(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 433 024 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **90313464.1**

(51) Int. Cl.5: **B41M 5/136**, B41M 5/30

(22) Date of filing: **11.12.90**

(30) Priority: **13.12.89 JP 323458/89**
05.02.90 JP 25505/90
11.04.90 JP 95636/90

(43) Date of publication of application:
19.06.91 Bulletin 91/25

(84) Designated Contracting States:
FR GB

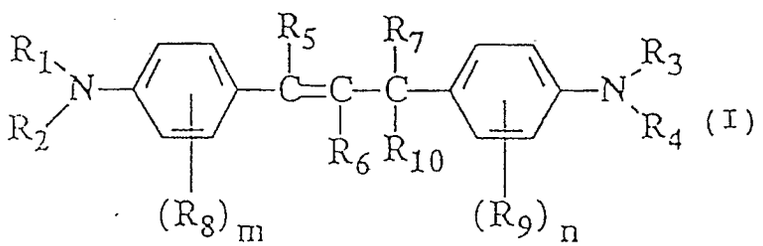
(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma Minami Ashigara-shi
Kanagawa(JP)

(72) Inventor: **Sano, Shojiro**
c/o Fuji Photo Film Co., Ltd., No, 200,
Onakazato
Fujinomiya-shi, Shizuoka(JP)
Inventor: **Takashima, Masanobu**
c/o Fuji Photo Film Co., Ltd., No, 200,
Onakazato
Fujinomiya-shi, Shizuoka(JP)
Inventor: **Satomura, Masato**
c/o Fuji Photo Film Co., Ltd., No, 200,
Onakazato
Fujinomiya-shi, Shizuoka(JP)

(74) Representative: **Diamond, Bryan Clive et al**
Gee & Co., Chancery House, Chancery Lane
London WC2A 1QU(GB)

(54) Colour recording medium containing leuco dye.

(57) A recording material comprises a support having thereon a recording layer comprising a binder and at least one electron-donating leuco dye represented by formula (I):



(I)

wherein R_1 to R_4 each represents a hydrogen atom, an optionally substituted alkyl or aryl group; R_5 to R_9 each represents a hydrogen atom or a univalent group, e.g. alkyl or aryl; m and n each represent an integer of from 1 to 4; and R_{10} is $-XR_{11}$, $-PO(OR_{12})_2$, $-CR_{13}R_{14}R_{15}$, or $-NR_{16}R_{17}$ where X is an oxygen or sulfur atom, and R_{11} to R_{17} each represent a hydrogen atom or a univalent group, e.g. alkyl and/or heterocylic and at least one of R_{13}, R_{14} and R_{15} is an electron-attracting group. 86 such dyes are shown. Other electron-donating dyes may be present.

The dye may be microencapsulated alone or in a solvent. The material may be pressure- or heat-sensitive.

When the recording layer is contacted with a layer of electron-acceptor, e.g. acid clay, color, e.g. bluish green, is developed, of good density and fastness.

EP 0 433 024 A1

COLOUR RECORDING MEDIUM CONTAINING LEUCO DYE

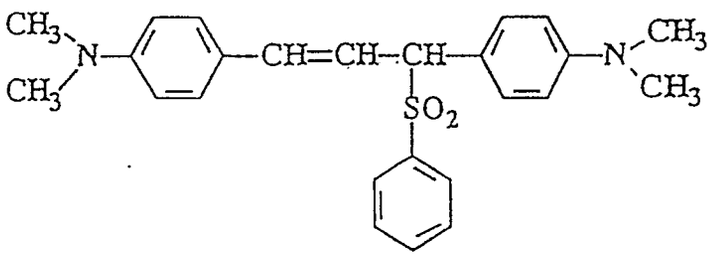
The present invention relates to a recording medium, and particularly to a recording medium having an improved stability of the developed color image.

Recording media which employ an electron-donating leuco dye and an electron-accepting compound include pressure sensitive paper, thermosensitive paper, light- and pressure-sensitive paper, electric heat-sensitive paper, thermosensitive transfer paper, and the like, as disclosed in detail, for example, in British Patent 2,140,449, U.S. Patents 4,480,052 and 4,436,920, JP-B-60-23992 (the term "JP-B" as used herein means an "examined Japanese patent publication"), and JP-A-57-179836, JP-A-60-123556, and JP-A-60-123557 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

These recording media are presently being comprehensively investigated to improve (1) developed color density and color developing sensitivity, and (2) storage stability of the recording medium and fastness of images after color development.

Among these, improvement of storage stability and image fastness as described in (2) above is strongly desired, particularly for blue color developing type recording media.

For example, a blue-color-developing agent, 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide (namely, Crystal Violet lactone), rapidly develops a deep blue color, but exhibits poor light-fastness and plasticizer resistance of the developed color image. As another example, the dye of the formula below:

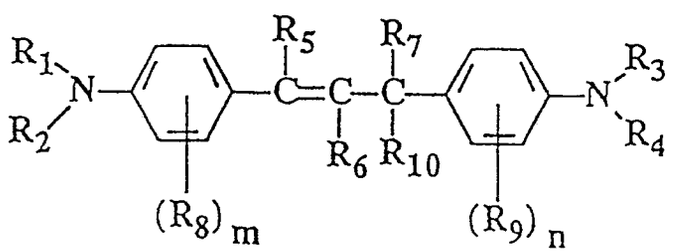


exhibits satisfactory fastness (light resistance and plasticizer resistance), but is disadvantageous in that the dye has a low solubility in an encapsulation solvent, the dye is inherently blue-colored, and the density of the developed color is low.

The present inventors have discovered that a recording medium employing a specific electron-donating leuco dye solves the above described problems.

An object of the present invention is to provide a recording medium having good stability of the developed color image and which satisfies other necessary requirements such as high density of the formed color and high color-forming speed.

The above objectives are achieved by providing a recording medium utilizing a color development of an electron-donating leuco dye by contact with an electron-accepting compound to provide a color dye image, comprising a support having thereon a recording layer comprising a binder and at least one electron-donating leuco dye represented by formula (I):



(I)

wherein R_1 to R_4 each represents a hydrogen atom, an alkyl group, or an aryl group; R_5 to R_9 each represents a hydrogen atom or a univalent group; m and n each represents an integer of from 1 to 4; and R_{10} is a group $-XR_{11}$, $-PO(OR_{12})_2$, $-CR_{13}R_{14}R_{15}$ or $-\overline{N}R_{16}\bar{R}_{17}$ where X is an oxygen atom or a sulfur atom, and R_{11} to R_{17} each represents a hydrogen atom or a univalent group and at least one of R_{13}, R_{14} and R_{15} is an electron-attracting group.

Preferably, R_1 to R_4 each represents a hydrogen atom, an alkyl group, or an aryl group; R_5 to R_7 each represents a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an alkoxycarbonyl group, an aryl group, an aryloxy group, an arylthio group, an aryloxycarbonyl group, or a cyano group; R_8 and R_9 each represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a cyano group, a nitro group, an amino group, a substituted amino group, a hydroxy group, a halogen atom, an alkoxycarbonyl group, an aryloxycarbonyl group or an acyloxy group; m and n each represents an integer of from 1 to 4; and R_{10} is a group $-XR_{11}$, $-PO(OR_{12})_2$, $-CR_{13}R_{14}R_{15}$ or $-\overline{N}R_{16}\overline{R}_{17}$.

In the above formula, X is an oxygen atom or sulfur atom, and R_{11} preferably represents an alkyl group, an aryl group, a heterocyclic group, COR_{18}, SO_2R_{19}, $N=CR_{20}R_{21}$, or $NR_{22}R_{23}$ where R_{18} and R_{19} each represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group; and R_{20}, R_{21}, R_{22}, and R_{23} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, COR_{24}, or SO_2R_{25} where R_{24} and R_{25} each represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group.

R_{12} preferably is a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group. Two of R_{12} may join together to form a 4- to 12-membered ring which may contain a hetero atom.

Preferably, R_{13}, R_{14}, and R_{15} each represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a halogen atom, a cyano group, a nitro group, SO_2R_{26}, COR_{27}, or $NR_{28}R_{29}$ where R_{26} and R_{27} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a hydroxy group, or $NR_{30}R_{31}$; R_{28}, R_{29}, R_{30}, and R_{31} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, SO_2R_{32} or COR_{33}, where R_{32} and R_{33} each represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group. Among them, examples of electron-attracting groups include a halogen atom, a cyano group, a nitro group, SO_2R_{26}, COR_{27} and $NR_{28}R_{29}$ in which at least one of R_{28} and R_{29} is SO_2R_{32} or COR_{33}. R_{13} and R_{14} may join together to form a 4- to 12-membered ring which may contain a hetero atom.

Preferably, R_{16} and R_{17} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, SO_2R_{34}, COR_{35}, a hydroxy group, or $NR_{36}R_{37}$, where R_{34} and R_{35} each represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a heterocyclic group, or $NR_{38}R_{39}$, R_{36}, R_{37}, R_{38}, and R_{39} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, SO_2R_{40}, or COR_{41} where R_{40}, and R_{41} each represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group. R_{16} and R_{17} may join together to form a 4- to 12-membered ring which may contain a hetero atom.

The term "a heterocyclic group" used in the above means a 5- to 7-membered mono- or polycyclic group having S, O or N as a hetero atom.

The alkyl groups, the aryl groups and the heterocyclic groups described above may be substituted by an alkyl group, an alkyoxy group, an aryl group, an aryloxy group, a halogen atom, a nitro group, a cyano group, a substituted carbamoyl group, a substituted sulfamoyl group, a substituted amino group, a substituted oxycarbonyl group, a substituted oxysulfonyl group, an alkylthio group or a arylsulfonyl group.

More specifically, the groups represented by R_1 to R_4 are preferably a hydrogen atom, an alkyl group of from 1 to 18 carbons, or an aryl group of from 6 to 12 carbons.

Preferably, R_1 - R_4 each represents hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, isoamyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-dodecyl, n-octadecyl, β-methoxyethyl, β-ethoxyethyl, γ-methoxypropyl, γ-ethoxypropyl, β-phenoxyethyl, β-cyanoethyl, β-chloroethyl, β-hydroxyethyl, cyclopentyl, cyclohexyl, tetrahydrofurfuryl, phenyl, tolyl, chlorophenyl, methoxyphenyl, benzyl, phenethyl, methylbenzyl, chlorobenzyl or methoxybenzyl.

Preferably, at least one of the groups R_1 - R_4 do not represent hydrogen.

R_1 and R_2, or R_3 and R_4 may join together to form a 5-to 8-membered ring with the nitrogen atom to which they are commonly bonded, which ring may contain another heteroatom, exemplary rings of which include pyrrolidine, piperidine, morpholine, thiomorpholine, piperazine, caprolactam, and the like. Further, R_1 to R_4 may join to the carbon atoms at the ortho-position relative to the nitrogen atoms to which they are bonded, to form 5- to 8-membered rings. Examples of the rings formed thereby include an indoline ring, 1,2,3,4-tetrahydro quinoline ring or julolidine ring.

Preferably, R_5 - R_7 each represents a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, or an alkoxycarbonyl group having 1 - 18 carbons; an aryl group, an aryloxy group, an arylthio group, or an aryloxycarbonyl group having from 6 - 12 carbons; or a cyano group.

More specifically, preferable R_5 - R_7 groups include hydrogen, methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, octadecyl, methoxypropyl, ethoxypropyl, phenoxyethyl, cyclopentyl, cyclohexyl, allyl, benzyl, phenethyl, phenyl, 4-methylphenyl, 3-methylphenyl, 2-methylphenyl, 4-methoxyphenyl, 3-methoxyphenyl, 2-

methoxyphenyl, 4-N,N-dimethylaminophenyl, 3-N,N-dimethylaminophenyl, 2-N,N-dimethylaminophenyl, cyano, methoxycarbonyl, ethoxycarbonyl and methylthio.

In particular, the R_5 - R_7 groups each preferably represents a hydrogen atom in order to simplify the synthesis of the dye.

In the above, examples of heteroatoms include S, O and N.

The groups R_8 - R_9 each preferably represents a hydrogen atom; an alkyl group or an alkoxy group having from 1 - 12 carbons; an alkoxycarbonyl group or an acyloxy group having from 2 - 12 carbons; an aryl group or an aryloxy group having from 6 - 12 carbons; an aryloxycarbonyl group having from 7 - 12 carbons; a hydroxy group, a chlorine atom, a bromine atom, a fluorine atom, a nitro group, a cyano group, an amino group, a mono- or di-alkylamino group having from 1 to 12 carbons, a mono- or di-arylamino group having from 6 - 12 carbons, or an acylamino group having from 1 - 12 carbons.

Preferable R_8 and R_9 groups include hydrogen, methyl, ethyl, propyl, butyl, octyl, phenyl, tolyl, benzyl, phenetyl, methoxy, ethoxy, propoxy, butoxy, octyloxy, benzyloxy, phenoxyethoxy, phenoxy, chlorine, bromine, fluorine, nitro, cyano, dimethylamino, diethylamino, acetylamino, acetyloxy and methoxycarbonyl.

R_8 and R_9 are each preferably located at a meta-position relative to $-NR_1,R_2$, and $-NR_3R_4$ in order to simplify the synthesis of the dye.

The group represented by R_{10} preferably contains from 1 to 20 carbons.

