

(19)



Europäisches Patentamt

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(11)

EP 0 844 099 A1

(12)

EUROPEAN PATENT APPLICATION(43) Date of publication:
27.05.1998 Bulletin 1998/22(51) Int. Cl.⁶: **B41M 5/30**(21) Application number: **97120382.3**(22) Date of filing: **20.11.1997**

(84) Designated Contracting States:

**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**

Designated Extension States:

AL LT LV MK RO SI(30) Priority: **21.11.1996 JP 311106/96**

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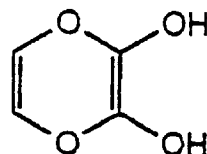
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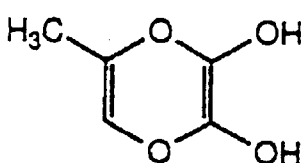
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81543 München (DE)****(54) Heat-sensitive recording material**

(57) The present invention discloses a heat-sensitive recording material including a support and a heat-sensitive color generating layer provided on the support, the heat-sensitive color generating layer containing a substantially colorless color-generating component A, a substantially colorless color-generating component B which reacts with the color-generating component A to generate color, acetoacetyl-modified polyvinyl alcohol which serves as a binder, and at least one of the compounds represented by formulas (1) to (5) which serves as a hardener.

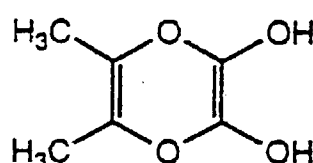
formula (1)



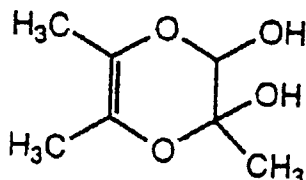
formula (2)



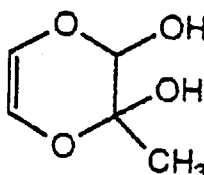
formula (3)



formula (4)



formula (5)

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The invention also provides a heat-sensitive recording material including a support and a heat-sensitive color generating layer provided on the support, the heat-sensitive color generating layer containing a substantially colorless color-generating component A, a substantially colorless color-generating component B which reacts with the color-generating component A to generate color, acetoacetyl-modified polyvinyl alcohol which serves as a binder, and an aldehyde compound which serves as a hardener, wherein the aldehyde compound is contained in an amount of between 40 to 200 parts by weight inclusive with respect to 100 parts by weight of the acetoacetyl-modified polyvinyl alcohol.

The heat-sensitive recording materials of the present invention have excellent water resistance, coating strength (printability), and storability (both image and non-image areas) and capable of preventing both smudge on a recording head and sticking.

Description**BACKGROUND OF THE INVENTION**

5 Field of the Invention:

The present invention relates to a heat-sensitive recording material. More particularly, the present invention relates to a heat-sensitive recording material having excellent coating strength (printability) and storability (image area and non-image area) and adapted to prevent smudge on and sticking to a recording head.

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Description of the Related Art:

Recording materials using electron donating colorless dyes and electron accepting compounds as color-generating components are well known in the forms of pressure-sensitive paper, heat-sensitive paper, photosensitive pressure-sensitive paper, conductive heat-sensitive recording paper, and heat-sensitive transfer paper. Examples of such recording materials are described, for example, in UK Patent No. 2,140,449, US Patent Nos. 4,480,052 and 4,436,920, Japanese Patent Application Publication (JP-B) No. 60-23992, and Japanese Patent Application Laid-Open (JP-A) Nos. 57-179836, 60-123556, and 60-123557. Heat-sensitive recording materials using electron donating dye precursors and electron accepting compounds are disclosed in JP-B Nos. 45-14039 and 43-4160. Heat-sensitive recording materials using diazo compounds are disclosed in JP-A No. 59-190886.

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In recent years, heat-sensitive recording systems have been applied in many areas such as facsimiles, printers, labels, meter readers' terminals, medical image output terminals, and prepaid cards, and thus needs therefor are increasing. Under these circumstances, market demand for water resistance of recording paper is increasing in view of increased opportunities of household and outdoor use of heat-sensitive recording paper, which involves handling recording paper with wet hands and wetting the coating surface of recording paper with rain or snow, resulting in adhesion or separation of the coating surface.

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In order to attain water resistance of recording paper, there have been proposed various methods including the following: cross linking agents such as formalin and glyoxal are used as water-resistance agents; and polyvinyl alcohol (PVA) is cross-linked through use of metal chelate. However, since a drying temperature or a heat treatment temperature is limited to a relatively low range in view of properties of color generation substances, these methods have failed to provide sufficient cross-linking, resulting in insufficient water resistance.

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Due to insufficient cross-linking derived from a drying temperature or a heat treatment temperature being limited to a relatively low range as mentioned above, the strength of coating also becomes insufficient. As a result, in recording, a resin layer sticks to a recording head (hereinafter referred to as sticking), and recording head smudges. Sticking and smudge on a recording head significantly affect feed of a recording material. However, effective measures to solve these problems have not been proposed, since many factors such as the film strength and glass transition temperature of a resin used as a binder are also involved in the problems. Also, when the plasticizer resistance of coating is low, image density after printing decreases, raising a problem in storability.

