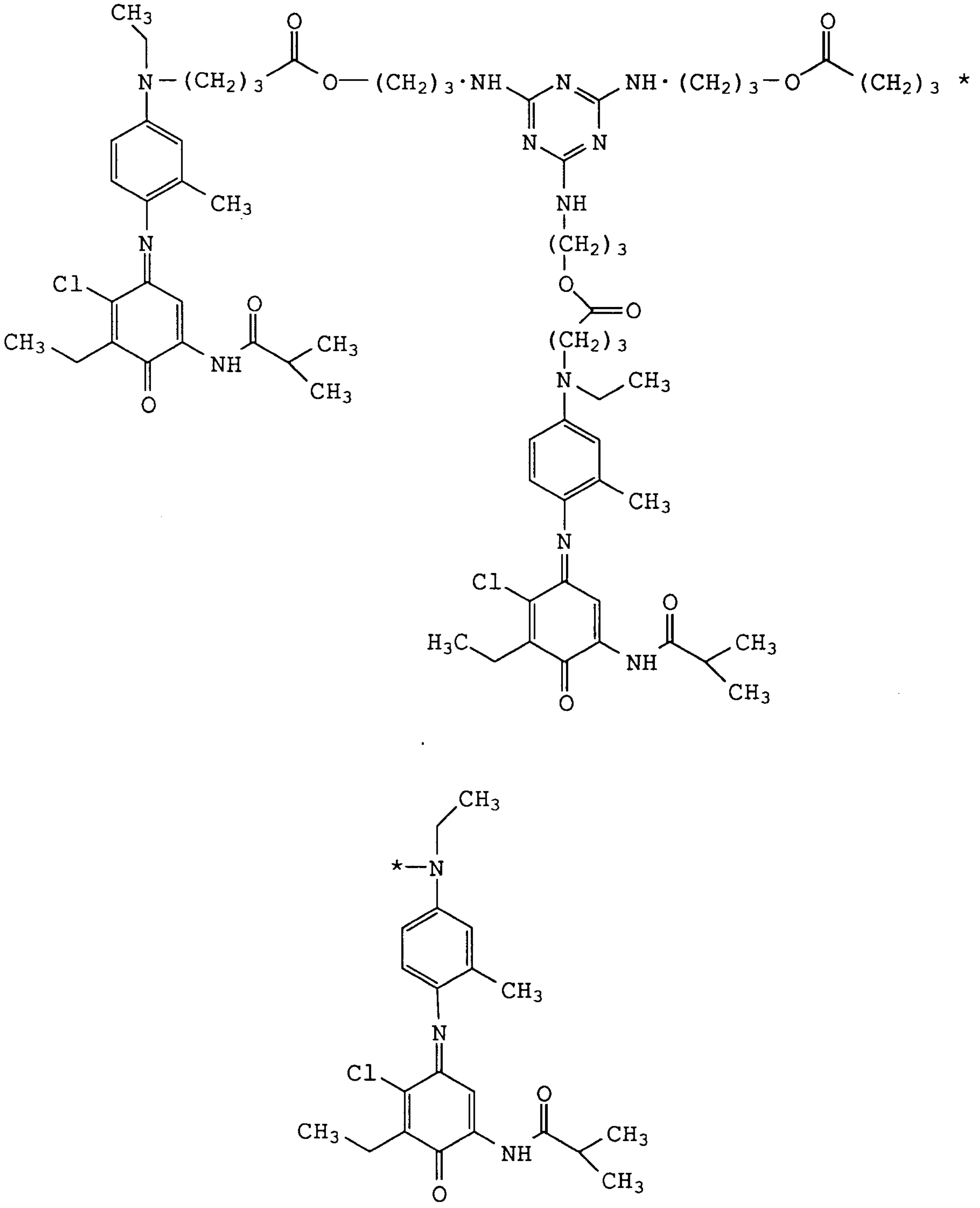

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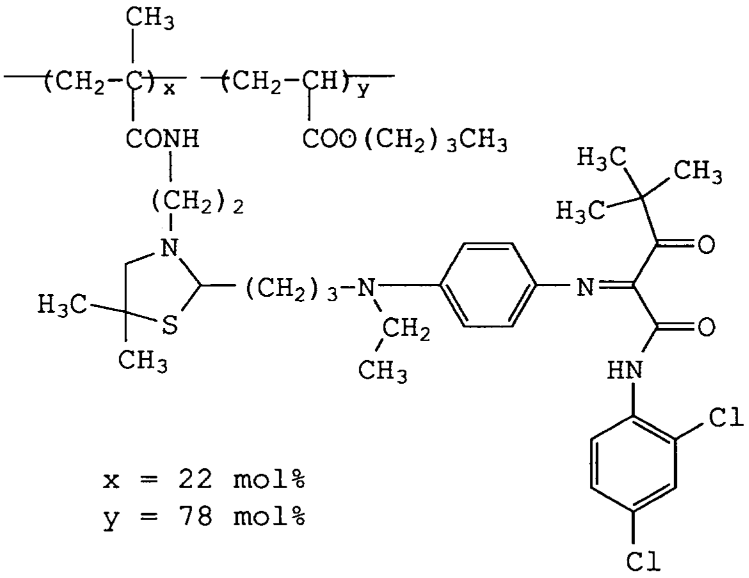
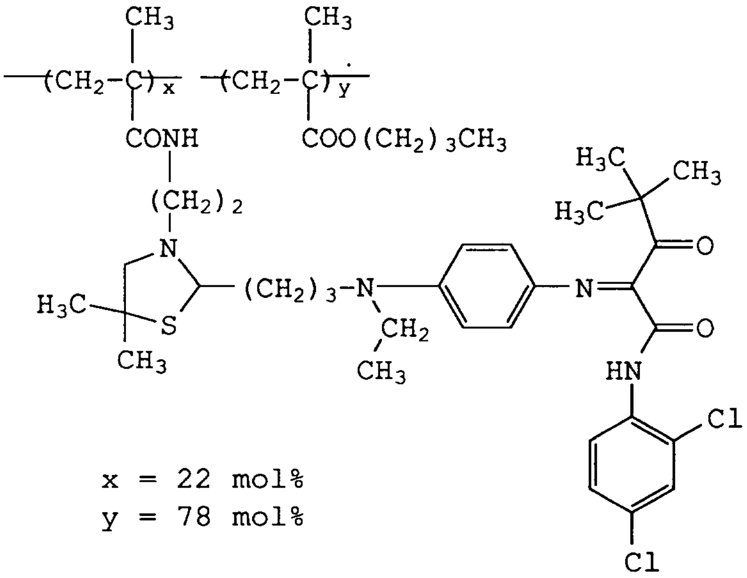