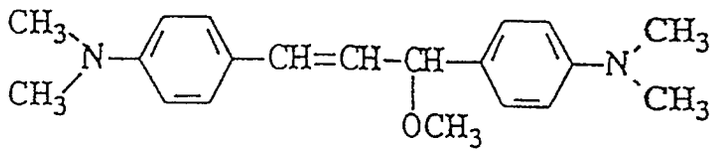
The group R_{10} preferably represents a group of $-XR_{11}$, $-CR_{13}R_{14}R_{15}$, or $-NR_{16}R_{17}$ in order to simplify the synthesis. In particular, $-CR_{13}R_{14}R_{15}$ is preferable in terms of the stability of the leuco type color former used for a recording medium.

Specific examples of R_{10} include methoxy, ethoxy, propoxy, butoxy, cyclohexyloxy, octyloxy, docecyloxy, octadecyloxy, benzyloxy, phenethyloxy, phenylbutyloxy, 4-methylbenzyloxy, 4-chlorobenzyloxy, 4-methoxybenzyloxy, β-phenoxyethoxy, β-(4-methylphenoxy)ethoxy, β-(3-methylphenoxy)ethoxy, β-(2-methylphenoxy)ethoxy, β-(4-methoxyphenoxy)ethoxy, β-phenylthioethoxy, β-phenylsulfonylethoxy, β-naphthyloxyethoxy, phenoxyethoxyethoxy, pyridylmethoxy, phenoxy, naphthyloxy, 4-chlorophenoxy, 4-methylphenoxy, 3-methylphenoxy, 2-methylphenoxy, 4-ethylphenoxy, 2,4-dichlorophenoxy, methyliminoxy, dimethyliminoxy, phenyliminoxy, diethylphosphonyl, dibutylphosphonyl, diphenylphosphonyl, di(4-tolyl)-phosphonyl, di(4-chlorophenyl)phosphonyl, di(4-methoxyphenyl)phosphonyl, di(4-nitrophenyl)phosphonyl, di-(4-cyanophenyl)phosphonyl, di(naphathalen-1-yl)phosphonyl ,di(naphthalen-2-yl)phosphonyl, di(2,4-dichlorophenyl)phosphonyl, di(4-chloro-3-methylphenyl)phosphonyl, anilino, 2-chloroanilino, 2-methoxycarbonylanilino, 2-nitroanilino, 2-methoxyanilino, 3-ethylanilino, 4-fluroanilino, 4-butoxyanilino, 2,4-dichloroanilino, 2,5-dimethylanilino, β-naphthylamino, N-methylanilino, N-butylanilino, N-acetylanilino, pyridylamino, quinolylamino, cyclohexylamino, indol-1-yl, carbazol-1-yl, succinylimido, phthalimido, acetylamino, benzoylamino, 2-methylbenzolyamino, 4-methylbenzolyamino, 4-chlorobenzoylamino, phenylsulfonylamino, 4-methylphenylsulfonylamino, 4-chlorophenylsulfonylamino, pyrrolidino, piperidino, morpholino, piperazino. phenylhydrazino, N-hydroxy-N-phenylsulfonylamino, N-hydroxy-N-4-chlorophenylsufonylamino, benzoylhydrazino, phenylsulfonylhydrazino, benzoyloxy, acetyloxy, methylthio, ethylthio, phenylthio, tolylthio, benzylthio, naphthylthio, benzothiazol-2-ylthio, benzoimidazol-2-ylthio, benzoxazol-2-ylthio, 1,1-diacetylmethyl, 1,1-dicyanomethyl, 1-acetyl-1-benzoylmethyl, 1,1-dimethoxycarbonylmethyl, 1,1-diethoxycarbonylmethyl, 1,1-diphenyloxycarbonylmethyl, 1,1-di-n-butoxycarbonylmethyl, 1,1-di-t-butoxycarbonylmethyl, 1,1-di-benzyloxycarbonylmethyl, 1,1-dioctyloxycarbonylmethyl, 1-acetyl-1-methoxycarbonylmethyl, 1-acetyl-1-ethoxycarbonylmethyl, 1-acetyl-1-isopropoxycarbonylmethyl, 1-acetyl-1-butoxycarbonylmethyl, 1-acetyl-1-hexyloxycarbonylmethyl, 1-acetyl-1-octyloxycarbonylmethyl, 1-acetyl-1-benzyloxycarbonylmethyl, 1-acetyl-1-phenoxycarbonylmethyl, 1-propyonyl-1-methoxycarbonylmethyl, 1-acetyl-1-ethoxycarbonylethyl, 1,1-diacetylethyl, 1-pivaloyl-1-methoxycarbonylmethyl, 1-cyano-1-ethoxycarbonylmethyl, 1-benzoyl-1-ethoxycarbonylmethyl, 1-acetyl-1-morpholinocarbonylmethyl, 1-methoxycarbonyl-1-ethoxycarbonylmethyl, 1,1-diphenylsulfonylmethyl, 1-tolysulfonyl-1-benzoylmethyl, 1,1-di(trifluoromethylcarbonyl)methyl, 1,1-dipivaloylmethyl, 1-furoyl-1-trifluoromethylcarbonylmethyl, 1-thienylcarbonyl-1-trifluoromethylcarbonylmethyl, 1,1-dicarbamoylmethyl, 1-acetyl-1-phenylcarbamoylmethyl, 1,1-dibenzoylmethyl, 1,1-dimethoxycarbonylethyl, 1,1-diethoxycarbonylethyl, 1,1-diphenyloxycarbonylethyl, 1,1-di-n-butoxycarbonylethyl, 1,1-di-t-butoxycarbonylethyl, 1,1-dibenzyloxycarbonylethyl, 1,1-dimethoxycarbonyl-n-propyl, 1,1-dimethoxycarbonyl-n-butyl, α,α-dimethoxycarbonylbenzyl, 1,1-dimethoxycarbonyl-1-methoxmethyl, 1,1-diethoxycarbonyl-n-propyl, 1,1-diethoxycarbonyl-n-pentyl, 1,1-diethoxycarbonyl-n-butyl, 1,1-diethoxycarbonyl-1-isopropylmethyl, 1,1-diethoxycarbonyl-1-tert-butyl methyl, α,α-diethoxycarbonylbenzyl, β,β-diethoxycarbonylphenethyl, 1,1-diethoxycarbonyl-1-allylmethyl, 1,1-diethoxycarbonyl-1-acetaminomethyl, 1,1-diethoxycarbonyl-1-chloromethyl, 1,1-diethoxycarbonyl-1-cyclopentylmethyl, 1,1-diethoxycarbonyl-1-phthalimidomethyl, 1,1-diethoxycarbonyl-2-ethoxycarbonylethyl, 1,1,1-triethoxycarbonylmethyl, benzoylmethyl, 4-chlorobenzoylmethyl, 4-nitrobenzoylmethyl, 1-chloro-1-acetylmethyl, 1-chloro-1-methoxycarbonylmethyl, 1-bromo-1-ben-

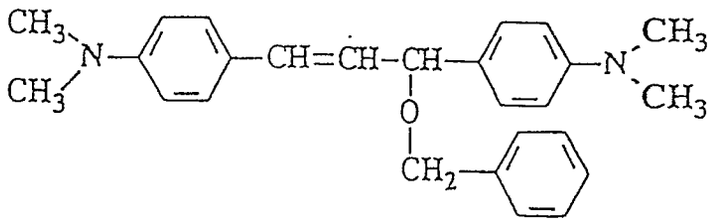
zoylmethyl, nitromethyl and 1-nitroethyl.

Specific examples of the leuco dye represented by formula (I) are shown below.

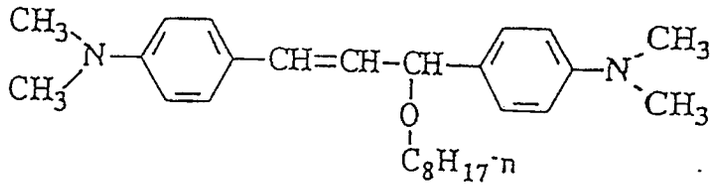
(1)



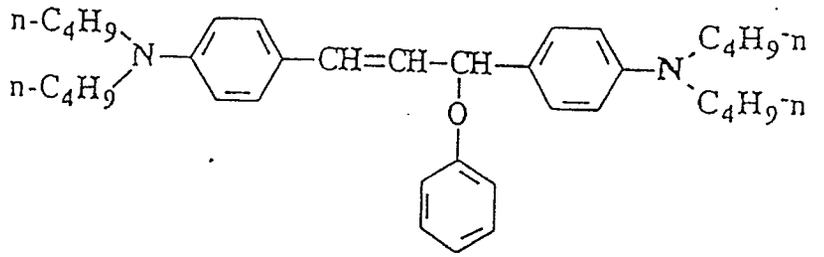
(2)



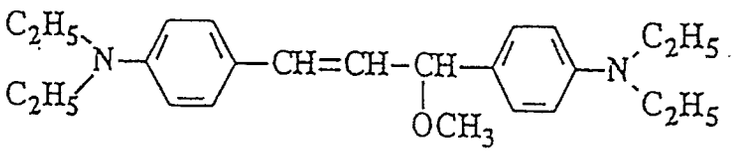
(3)



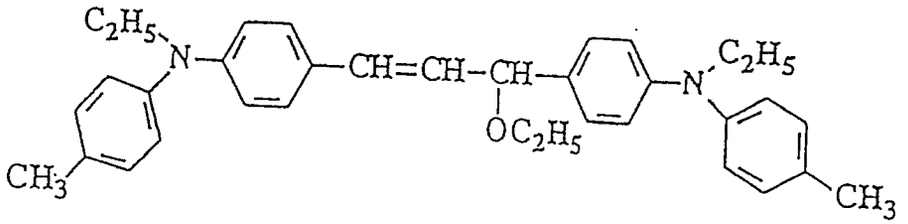
(4)



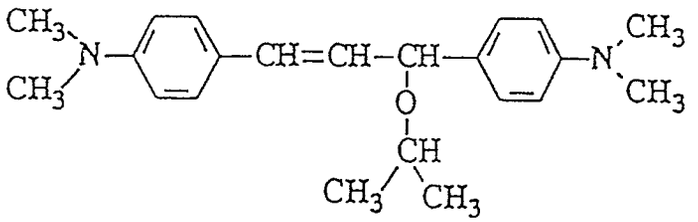
(5)



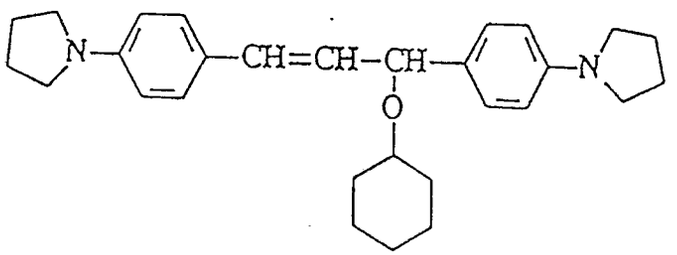
(6)



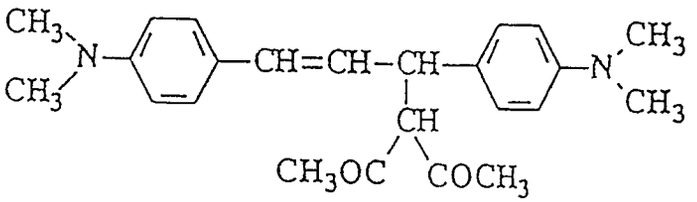
(7)



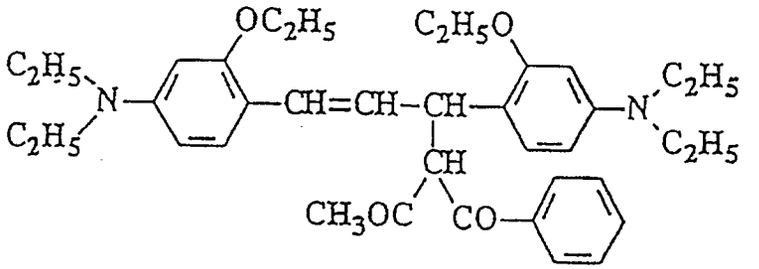
(8)



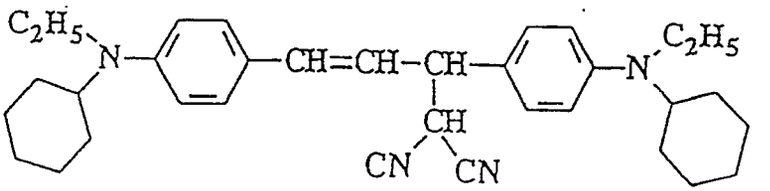
(9)



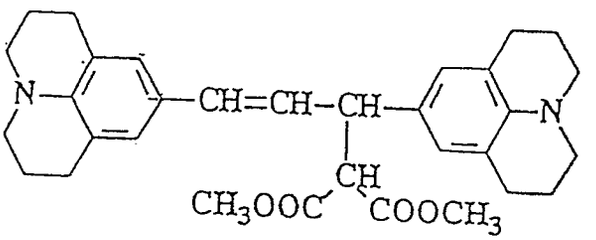
(1 0)



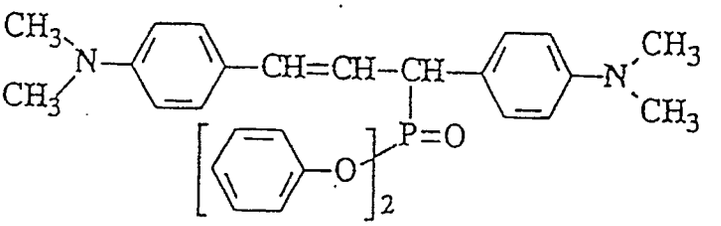
(1 1)



