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

(11) EP 0 675 002 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
25.02.1998 Bulletin 1998/09

(51) Int. Cl.^{6}: **B41M 5/30**

(21) Application number: **95301790.2**

(22) Date of filing: **17.03.1995**

(54) Heat-sensitive recording material

Wärmeempfindliches Aufzeichnungsmaterial

Matériau d'enregistrement thermosensible

(84) Designated Contracting States:
DE ES FR GB

(30) Priority: **18.03.1994 JP 48996/94**
16.05.1994 JP 101261/94

(43) Date of publication of application:
04.10.1995 Bulletin 1995/40

(73) Proprietor:
FUJI PHOTO FILM CO., LTD.
Kanagawa (JP)

(72) Inventors:
- **Kawakami, Hiroshi,**
  c/o Fuji Photo Film Co., Ltd
  Fujinomiya-shi, Shizuoka (JP)
- **Yanagihara, Naoto,**
  c/o Fuji Photo Film Co., Ltd
  Fujinomiya-shi, Shizuoka (JP)
- **Yamamoto, Hiroshi,**
  c/o Fuji Photo Film Co., Ltd
  Fujinomiya-shi, Shizuoka (JP)

(74) Representative:
Dixon, Donald Cossar et al
Gee & Co.
Chancery House
Chancery Lane
London WC2A 1QU (GB)

(56) References cited:
EP-A- 0 253 666 **EP-A- 0 534 257**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Xerox (UK) Business Services
2.15.9/3.4

Description

The present invention relates to a heat-sensitive recording material and, more particularly, to a heat-sensitive recording material comprising a support having provided thereon a color forming layer containing an electron donating colorless dye and an electron accepting compound, wherein provided between said support and said heat-sensitive color forming layer is a subbing layer containing at least one of calcined kaolin, a sizing agent and a wax, the material exhibiting improved color forming properties, storage stability before printing and colored image stability after printing.

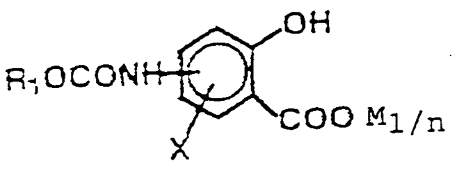
A recording material using an electron donating colorless dye and an electron accepting compound is well known as a pressure-sensitive paper, a heat-sensitive paper, a light- and pressure-sensitive paper, an electro-heat-sensitive recording paper, a heat-sensitive transfer paper and the like. These recording materials are disclosed, 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"), JP-A-57-179836, JP-A-60-123556 and JP-A-60-123557 (the term "JP-A" as used herein means a "published unexamined Japanese patent application"). Particularly, heat-sensitive recording materials are disclosed in JP-B-43-4160 and JP-B-45-14039. These heat-sensitive recording systems have been widely utilized in various fields such as facsimiles, printers and labels, and the demand therefor has increased. However, heat-sensitive recording materials have drawbacks such as fog generated by solvents and the like, and discoloration due to the action of oils and chemicals on the color formers. Consequently, their commercial value in the fields of, in particular, labels, slips, papers for word processors and plotters has been greatly impaired.

A heat-sensitive material using a salicylic acid derivative has been known from EP-A-534257 and EP-A-253666. However, heat-sensitive materials disclosed in these publications are insufficient in performance such as the light fastness of white portions and image portions and the heat fastness of white portions.

The present inventors have extensively studied the oil solubility, water solubility, distribution coefficient, pKa, substituent polarity, and substituent position of electron donating colorless dyes and electron accepting compounds with a view to developing excellent recording materials. However, they encountered a further problem in that by imparting sufficient resistance to minimise the above-mentioned drawbacks, the sensitivity of the material was greatly reduced.

Accordingly, an object of the present invention is to provide a heat-sensitive recording material which is highly sensitive, has excellent storage stability before printing and provides a stable colored image on printing.

The above and other objects of the present invention have been attained by a heat-sensitive recording material comprising a support having provided thereon a heat-sensitive color-forming layer containing an electron donating colorless dye and an electron accepting compound, wherein provided between said support and said heat-sensitive color forming layer is a subbing layer containing at least one of calcined kaolin, a sizing agent and a wax, wherein the heat-sensitive color forming layer contains a salicylic acid derivative represented by formula (1) or a metal salt thereof and a metal compound:



(1)

wherein R_1 represents an alkyl group or an aryl group; X represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, or a halogen atom; M represents a hydrogen atom or an n-valent metal atom; and n represents an integer, provided that n is 1 when M represents a hydrogen atom.

In formula (1), R_1 preferably represents an alkyl group having from 1 to 20 carbon atoms or an aryl group having from 6 to 15 carbon atoms. The alkyl group may be substituted with an alkoxy group having from 1 to 10 carbon atoms, an aryl group having from 6 to 10 carbon atoms, or a halogen atom. The aryl group may be substituted with an alkyl group having from 1 to 10 carbon atoms, an alkoxy group having from 1 to 10 carbon atoms, an aryl group having from 6 to 10 carbon atoms, or a halogen atom. Specific examples of preferred R_1 include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, an n-amyl group, an n-hexyl group, an n-octyl group, a 2-ethylhexyl group, an n-decyl group, an n-dodecyl group, an n-pentadecyl group, a methoxyethyl group, a benzyl group, a 4-methylbenzyl group, a phenyl group, a tolyl group and a methoxyphenyl group.

In formula (1), X preferably represents a hydrogen atom, a chlorine atom, an alkyl group having from 1 to 8 carbon atoms, an aryl group having from 6 to 10 carbon atoms, or an alkoxy group having from 1 to 8 carbon atoms. The alkyl group, the aryl group and the alkoxy group may be substituted. Specific examples of preferred X include a hydrogen atom, a chlorine atom, a methyl group, an ethyl group, an isopropyl group, a t-butyl group, a t-octyl group, a benzyl group, an α-methylbenzyl group, an α,α-dimethylbenzyl group, and a phenyl group.

In formula (1), of the metal atoms represented by M, divalent or trivalent metals are preferred. n preferably represents 2 or 3. Specific examples of preferred M include metals such as zinc, magnesium, barium, calcium, aluminum, tin, titanium, nickel, cobalt, manganese and iron, and particularly zinc, aluminum, magnesium and calcium are preferred.

The substitution position of an R_1OCONH- group in formula (1) is preferably the 4- or 5-position of the salicylic acid.

Specific examples of salicylic acid derivatives which are used in the present invention are described below, but the present invention is not limited thereto.