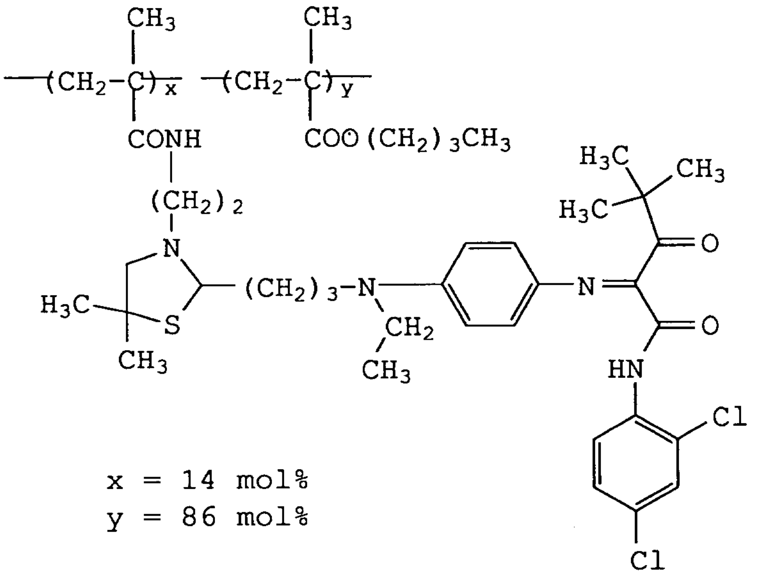
x = 22 mol%
y = 78 mol%

(65)



x = 22 mol%
y = 78 mol%

(66)



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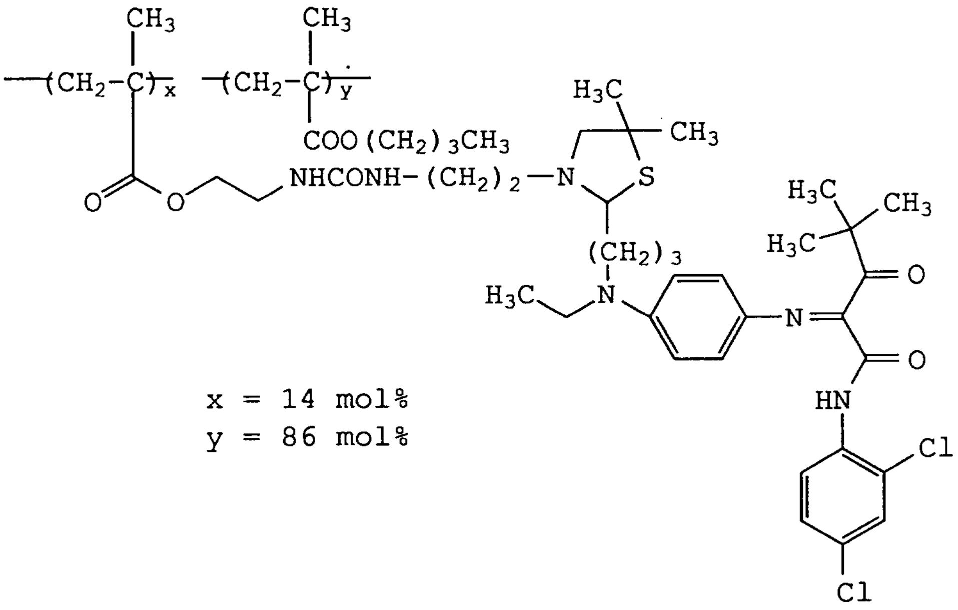


Known organic silver salts can be added to the recording material of the present invention.

Examples of organic silver salts which can be used for the present invention include the silver salts of long-chain aliphatic carboxylic acid and silver salts of carboxylic acid having a heterocyclic ring, such as silver laurate, silver myrystate, silver palmitate, silver stearate, silver arachidonate, silver behenate and silver α-(1-phenyltetrazolethio)acetate, and the silver salts of aromatic carboxylic acid such as silver benzoate and silver phthalate, described in Japanese Patent Examined Publication No. 4921/1968, Japanese Patent O.P.I. Publication Nos. 52626/1974, 141222/1977, 36224/1978 and 37610/1978, and US Patent Nos. 3,330,633, 3,794,496 and 4,105,451, and the silver salts of compounds having an imino group described in Japanese Patent Examined Publication Nos. 26582/1969, 12700/1970, 18416/1970 and 22185/1970, Japanese Patent O.P.I. Publication Nos. 137321/1977, 118638/1983 and 118639/1983, and US Patent No. 4,123,274.

Examples of silver salts having an imino group include benzotriazole silver, which may be substituted or not. Typical examples of substituted benzotriazole silver include alkyl-substituted benzotriazole silver, alkylamidobenzotriazole silver, alkylsulfamoylbenzotriazole silver, halogen-substituted benzotriazole silver salts, alkoxybenzotriazole silver, 5-nitrobenzotriazole silver, 5-aminobenzotriazole silver, 4-hydroxybenzotriazole silver, 5-carboxybenzotriazole silver, 4-sulfobenzotriazole silver and 5-sulfobenzotriazole silver.

Examples of other silver salts having an imino group include imidazole silver, benzimidazole silver, 2-methylbenzimidazole silver, 6-nitrobenzimidazole silver, pyrazole silver, urazol silver, 1,2,4-triazole silver, 1H-tetrazole silver, 3-amino-5-benzylthio-1,2,4-triazole silver, saccharin silver, phthalazinone silver and phthalimide silver, and silver salts of mercapto compound such as 2-mercaptobenzoxazole silver, mercaptooxadiazole silver, 2-mercaptobenzothiazole silver, 2-mercaptobenzimidazole silver, 3-mercapto-4-phenyl-1,2,4-triazole silver, 1-phenyl-5-mercaptotetrazole silver, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene silver and 5-methyl-7-hydroxy-1,2,2,4,6-pentazaindene silver.

Examples also include the silver salts of carboxylic acid which decarboxylate at high temperatures described in Japanese Patent O.P.I. Publication No. 211454/1985 and the silver salts of acetylene derivative described in Japanese Patent O.P.I. Publication Nos. 226744/1986 and 231542/1986.

Silver complex compounds having a stability constant of 4.5 to 10.0 as described in Japanese Patent O.P.I. Publication No. 31728/1977 and silver salts of imidazolinethione as described in US Patent No. 4,168,980 can also be used.

Of the organic silver salts mentioned above, silver salts of compounds having an imino group, particularly silver salts of benzotriazole derivatives are preferred, with more preference given to silver salts of benzotriazole, 5-methylbenzotriazole and derivatives thereof, sulfobenzotriazole and N-alkylsulfamoylbenzotriazole.

Other known organic silver salts can be used in the recording material of the present invention.

The organic silver salts described above may be used singly or in combination. They may be used as such after removing soluble salts in an aqueous solution of hydrophilic colloid such as gelatin, or may be used as fine grains of solid obtained by mechanical pulverization and dispersion of the organic silver salt after its isolation. The amount of organic silver salt used is normally 0.01 to 20 g, preferably 0.1 to 5 g per m^2 of recording material.