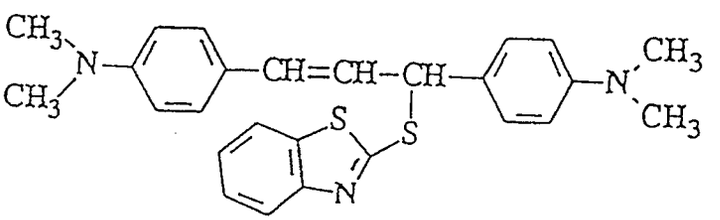
(1 2)



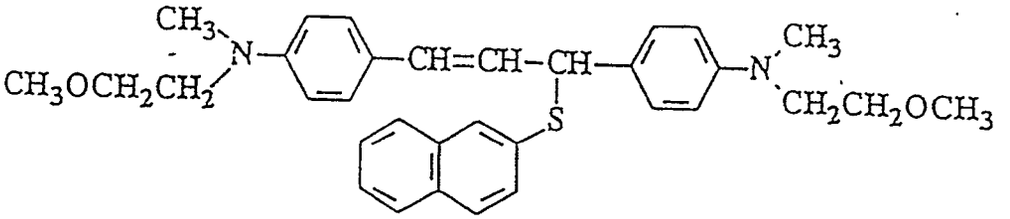
(1 3)



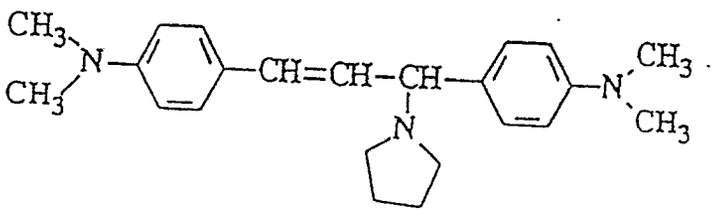
(1 4)



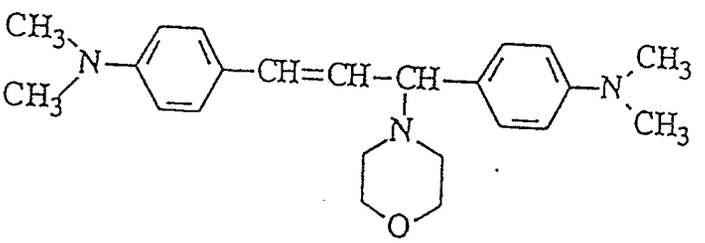
(1 5)



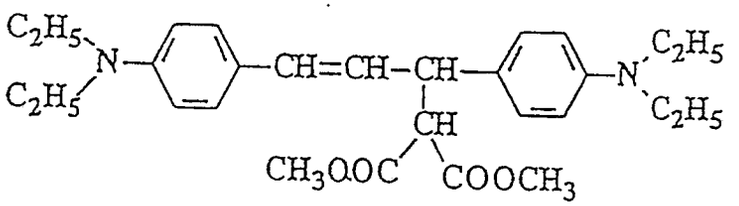
(1 6)



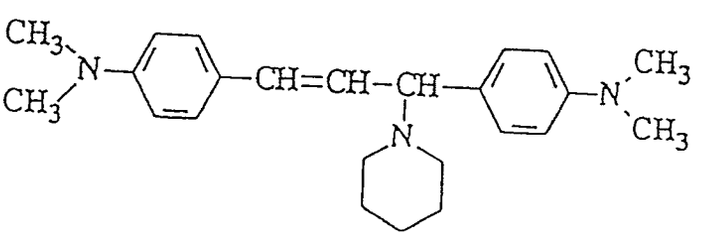
(1 7)



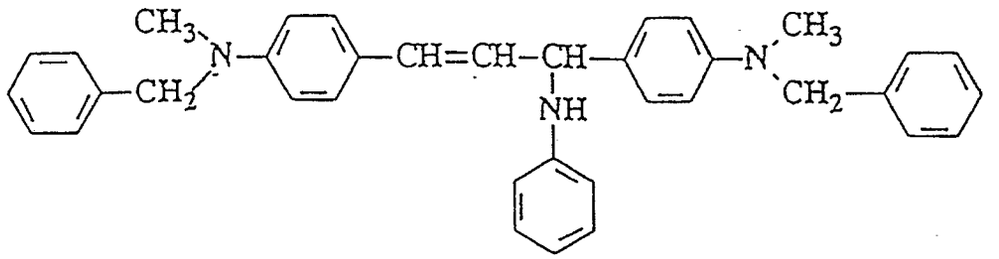
(1 8)



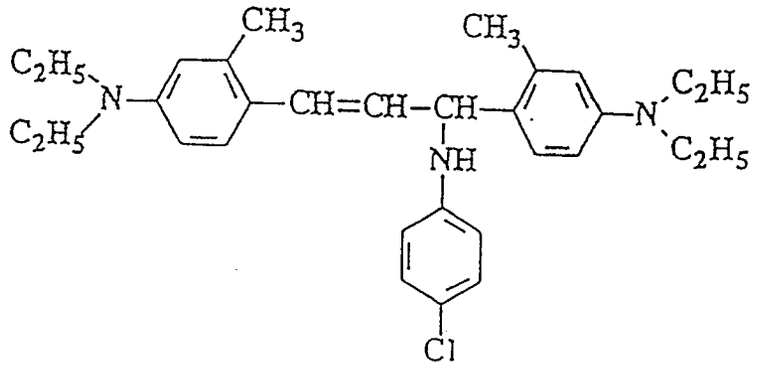
(1 9)



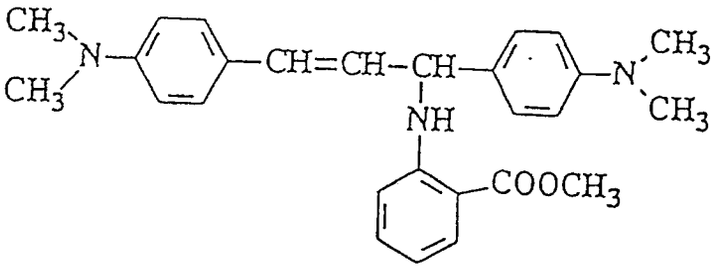
(2 0)



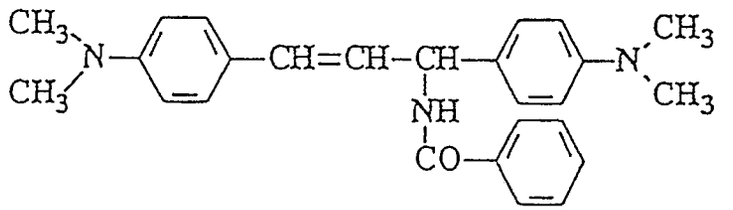
(2 1)



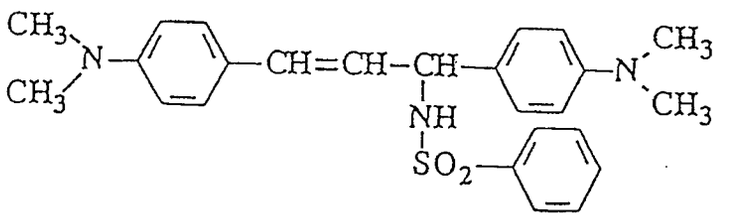
(2 2)



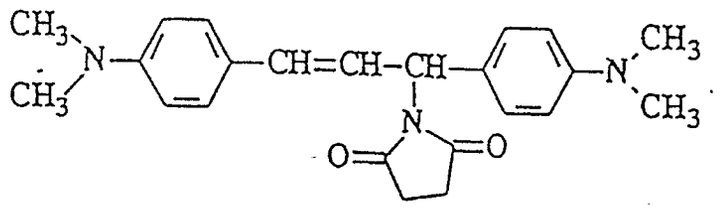
(2 3)



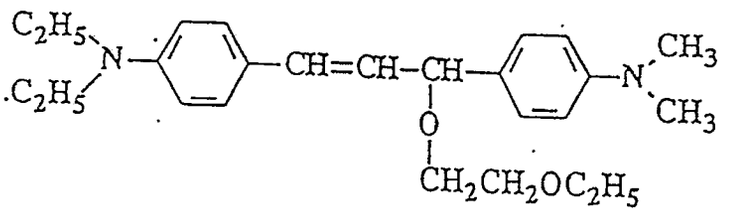
(2 4)



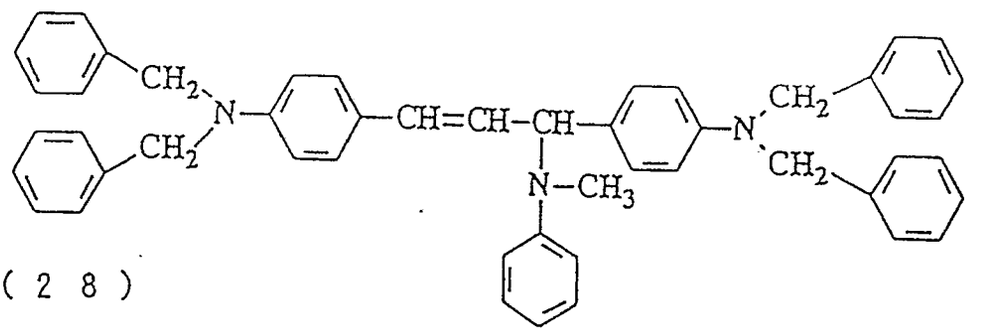
(2 5)



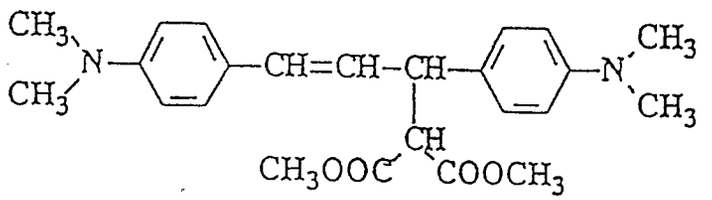
(2 6)



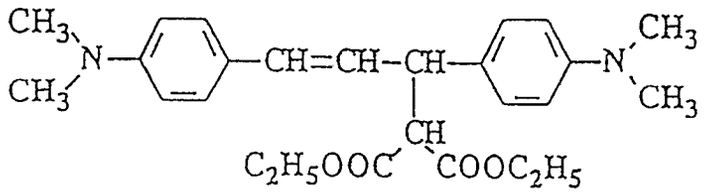
(2 7)



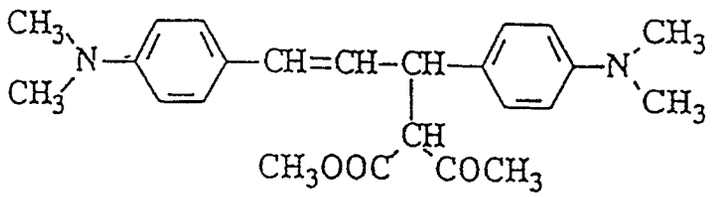
(2 8)



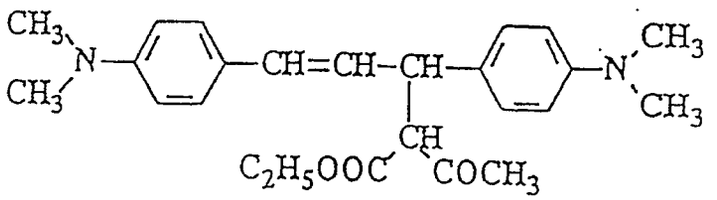
(2 9)



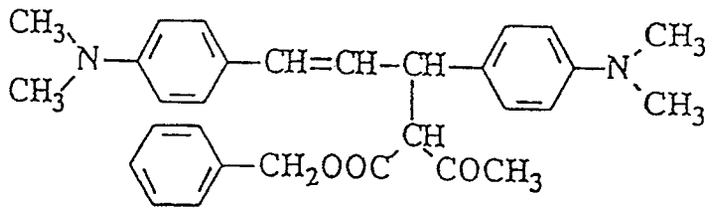
(3 0)



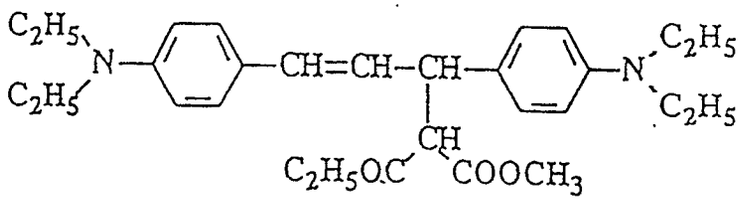
(3 1)



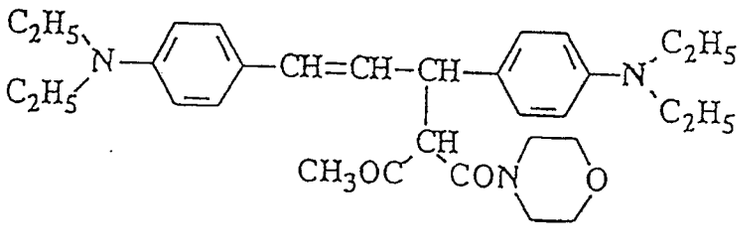
(3 2)



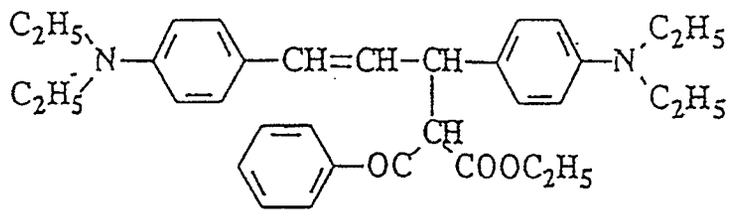
(3 3)