Specific examples include 4-methoxycarbonylaminosalicylic acid, 4-ethoxycarbonylaminosalicylic acid, 4-n-propyloxycarbonylaminosalicylic acid, 4-isopropyloxycarbonylaminosalicylic acid, 4-n-butoxycarbonylaminosalicylic acid, 4-isobutyloxycarbonylaminosalicylic acid, 4-n-hexyloxycarbonylaminosalicylic acid, 4-n-octyloxycarbonylaminosalicylic acid, 4-(2-ethylhexyloxycarbonylamino)salicylic acid, 4-n-decyloxycarbonylaminosalicylic acid, 4-n-dodecyloxycarbonylaminosalicylic acid, 4-(2-methoxyethoxycarbonylamino)salicylic acid, 4-benzyloxycarbonylaminosalicylic acid, 4-phenoxycarbonylaminosalicylic acid, 4-p-tolyloxycarbonylaminosalicylic acid, 5-methyl-4-n-octyloxycarbonylaminosalicylic acid, 5-phenyl-4-n-octyloxycarbonylaminosalicylic acid, 5-methoxycarbonylaminosalicylic acid, 5-ethoxycarbonylaminosalicylic acid, 5-n-propyloxycarbonylaminosalicylic acid, 5-isopropyloxycarbonylaminosalicylic acid, 5-n-butoxycarbonylaminosalicylic acid, 5-isobutyloxycarbonylaminosalicylic acid, 5-n-hexyloxycarbonylaminosalicylic acid, 5-n-octyloxycarbonylaminosalicylic acid, 5-(2-ethylhexyloxycarbonylamino)salicylic acid, 5-n-decyloxycarbonylaminosalicylic acid, 5-n-dodecyloxycarbonylaminosalicylic acid, 5-(2-methoxyethoxycarbonylamino)salicylic acid, 5-benzyloxycarbonylaminosalicylic acid, 5-phenoxycarbonylaminosalicylic acid, 5-p-tolyloxycarbonylaminosalicylic acid, 3-t-butyl-5-n-octyloxycarbonylaminosalicylic acid, 3-n-octyloxycarbonylaminosalicylic acid, and 6-n-octyloxycarbonylaminosalicylic acid 4-n-Octylcarbonylaminosalicylic acid is particularly preferred.

When the salicylic acid derivative represented by formula (1) is used in combination with at least one metal compound selected from an oxide, a hydroxide, a carbonate and a carboxylate of zinc, aluminum, titanium, silicon, boron, magnesium or calcium, etc., the storage stability of images is further improved. Of the metal compounds used in combination, zinc oxide, aluminum hydroxide, calcium carbonate, silicon dioxide, and aluminum silicate are preferred, and zinc oxide is particularly preferred.

The particle size of the dispersion of the salicylic acid derivative represented by formula (1) of the present invention or the metal salt thereof after being pulverized by means of a sand mill, etc., is 3 μm or less, preferably 2 μm or less, for obtaining color generation sensitivity. When the salicylic acid derivative of the present invention is used, it is preferred to use the solid dispersion solution obtained by mixing the derivative with a metal compound and dispersing using water as a dispersion medium. In this case, of the metal compounds which are used in combination, the above described zinc oxide, aluminum hydroxide, calcium carbonate, silicon dioxide, and aluminum silicate are preferred, and zinc oxide is particularly preferred.

Other electron accepting compounds such as conventionally well known salicylic acid derivatives other than the salicylic acid derivatives of the present invention, metal salts of aromatic carboxylic acids, phenol derivatives, phenol resins, novolak resins, metal treated novolak resins, metal complexes, acid clay, bentonite, etc., may be used in combination in the present invention. Examples of these electron accepting compounds are disclosed 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 and JP-A-61-95988.

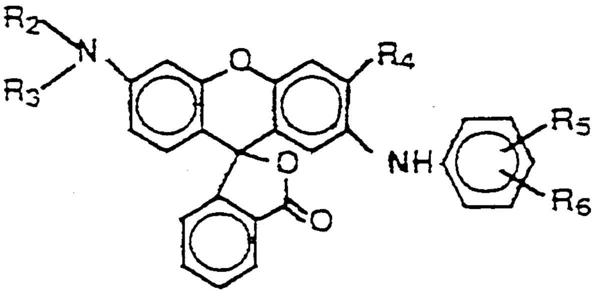
Specific examples of some of them include 4-tert-butylphenol, 4-phenylphenol, 2,2'-dihydroxybiphenyl, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), 4,4'-sec-butylidenediphenol, 4,4'-cyclohexylidenediphenol, bis(3-allyl-4-hydroxyphenyl)sulfone, 4-hydroxyphenyl-3',4'-dimethylphenylsulfone, 4-(4-isopropoxyphenylsulfonyl)phenol, 4,4'-dihydroxydiphenylsulfide, 1,4-bis(4'-hydroxycumyl)benzene, 1,3-bis(4'-hydroxycumyl)benzene, 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-dihydroxydiphenylsulfone, 4-hydroxybenzoic acid benzyl ester, 3,5-di-tert-butylsalicylic acid, 3-phenyl-5-(α,α-dimethylbenzyl)salicylic acid, 3-cumyl-5-t-octylsalicylic acid, 3,5-di-t-butylsalicylic acid, 3-phenyl-5-t-octylsalicylic acid, 3-methyl-5-α-methylbenzylsalicylic acid, 3-methyl-5-cumylsalicylic acid, 3,5-di-t-octylsalicylic acid, 3,5-bis(α-methylbenzyl)salicylic acid, 3-cumyl-5-phenylsalicylic acid, 5-n-octadecylsalicylic acid, 4-pentadecylsalicylic acid, 3,5-bis(α,α-dimethylbenzyl)salicylic acid, 3,5-bis-t-octylsalicylic acid, 4-β-dodecyloxyethoxysalicylic acid, 4-methoxy-6-dodecyloxysalicylic acid, 4-β-phenoxyethoxysalicylic acid, 4-β-p-ethylphenoxyethoxysalicylic acid, 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid, N-(phenoxyacetyl)anthranyl acid, etc., and metal salts of them, etc. Above all, it is particularly preferred to use in combination with 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid and metal salt thereof.

The above described electron accepting compounds are used in an amount of preferably from 10 to 200% by weight, more preferably from 10 to 100% by weight, based on the amount of the salicylic acid derivative of the present invention.

It is further preferred to use two or more of the above described electron accepting compounds in combination. In particular, the combined use of 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid (metal salt thereof) with at least one of 2,2-bis(4-hydroxyphenyl)propane, 4-(4-isopropoxyphenylsulfonyl)phenol and 1,4-bis(4'-hydroxycumyl)benzene is preferred. In the case of using two or more kinds of electron accepting compounds in combination in addition to the salicylic acid derivative represented by formula (1), it is preferred, from the viewpoint of high sensitization, to carry out dispersion processing after each electron accepting compound is mixed.

The electron accepting compound including the salicylic acid derivative represented by formula (1) is used in an amount of preferably from 50 to 800% by weight, and more preferably from 100 to 500% by weight, based on the amount of the electron donating colorless dye.