For the purpose of acceleration of the reaction of 1,3-sulfur-nitrogen-containing compound and organic silver salt taking place upon heating, promotion of the transfer of the dye formed and other purposes, it is preferable to add a thermal solvent (hot melting substance) to the recording material of the present invention. The thermal solvent is a compound which liquifies upon heating and acts to accelerate the image formation. It is preferably in a solid state at normal temperature, and its melting point is preferably 70 to 170 °C. For use for the present invention, the thermal solvent preferably has the following nature.

Occurs as a white solid at normal temperature and becomes colorless and transparent upon melting.

The heating volatility is minimum.

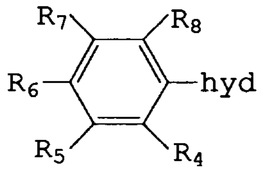
Examples of thermal solvents which can be used for the present invention include the compounds described in US Patent Nos. 3,347,675, 3,438,776, 3,666,477 and 3,667,959, RD No. 17643 and Japanese Patent O.P.I. Publication Nos. 19525/1976, 24829/1978, 60223/1978, 118640/1983, 198038/1983, 68730/1984, 84236/1984, 229556/1984, 14241/1985, 191251/1985, 232547/1985, 52643/1986, 42153/1987, 44737/1987, 78554/1987, 136645/1987, 139545/1987, 53548/1988, 161446/1988, 224751/1989, 227150/1989, 863/1990, 120739/1990 and 123354/1990.

Thermal solvents which are preferably used in the recording material of the present invention are described below.

The thermal solvent preferably has an i/o value of not less than 0.5 and not more than 4. Here, the i/o value indicates the degree of organicity or inorganicity of compounds, calculated by the method described in "Kagaku no Ryoiki", vol. 11, pp. 719-725 (1957), published by Nankodo Shuppan.

Compounds which are more preferably used as thermal solvents for the present invention are represented by the following formula 2.

Formula 2



wherein hyd represents a group whose π value is -0.9 to -1.9 (π value is a parameter indicating hydrophobicity; the values used were obtained from "Kagaku no Ryoiki", supple. No. 122, "Yakubutsu no Kozo Kassei Sokan" (Nankodo), pp. 96-103.

Examples of groups preferred for hyd include $-NHCOCH_3$, $-CH_2OH$, $-NHSO_2CH_3$, $-CONHCH_3$, $-NHCONH_2$, $-CONH_2$, $-NHCSNH_2$, $-SO_2CH_3$, $-CH_2CONH_2$, $-SO_2NH_2$; $-OCONH_2$, $-OCH_2CONH_2$ and $-N(SO_2CH_3)_2$.

R_4 through R_8 in Formula 2 can be selected according to the hyd group so that the i/o value of the compound falls in the range from 1 to 3. Examples of R_4 through R_8 include hydrogen atoms, and alkyl groups, aryl groups, alkoxy groups, aryloxy groups, alkoxycarbonyl groups, acyloxy groups and halogen atoms which may have various substituents.

Of the compounds represented by Formula 2, thermal solvents which are solid at room temperature and sparingly water-soluble are preferred.

Examples of thermal solvents which can be used for the present invention, with their i/o values, are given below, but these are not to be construed as limitative.

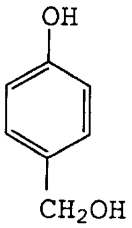
TS-1

$HOCH_2C(CH_3)_2CH_2OH$

TS-2

$HOCH_2C(CH_2)_4CH_2OH$

TS-3



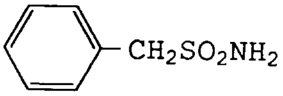
i/o=1.5

TS-4

$H_2NCOCH_2C(CH_3)_2C(CH_3)_3$

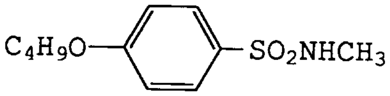
i/o=1.4

TS-5



i/o=1.8

TS-6



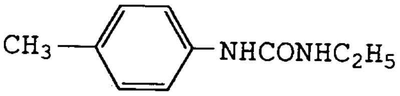
i/o=1.25

TS-7

$C_2H_5NHCONHC_2H_5$

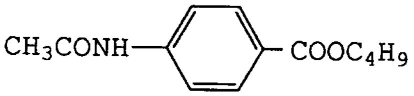
i/o=2.2

TS-8



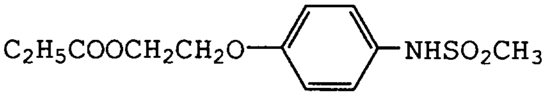
i/o=1.2

TS-9



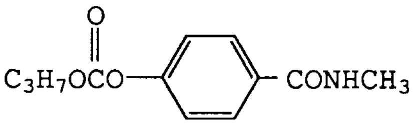
i/o=1.1

TS-10



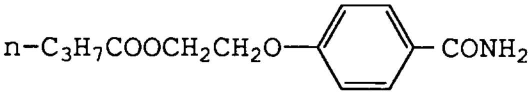
i/o=1.4

TS-11



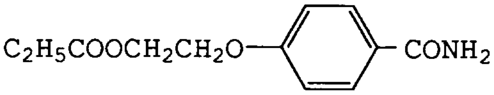
i/o=1.2

TS-12



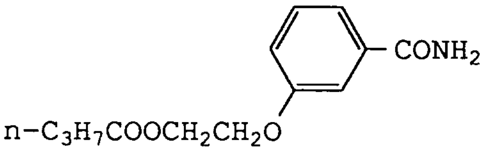
i/o=1.1

TS-13



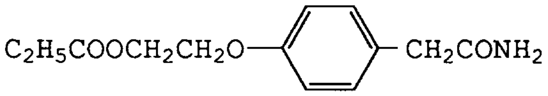
i/o=1.2

TS-14



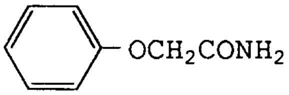
i/o=1.1

TS-15



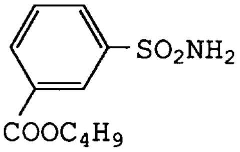
i/o=1.1

TS-16



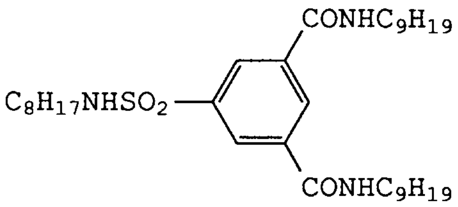
i/o=1.5

TS-17



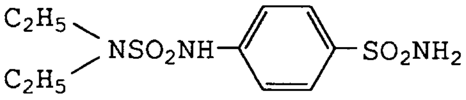
i/o=1.4

TS-18



i/o=1.0

TS-19



i/o=2.5

TS-20

$CH_3NHCONHCH_3$

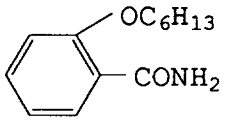
i/o=3.7

TS-21

$C_2H_5CONH_2$

i/o=3.3

TS-22



i/o=0.9

The compounds which are most preferably used as thermal solvents for the present invention are the thermal solvents whose i/O value falls in the range from 0.8 to 3, which are solid at room temperature and sparingly water-soluble, specifically TS-10, TS-11, TS-12, TS-13 and TS-14.