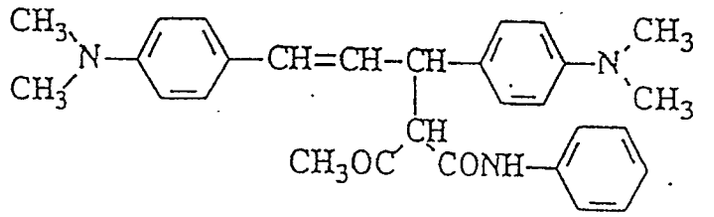
(3 4)



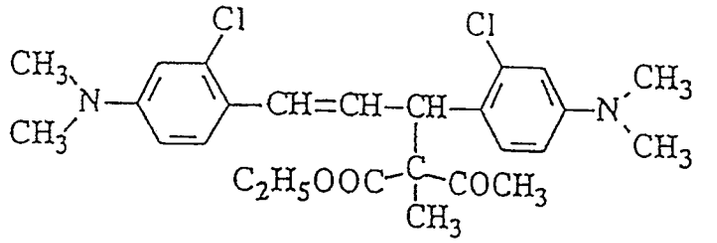
(3 5)



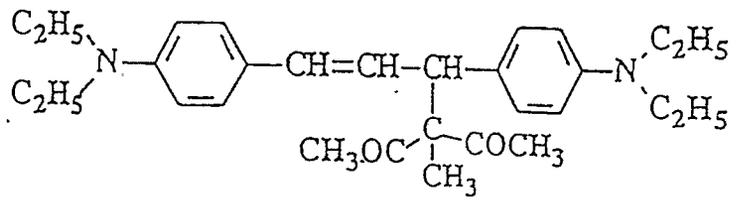
(3 6)



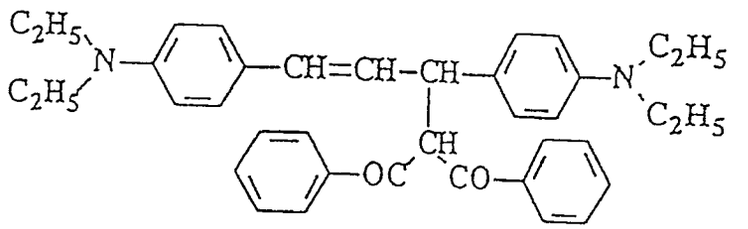
(3 7)



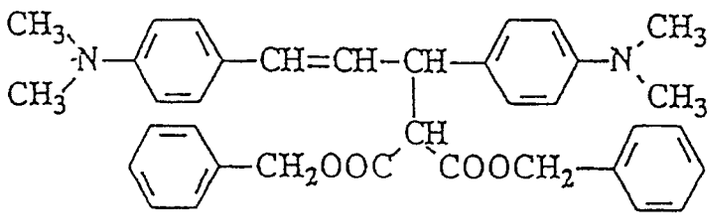
(3 8)



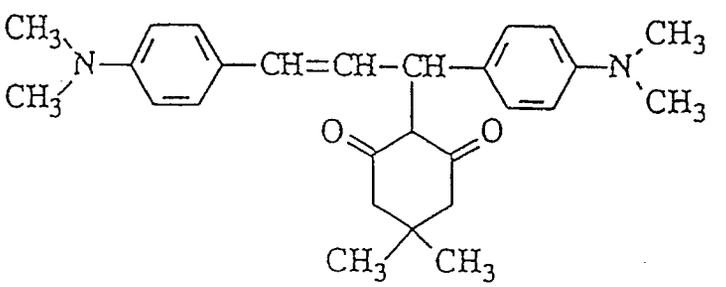
(3 9)



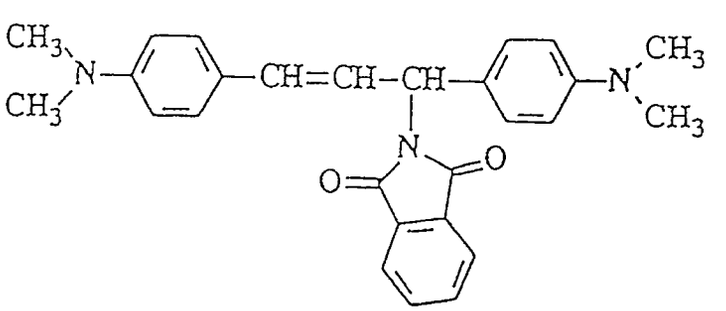
(4 0)



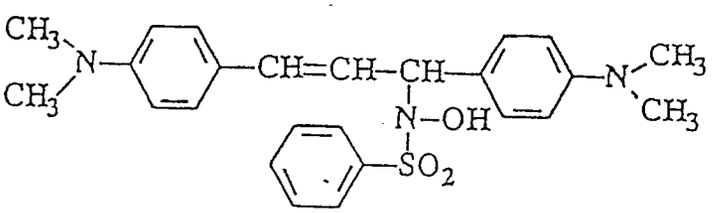
(4 1)



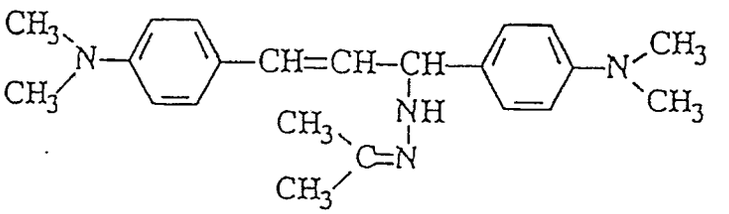
(4 2)



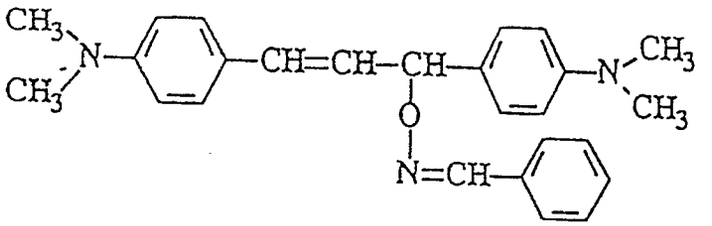
(4 3)



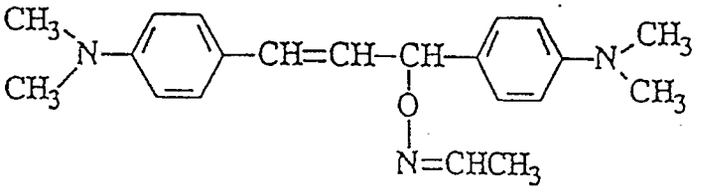
(4 4)



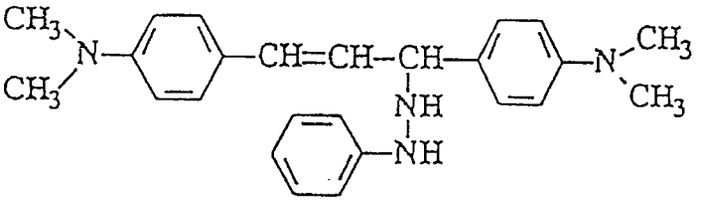
(4 5)



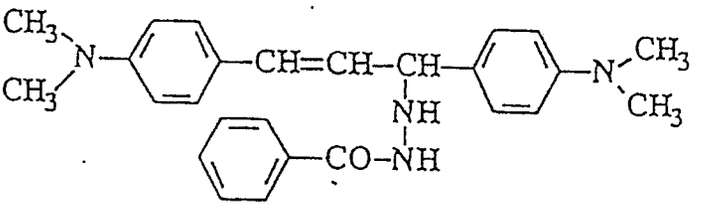
(4 6)



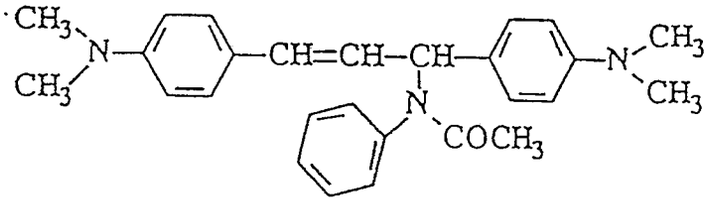
(4 7)



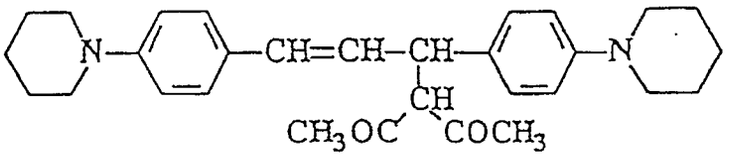
(4 8)



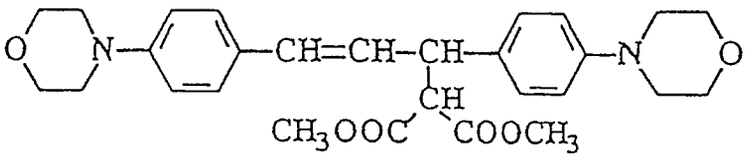
(4 9)



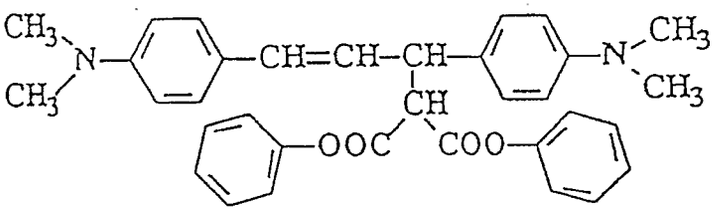
(5 0)



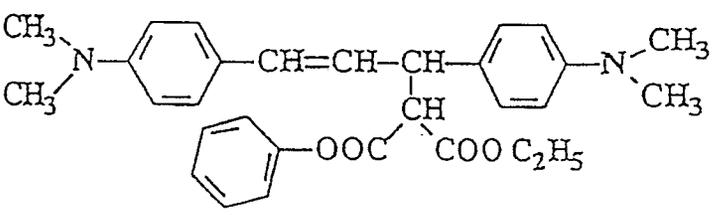
(5 1)



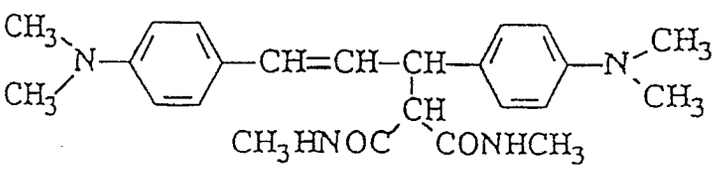
(5 2)



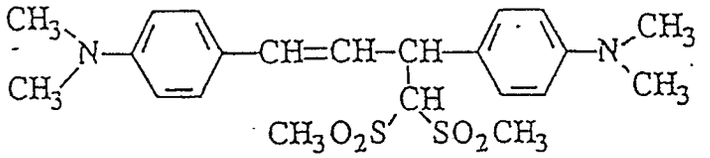
(5 3)



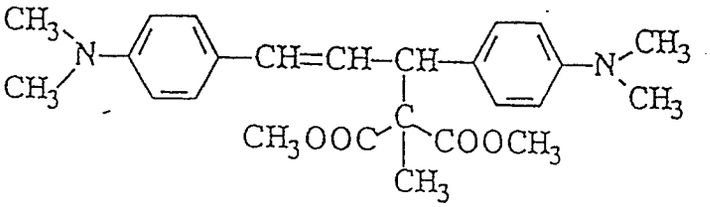
(5 4)



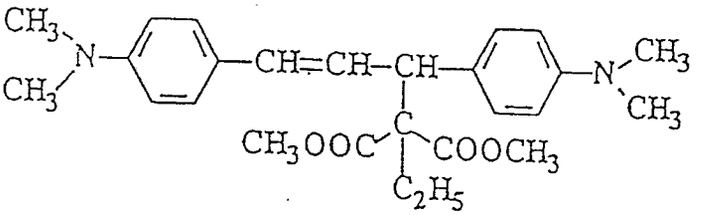
(5 5)



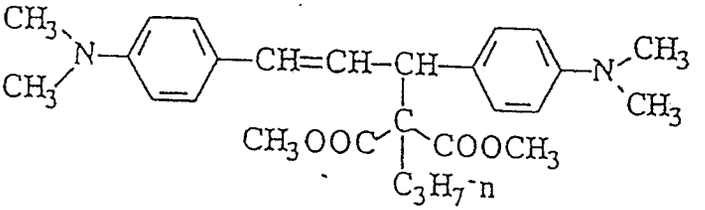
(5 6)



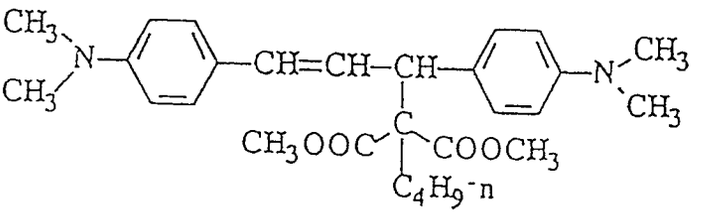
(5 7)



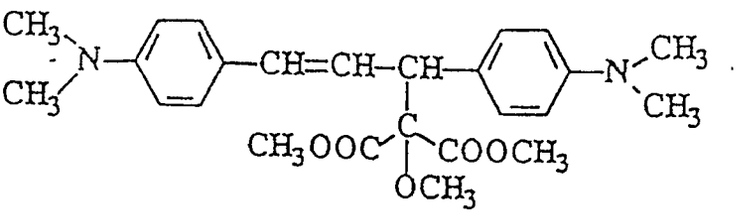
(5 8)