Various compounds are available as electron donating colorless dyes, such as triphenylmethanephthalide based compounds, fluoran based compounds, phenothiazine based compounds, indolylphthalide based compounds, leucoauramine based compounds, rhodaminelactam based compounds, triphenylmethane based compounds, triazene based compounds, spiropyran based compounds and fluorene based compounds. Specific examples of phthalides are disclosed in U.S. Reissued Patent 23,024, U.S. Patents 3,491,111, 3,491,112, 3,491,116 and 3,509,174, those of fluorans are disclosed 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, those of spirodipyrans are disclosed in U.S. Patent 3,971,808, those of pyridine based and pyrazine based compounds are disclosed in U.S. Patents 3,775,424, 3,853,869 and 4,246,318, and those of fluorene based compounds and disclosed in JP-A-63-94878. Preferred electron donating colorless dyes which are preferably used in the present invention are fluoran compounds represented by formula (2):



(2)

wherein R_2 and R_3 represent an alkyl group or an aryl group; and R_4, R_5 and R_6 represent a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group.

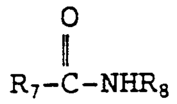
Black coloring 2-arylamino-3-H, halogen- or alkyl-6-substituted aminofluoran are particularly useful among those represented by formula (2). Specific examples include 2-anilino-3-methyl-6-diethylaminofluoran, 2-anilino-3-methyl-6-N-cyclohexyl-N-methylaminofluoran, 2-p-chloroanilino-3-methyl-6-dibutylaminofluoran, 2-anilino-3-chloro-6-diethylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-isoamylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-dodecylaminofluoran, 2-o-chloroanilino-6-dibutylaminofluoran, 2-anilino-3-pentadecyl-6-diethylaminofluoran, 2-anilino-3-methyl-6-dibutylaminofluoran, 2-o-toluidino-3-methyl-6-diisopropylaminofluoran, 2-anilino-3-methyl-6-N-isobutyl-N-ethylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-tetrahydrofurfurylaminofluoran, 2-anilino-3-chloro-6-N-ethyl-N-isoamylaminofluoran, 2-anilino-3-methyl-6-N-methyl-N-γ-ethoxypropylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-γ-ethoxypropylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-γ-propoxypropylaminofluoran, and 2-anilino-3-methyl-6-N-methyl-N-propylaminofluoran. 2-Anilino-3-methyl-6-dibutylaminofluoran is preferred and 2-anilino-3-methyl-6-N-methyl-N-n-propylaminofluoran is particularly preferred.

The coated amount of the electron donating colorless dye is generally from 0.1 to 2.0 g/m^2, and preferably from 0.2 to 1.0 g/m^2.

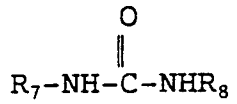
Sensitizers may be used in addition to electron donating colorless dyes and electron accepting compounds in the present invention. Compounds which are described in JP-A-58-57989, JP-A-58-87094 and JP-A-63-39375 are examples of such sensitizers. Representative examples include aromatic ethers (particularly, benzyl ethers, di(substituted-phenoxy)alkanes, diphenyl ethers, particularly preferably 2-benzyloxynaphthalene, 1,2-di(3-methylphenoxy)ethane, and 4-biphenyl-p-tolyl ethers), aromatic esters (particularly, oxalic acid dibenzyl ester derivatives, particularly preferably di(p-methylbenzyl)oxalate, and biphenyl derivatives (particularly, p-benzylbiphenyl, m-terphenyl), or aliphatic amide and aliphatic urea, or aromatic amide and aromatic urea.

A sensitizer is used in an amount of preferably from 50 to 800% by weight, and more preferably from 100 to 500% by weight, based on the amount of the electron donating colorless dye.

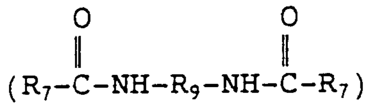
The use of sensitizers such as aromatic ether, aromatic ester and biphenyl derivative in combination with aliphatic amide and aliphatic urea is particularly preferred. Aliphatic amide and aliphatic urea which are preferably used are represented by formulae (3) to (5):



$$R_7-\overset{\overset{O}{\|}}{C}-NHR_8 \qquad (3)$$



$$R_7-NH-\overset{\overset{O}{\|}}{C}-NHR_8 \qquad (4)$$



$$(R_7-\overset{\overset{O}{\|}}{C}-NH-R_9-NH-\overset{\overset{O}{\|}}{C}-R_7) \qquad (5)$$

wherein R_7 represents an alkyl group having from 12 to 24 carbon atoms or an alkenyl group; R_8 represents a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms or a methylol group; and R_9 represents an alkylene group having from 1 to 8 carbon atoms.

Specific examples thereof include stearic acid amide, palmitic acid amide, oleic acid amide, stearylurea, and palmitylurea. In addition, N-substituted amide compounds of methylolstearic acid amide and ethylenebis-stearic acid amide are also included. These amide compounds or urea compounds are used in an amount of preferably from 1 to 100% by weight, and more preferably from 2 to 50% by weight, based on the amount of the sensitizers such as aromatic ethers, aromatic esters and bisphenyl derivatives.

The typical process of producing the heat-sensitive color forming layer of the present invention is described below. An electron donating colorless dye, an electron accepting compound and a sensitizer are dispersed in an aqueous solution of a water-soluble high molecular weight compound, such as polyvinyl alcohol, by means of a ball mill, a sand mill, etc., to a particle size of several microns or less. A sensitizer may be added to either or both of an electron donating colorless dye or/and an electron accepting compound and dispersed simultaneously, or a solution soluble with an electron donating colorless dye or an electron accepting compound is previously prepared and may be dispersed in the solution. These dispersions are mixed after dispersing and, if necessary, a surfactant, a binder, a metal soap, a wax, an antioxidant, an ultraviolet absorber, etc., are added to produce a heat-sensitive coating solution. The thus-obtained heat-sensitive coating solution is coated on a high quality paper, a high quality paper having a subbing layer, a synthetic paper, a plastic film, etc., dried and imparted with smoothness by subjecting to calendering to produce an objective heat-sensitive recording material.

A support for use in the present invention is preferably a support having smoothness regulated by JIS-8119 of 500 sec or more, preferably 800 sec or more, from the viewpoint of dot reproduction. There are various means to obtain a support having smoothness of 500 sec or more, for example,

(1) using a high smoothness paper such as a synthetic paper or a plastic film,
(2) providing a subbing layer comprising a pigment as a major component on a support,
(3) raising the smoothness of a support by subjecting to supercalendering, etc.

The present inventors have found that, by providing a subbing layer comprising a pigment as a major component, not only good dot reproduction can be achieved, but it also becomes difficult to generate fog at the white portions when the material is stored under high temperature conditions. Examples of pigments for use in the present invention for the subbing layer include calcined kaolin, aluminum hydroxide, calcium carbonate, barium sulfate, zinc oxide, lithopone, agalmatolite, kaolin, silica and noncrystal silica. Two or more of these pigments may be used in combination. Calcined kaolin is particularly preferred. The coated amount of the pigment in the subbing layer is generally from 1 to 20 g/m^2, and preferably from 3.0 to 15.0 g/m^2.