When added to a recording material comprising a plurality of layers, these thermal solvents may be added to any structural layer. The thermal solvent for the present invention is added at ratios of preferably 10 to 500% by weight, more preferably 20 to 250% by weight of the total amount of binder in the recording material. The thermal solvent of the present invention is added preferably as a suspension of fine particles in an aqueous colloidal medium using a ball mill, sand mill or another means.

The thermal solvents for the present invention may be used in combination of two or more kinds.

The recording material of the present invention is embodied by coating on a support a composition comprising a 1,3-sulfur-nitrogen-containing compound, an organic silver salt and a thermal solvent along with a binder.

When using the recording material of the present invention as a thermal recording material, the desired compound can be formed by heating the coating product using a thermal head or a condensed laser beam or the like to cause reaction between a 1,3-sulfur-nitrogen-containing compound above and silver ion at the heated portion.

Imagewise heating makes imagewise formation of the desired compound possible. For example, introducing a dye or a group capable of becoming a dye intermediate to a substituent makes imagewise distribution of the dye. In short, a dye image can be formed, which has a potential for application to a thermal image forming material.

The recording material of the present invention can be embodied as a thermal transfer recording material when the 1,3-sulfur-nitrogen-containing compound of the present invention is a non-diffusible dye and the product of reaction with organic silver salt is a diffusible dye.

The thermal transfer recording material of the present invention comprises a support and a thermal transfer layer formed thereon which contains the composition of the present invention. The 1,3-sulfur-nitrogen-containing compound content in the thermal transfer layer is preferably 0.05 to 10 g per m^2 of support.

The thermal transfer layer can be formed by dissolving in a solvent one or more kinds of the 1,3-sulfur-nitrogen-containing compound of the present invention along with a binder or dispersing them in a dispersant in the form of fine grains to yield an ink solution for thermal transfer layer formation, and coating and drying the ink on the support. The dry thickness of the thermal transfer layer is preferably 0.1 to 10 μm.

Examples of preferred binders include solvent-soluble polymers such as acrylic resin, methacrylic resin, polystyrene, polycarbonate, polysulfone, polyether sulfone, polyvinylbutyral, polyvinylacetal, nitrocellulose and ethyl cellulose. These binders may be used singly or in combination, and may be used in dispersion in latex as well as in solution in organic solvent.

The amount of binder used is preferably 0.1 to 20 g per m^2 of support. Examples of such organic solvents include alcohols such as ethanol and propanol, cellosolves such as methyl cellosolve, aromatic compounds such as toluene and xylene, esters such as acetates, ketones such as acetone and methyl ethyl ketone and ethers such as tetrahydrofuran and dioxane.

Any material can be used for the support, as long as it is dimensionally stable and endures heating by thermal head etc. upon recording. Examples of preferred materials include thin papers such as condenser paper and glassine paper, and heat stable plastic films such as those of polyethylene terephthalate, polyamide and polycarbonate. The thickness of the support is preferably 2 to 30 μm, and the support preferably has a subbing layer comprising a polymer selected for the purpose of improving the binder adhesion and preventing dye transfer and deposition on the support. Moreover, the back face (the side opposite to the thermal transfer layer) of the support may have a slipping layer for the prevention of head cohesion to the support.

For applying the thermal transfer recording material relating to the present invention to a thermal recording material permitting full-color image recording, it is preferable to repeatedly coat on a support a total of three layers, namely a magenta thermal transfer layer containing a magenta image forming thermally-diffusible dye, a cyan thermal transfer layer containing a cyan image forming thermally-diffusible dye and a yellow thermal transfer layer containing a yellow image forming thermally-diffusible dye. A total of four layers, namely a thermal transfer layer containing a black image forming substance and the three layers described above may be repeatedly coated on the same surface.

On the other hand, the recording material of the present invention is embodied as a light-sensitive thermal recording material by adding a light-sensitive-containing material to a composition comprising a 1,3-sulfur-nitrogen-containing compound, an organic silver salt and a thermal solvent and coating the mixture along with a binder on the support. In such a material, image recording is achieved optically, wherein images are formed upon uniform heating. This type of materials are referred to as heat developable light-sensitive materials.

The heat developable light-sensitive material relating to the present invention is described below.

In the heat developable light-sensitive material relating to the present invention, a light-sensitive silver halide is used as the light-sensitive material.

The organic silver salt described above is reduced with a reducing agent as described below under heating conditions. This reaction is accelerated by so-called latent images formed on the exposed fine grains of silver halide. In other words, in the heat developable light-sensitive material, the organic silver salt undergoes reduction in the exposed portion. Taking place concurrently with this reaction, the reaction of 1,3-sulfur-nitrogen-containing compound and organic silver salt is suppressed in the exposed portion.

Consequently, it is possible to cause the reaction of 1,3-sulfur-nitrogen-containing compound and organic silver salt selectively in the unexposed portion, i.e., reverse-imagewise formation of the desired compound is possible.

This principle is applicable to the formation of positive images, for instance.

When embodying the present invention as a transfer type heat developable light-sensitive material, for instance, dye transfer occurs in the unexposed portion provided that a dye or a group capable of becoming a dye intermediate is introduced to the substituent for the 1,3-sulfur-nitrogen-containing compound and made non-diffusible and allowed to form a diffusible dye or dye intermediate after reaction with organic silver salt, i.e., positive images can be formed.

The compound released in the reverse-imagewise manner is not necessarily a dye; it may be any PUG, such as a developing inhibitor, fogging agent, developing agent, hardener, developing accelerator or brightening agent for controlling the image formed.

Examples of binders which can be used in the heat developable type light-sensitive material of the present invention include the binders described in Japanese Patent O.P.I. Publication No. 863/1990, line 14, upper right column, through line 10, lower left column, page 10, including preferable combinations thereof. More preference is given to gelatin, polyvinyl pyrrolidone and combinations thereof.

With respect to the silver halide reducing agent, dye providing substance and additive, binder support, image receiving material, constituting the heat developable light-sensitive material, exposure and development, any material or means can be used. Examples thereof are given in Japanese Patent Application Nos. 256079/1989 (pp. 14-47) and 158931/1990 (pp. 13-41), filed by the present applicants.

Any known conventional light-sensitive silver halide can be used in the heat developable light-sensitive material of the present invention. Examples of such light-sensitive silver halides include silver chloride, silver bromide, silver iodobromide, silver chlorobromide and silver chloroiodobromide.