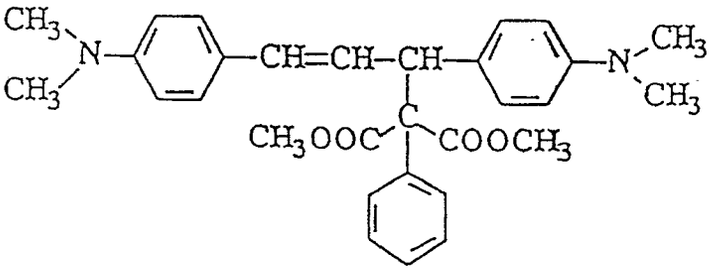
(5 9)



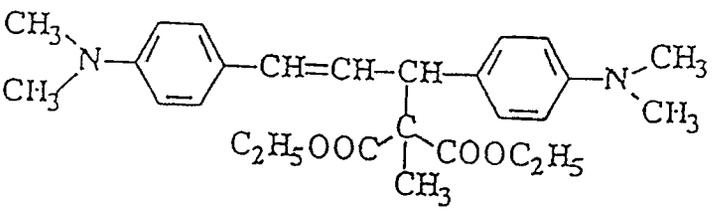
(6 0)



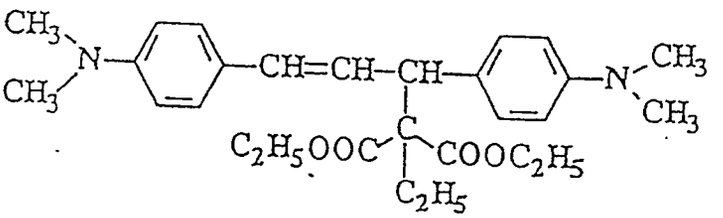
(6 1)



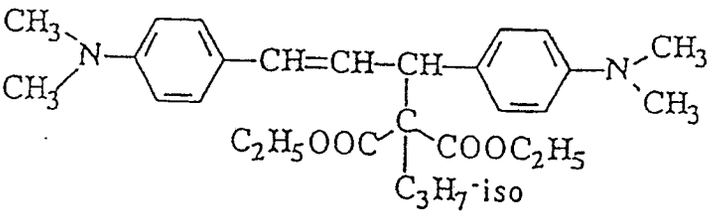
(6 2)



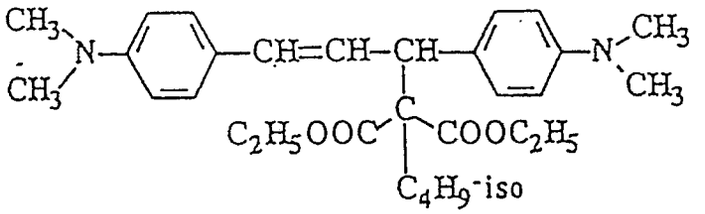
(6 3)



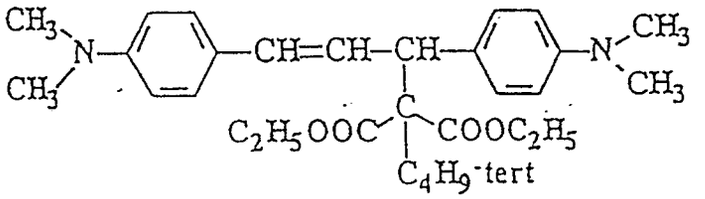
(6 4)



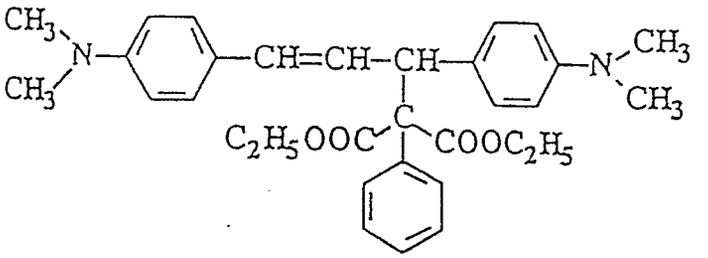
(6 5)



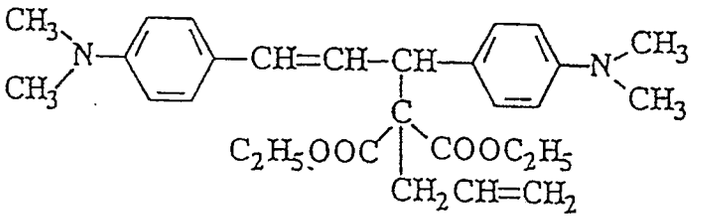
(6 6)



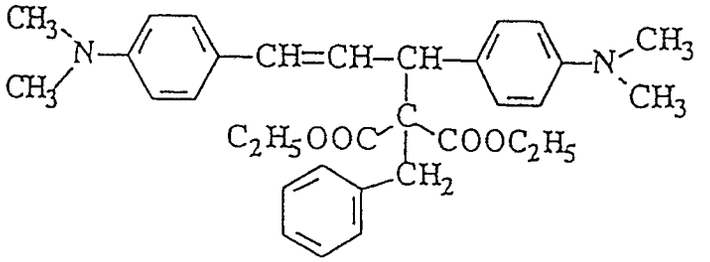
(6 7)



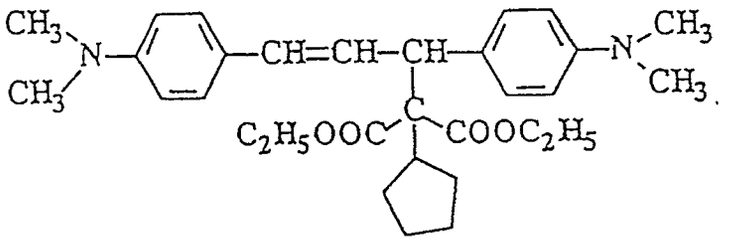
(6 8)



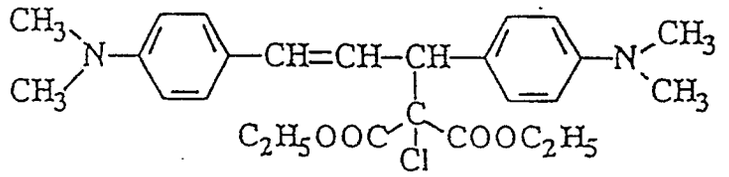
(6 9)



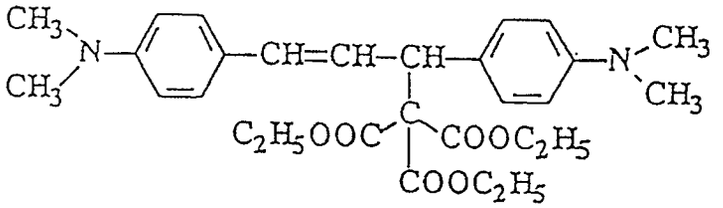
(7 0)



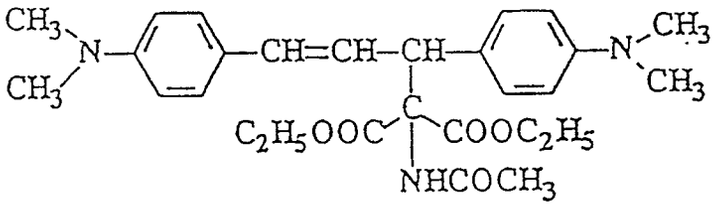
(7 1)



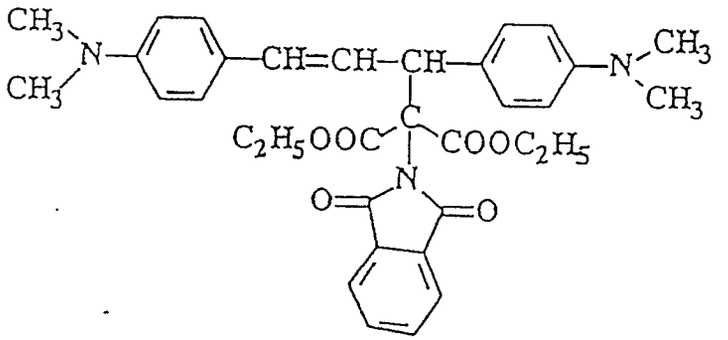
(7 2)



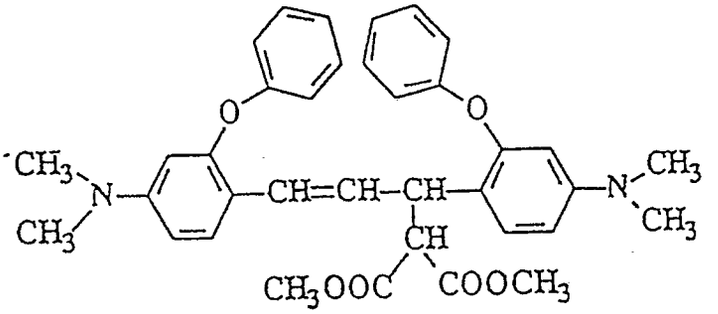
(7 3)



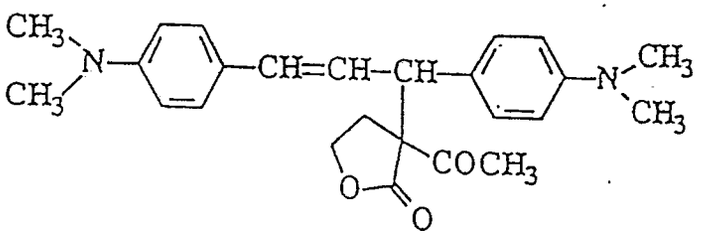
(7 4)



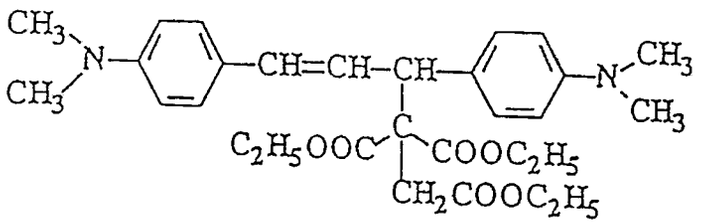
(7 5)



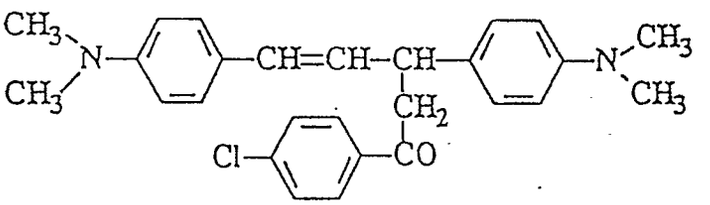
(7 6)



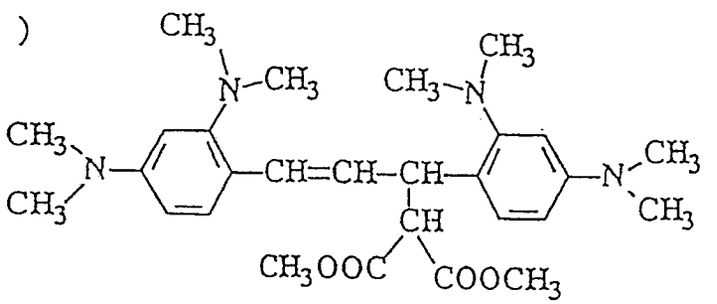
(7 7)



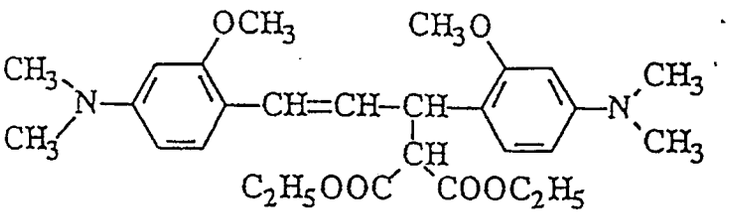
(7 8)



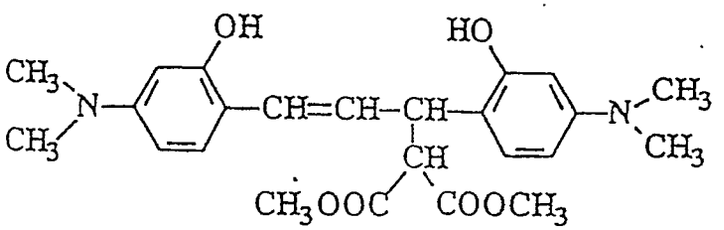
(7 9)



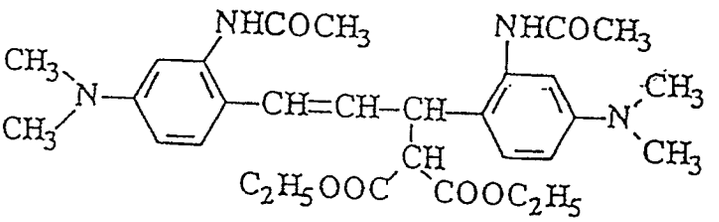
(8 0)



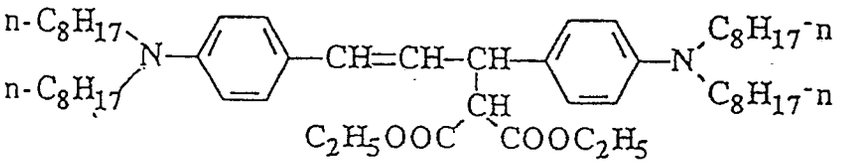
(8 1)