A coating solution for a subbing layer can be prepared by mixing a binder with a solution of pigment dispersion. Further, a mold releasing agent, a waterproofing agent, a surfactant, a sizing agent, a wax, etc., may be added, if necessary. The preservability of the white portions can be further improved by the addition of, in particular, a sizing agent such as alkenyl succinate, an alkyl ketene dimer, a rosin compound, etc., and a water repellant such as a wax, e.g., paraffin wax, microcrystalline wax, carnauba wax, montan wax, polyethylene wax, etc. A sizing agent and a water repellant are used in amounts of generally from 0.2 to 20% by weight, preferably from 0.5 to 5% by weight, based on the amount of the pigment contained in the subbing layer.

The obtained coating solution for a subbing layer is coated on a support using a coating apparatus such as a bar coater, an air knife coater, a blade coater, a curtain coater, etc., and dried to obtain a subbing layer of the present invention. A heat-sensitive recording material can be obtained by coating a heat-sensitive color forming layer on the thus obtained subbing layer. A subbing layer may be coated at the same time with a heat-sensitive color forming layer; alternatively, a subbing layer is coated, dried, and then a heat-sensitive color forming layer may be coated. The dry coating weight of the subbing layer is preferably from 3.0 to 20.0 g/m^2, more preferably from 5.0 to 12.0 g/m^2. When the coating amount is too small, heat sensitivity is extremely reduced: on the contrary, when it is too great, sufficient coated film strength and paper strength cannot be obtained. A calendering treatment may be carried out after coating of the subbing layer and after coating of the heat-sensitive color forming layer, as required.

A protective layer may be provided in the present invention, if necessary. Examples of pigments for a protective layer include aluminum hydroxide, calcium carbonate, barium sulfate, zinc oxide, lithopone, agalmatolite, kaolin, silica and noncrystal silica. Two or more of these pigments may be used in combination. Particularly, when aluminum hydroxide is used, surface slipperiness is good when the surface of the heat-sensitive paper is written with a pencil and also sensitivity is difficult to reduce. The coated amount of the pigment in the protective layer is generally from 0 to 5 g/m^2, and preferably from 0.1 to 2.0 g/m^2.

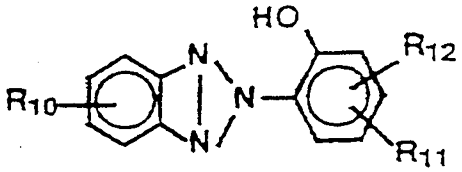
A coating solution for a protective layer of the present invention can be prepared by mixing a binder with a solution of pigment dispersion. Further, a mold releasing agent, a waterproofing agent, a surfactant, a wax, etc., may be added, if necessary. The obtained coating solution for a protective layer is coated on a heat-sensitive color forming layer using a coating apparatus such as a bar coater, an air knife coater, a blade coater, a curtain coater, etc., and dried to obtain a protective layer of the present invention. A protective layer may be coated at the same time with a heat-sensitive color forming layer; alternatively, a heat-sensitive color forming layer is coated, dried, and then a protective layer may be coated. The dry coating weight of the protective layer is preferably from 0.5 to 5.0 g/m^2, more preferably from 0.8 to 3.0 g/m^2. When the coating amount is too great, heat sensitivity is extremely reduced: on the contrary, when it is too small, a sufficiently protective effect cannot be obtained. A calendering treatment may be carried out after coating of the protective layer, as required.

A binder which can be used in the present invention is preferably a compound having a water solubility of 5% by weight or more in water at 25°C, and specific examples thereof include polyvinyl alcohols (including modified polyvinyl alcohols such as carboxy-modified, acetoacetyl-modified, itaconic acid-modified, maleic acid-modified and silica-modified), methyl cellulose, carboxymethyl cellulose, starches (including modified starch), gelatin, gum arabic, casein, a hydrolyzed product of a styrene-maleic anhydride copolymer, polyacrylamide, and a saponification product of a vinyl acetate-polyacrylic acid copolymer. These binders are used not only for the dispersing process, but also for the purpose of improving the coated film strength; and for this purpose a synthetic high molecular weight latex series binder can be used in combination, such as a styrene-butadiene copolymer, a vinyl acetate copolymer, an acrylonitrile-butadiene copolymer, a methyl acrylate-butadiene copolymer, and a polyvinylidene chloride. Further, an appropriate crosslinking agent for a binder may be added according to the kind of a binder, if necessary.

Examples of pigments for use in the present invention include calcium carbonate, barium sulfate, lithopone, agalmatolite, kaolin, silica and noncrystal silica. Metal salts of higher fatty acids are used as a metal soap, such as zinc stearate, calcium stearate, and aluminum stearate. Further, a surfactant, an antistatic agent, an ultraviolet absorber, a defoaming agent, an electroconductive agent, a fluorescent dye, a coloring dye, etc., may be added, if necessary.

When the salicylic acid derivatives and metal salts thereof of the present invention are used, white portions and images portions show excellent resistance to chemicals, and by the addition of an ultraviolet absorber for the purpose of improving discoloration of white portions due to light, light fastness of white portions can be improved. An ultraviolet absorber may be added to any of a heat-sensitive color forming layer, a subbing layer, a backing layer, or a protective layer, but the addition to a color forming layer or a protective layer is preferred. When an ultraviolet absorber is included in a protective layer, a protective layer not containing an ultraviolet absorber may further be provided on the first protective layer.

Examples of the ultraviolet absorber include benzophenone based ultraviolet absorbers, benzotriazole based ultraviolet absorbers, cyanoacrylate based ultraviolet absorbers, and hindered amine based ultraviolet absorbers, and benzotriazole based ultraviolet absorbers are preferred of these. Particularly, benzotriazole based ultraviolet absorbers represented by formula (6) are preferred:


(6)

wherein R_{10}, R_{11} and R_{12} represent a hydrogen atom, an alkyl group having from 1 to 15 carbon atoms, an alkoxy group, an aralkyl group, an aryl group or a halogen atom, which group may be further substituted.

Specific examples include 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-5'-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-sec-butyl-5'-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-(α,α-dimethylbenzyl)phenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole, 2-(2'-hydroxy-3'-dodecyl-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-4'-(2''-ethylhexyl)oxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-tert-octylphenyl)benzotriazole, and a polyethylene glycol (molecular weight: 300) solution of methyl-3-(3-tert-butyl-5-(2H-benzotriazol-2-yl)-4-hydroxyphenyl)propionate
The amount used of an ultraviolet absorber is preferably from 10 to 500% by weight, more preferably from 50 to 400% by weight, based on the amount of the electron donating colorless dye in the heat-sensitive color forming layer.