The reducing agent used in the heat developable light-sensitive material of the present invention is selected as appropriate out of the known conventional reducing agents in use for heat developable light-sensitive materials according to the developing mechanism and dye formation or release mechanism. The reducing agent referred here includes reducing agent precursors which release a reducing agent upon heat development.

The heat developable light-sensitive material of the present invention is used as a black-and-white or color light-sensitive material. When it is used as a color light-sensitive material, a dye-providing material is used.

Although it is of course possible to use the 1,3-sulfur-nitrogen-containing compound of the present invention as a dye-providing material as stated above, it may be used in combination with other dye-providing materials. The 1,3-sulfur-nitrogen-containing compound may be designed to release a photographically useful compound other than a dye and may be used to form a color image in the presence of other dye-providing materials.

Examples of such dye-providing materials include the diffusible dye forming couplers described in Japanese Patent O.P.I. Publication Nos. 44737/1987, 129852/1987 and 169158/1987 and Japanese Patent Application No. 200859/1989, the leuko dye described in Japanese Patent O.P.I. Publication No. 88254/1986 and the azo dyes used for the heat developable dye bleaching method described in US Patent No. 4,235,957. It is preferable to use a dye-providing material which forms or releases a diffusible dye, with more preference given to a compound which forms a diffusible dye upon coupling reaction.

In addition to the substances described above, the heat developable light-sensitive material of the present invention may incorporate various additives as necessary.

The heat developable light-sensitive material of the present invention contains (a) a 1,3-sulfur-nitrogen-containing compound, (b) an organic silver salt, (c) a reducing agent, and (d) a light-sensitive silver halide. When it is used as a color light-sensitive material, it further contains (e) a dye-providing material, which may be identical to (a) or (c). These substances may be contained in a single photographic component layer or in two or more layers. Specifically, it is possible to add the components (a), (b) and (d) to a single layer and the component (c) to an adjoining layer, or to add (b), (c) and (d) to a single layer and (a) to another layer.

Two or more light-sensitive layers may have substantially the same kind of color sensitivity, which layers may be prepared as low and high speed layers, respectively.

When using the heat developable light-sensitive material of the present invention as a full-color recording material, it usually has three light-sensitive layers with different kinds of color sensitivity, in which respective dyes with different hues are formed or released upon heat development. In this case, it is the common practice that the blue-sensitive layer (B) contains a yellow dye (Y), the green-sensitive layer (G) contains a magenta dye (M) and the red-sensitive layer (R) contains a cyan dye (C), i.e. (B-Y)-(G-M)-(R-C), but the present invention is not limited to these combinations, i.e., any combination is acceptable. Specifically, possible combinations include (B-C)-(G-M)-(R-Y) and (infrared-sensitive layer-C)-(G-Y)-(R-M).

These layers may take any configuration, including the layer configurations of R-G-B, G-R-B, R-G-infrared and G-R-infrared as arranged from the support side.

The heat developable light-sensitive material of the present invention may be provided with non-light-sensitive layers such as subbing layers, interlayers, protective layers, filter layers, backing layers and peeling layers as well as light-sensitive layers.

When using the heat developable light-sensitive material of the present invention for the dye transfer method, it is preferable to use an image receiving material. The image receiving material comprises a support and an image receiving layer capable of dye reception formed thereon, but the support itself may also serve as an image receiving layer with such capability.

The heat developable light-sensitive material of the present invention can be so-called a mono-sheet type heat developable light-sensitive material wherein a light-sensitive layer and an image receiving layer have previously been laminated on the same support as described in RD No. 15108 and Japanese Patent O.P.I. Publication Nos. 198458/1982, 207250/1982 and 80148/1986 and other publications.

The image receiving material for the present invention may incorporate various known additives. Examples of such additives include antistaining agents, UV absorbents, brightening agents, image stabilizers, developing accelerators, antifogging agents, pH regulators (e.g., acids, acid precursors), thermal solvents, organic fluorine compounds, oil drops, surfactants, hardeners, matting agents, antifungal agents and various metal ions.

The heat developable light-sensitive material of the present invention can be exposed to light in accordance with known exposure means suitable to the color sensitivity of the light-sensitive material.

Examples of usable exposure light sources include tungsten lamps, halogen lamps, xenon lamps, mercury lamps, CRT light sources, FO-CRT light sources, light emitting diodes and laser sources (e.g., gas laser, dye laser, YAG laser, semiconductor laser), all of which may be used singly or in combination. It is also possible to use light sources comprising a combination of semiconductor laser and SHG element (second harmonic wave generating element). Also, phosphors excited by electron beams, X-rays, γ-rays or α-rays can also be used as light sources for exposure.

In the heat development of the heat developable light-sensitive material of the present invention, a known heating means can be used; for example, it may be brought into contact with a heated heat block, surface heater, heat roller or heat drum, it may be passed through a hot atmosphere, it may be heated using high frequency wave heating, and it may be heated with the Joule heat generated by supplying current to a heat generating electroconductive material like a carbon black layer on the back face of the light-sensitive material or image receiving material.

Heating for image formation using a recording material relating to the invention (heat-sensitive recording material or heat developing type light-sensitive material) is carried out substantially in the absence of water and base.

Hereinafter, the advantageous feature of the present invention will be illustrated by exemplifying a transfer-type heat developable light-sensitive material containing 1-3-sulfur-nitrogen-containing compound as a dye-providing substance.

In other words, neither water nor base is externally added for this heating, nor does the recording material itself contain a base or base precursor. When a hydrophilic binder such as gelatin is used in the recording material or image-receiving material, a trace amount of water is retained therein because of equilibrium with the atmosphere; this condition is also included in "substantially in the absence of water" in the present invention.

When the recording material containing a 1,3-sulfur-nitrogen-containing compound contains a base or base precursor, a cleavage reaction of the 1,3-sulfur-nitrogen-containing compound proceeds and results in image quality deterioration during long-term storage or high-temperature or high-humidity storage of the recording material. Particularly when the 1,3-sulfur-nitrogen-containing compound releases a dye, a problem of increased fogging is posed.

When a base or base precursor exists during heating, imagewise regulation of the reaction is difficult and image quality deterioration occurs. For example, when the 1,3-sulfur-nitrogen-containing compound releases a dye, fogging is markedly suppressed as a result of acceleration of silver development by the base, but maximum density reduction is also considerable.

Hitherto, 1,3-sulfur-nitrogen-containing compounds have been known to be used in the presence of base. However, in the present invention, the presence of base is unnecessary, on the contrary, the relationship between fog and maximum density improves significantly because 1) reaction is carried out at high temperatures, and 2) the reaction is accelerated by the presence of a thermal solvent.

The advantageous effects of the present invention can be ahieved especially noticeably when the formation of image dyes by heat development and the transfer thereof to the image-receiving material are conducted substantially not in the presence of water.