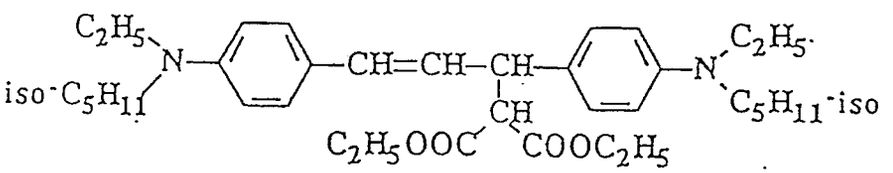
(8 2)



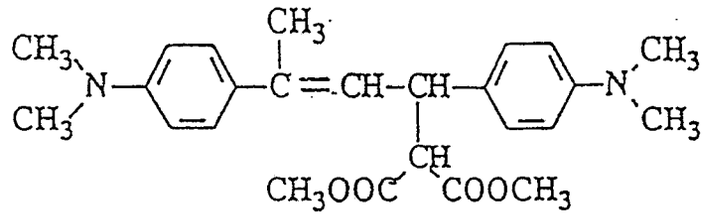
(8 3)



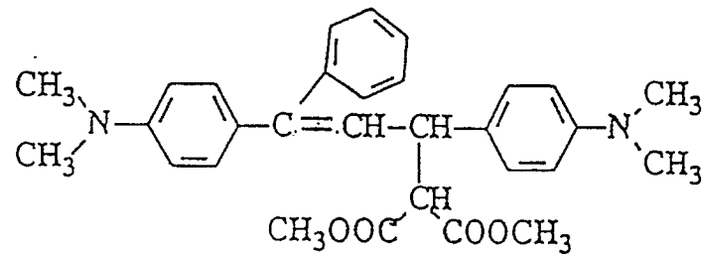
(8 4)



(8 5)



(8 6)



In preparing a recording medium in accordance with the present invention, the leuco dye represented by formula (I) may be used together with other electron-donating dyes such as a triphenylmethane phthalide, a fluoran, a phenothiazine, an indolylphthalide, a leucoauramine, a leucorhodamine, a triphenylmethane, a triazene, a spiropyrane, a fluorene, a spirodipyran, a pyridine or a pyrazine.

In the above described combination, the leuco dye represented by formula (I) is preferably used in an amount of not less than 30 % by weight with respect to the total content of the electron-donating dyes in order to sufficiently improve the properties of the recording medium. Specific examples of phthalides for use in the present invention include those described in U.S. Reissued Patent 23,024, and U.S. Patents 3,491,111, 3,491,112, 3,491,116 and 3,509,174. Useful examples of the fluorans are described in U.S. Patents 3,624,107, 3,627,787, 3,641,011, 3,462,828, 3,681,390, 3,920,510, and 3,959,571. Useful examples of the spirodipyrans are described in U.S. Patent 3,971,808. The useful examples of the pyridines and pyrazines are described in U.S. Patents 3,775,424; 3,853,869; and 4,246,318. Useful examples of the fluorenes are described in EP 278614A and Japanese Patent application No. 61-240989.

The leuco dye represented by formula (I) provides a color when contacted with an electron-accepting compound as a color developing agent. Useful electron-accepting compounds include phenol derivatives, salicylic acid derivatives, metal salts of aromatic carboxylic acids, acid clay, bentonite, novolak resins, metal-treated novolak resins, metal complexes, and the like, and mixtures thereof. specific examples of the electron accepting compound for use in the present invention include those described in JP-B-40-9309, JP-B-45-14039, JP-A-52-140483, JP-A-48-51510, JP-A-57-210886, JP-A-58-87089, JP-A-59-11286, JP-A-60-176795, JP-A-61-95988, and U.S. Patents 3,767,449, 4,219,219, 4,269,893, 4,374,671 and 4,687,869, etc. In particular, the use of a salicylic acid derivative, a phenol derivative, a metal complex, acid clay, or bentonite as the electron accepting compound is preferable. Among them, acid clay and bentonite are more preferable. These substances are applied to the recording medium, e.g., in the form of a fine dispersion or fine droplets.

A recording medium of the present invention comprises a support having thereon a recording layer comprising a binder and at least one electron-denoting leulo dye represented by formula (I). The type of support and binder to be employed depends on the usage of the recording medium as discussed below.

A recording layer of the present invention may contain a variety of additives which are known in the field of recording media and high-molecular weight resins, such as a pigment, a wax, an antistatic agent, an ultraviolet absorbing agent, an antifoaming agent, an electricity-conducting agent, a fluorescent dye, a surfactant, and the like, depending upon the application of the recording medium.

The present invention may be used to prepare a pressure-sensitive paper, as described, for example, in U.S. Patents 2,505,470, 2,505,471, 2,505,489, 2,548,366, 2,712,507, 2,730,456, 2,730,457, 3,103,404, 3,418,250, and 4,010,038. Generally, the pressure-sensitive paper comprises at least one pair of sheets, each sheet of which separately containing either the electron-donating leuco dye or the electron-accepting compound.

The electron donating leuco dye represented by formula (I) and the electron-accepting compound may

be respectively contained in microcapsules, which microcapsules are dispersed in the recording layer. The microcapsules can be produced for example, by the techniques of coacervation of a hydrophilic colloid sol as described in U.S. Patents 2,800,457 and 2,800,458, interfacial polymerization as described in British Patents 867,797, 950,443, 989,264, and 1,091,076, and the method described in U.S. Patent 3,103,404.

The materials for the capsule wall are preferably of a synthetic resin type: for example, a polyurethane and/or polyurea type, or a melamine resin type.

Generally a recording sheet of the present invention containing the color forming agent is prepared by encapsulating an electron-donating leuco dye represented by formula (I) alone or as a solution in a solvent such as a synthetic oil (e.g., an alkylated naphthalene, an alkylated diphenyl, an alkylated diphenylmethane, an alkylated terphenyl, chlorinated paraffin), a vegetable oil (e.g., cotton oil, castor oil); an animal oil, a mineral oil; and mixtures thereof, and the like, and then applying the microcapsules, by means, for example, of air-knife applying onto a sheet of paper or wood-free paper, a plastic sheet or a resin-coated paper sheet.

The microcapsule may also contain an additive such as an ultraviolet absorbing agent and an antioxidant in addition to the electron-accepting leuco dye represented by formula (I). Particularly for the purpose of improving the storage property of the electron-accepting leuco dye before use, an ultraviolet absorbing agent of the benzotriazole type, an antioxidant of a hindered amine type, a hindered phenol type, an aniline type, or a quinoline type, and the like may be used.

A sheet comprising a recording layer containing a color-developing agent is prepared by mixing an electron-accepting compound with an optional additive, dispersing the resulting mixture in a binder such as a styrene-butadiene latex and polyvinyl alcohol, and applying the dispersion together with a pigment as described below onto a support such as a paper sheet, a plastic sheet, and a resin-coated paper sheet.

The amounts of the electron-donating leuco dye and the electron-accepting compound to be used are appropriately determined depending on the coating thickness, the type of the pressure-sensitive recording paper, the method of preparation of the microcapsule, and other conditions. The amounts are readily determined by an artisan.

A thermosensitive paper containing the leuco dye represented by formula (I) may be prepared as described in GB 2200220A, JP-A-62-144989, Japanese Patent Application No. 62-244883, and others. Specifically, the electron-donating leuco dye and the electron-accepting compound are pulverized and dispersed to a particle diameter of 10 μ or less, and preferably 3 μ in a dispersion medium before use. The dispersion medium is generally an aqueous solution of a water-soluble polymer in a concentration of approximately from 0.5 to 10 wt%. The dispersion is prepared by means of a ball mill, a sand mill, a horizontal sand mill, an attritor, a colloidal mill, or the like.

The ratio of the electron-donating leuco dye and the electron-accepting compound to be used in the thermosensitive paper is preferably in the range of 1:10 to 1:1, particularly preferably from 1:5 to 2:3 by weight. A heat-fusible substance is preferably used together with the color forming components. The heat-fusible substance is finely dispersed simultaneously with the electron-donating leuco dye or with the electron-accepting compound. The addition amount of the heat-fusible substance is in the range of from 20 % to 300 %, preferably from 40 % to 150 % by weight based on the electron-accepting compound.

The coating liquid thus prepared may further contain an additive, generally used for thermosensitive papers, including, for example, an oil-absorbing substance such as an inorganic pigment, a polyurea filler, and the like which is dispersed in the binder to prevent soiling of the recording head. Furthermore, to reduce sticking to the recording head, a fatty acid, a metal soap, or the like may be added. Thus, in addition to the electron-donating leuco dye and the electron-accepting compound which serve as color forming components, additives such as a heat-fusible material, a pigment, a wax, an antistatic agent, an ultraviolet absorbing agent, an antifoaming agent, an electricity-conducting agent, a fluorescent dye, a surfactant and the like may be contained in the coating liquid. The coating liquid is then applied onto a support and dried to constitute a recording medium.

Further, a protective layer may be provided on the surface of the thermosensitive recording layer, as required. The protective layer may comprise a lamination of two or more layers. Onto the back side of the recording medium, a coating solution analogous to the one employed for the protective layer may be applied for correcting the curl balance of the support or for improving the chemical resistance of the back side. A label may be prepared by applying an adhesive and a release paper onto the backside of the recording medium.

The electron-donating leuco dye and the electron-accepting compound are usually applied onto a support as a dispersion in a binder. The binder is generally water-soluble, and useful examples thereof include polyvinyl alcohol, hydroxyethylcellulose, hydroxypropylcellulose, epichlorohydrin-modified polyamides, ethylene-maleic anhydride copolymers, styrene-maleic anhydride copolymers, isobutylene-maleic salicylic anhydride copolymers, polyacrylic acids, polyacrylamides, methylol-modified

polyacrylamide, starch derivatives, casein and gelatin. The binder may further contain a water-resistance-improving agent, or a hydrophobic polymer emulsion such as styrene-butadiene rubber latex or acrylic resin emulsion for improving the water-resistance. The coating liquid is applied onto base paper, wood-free paper, synthetic paper, a plastic sheet, resin-coated paper or neutralized paper.

Useful examples of the heat-fusible substance are disclosed in JP-A-58-57989, JP-A-58-87094, Specific examples of the heat-fusible substance include ether compounds such as 2-benzyloxynaphthalene, 4-benzylbiphenyl, 1,2-di-m-tolyloxyethane, 1,2-diphenoxyethane, 1,4-diphenoxybutane, bis[β-(p-methoxyphenoxy)ethyl] ether, 1-phenoxy-2-p-ethylphenoxyethane, 1-p-methoxyphenoxy-2-phenoxypropane, 1-phenoxy-2-p-methoxyphenoxypropane, 1,2-bis(p-methoxyphenoxy)propane, 1,3-bis(p-methoxyphenoxy)-propane, 1-p-methoxyphenoxy-2-o-chlorophenoxyethane, 4-(p-methoxybenzylthio)anisole, 1-phenoxy-2-p-methoxyphenylthioethane, 1,2-bis(p-methoxyphenylthio)ethane, 1-p-methylphenoxy-2-p-methoxyphenylthioethane and 4-(4-chlorobenzyloxy)ethoxybenzene; stearic amide, methylene-bis-stearamide, stearic anisidide, behenic amide, stearic anilide and stearyl urea.

Useful pigments includes kaolin, calcined kaolin, talc, diatomaceous earth, calcium carbonate, aluminum hydroxide, magnesium hydroxide, zinc oxide, lithopone, amorphous silica, colloidal silica, calcined gypsum, silica, magnesium carbonate, titanium oxide, alumina, barium carbonate, barium sulfate, mica, microbaloon, urea-formalin fillers, particulate polyesters and cellulose fillers.

Useful metal soaps include polyvalent metal salts of higher fatty acids such as zinc stearate, aluminum stearate, calcium stearate and zinc stearate.

Useful waxes include paraffin wax, carboxy-modified paraffin wax, carnauba wax, microcrystalline wax, polyethylene wax, polystyrene wax, higher fatty acid esters and amides.

Useful hindered phenol compounds, preferably include phenol derivatives which are substituted at the 2- and/or 6-position by a branched alkyl group. Examples thereof include 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,1,3-tris(2-ethyl-4-hydroxy-5-t-butylphenyl)butane, 1,1,3-tris(3,5-di-t-butyl-4-hydroxyphenyl)butane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)propane, 4,4-butylidenebis(6-t-butyl-3-methylphenol, 4,4-thiobis(3-methyl-6-t-butylphenol), 2,2-methylenebis(6-t-butyl-4-methylphenol), 2,2-methylenebis-(6-t-butyl-4-ethylphenol), octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, 1,3,5-trimethyl-2,4,6-tris-(3,5-di-t-butyl-4-hydroxybenzyl)benzene, tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]-methane and 2,2,6,6-tetramethyl-4-piperidinyl sebacate.

The amount of the hindered phenol contained in the recording layer is preferably in the range of from 1 % to 200 %, more preferably from 5 % to 100 % by weight based on the electron-accepting compound.

Useful ultraviolet absorbing agents include cinnamic acid derivatives, benzophenone derivatives, benzotriazolylphenol derivatives. Specific examples thereof include butyl α-cyano-β-phenyl cinnamate, o-benzotriazolyl phenol, o-benzotriazolyl-p-chlorophenol, o-benzotriazolyl-p-methylphenol, o-benzotriazolyl-2,4-di-t-butylphenol, o-benzotriazolyl-2,4-di-t-octylphenol.

Useful water-resistance improving agents include water-soluble precondensates of, e.g., N-methylol urea, N-methylolmelamine, urea-formalin; dialdehyde compounds such as glyoxal, glutalaldehyde; inorganic crosslinking agents such as boric acid, borax; polyacrylic acid, methyl vinyl ether-maleic anhydride copolymers, and their mixtures.