Ultraviolet absorbers may be used in the form of a solid dispersion, or those having low melting points or those which are liquid at normal temperature may be used by being microencapsulated. Microcapsules for use in the present invention can be prepared according to various conventionally known methods. In general, microcapsules are prepared by a method in which a core material (oily liquid) obtained by dissolving an ultraviolet absorber in an organic solvent as appropriate is emulsified and dispersed in an aqueous medium, and a thin shell comprising a high molecular weight material is formed around each oily droplet. Specific examples of high molecular weight materials useful for forming microcapsule shells include a polyurethane resin, a polyurea resin, a polyester resin, a polycarbonate resin, an aminoaldehyde resin, a melamine resin, a polystyrene resin, a styrene-acrylate copolymer resin, a styrene-methacrylate copolymer resin, gelatin and polyvinyl alcohol. Organic solvents which are used for core materials include low boiling point solvents such as ethyl acetate, butyl acetate, and oils used for pressure-sensitive recording materials.

When an ultraviolet absorber is added to a protective layer in the present invention, a pigment dispersion solution and a binder are mixed with an ultraviolet absorber dispersion solution or ultraviolet absorber-containing microcapsules to obtain a coating solution for a protective layer. Further, a mold releasing agent, a waterproofing agent, a surfactant, a wax, etc., may be added, if necessary. The obtained coating solution for a protective layer is coated on a heat-sensitive color forming layer using a coating apparatus such as a bar coater, an air knife coater, a blade coater, a curtain coater, etc., and dried to obtain a protective layer of the present invention. A protective layer may be coated at the same time with a heat-sensitive color forming layer; alternatively, a heat-sensitive color forming layer is coated, dried, and then a protective layer may be coated. Moreover, a protective layer not containing an ultraviolet absorber may further be provided on the protective layer containing an ultraviolet absorber, if necessary. The dry coating weight of the protective layer is preferably from 0.5 to 5.0 g/m^2, more preferably from 0.8 to 3.0 g/m^2. When the coating amount is too great, heat sensitivity is extremely reduced: on the contrary, when it is too small, a sufficiently protective effect cannot be obtained. A calendering treatment may be carried out after coating of the protective layer, if required.

A back coating layer may be provided on the opposite side of the heat-sensitive color forming layer of the support, if necessary. Any back coating layers conventionally known as back coating layers for heat-sensitive recording materials can be used.

The present invention is described in detail with reference to the Examples; however, it should not be construed as being limited thereto.

EXAMPLE 1

20 g of 2-anilino-3-methyl-6-dibutylaminofluoran as an electron donating colorless dye and 20 g of di(p-methylbenzyl)oxalate as a sensitizer were respectively dispersed with 100 g of a 5% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) in a ball mill over a whole day and night so that the average particle size became 1.5 μm or less to thereby obtain each dispersion solution. Further, 20 g of 4-benzyloxycarbonylaminosalicylic acid as an electron accepting compound were mixed with 5 g of zinc oxide and the mixture was then dispersed with 100 g of a 5% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) in a ball mill over a whole day and night so that the average

particle size became 1.5 μm or less to thereby obtain a dispersion solution of electron accepting compound. Still further, 80 g of calcium carbonate was dispersed with 160 g of a 0.5% solution of sodium hexametaphosphate in a homogenizer to thereby obtain a pigment dispersion solution. Each of the thus-obtained dispersion solutions were mixed with the ratio of the dispersion solution of the electron donating colorless dye being 5 g, the dispersion solution of the electron accepting compound being 10 g, the dispersion solution of di(p-methylbenzyl)oxalate being 10 g, and the dispersion solution of calcium carbonate being 5 g, and further 3 g of a 21% emulsion of zinc stearate was added thereto to thereby obtain a coating solution for a heat-sensitive layer. This coating solution for a heat-sensitive layer was coated on an undercoat paper using a wire bar coater so as to the dry weight of the coated layer became 5 g/m^2, and dried at 50°C for 60 s (1 min) to obtain a heat-sensitive recording paper.

Preparation of Undercoat Paper 1

80 g of calcined kaolin (Ansilex 90, Engelhardt) was dispersed in a homogenizer with 160 g of a 0.5% solution of sodium hexametaphosphate, and 100 g of a 10% aqueous solution of polyvinyl alcohol (PVA-105, a product of Kuraray) was added to the above dispersion solution to thereby obtain a coating solution for a subbing layer. This coating solution for a subbing layer was coated on a high quality paper of weighing 50 g/m^2 using a wire bar coater so that the dry weight of the subbing layer became 7.0 g/m^2, and dried at 50°C for 60 s (1 min) to obtain an undercoat paper. The thus-obtained undercoat paper was subjected to a surface treatment by calendering so as to adjust the smoothness to be 300 ± 100 sec as Bekk smoothness.

EXAMPLE 2

A heat-sensitive recording material was prepared in the same manner as in Example 1 except that a subbing layer coating solution was prepared by the addition of 15 g of a 15.5% alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.)with noncrystal silica (Mizukasil P-832, a product of Mizusawa Chemical Co., Ltd.).

EXAMPLE 3

A heat-sensitive recording material was prepared in the same manner as in Example 2 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd) with 12 g of an alkyl ketene dimer compound (Sizepine K287, a product of Arakawa Chemical Co., Ltd.).

EXAMPLE 4

A heat-sensitive recording material was prepared in the same manner as in Example 2 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 9 g of a 30% paraffin wax dispersion solution (Sizepine W116H, a product of Arakawa Chemical Co., Ltd.).

EXAMPLE 5

A heat-sensitive recording material was prepared in the same manner as in Example 2 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 9 g of a 30% paraffin wax dispersion solution (Hidrin D-337, a product of Chukyo Yushi K.K.).

EXAMPLE 6

A heat-sensitive recording material was prepared in the same manner as in Example 2 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 9 g of a 30% paraffin wax dispersion solution (Hidrin P-7, a product of Chukyo Yushi K.K.).

EXAMPLE 7

A heat-sensitive recording material was prepared in the same manner as in Example 2 except that a subbing layer coating solution was prepared by replacing the alkyl ketene dimer compound (Sizepine K903, a product of Arakawa Chemical Co., Ltd.) with 9 g of a 30% reinforced rosin sizing agent (Sizepine E, a product of Arakawa Chemical Co., Ltd.).

EXAMPLE 8

A heat-sensitive recording paper was prepared in the same manner as in Example 2 except that a subbing layer coating solution was prepared by replacing calcined kaolin with calcium carbonate (Cal-light KT, manufactured by Shiraishi Chuo Kenkyusho).

EXAMPLE 9

A heat-sensitive recording paper was prepared in the same manner as in Example 2 except that a subbing layer coating solution was prepared by replacing calcined kaolin with noncrystal silica (Mizukasil P-832, a product of Mizusawa Chemical Co., Ltd.).

EXAMPLE 10

A heat-sensitive recording paper was prepared in the same manner as in Example 2 except that a heat-sensitive layer coating solution was prepared by replacing 80 g of the calcined kaolin with 70 g of calcined kaolin and 10 g of calcium carbonate.