In the present invention, it is preferable to employ a hydrophobic polymer in an image-receiving layer of the image-receiving material.

As hydrophobic polymers, polyvinyl chloride, polycarbonates, polyesters, polyarylates and polystyrene are preferable, and polyvinyl chloride is especially preferable.

When a hydrophilic binder is used in the recording material of the present invention, it is preferable to set the film surface pH of the recording layer at not more than 8.0, more preferably not more than 7.0 at 25 ° C. The film surface pH of the recording layer is preferably kept within the above-mentioned range both before, during and after heating for image formation.

Here, the film surface pH of the recording layer can easily be measured by dropwise adding a small amount of pure water onto the surface of the recording layer and applying a flat pH electrode thereon. The pure water used for this purpose is ion exchange water or distilled water whose pH is 5 to 8 and whose electroconductivity is not more than 1 µs/cm at 25 ° C. Specifically, a microsyringe is used to dropwise add about 10 µl of the pure water onto the surface of the light-sensitive layer, and a flat electrode is applied thereto to obtain measurements.

EXAMPLES

The present invention is hereinafter described in more detail by means of the following examples, but the invention is not by any means limited by them.

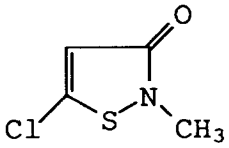
Example 1

Preparation of organic silver salt emulsion

While keeping a temperature of 50 ° C, to an aqueous solution (OA-1) containing 300 g of modified gelatin wherein over 90% of the amino groups have been substituted by phenylcarbamoyl groups, 2400 ml of deionized water, 9.18 g of benzotriazole and 51 ml of 28% aqueous ammonia, 1420 ml of another aqueous solution (OB-2) containing 250 g of benzotriazole and 169 ml of 28% aqueous ammonia and 1420 ml of still another aqueous solution (OC-1) containing 360 g of silver nitrate and 336 ml of 28% aqueous ammonia were added at constant flow rate by the double jet precipitation method using the mixer agitator described in Japanese Patent O.P.I. Publication Nos. 92523/1982 and 92524/1982. During the mixing process, pH and pAg were kept constant at 9.3 and 11, respectively. After completion of addition, a 20% aqueous solution of 60 g of modified gelatin wherein over 90% of the amino groups have been substituted by phenylcarbamoyl groups. Subsequently, 56% acetic acid was added to reach a pH level of 5.5. After precipitation, the dissolved excess soluble salts were removed.

Further, 4800 ml of deionized water was added, and a 10% aqueous solution of potassium hydroxide was added to reach a pH level of 6.0. After 5 minutes of dispersion, a 20% aqueous solution of 30 g of the modified gelatin described above was added. Subsequently, 3.5 N sulfuric acid was added to reach a pH level of 4.5. After precipitation, the dissolved excess soluble salts were removed. After adjusting to a pH level of 6.0 and adding 0.45 g of the following compound ST-1, deionized water was added to reach a total quantity of 2520 ml, followed by 30 minutes of dispersion at 50 ° C to yield an organic silver salt emulsion.

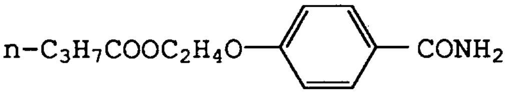
ST-1



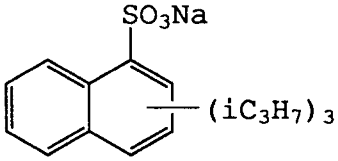
Preparation of thermal solvent dispersion 1

Using an alumina ball mill, 25 g of the following thermal solvent TS-12 was dispersed in 100 ml of a 0.5% aqueous solution of polyvinylpyrrolidone containing 0.04 g of surfactant 1 (Alkanol XC, produced by Du-Pont) to yield 120 ml of a dispersion.

Thermal solvent TS-12



Surfactant 1



Preparation of 1,3-sulfur-nitrogen-containing compound dispersion 1

Using an alumina ball mill, 12 g of the compound 37 of the present invention was dispersed in 100 ml of a 1.5% aqueous solution of polyvinyl alcohol containing 0.01 g of surfactant 1 (Alkanol XC, produced by Du-Pont) to yield 120 ml of a dispersion.

Preparation of recording material 1

The following recording material was prepared using the organic silver salt dispersion, thermal solvent dispersion and 1,3-sulfur-nitrogen-containing compound dispersion prepared above.

Gelatin	3.6 g/m^2
Compound 37 of the present invention	1.3 g/m^2
Silver benzotriazole	0.68 g/m^2 (as silver)
Thermal solvent TS-12	6.0 g/m^2
Polyvinyl alcohol	0.13 g/m^2

The support used was a latex-subbed transparent polyethylene terephthalate film having a thickness of 100 μm.

Preparation of recording material 2

A recording material 2 was prepared in the same manner as with recording material 1 except that silver benzotriazole was not used.

Evaluation

The recording materials 1 and 2 thus obtained were heated by keeping in contact with a 120 ° C metal plate for 60 seconds, followed by extraction with a 10:1 mixed solvent of dimethylformamide and water, after which thin-layer chromatography (developing solvent: $CHCl_3$:MeOH = 8:2) for evaluation. The recording material 1, which contained silver benzotriazole, yielded a diffusible dye released from the compound 37 of the present invention, while the recording material 2 yielded an unchanged form of the compound 37 of the present invention. It can therefore be said that the use of the recording material of the present invention and a heating means such as a thermal head makes it possible to provide a thermal recording material and a method of image formation using it.

Example 2

Recording materials 1 (b) and 2 (b) were prepared in the same manner as in Example 1 except that the compound 37 of the present invention was replaced with the compound 38 of the present invention for the recording material 1 (b) and silver benzotriazole was not used for the recording material 2 (b).

Heating was followed by extraction in the same manner as in Example 1, and evaluation was made by thin-layer chromatography (developing solvent: hexane:ethyl acetate = 1:2). The results obtained were similar to those obtained in Example 1.

The recording materials 1 (b) and 2 (b) were heated at 120 ° C for 60 seconds and then uniformly sprayed with a solution of 1% o-dianisidine in acetic acid. The recording material 1 (b) developed an orange color, while the recording material 2 (b) remained colorless. When the compound (38) was heated in the presence of benzotriazole silver, a thiazolizing ring was presumably cleaved to form a diffusible aldehyde compound.

Example 3

Recording materials 3 through 19 were prepared in the same manner as in Example 1 except that the thermal solvent TS-12 used in Example 1 was replaced with the thermal solvents listed in Table 1 below.

The recording materials 1 through 19 thus obtained were heated by keeping them in contact with a 120 ° C hot metal plate for 45 seconds, followed by extraction using the same solvent as in Example 1 and evaluation by thin-layer chromatography.