Useful components of the protective layer include water-soluble polymers such as polyvinyl alcohol, carboxy-modified polyvinyl alcohol, vinyl acetate-acrylamide copolymers, silicone-modified polyvinyl alcohol, starch, modified starch, methylcellulose, carboxymethylcellulose, hydroxymethylcellulose, gelatins, gum arabic, casein, styrene-maleic acid copolymer hydrolyzate, styrene-maleic acid copolymer half ester hydrolyzate, isobutylene-maleic anhydride copolymer hydrolyzate, polyacrylamide derivatives, polyvinylpyrrolidone, sodium polystyrenesulfonate, sodium alginate; and water-insoluble polymers such as styrene-butadiene rubber latexes, acrylonitrile-butadiene rubber latexes, methyl acrylate-butadiene latexes, vinyl acetate emulsion.

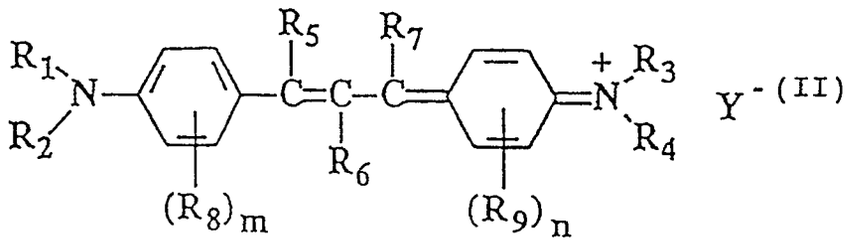
The protective layer may contain a pigment, a metal soap, a wax, a water-resistance improving agent or the like for compatibility with the thermosensitive recording head.

For uniformly applying the protection layer onto the thermosensitive color-forming layer, a surfactant may be added to the coating liquid thereof. Useful surfactants include metal salts of sulfosuccinic acid type compounds, fluorine-containing surfactants, etc. Specifically, sodium salts or ammonium salts of di-(n-hexyl)sulfosuccinic acid or di-(2-ethylhexyl)sulfosuccinic acid are preferred. Any anionic surfactant, however, is effective.

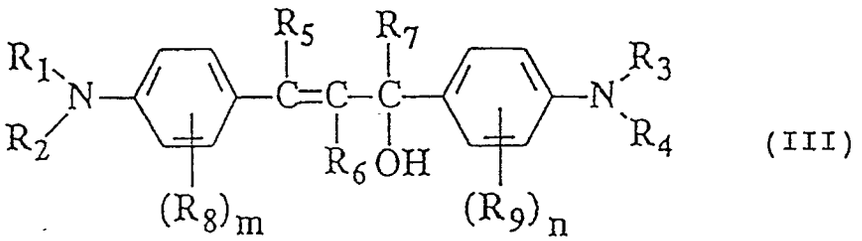
Photosensitive pressure-sensitive paper containing the leuco dye represented by formula (I) can be prepared as described, for example, in U.S. Patent 4,800,149, JP-A-57-179836, etc. Generally, a photopolymerization initiator such as silver iodide, silver bromide, silver behenate, Michler's ketone, a benzoin derivative, a benzophenone derivative, etc. and a polyfunctional monomer as a crosslinking agent

such as a polyallyl compound, poly(meth)acrylate, poly(meth)acrylamide, and the like together with an electron-donating leuco dye and optionally a solvent are enclosed in a capsule made of a synthetic resin such as polyether urethane or polyurea. After imagewise exposure, the electron-donating leuco dye in the unexposed portion is brought into contact with the electron-accepting compound to form color.

The electron-donating leuco dye used in the invention is readily prepared, for example, from compounds of the general formula (II) or (III) below according to known methods, for example, with reference to British Patent 2,101,648, U.S. Patent 4,287,336, JP-B-60-6794, JP-A-48-729, JP-A-63-208558, and JP-A- 60-231766.



(II)



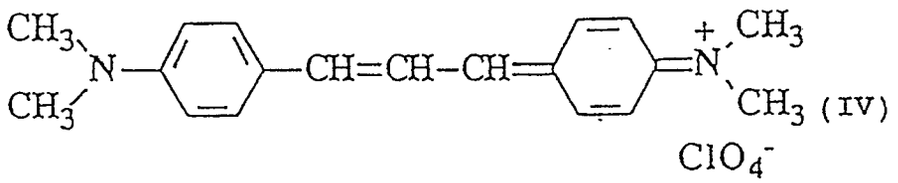
(III)

In the above formulae, R_1 to R_9, m, and n have the same meaning as described above for formula (I), and Y represents an anion necessary for forming a dye, for example, Cl, Br, ClO_4, PF_6 or BF_4.

SYNTHESIS EXAMPLE 1

Exemplary Compound (1):

0.15 mole of 4N,N-dimethylaminobenzaldehyde, 0.15 mole of 4-N,N-dimethylaminoacetophenone, 0.05 mole of 28 % sodium methoxide solution in methanol, and 200 ml of ethanol were placed in a three-neck flask equipped with a stirrer. The mixture was refluxed and stirred for 10 hours. After cooling, the precipitated crystalline matter was separated by filtration and washed with methanol, to obtain 0.13 mole of 1-(4-N,N-dimethylaminobenzoyl)-2-(4-N,N-dimethylaminophenyl)ethylene. Subsequently, 0.15 mole of lithium aluminum hydride and 500 ml of tetrahydrofuran were weighed out. Thereto, 0.1 mole of the above noted ketone was gradually added with stirring at room temperature, and the stirring was continued for an additional one hour at room temperature. The reaction mixture was cooled and 120 ml of water was added thereto dropwise. Additionally, a mixture of 0.1 mole of 70 % perchloric acid with 200 ml of acetic acid and 1 liter of water were sequentially gradually added thereto. The precipitated crystals were collected by filtration and washed with water, to obtain the compound (IV) below.



(IV)

0.01 mole of this compound and 50 ml of methanol were weighed out, and thereto 0.011 mole of 28 wt% sodium methoxide solution was added dropwise, and the mixture was stirred for an additional one hour at room temperature. The reaction mixture was poured into water, and filtered and dried to obtain the

exemplary compound (1) as a pale yellow crystal (m.p. 63 - 65 °C).

SYNTHESIS EXAMPLE 2
Exemplary Compound (9):

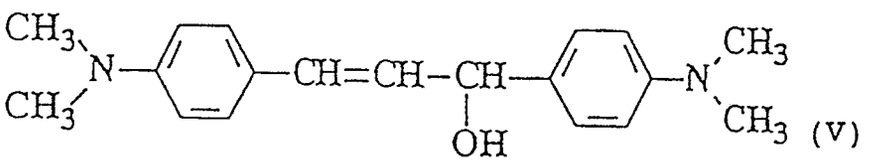
0.011 mole of sodium hydride and 40 ml of tetrahydrofuran were placed in a three-neck flask equipped with a stirrer. Thereto, 0.0105 mole of acetylacetone was added dropwise with stirring. After stirring for 5 minutes at room temperature, 0.01 mole of the compound (IV) was added gradually, and stirred at 50 C for one hour. The reaction mixture was poured into water, and was filtered and dried to obtain the exemplary compound (9) as a white crystal (m.p.: 102 - 104 °C).

SYNTHESIS EXAMPLE 3
Exemplary Compound (19):

0.011 mole of sodium hydride and 40 ml of tetrahydrofuran were placed in a three-neck flask equipped with a stirrer. Thereto, 0.0105 mole of piperidine was added dropwise with stirring. After stirring for 5 minutes at room temperature, 0.01 mole of the compound (IV) was added gradually, and stirred at room temperature for 5 hours. The reaction mixture was poured into water, and was filtered and dried to obtain the exemplary compound (19) as a white crystal (m.p.: 88 - 90 °C).

SYNTHESIS EXAMPLE 4
Exemplary Compound (28):

0.01 mole of the compound (V) below



(V)

together with 0.01 mole of dimethyl malonate and 30 ml of ethylcelllosolve were placed in a three-neck flask equipped with a stirrer, and were stirred at 100 °C for 3 hours. The reaction mixture was poured into water, and was filtered and dried to obtain the exemplary compound (28) as a white crystal (m.p.: 116 - 118 °C).

SYNTHESIS EXAMPLE 5
Exemplary Compound (31):

0.01 mole of sodium hydride and 40 ml of tetrahydrofuran were placed in a three-neck flask equipped with a stirrer. Thereto, 0.01 mole of ethyl acetoacetate was added dropwise with stirring. After stirring for 5 minutes at room temperature, 0.01 mole of the compound (IV) was added gradually, and stirred at room temperature for 1 hour. The reaction mixture was poured into water, and was filtered and dried to obtain the exemplary compound (31) as a white crystal (m.p.: 81 - 83 °C).

The present invention is described below by reference to the following detailed Examples; however, the present invention is not to be construed as being limited thereby. The terms "%" and "parts" are based on weight unless indicated otherwise.

EXAMPLE 1

20 g each of exemplary compound (9), bisphenol A as an electron-accepting compound, and 4-(4-chlorobenzyloxy)-ethoxybenzene were individually dispersed in 100 g of aqueous 5% polyvinyl alcohol solution (Kuraray PVA 105) for one day by means of a ball mill to prepare three separate liquid dispersions each having a volume-average particle diameter of 1.5 μm or less. Separately, 80 g of calcium carbonate was dispersed in 160 g of 0.5% sodium hexametaphosphate solution by means of a homogenizer to prepare a pigment liquid dispersion.

The liquid dispersions as prepared above were mixed in the following proportions: 5 g of the electron-donating leuco dye liquid dispersion, 10 g of the electron-accepting compound liquid dispersion, 10 g of the

heat-fusible substance liquid dispersion, and 15 g of the pigment liquid dispersion. To this mixture were added 3 9 of a 21% zinc stearate emulsion to obtain a thermosensitive coating liquid.

The coating liquid was applied on wood-free paper with a coating bar to provide a dry coat layer weight of 5 g/m^2. The coated material was dried at 50 °C for one hour, and was subjected to supercalender treatment, to thereby obtain a thermosensitive recording paper.

The resulting thermosensitive recording paper exhibited superior storage properties prior to recording without the formation of fog.

Printing was conducted on the thermosensitive paper by means of a thermosensitive printing test apparatus provided with a thermal head (KLT-216-8MPD1, made by Kyocera K.K.) and a press roll having an applied pressure of 100 kg/cm^2 at a recording head voltage of 24 V, a pulse cycle of 10 ms, and a pulse width of 1.0 ms. A blue image was produced. The resulting developed image exhibited satisfactory resistance to chemicals and sunlight.

EXAMPLES 2 TO 3

Coated paper was prepared in the same manner as in Example 1, except that liquid dispersions of the electron-donating leuco dyes and the electron-accepting compounds shown below were prepared in the same manner as in Example 1 and used in place of those employed in Example 1, respectively.

Example 2:

Electron-donating leuco dye: 10 g of exemplary compound (22) dispersion and 10 g of Crystal Violet lactone dispersion.

Electron-accepting compound: 5 g of bis(4-hydroxyphenyl)sulfone dispersion, and 15 g of zinc rhodanidebenzimidazole complex dispersion.

Example 3:

Electron-donating leuco dye: 10 g of exemplary compound (14) dispersion, and 10 g of 3-(1-n-octyl-2-methylindol-3-yl)-3-(4-N,N-diethylamino-2-ethoxyphenyl)phthalide dispersion.

Electron-accepting compound: 8 g of 1,1-bis(4-hydroxyphenyl)cyclohexane dispersion, 8 g of zinc 4-β-p-methoxyphenoxyethoxysalicylate dispersion, and 4 g of the complex of zinc rhodanide with 1-phenyl-2,3-dimethyl-3-pyrazolin-5-one dispersion.

In both of Examples 2 and 3, the resulting developed images exhibited satisfactory resistance against chemicals and sunlight.

EXAMPLE 4

(1) Preparation of an electron-donating leuco dye-containing capsule sheet:

Five parts of a partial sodium salt of polyvinylbenzene-sulfonic acid (Versa TL500, made by National Starch Co.) was dissolved in 95 parts of hot water, and the resulting solution was cooled. The pH of the solution was adjusted to 4.0 by addition of an aqueous sodium hydroxide solution. To 100 parts of this aqueous 5% aqueous solution of the partial sodium salt of polyvinylbenzenesulfonic acid, 100 parts of diisopropylnaphthalene solution containing the exemplary compound (1) at a concentration of 3.5 wt% was dispersed and emulsified to prepare a liquid emulsion having a particle size of 4.0 μ. Separately, 6 parts of melamine, 11 parts of aqueous 37 wt% formaldehyde solution, and 30 parts of water were heated and stirred at 60 °C for 30 minutes to prepare a transparent aqueous solution of a prepolymerizate of melamine-formaldehyde.

This aqueous solution was mixed with the above described liquid emulsion. The pH of the solution was adjusted to 6.0 by adding 2M phosphoric acid solution with stirring, and the temperature of the solution was raised to 65 °C and stirred for 6 hours. This liquid microcapsule dispersion was cooled to room temperature, and was adjusted to pH 9.0.

To this liquid dispersion, 200 parts of an aqueous 10% polyvinyl alcohol solution, and 50 parts of particulate starch were added, and the solid content of the microcapsule liquid dispersion was adjusted to a solid content of 20 % by addition of water.

The resulting coating liquid was applied onto a base paper having a basis weight of 50 g/m^2 in a solid coating amount of 5 g/m^2 with an air knife coater, and the coated material was dried to prepare an electron-donating leuco dye-containing capsule sheet.