EXAMPLE 11

A heat-sensitive recording paper was prepared in the same manner as in Example 2 except that a heat-sensitive layer coating solution was prepared by replacing 80 g of the calcined kaolin with 60 g of calcined kaolin and 20 g of calcium carbonate.

The thus obtained heat-sensitive recording papers were subjected to a surface treatment by calendering so as to adjust the smoothness to be 300 ± 50 sec as Bekk smoothness. The evaluation of heat-sensitive recording papers was conducted as follows. (1) Printing was conducted using a Kyocera printing tester at a printing energy of 30 mJ/mm^2 and color density was measured using a Macbeth densitometer. The higher value means the higher sensitivity of the heat-sensitive recording paper. (2) Chemical resistance was evaluated by the degree of fog at white portions and discoloration (fading) of colored portions by writing down on the coloring face of the above obtained recording paper with a fluorescent pen (Spotliter, pink, a product of PILOT Co., Ltd.). (3) Light fastness was evaluated by the density of white portions (yellow density) and image density after the above-obtained recording paper was directly exposed to the sun for 1 week (Fujinomiya, Japan on January). (4) Heat fastness was evaluated by measuring the white portion density after a recording paper was stored in a constant temperature constant humidity bath of 60°C 30% RH for 24 hours. (5) Plasticizer resistance test was evaluated by the degree of discoloration of colored portions after a recording paper was contacted with a polyvinyl chloride film (a product of Sinetsu Seien) for 120 hours. The results obtained are shown in Table 1.

As can be seen from the following Table 1, the recording material of the present invention exhibits high sensitivity, fog coloration or discoloration of colored portions due to chemicals does not occur; discoloration of colored portions due to plasticizers does not occur; and, in particular, the sharpness of the colored portions can be maintained. Therefore, the recording material of the present invention possesses extremely excellent properties.

TABLE 1

	Light Fastness of Image Portion		Fluorescent Pen		Light Fastness of White Portion (Y)		Heat Fastness of White Portion	
	Initial Density	After Processing	Fog	Discoloration	Initial Density	After Processing	Initial Density	After Processing
Example 1	1.36	1.24	o	o	0.07	0.11	0.05	0.09
Example 2	1.37	1.25	o	o	0.06	0.10	0.05	0.08
Example 3	1.36	1.23	o	o	0.05	0.09	0.05	0.08
Example 4	1.38	1.25	o	o	0.06	0.10	0.05	0.08
Example 5	1.37	1.24	o	o	0.07	0.11	0.06	0.08
Example 6	1.39	1.24	o	o	0.06	0.10	0.05	0.08
Example 7	1.35	1.21	o	o	0.07	0.11	0.05	0.08
Example 8	1.34	1.22	o	o	0.07	0.11	0.05	0.09
Example 9	1.33	1.21	o	o	0.08	0.11	0.06	0.10
Example 10	1.38	1.26	o	o	0.07	0.11	0.05	0.08
Example 11	1.38	1.25	o	o	0.06	0.10	0.05	0.08

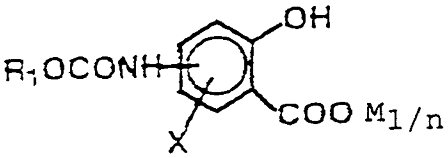
⊚: Very excellent (no change)

o: Excellent (little change)

x: Impracticable (images were very difficult to read)

Claims

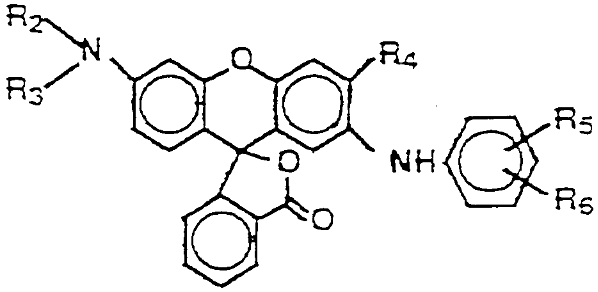
1. A heat sensitive recording material comprising a support having provided thereon a heat-sensitive color forming layer containing an electron donating colorless dye and an electron accepting compound, wherein provided between said support and said heat-sensitive color forming layer is a subbing layer containing at least one of calcined kaolin, a sizing agent and a wax, wherein said heat-sensitive color forming layer contains a salicylic acid derivative represented by formula (1) or a metal salt thereof, and a metal compound:



(1)

Wherein R_1 represents an alkyl group or an aryl group; X represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, or a halogen atom; M represents a hydrogen atom or an n-valent metal atom; and n represents an integer, provided that n is 1 when M represents a hydrogen atom.

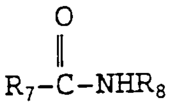
2. A recording material as claimed in Claim 1, wherein said heat-sensitive color forming layer contains zinc oxide and a fluoran compound represented by formula (2):

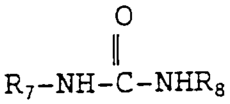


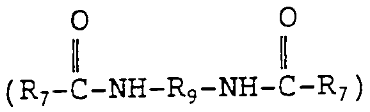
(2)

wherein R_2 and R_3 each independently represent an alkyl group or an aryl group; and R_4, R_5 and R_6 each independently represent a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group.

3. A recording material as claimed in claim 1 or 2, wherein said heat-sensitive color forming layer contains a sensitizer selected from di(p-methylbenzyl)oxalate, 2-benzyloxy-naphthalene, p-benzylbiphenyl, m-terphenyl, 4-biphenyl-p-tolyl ether, 1,2-di(3-methylphenoxy)ethane, aliphatic amide compounds, and aliphatic urea compounds represented by the following formulae (3) to (5):


$$R_7-\overset{O}{\overset{\|}{C}}-NHR_8 \qquad (3)$$

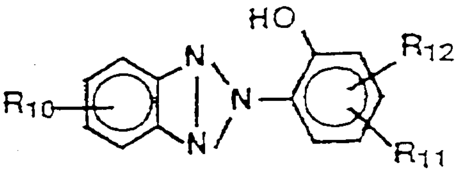

$$R_7-NH-\overset{O}{\overset{\|}{C}}-NHR_8 \qquad (4)$$


$$(R_7-\overset{O}{\overset{\|}{C}}-NH-R_9-NH-\overset{O}{\overset{\|}{C}}-R_7) \qquad (5)$$

wherein R_7 represents an alkyl group having from 12 to 24 carbon atoms, or an alkenyl group; R_8 represents a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms, or a methylol group; and R_9 represents an alkylene group having from 1 to 8 carbon atoms.

4. A recording material as claimed in any one of Claims 1 to 3, wherein a protective layer is provided on said heat-sensitive color forming layer, said protective layer containing aluminum hydroxide.