The results obtained are given in Table 1. The figures for reactivity in Table 1 were obtained on the basis of the size and density of the spots of the compound of the present invention and a diffusible dye resulted from reaction with silver ions on the thin-layer chromatograms. The relationship between reactivity and corresponding spots on thin-layer chromatograms are as follows.

Reactivity (condition of the spot of the compound of the present invention or corresponding aldehyde derivative)

5: The spot of the compound of the present invention disappeared; the diffusible dye alone is present.

4: A thin spot of the compound of the present invention remains; almost the entire spot is assigned to the diffusible dye.

3: The compound of the present invention and the diffusible dye each account for nearly 50%.

2: Almost the entire spot is assigned to the compound of the present invention; the contribution of the diffusible dye is very small.

1: The spot of the compound of the present invention alone is present; no diffusible dye formation noted.

Table 1

Recording material	Hot melting substance	Reactivity
1	TS-12	5
2	TS-12	1
3	TS-1	3
4	TS-3	3
5	TS-4	3
6	TS-5	4
7	TS-6	4
8	TS-7	3
9	TS-8	4
10	TS-9	4
11	TS-10	4
12	TS-11	4
13	TS-14	5
14	TS-16	4
15	TS-17	4
16	TS-18	4
17	TS-19	4
18	TS-20	4
19	TS-21	4

Example 4

A recording material 20 was prepared with the organic silver salt dispersion, thermal solvent dispersion and 1,3-sulfur-nitrogen-containing compound dispersion prepared in Example 1 and a monodispersed silver iodobromide grain emulsion with an average grain size of 0.25 μm chemically sensitized with sodium thiosulfate and the following reducing agent 1. The amounts of these components used per m^2 are as follows.

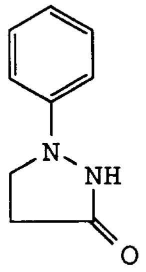
Gelatin	3.6 g
Compound 37 of the present invention	1.3 g
Silver benzotriazole	0.68 g (as silver)
Thermal solvent TS-12	6.0 g
Polyvinyl alcohol	0.13 g
Silver iodobromide	0.45 g (as silver)
Reducing agent 1	1.02 g

The support used was a latex-subbed transparent polyethylene terephthalate film having a thickness of 100 μm.

A recording material 20 (b) was prepared in the same manner as above except that the compound 37 of the present invention was replaced with the compound 38 of the present invention. The recording materials 20 (a) and 20 (b) were subjected to exposure using a tungsten lamp as the light source. Exposed and unexposed recording materials 20 (a) and 20 (b) were heated, extracted and evaluated by thin-layer chromatography in the same manner as in Examples 1 and 2. The exposed samples yielded an evidently smaller amount of diffusible compounds corresponding to the compounds 37 and 38 of the present invention in comparison with the unexposed samples.

It can therefore be said that the present invention makes it possible to suggest the potential of the present invention for embodiment as a heat developable light-sensitive material.

Reducing agent 1



Example 5

Preparation of a 1,3-sulfur-nitrogen-containing compound dispersion- 2

1,3-sulfur-nitrogen-containing compound of the present invention, as shown in Table 2 and 180 mg of tricrezylphosphate were dissolved in 1.2 ml of ethylacetate. Then, the solution was mixed with 6.5 ml of an aqueous solution containing 132 mg of the aforesaid surfactant and 150 mg of gelatin. Then, the mixed solution was emulsified and dispersed with a supersonic homogenizer. After that, ethylacetate was distilled off therefrom and deionized water was added to make 10 g in total. Thus, solutions each containing therein 1,3-sulfur-nitrogen-containing compound were prepared.

Table 2

Compound	Addition amount (mg)
(41)	672
(42)	318
(45)	612
(47)	360
(58)	491
(65)	716

Preparation of a reducing agent dispersion

A Dimezone-dispersing solution was prepared by dispersing the mixture of 5.0 g of Dimezone (1-phenyl-4,4-dimethyl-3-pyrazolidone), 5.0 ml of 5 weight % aqueous solution of the above-mentioned surfactant-1 and 40 ml of ion-exchanged water by means of an alumina ball mill. In the same manner as above except that Dimezone was replaced with dimezone-S (4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone), a Dimezone-S dispersion was prepared.

Preparation of heat developable light-sensitive material

Using dispersion prepared as above, an organic silver salt emulsion prepared in Example-1 (silver benzotriazole), a thermal solvent dispersion (TS-12) and a silver iodobromide emulsion (an iodide content of 2 mol %), heat developable light-sensitive materials 101 and 102 were prepared.

An emulsion layer was coated on a 180 µm-thick PET support having thereon a subbed layer, and dried. The coating amount of each compound in the emulsion layer is shown as follows:

Gelatin Polyvinyl pyrrolidone Thermal solvent TS-12	3.0 g/m^2 0.02 g/m^2 1.5 g/m^2
1,3-Sulfur-nitrogen compounds as described in Table 3	
Dimezone Silver iodobromide Silver benzotriazole 1,2,4-Triazole Glyoxal	2.0 mmol/m^2 2.0 mmol/m^2 1.0 mmol/m^2 24 mmol/m^2 0.06 g/m^2

In coating an emulsion layer, a small amount of the above-mentioned surfactant-1 and a small amount of Zonyl FSN (produced by Du Pont) were added as coating aids.

Preparation of an image-receiving material

On a baryta paper support for photographic use of 150 g/m^2, polyvinyl chloride of 12 g/m^2 was coated so that an image-receiving material was prepared.

Evaluation

By the use of a Xenon flash lamp, heat developable light-sensitive materials 101 and 102 were subjected to partial exposure for 10^{-3} seconds. Then, each of them was superposed on an image-receiving material, and, they were heated uniformly for 60 seconds while being kept in contact with a metallic heat plate at 120 °C with a pressure of 2 kg/cm^2.

After cooling, when the light-sensitive material was separated from the image-receiving material, a positive type yellow image was obtained on the image-receiving layer.

The reflection density of the image was measured using a reflection densitometer PDA-65 (produced by Konica). Results are shown in Table 3.

Table 3

Light-sensitive material	Kind and added amount of 1,3-sulfur-nitrogen compound	Reflective density	
		Unexposed portion	Exposed portion
101	(41) 0.5 mmol/m^2	1.08	0.67
102	(45) 0.5.mmol/m^2	0.51	0.31

Example 6

Using an organic silver salt emulsion prepared in Example-1 (silver benzotriazole), a thermal solvent-dispersion (TS-12), 1,3-sulfur-nitrogen-containing compound dispersion prepared in Example 5, a reducing agent dispersion and a silver iodobromide emulsion (an iodide content of 2 mol %), heat developable light-sensitive materials 201 through 207 having 2-layer constitution were prepared.

The first layer (layer-1) was coated on a 180 µm-thick PET support having thereon a subbed layer, and dried. Then, the second layer (layer-2) was coated thereon and dried.

Coating amount of each compound in the first layer and the second layer is shown below.