(2) Preparation of an electron-accepting compound sheet:

10 parts of zinc 3,5-bis-α-methylbenzylsalicylate was dissolved in 20 parts of 1-isopropylphenyl-2-phenylethane. This solution was mixed with 50 parts of aqueous 2% polyvinyl alcohol solution and 0.1 part of aqueous 10% triethanolamine dodecylbenzenesulfonate solution, and emulsified to provide an average particle diameter of 3 μm.

Subsequently, a liquid dispersion consisting of 80 parts of calcium carbonate, 20 parts of zinc oxide, 1 part of sodium hexametaphosphate, and 200 parts of water was mixed with the emulsion prepared above. Thereto as a binder, 100 parts of aqueous 10% PVA solution and 10 parts (as solid) of a carboxy-modified SBR (styrene butadiene rubber) latex were added, and the solid content was adjusted by addition of water, to thereby obtain Coating liquid (A).

A dispersion consisting of 10 parts of the above described electron-accepting compound, 20 parts of silton clay, 60 parts of calcium carbonate, 20 parts of zinc oxide, 1 part of sodium hexametaphosphate, and 200 parts of water was dispersed by use of a sand grinder to provide an average particle diameter of 3 μm.

To this dispersion, 16 parts of aqueous 10% PVA solution, 100 parts of an aqueous 10% PVA solution, and 10 parts (as solid) of a carboxy-modified SBR latex were added, and the solid concentration was adjusted to 20 % by the addition of water, to thereby obtain Coating liquid (B).

Coating liquid (A) and Coating liquid (B) were mixed in a ratio of 1:1 based on the content of the electron-accepting compound, and applied onto a base paper having a basis weight of 50 g/m^2 in a solid coating amount of 5.0 g/m^2 with an air knife coater. The coated material was then dried to thereby an electron-accepting compound sheet.

The face of the electron-donating leuco dye-containing microcapsule sheet was overlaid on the electron-accepting compound sheet, and the letter "m" were continuously pressure-typed thereon using an electric typewriter (IBM 6747 type). A bluish green color was rapidly developed. The resulting colored image had satisfactory resistance against chemicals and sunlight.

EXAMPLE 5

An electron-donating leuco dye-containing microcapsule sheet was prepared in the same manner as in Example 4, except that exemplary compound (19) was used in place of the electron-donating leuco dye of Example 4. The face of the sheet was overlaid on the electron-accepting compound sheet of Example 4, and the letter "m" were continously pressure-typed thereon using the electric typewriter. A bluish green color was rapidly developed. The resulting colored image had satisfactory resistance against chemicals and sunlight.

EXAMPLE 6

An electron-accepting compound sheet described below was employed instead of the sheet of Example 4.

(2') Preparation of an electron-accepting compound sheet:

100 parts of acid clay was dispersed in 400 parts of aqueous 0.5% sodium hydroxide solution. 20 parts (as solid) of styrene-butadiene copolymer latex and 40 parts of aqueous 10 % starch solution were added thereto, and stirred and mixed sufficiently to prepare an electron-accepting compound-coating solution.

The coating liquid thus prepared was applied onto a base paper having a basis weight of 50 g/m^2 in a solid coating amount of 5.0 g/m^2 using an air knife coater. The coated material was then dried to obtain an electron-accepting compound sheet.

The electron-donating leuco dye-containing microcapsule sheet of Example 4 was overlaid onto the above described electron-accepting compound sheet, and the letter "m" were continuously pressure-typed thereon using the electric typewriter to develop a color. The density of the color was measured 24 hours after developing with reflection densitometer Model RD 918, made by Macbeth Co. (D_0). This developed color image was further irradiated for 36 hours using a xenon fade meter Model FAL-25AX-HC, made by Suga Shikenki Co. followed by measuring the reflection density thereof (DL). The light-resistance value of the developed color image was calculated by the ratio of DL to D_0 to obtain the value of 0.93.

EXAMPLE 7

The light-resistance value of the developed color image was determined in the same manner as in Example 6 except, that exemplary compound (28) was used in place of the electron-donating leuco dye of Example 6. The resulting light-resistance value was 0.87.

EXAMPLE 8

The light-resistance value of the developed color image was measured in the same manner as in Example 6, except that exemplary compound (31) was used in place of the electron-donating leuco dye of Example 6. The resulting value was 0.87.

EXAMPLE 9

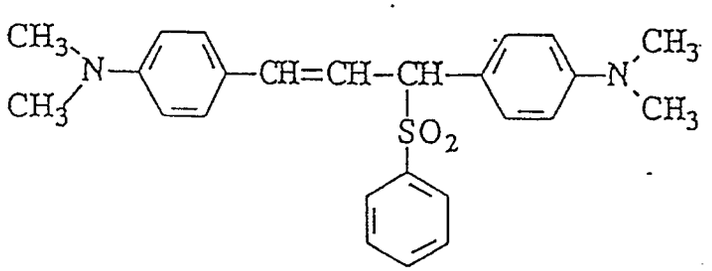
The light-resistance value of the developed color image was measured in the same manner as in Example 6, except that exemplary compound (29) was used in place of the electron-donating leuco dye of Example 6. The resulting value was 0.86.

EXAMPLE 10

The light-resistance value of the developed color image was measured in the same manner as in Example 6, except that exemplary compound (56) was used in place of the electron-donating leuco dye of Example 6. The resulting value was 0.90.

COMPARATIVE EXAMPLE

The light-resistance value of the developed color image was measured in the same manner as in Example 6, except that the compound having the formula below was used in place of the electron-donating leuco dye of Example 6:

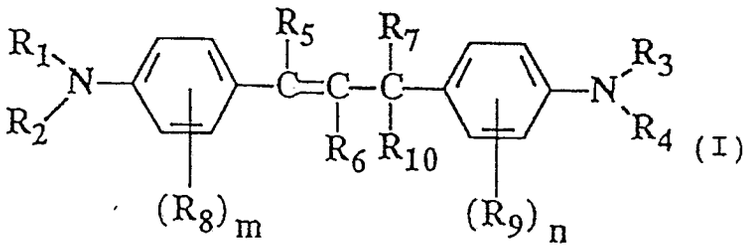


The resulting value was 0.65.

From the above results, the recording medium of the present invention appear superior to conventional those in the light-resistance of the developed color image.

Claims

1. A recording medium utilizing color development of an electron-donating leuco dye by contact with an electron-accepting compound to provide a color dye image, comprising a support having thereon a recording layer comprising a binder and at least one electron-donating leuco dye represented by formula (I):



(I)

wherein R_1 to R_4 each represents a hydrogen atom, an optionally substituted alkyl or aryl group; R_5 to R_9 each represents a hydrogen atom or a univalent group; m and n each represents an integer of from 1 to 4; and R_{10} is a group $-XR_{11}$, $-PO(OR_{12})_2$, $-CR_{13}R_{14}R_{15}$, or $-N\bar{R}_{16}R_{17}$ wherein X is an oxygen atom or a sulfur atom, and R_{11} to R_{17} each represents a hydrogen atom or a univalent group and at least one of R_{13}, R_{14} and R_{15} is an electron-attracting group.

2. A recording medium as in claim 1, wherein R_1 to R_4 each represents a hydrogen atom, an alkyl group, or an aryl group; R_5 to R_7 each represents a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an alkoxycarbonyl group, an aryl group, an aryloxy group, an arylthio group, an aryloxycarbonyl group, or a cyano group; R_8 and R_9 each represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a cyano group, a nitro group, an amino group, a substituted amino group, a hydroxy group, a halogen atom, an alkoxycarbonyl group, an aryloxycarbonyl group, or an acyloxy group; m and n each represents an integer of from 1 to 4; and R_{10} is a group of $-XR_{11}$, $-PO(OR_{12})_2$, $-CR_{13}\bar{R}_{14}R_{15}$, or $-NR_{16}R_{17}$; X is an oxygen atom or a sulfur atom, and R_{11} represents an alkyl group, an aryl group, a heterocyclic group, COR_{18}, SO_2R_{19}, $N=CR_{20}R_{21}$, or $NR_{22}R_{23}$ where R_{18} and R_{19} each represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group; R_{20}, R_{21}, R_{22}, and R_{23} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, COR_{24}, or SO_2R_{25} where R_{24} and R_{25} each represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group; R_{12} is a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group, or two of R_{12} may join together to form a 4- to 12-membered ring which may contain a hetero atom; R_{13}, R_{14}, and R_{15} each represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a halogen atom, a cyano group, a nitro group, SO_2R_{26}, COR_{27}, or $NR_{28}R_{29}$ where R_{26} and R_{27} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a hydroxy group, or $NR_{30}R_{31}$; R_{28}, R_{29}, R_{30}, and R_{31} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, SO_2R_{32}, or COR_{33} where R_{32}, and R_{33} each represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group, and R_{13} and R_{14} may join together to form a 4- to 12-membered ring which may contain a hetero atom, with the proviso that at least one of R_{13}, R_{14} and R_{15} is a halogen atom, a cyano group, a nitro group, SO_2R_{26}, COR_{27} $NR_{28}SO_2R_{32}$ or $NR_{28}COR_{33}$; R_{16} and R_{17} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, SO_2R_{34}, COR_{35}, a hydroxy group, or $NR_{36}R_{37}$ where R_{34} and R_{35} each represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a heterocyclic group, or $NR_{38}R_{39}$; R_{36}, R_{37}, R_{38}, and R_{39} each represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, SO_2R_{40}, or COR_{41} where R_{40}, and R_{41} each represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group; and R_{16} and R_{17} may join together to form a 4- to 12-membered ring which may contain a hetero atom.

3. A recording medium as in Claim 2, wherein R_1 to R_4 each represents a hydrogen atom, an alkyl group having from 1 to 18 carbon atoms, or an aryl group having from 6 to 12 carbon atoms.

4. A recording medium as in any of Claims 1 to 3, wherein R_5 to R_7 each represents a hydrogen atom, an alkyl group , an alkoxy group, an alkylthio group, or an alkoxycarbonyl group having from 1 to 18 carbon atoms; an aryl group, an aryloxy group, an arythio group, or an aryloxycarbonyl group having from 6 to 12 carbon atoms; or a cyano group.

5. A recording medium as in any of Claims 1 to 4, wherein R_8 and R_9 each represents a hydrogen atom; alkyl group or alkoxy group having from 1 to 12 carbon atoms; an alkoxycarbonyl group or an acyloxy

group having from 2 to 12 carbon atoms; an aryl group or an aryloxy group having from 6 to 12 carbon atoms; an aryloxycarbonyl group having from 7 to 12 carbon atoms; a hydroxy group, a chlorine atom, a bromine atom , a fluorine atom, a nitro group, a cyano group, an amino group, a mono- or di-alkylamino group having from 1 to 12 carbon atoms, a mono- or di-arylamino group having from 6 to 12 carbon atoms, or an acylamino group having from 1 to 12 carbon atoms.

6. A recording medium as in any of Claims 1 to 5, wherein R_8 and R_9 are each located at a meta-position relative to $-NR_1R_2$ and $-NR_3R_4$.

7. A recording medium as in any of Claims 1 to 6, wherein R_{10} contains 1 to 20 carbon atoms.

8. A recording medium as in any of Claims 1 to 7, wherein said recording medium is a pressure-sensitive paper, said recording layer further comprising microcapsules containing the at least one electron-donating leuco dye represented by formula (I).

9. A recording medium as in any of Claims 1 to 7, wherein said recording medium is a thermonsensitive paper, said recording layer further comprising a heat-fusible substance and an electron-accepting compound.

10. A recording medium as in any preceding claim, wherein said recording medium further comprises a second electron-donating dye selected from triphenylmethane phthalide, a fluoran, a phenothiazine, an indolylphthalide, a leucoauramine, a leucorhodamine, a triphenylmethane, a triazene, a spiropyrane and a fluorene.

11. A recording medium as in Claim 10, wherein the leuco dye represented by formula (I) is contained in the recording layer in an amount of not less than 30% by weight with respect to the total content of the electron-donating dye.

12. A recording medium as in any preceding claim, wherein said electron-accepting compound is selected from a phenol derivative, a salicylic derivative, a metal salt of an aromatic carboxylic acid, an acid clay, bentonite, a novolak resin, a metal-treated novolak resin and a metal complex.

13. A method for recording using a recording medium as claimed in any preceding claim, comprising contacting the electron-donating leuco dye with an electron-accepting compound.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 3464

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	US-A-4 795 736 (W.M.HUNG ET AL) * column 2, line 1 - column 4, line 25 *	1-13	B 41 M 5/136 B 41 M 5/30
Y	EP-A-0 339 383 (BASF AKTIENGESELLSCHAFT) * page 1, line 1 - page 5, line 46 * * examples *	1-13	
A	US-A-3 957 288 (R.G.LEMAHIEU ET AL) * abstract * * table *	1	
A	US-A-3 958 815 (A.L.POOT ET AL) * abstract * * table *	1	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 496 (C-555)(3343) 23 December 1988, & JP-A-63 208558 (HODOGAYA CHEM IND CO LTD) 30 August 1988, * the whole document *	1	
A	GB-A-2 101 648 (FUJI PHOTO FILM CO LTD) * abstract *	1	
A	GB-A-1 586 937 (FUJI PHOTO FILM CO LTD) * claims 1, 8 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5) B 41 M
A	FR-A-2 298 442 (CIBA-GEIGY AG) * claim 1 * * table *	1	
A	US-A-3 489 800 (F.L.TEWKSBURY JR. ET AL) * abstract *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	03 April 91	MARKHAM R.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document