5. A recording material as claimed in any one of Claims 1 to 4, wherein said heat-sensitive recording material contains an ultraviolet absorber represented by formula (6):



(6)

wherein R_{10}, R_{11} and R_{12} represent a hydrogen atom, an alkyl group having 1 to 15 carbon atoms, an alkoxy group, an aralkyl group, an aryl group, or a halogen atom.

6. A recording material as claimed in any one of Claims 1 to 5, wherein said heat-sensitive recording material contains a salicylic acid derivative represented by formula (1) or a metal salt thereof and 4-(2'-(4-methoxyphenyloxy)ethyloxy)salicylic acid or a metal salt thereof.

7. A recording material as claimed in Claim 6, wherein said heat-sensitive recording material contains at least one of 2,2-bis(4-hydroxyphenyl)propane, 1,4-bis(4'-hydroxycumyl)benzene and 4-(4-isopropoxyphenylsulfonyl) phenol.

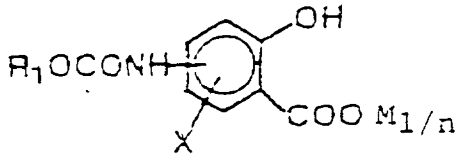
8. A recording material as claimed in Claim 6 or 7, wherein said salicylic acid derivative represented by formula (1) is 4-n-octyloxycarbonyl-aminosalicylic acid or a metal salt thereof.

9. A recording material as claimed in any one of Claims 1 to 8, wherein the coated amount of the calcined kaolin in the subbing layer is from 1.0 to 20.0 g/m^2.

10. A recording material as claimed in any one of Claims 1 to 8, wherein the coated amount of the calcined kaolin is the subbing layer is from 3.0 to 15.0 g/m^2.

Patentansprüche

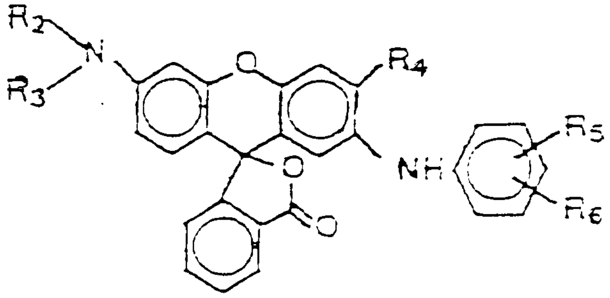
1. Wärmeempfindliches Aufzeichnungsmaterial, umfassend einen Träger mit einer darauf angeordneten wärmeempfindlichen farbbildenden Schicht, enthaltend einen farblosen, Elektronen-abgebenden Farbstoff und eine Elektronen-annehmende Verbindung, wobei zwischen dem Träger und der wärmeempfindlichen farbbildenden Schicht eine Unterschicht geschaffen ist, enthaltend wenigstens eines aus kalziniertem Kaolin, einem Leimungsmittel und einem Wachs, wobei die wärmeempfindliche farbbildende Schicht ein durch Formel (1) dargestelltes Salicylsäurederivat oder ein Metallsalz davon, und eine Metallverbindung enthält:



(1)

worin R_1 eine Alkylgruppe oder Arylgruppe bedeutet; X bedeutet ein Wasserstoffatom, eine Alkylgruppe, eine Arylgruppe, eine Alkoxygruppe oder ein Halogenatom; M bedeutet ein Wasserstoffatom oder ein n-wertiges Metallatom; und n bedeutet eine ganze Zahl, mit der Maßgabe, daß, falls M ein Wasserstoffatom bedeutet, n 1 ist.

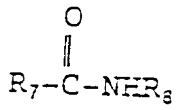
2. Aufzeichnungsmaterial nach Anspruch 1, worin die wärmeempfindliche Farbbildungsschicht Zinkoxid und eine durch Formel (2) dargestellte Fluoranverbindung enthält:



(2)

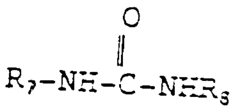
worin R_2 und R_3 jeweils unabhängig eine Alkylgruppe oder eine Arylgruppe bedeuten; und R_4, R_5 und R_6 bedeuten unabhängig ein Wasserstoffatom, ein Halogenatom, eine Alkylgruppe oder eine Alkoxygruppe.

3. Aufzeichnungsmaterial nach Anspruch 1 oder 2, worin die wärmeempfindliche farbbildende Schicht einen Sensibilisator enthält, ausgewählt aus Di(p-methylbenzyl)oxalat, 2-Benzyloxynaphthalin, p-Benzylbiphenyl, m-Terphenyl, 4-Biphenyl-p-tolylether, 1,2-Di(3-methylphenoxy)ethan, aliphatischen Amidverbindungen und aliphatischen Harnstoffverbindungen, dargestellt durch folgende Formeln (3) bis (5):



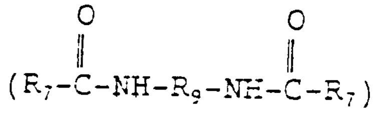
$$R_7-\overset{\overset{\displaystyle O}{\|}}{C}-NHR_8$$

(3)



$$R_7-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NHR_8$$

(4)



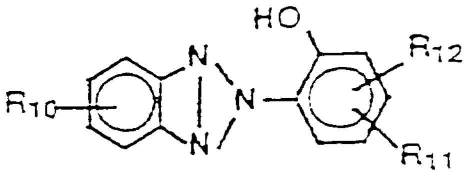
$$(R_7-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R_9-NH-\overset{\overset{\displaystyle O}{\|}}{C}-R_7)$$

(5)

worin R_7 eine Alkylgruppe mit 12 bis 24 Kohlenstoffatomen oder eine Alkenylgruppe bedeutet; R_8 bedeutet ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 24 Kohlenstoffatomen oder eine Methylolgruppe; und R_9 bedeutet eine Alkylengruppe mit 1 bis 8 Kohlenstoffatomen.

4. Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 3, worin eine Schutzschicht auf der wärmeempfindlichen farbbildenden Schicht geschaffen ist, wobei die Schutzschicht Aluminiumhydroxid enthält.

5. Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 4, worin das wärmeempfindliche Aufzeichnungsmaterial ein durch Formel (6) dargestelltes Ultraviolett-Absorptionsmittel enthält:



(6)

worin R_{10}, R_{11} und R_{12} ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 15 Kohlenstoffatomen, eine Alkoxygruppe, eine Aralkylgruppe, eine Arylgruppe oder ein Halogenatom bedeuten.

6. Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 5, worin das wärmeempfindliche Aufzeichnungsmaterial ein durch Formel (1) dargestelltes Salicylsäurederivat oder ein Metallsalz davon und 4-(2'-(4-Methoxyphenyloxyethyloxy)salicylsäure oder ein Metallsalz davon enthält.

7. Aufzeichnungsmaterial nach Anspruch 6, worin das wärmeempfindliche Aufzeichnungsmaterial wenigstens eines aus 2,2-Bis(4-hydroxyphenyl)propan, 1,4-Bis(4'-hydroxycumyl)benzol und 4-(4-Isopropoxyphenylsulfonyl)phenol enthält.