In coating the first layer and the second layer, a small amount of the above-mentioned surfactant-1 and a small amount of Zonyl FSN (produced by Du Pont) were added as coating aids.

Layer-1	
Gelatin	2.0 g/m^2
Thermal solvent TS-12	Amount described in Table 4
Polyvinyl pyrrolidone	0.02 g/m^2
1,3-Sulfur-nitrogen-containing compound, as described in Table 4	

Layer-2	
Gelatin	3.0 g/m^2
Polyvinyl pyrrolidone	0.02 g/m^2
Thermal solvent TS-12	1.5 g/m^2
Reducing agent, as described in Table 4	
Silver iodobromide	Amount described in Table 4
Silver benzotriazole	Amount described in Table 4
1,2,4-Triazole	24.0 mmol/m^2
Glyoxal	0.1 g/m^2

Table 4

Light-sensitive material	Layer-1		Layer-2			Heating condition		Reflective density		Image color
	TS-12 (g/m²)	1,3-sulfur-nitrogen-containing-compound	Reducing agent (mmol/m²)	Silver iodo-bromide (mmol/m²)	Silver benzo-triazole (mmol/m²)	Temp. (°C)	Time (sec.)	Un-exposed portion	Exposed portion	
201	0	(41) 0.25 mmol/m²	Dimezone 4.0	2.0	2.0	120	180	0.48	0.12	Yellow
202	0	(42) 0.25 mmol/m²	Dimezone 4.0	2.0	2.0	120	180	0.95	0.51	Magenta
203	0	(47) 0.25 mmol/m²	Dimezone 4.0	2.0	2.0	110	180	1.18	0.89	Yellow
204	0	(47) 0.25 mmol/m²	Dimezone-S 4.0	2.0	2.0	110	180	0.93	0.56	Yellow
205	0	(58) 0.19 mmol/m²	Dimezone 4.0	4.0	1.0	110	180	0.86	0.70	Yellow
206	1.5	(65) 990 mg/m²	Dimezone 4.0	2.0	1.0	120	180	0.74	0.40	Yellow
207	1.5	(41) 0.25 mmol/m²	Dimezone 4.0	2.0	2.0	120	180	0.60	0.40	Yellow

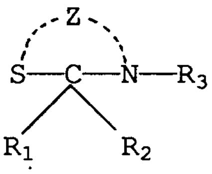
Heat developable light-sensitive materials 201 through 206 were subjected to light exposure and heat-developing in the same manner as in Example 5, provided that the conditions of heating were changed as shown in Table 4.

After cooling, when the light-sensitive material was separated from the image-receiving material, a positive-type yellow or magenta image was obtained on the image-receiving material.

Claims

1. A method of image formation wherein a recording material is subjected to imagewise heating substantially in the absence of water and a base or precursor thereof, wherein said recording material comprises a support having coated thereon a 1,3-sulfur-nitrogen-containing compound capable of being cleaved in the presence of a silver ion or silver complex ion, an organic silver salt and a thermal solvent, and wherein said 1,3-sulfur-nitrogen-containing compound is represented by the following formula 1

   formula 1

   wherein R_1 and R_2 independently represnt a hydrogen atom, aliphatic group, aromatic group or heterocyclic group; R_3 represents a hydrogen atom, aliphatic group, aromatic group, heterocyclic group or acyl group; Z represents a group of nonmetallic atoms necessary to form a ring, which may have a substituent, wherein at least one of R_1, R_2, R_3 and the substituent on the ring represented by Z is a photographically useful group or precursor thereof capable of being released upon reaction with a silver ion or water-soluble silver complex under heating.

2. A method of image formation wherein a recording material is subjected to heating, simultaneously with or after imagewise exposure, substantially in the absence of water and a base or precursor thereof, wherein said recording material comprises a support having coated thereon a 1,3-sulfur-nitrogen-containing compound capable of being cleaved in the presence of a silver ion or silver complex ion, an organic silver salt, a reducing agent, a light sensitivre silver halide and a thermal solvent, and wherein said 1,3-sulfur-nitrogen-containing compound is represented by formula 1 as claimed in claim 1.

3. The method of claim 2, wherein said photographically useful group is a dye, developing inhibitor, developing accelerator, fogging agent, coupler, toning agent or brightening agent.

4. A method of image formation wherein a recording material is subjected to heating, simultaneously with or after imagewise exposure, substantially in the absence of water and a base or precursor thereof, wherein said recording material comprises a support having coated thereon a thermal transfer layer containing a 1,3-sulfur-nitrogen-containing compound represented by formula 1 as claimed in claim 1 capable of being cleaved in the presence of a silver ion or silver complex ion, an organic silver salt, a reducing agent, a light sensitive silver halide and a thermal solvent, wherein said photographically useful group is a dye, said compound represented by formula 1 is used as a dye-providing material to form a dye, and the resulting dye is transferred to a image-receiving material.

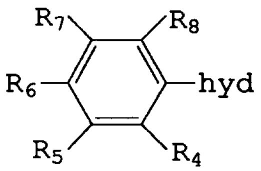
5. The method of claim 4, wherein formation of the dye and transfer thereof to the image-receiving material are each carried out in the absence of water and a base or precursor thereof.

6. The method of claim 5, wherein said image-receiving material comprises a support having thereon an image-receiving layer containing a hydrophobic polymer.

7. The method of claim 6, wherein said hydrophobic polymer is polyvinyl chloride.

8. The method of claim 5, wherein said thermal solvent is a compound represented by the following formula 2

formula 2



wherein hyd represents a group selected from -NHCOCH$_3$, -CH$_2$OH, -NHSO$_2$CH$_3$, -CONHCH$_3$, -NHCONH$_2$, -CONH$_2$, -NHCSNH$_2$, -SO$_2$CH$_3$, -CH$_2$CONH$_2$, -SO$_2$NH$_2$, -OCONH$_2$, -OCH$_2$CONH$_2$ and -N-(SO$_2$CH$_3$)$_2$; R$_4$ through R$_8$ each are a hydrogen atom, a halogen atom, or a group selected from alkyl, aryl, alkoxy, aryloxy, alkoxycarbonyl and acyloxy.

9. The method of claim 5, wherein said recording material comprised a support having thereon a layer containing a hydrophilic binder, wherein a surface pH value of the layer is not more than 8.0 at 25 ° C.

10. The method of claim 9, wherein said surface pH value is not more than 7.0 at 25 ° C.

11. The method of claim 5, wherein said photographically useful group is a dye; said thermal solvent is a compound represented by formula 2 as claimed in claim 8; and said recording material comprises a layer containing a hydrophilic binder, wherein a surface pH value of the layer is not more than 8.0 at 25 ° C.

12. The method of claim 11, wherein the resuting dye is transferred to an image-receiving layer comprising a hydrophobic polymer.

13. The method of claim 12, wherein said hydrophobic polymer is polyvinyl chloride.