8. Aufzeichnungsmaterial nach Anspruch 6 oder 7, worin das durch Formel (1) dargestellte Salicylsäurederivat 4-n-Octyloxycarbonylaminosalicylsäure oder ein Metallsalz davon ist.

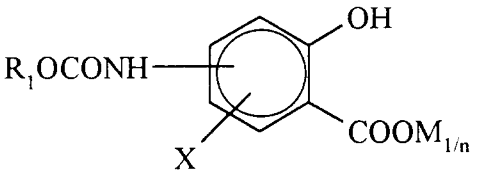
9. Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 8, worin die Beschichtungsmenge an kalziniertem Kaolin in der Unterschicht 1,0 bis 20,0 g/m^2 beträgt.

10. Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 8, worin die Beschichtungsmenge an kalziniertem Kaolin in der Unterschicht 3,0 bis 15,0 g/m^2 beträgt.

Revendications

1. Matériau d'enregistrement thermosensible comprenant un support muni sur son dessus d'une couche formant une

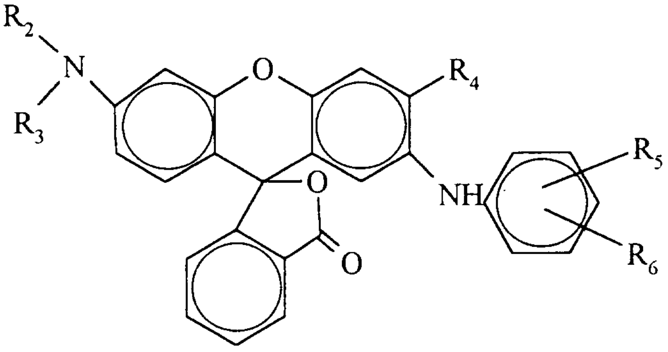
couleur thermosensible contenant un colorant sans couleur donneur d'électrons et un composé accepteur d'électrons, dans lequel il est fourni entre ledit support et ladite couche formant une couleur thermosensible une souscouche contenant au moins un composé parmi du kaolin calciné, un adhésif et une cire, dans lequel ladite couche formant une couleur thermosensible contient un dérivé de l'acide salicylique représenté par la formule (1) ou un sel métallique de celui-ci, et un composé métallique :



(1)

où R_1 représente un groupe alkyle ou un groupe aryle; X représente un atome d'hydrogène, un groupe alkyle, un groupe aryle, un groupe alcoxy ou un atome d'halogéne; M représente un atome d'hydrogène ou un atome métallique n-valent; et n représente un nombre entier à condition que n est égal à 1 lorsque M représente un atome d'hydrogène.

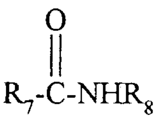
2. Matériau d'enregistrement selon la revendication 1, dans lequel ladite couche formant une couleur thermosensible contient de l'oxyde de zinc et un composé de fluoranne représenté par la formule (2) :



(2)

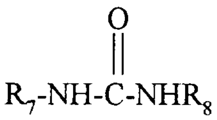
où R_2 et R_3 représentent indépendamment un groupe alkyle ou un groupe aryle; et R_4, R_5 et R_6 représentent chacun indépendamment un atome d'hydrogène, un atome d'halogène, un groupe alkyle ou un groupe alcoxy.

3. Matériau d'enregistrement selon la revendication 1 ou 2, dans lequel ladite couche formant une couleur thermosensible contient un sensibilisateur choisi parmi l'oxalate de di(p-méthylbenzyle), le 2-benzyloxynaphtalène, le p-benzylbiphényle, le m-terphényle, le 4-biphényl-p-tolyléther, le 1,2-di(3-méthylphénoxy)éthane, des composés d'amides aliphatiques, et des composés durée aliphatiques représentés par les formules (3) à (5) suivantes :



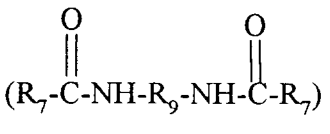
(3)

$$R_7\text{-}\overset{\overset{O}{\|}}{C}\text{-}NHR_8$$



(4)

$$R_7\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}NHR_8$$



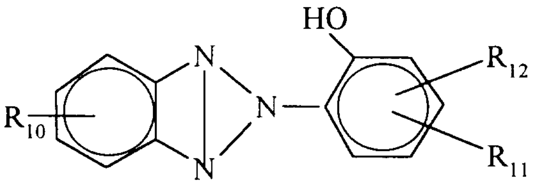
(5)

$$(R_7\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}R_9\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}R_7)$$

où R_7 représente un groupe alkyle ayant de 12 à 24 atomes de carbone ou un groupe alcényle; R_8 représente un atome d'hydrogène, un groupe alkyle ayant de 1 à 24 atomes de carbone ou un groupe méthylol; et R_9 représente un groupe alkylène ayant de 1 à 8 atomes de carbone.

4. Matériau d'enregistrement selon l'une quelconque des revendications 1 à 3, dans lequel une couche protectrice est fournie sur ladite couche formant une couleur thermosensible, ladite couche protectrice contenant de l'hydroxyde d'aluminium.

5. Matériau d'enregistrement selon l'une quelconque des revendications 1 à 4, dans lequel ledit matériau d'enregistrement thermosensible contient un absorbeur d'ultraviolets représenté par la formule (6) :



(6)

où R_{10}, R_{11} et R_{12} représentent un atome d'hydrogène, un groupe alkyle ayant de 1 à 15 atomes de carbone, un groupe alcoxy, un groupe aralkyle, un groupe aryle ou un atome d'halogène.

6. Matériau d'enregistrement selon l'une quelconque des revendications 1 à 5, dans lequel ledit matériau d'enregistrement thermosensible contient un dérivé de l'acide salicylique représenté par la formule (1) ou un sel métallique de celui-ci et l'acide 4-(2'-(4-méthoxyphényloxy)éthyloxy)salicylique ou un sel métallique de celui-ci.

7. Matériau d'enregistrement selon la revendication 6, dans lequel ledit matériau d'enregistrement thermosensible contient au moins un composé parmi le 2,2-bis(4-hydroxyphényl)propane, le 1,4-bis(4'-hydroxycumyl)benzène et le 4-(4-isopropoxyphénylsulfonyl)phénol.

8. Matériau d'enregistrement selon la revendication 6 ou 7, dans lequel ledit dérivé de l'acide salicylique représenté par la formule (1) est l'acide 4-n-octyloxycarbonylaminosalicylique ou un sel métallique de celui-ci.

9. Matériau d'enregistrement selon l'une quelconque des revendications 1 à 8, dans lequel la quantité déposée du kaolin calciné dans la sous-couche est de 1,0 à 20,0 g/m^2.

10. Matériau d'enregistrement selon l'une quelconque des revendications 1 à 8, dans lequel la quantité déposée du kaolin calciné dans la sous-couche est de 3,0 à 15,0 g/m^2.