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40 SUMMARY OF THE INVENTION

In view of the foregoing, an object of the present invention is to provide a heat-sensitive recording material having excellent water resistance, coating strength (printability), and storability (both image and non-image areas) and capable of preventing both smudge on a recording head and sticking.

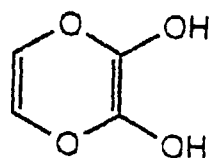
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The present invention provides a heat-sensitive recording material which includes a support and a heat-sensitive color generating layer provided on the support, the heat-sensitive color generating layer containing a substantially colorless color-generation component A, a substantially colorless color-generation component B which reacts with the color-generation component A to generate color, acetoacetyl-modified polyvinyl alcohol which serves as a binder, and at least one of compounds represented by formulas (1) to (5) which serves as a hardener.

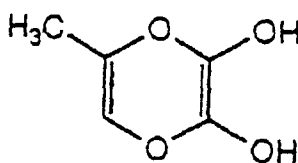
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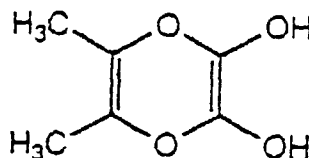
formula (1)



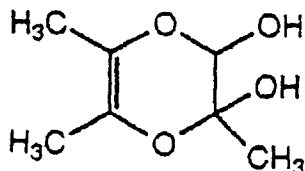
formula (2)



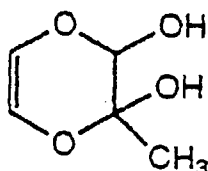
formula (3)



formula (4)



formula (5)



The present invention also provides a heat-sensitive recording material which includes a support and a heat-sensitive color generating layer provided on the support, the heat-sensitive color generating layer containing a substantially colorless color-generation component A, a substantially colorless color-generation component B which reacts with the color-generation component A to generate color, acetoacetyl-modified polyvinyl alcohol which serves as a binder, and an aldehyde compound which serves as a hardener, wherein the aldehyde compound is contained in an amount of between 40 to 200 parts by weight inclusive with respect to 100 parts by weight of the acetoacetyl-modified polyvinyl alcohol.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Acetoacetyl-modified polyvinyl alcohol contained as a binder in a heat-sensitive color generating layer is generally manufactured by allowing a liquid or gaseous diketene to react with a polyvinyl alcoholic resin in the form of solution, dispersion, or powder. The degree of acetylation of acetoacetyl-modified polyvinyl alcohol is selected as adequate in accordance with target quality of a heat-sensitive recording material, and is preferably 0.1 mol% to 20 mol%, more preferably 0.5 mol% to 10 mol%.

The above mentioned polyvinyl alcoholic resins include polyvinyl alcohol and its derivatives obtained through saponification of polyvinyl acetate in lower alcohol and saponified products of a copolymer of vinyl acetate and a monomer capable of copolymerizing with vinyl acetate. Examples of a monomer capable of copolymerizing with vinyl acetate include: unsaturated carboxylic acids such as maleic anhydride, maleic acid, fumaric acid, crotonic acid, itaconic acid, and (meth)acrylic acid, and esters thereof; α -olefin such as ethylene and propylene; olefinsulfonic acids such as (meth)acrylicsulfonic acid, ethylenesulfonic acid, and sulfomaleic acid; alkali salts of olefinsulfonic acid such as sodium (meth)acrylicsulfonate, sodium ethylenesulfonate, sodium sulfonate (meth)acrylate, sodium sulfonate (monoalkylmalate), and sodium disulfonate alkylmalate; monomers containing an amide group such as N-methylolacrylamide and alkali salts of acrylamide alkyl sulfonic acid; and N-vinylpyrrolidone derivatives.

As a binder, a compound which dissolves in water at 25°C in an amount of not less than 5 wt.% may be used as needed together with aforementioned acetoacetyl-modified polyvinyl alcohol. Examples of such a binder include polyvinyl alcohols (including carboxy-, itaconic acid-, maleic acid-, silica- and amino group-modified polyvinyl alcohol), methyl cellulose, carboxymethyl cellulose, starches (including modified starches), gelatin, acacia, casein, styrene-maleic anhydride copolymer hydrolyzate, polyacrylamide, and saponified products of a copolymer of vinyl acetate and polyacrylic acid. These binders are used for the purpose of improving not only dispersion but also coating strength and may be used in combination with synthetic polymer latex binders such as styrene-butadiene copolymer, vinyl acetate copolymer, acrylonitrile-butadiene copolymer, methyl acrylate-butadiene copolymer, and polyvinylidene chloride. Also, appropriate cross linking agents for binders may be added as needed in accordance with binders concerned.

For the aforementioned acetoacetyl-modified polyvinyl alcohol, at least one of the compounds represented by formulas (1)-(5) is used as a hardener. The compounds represented by formulas (1)-(5) are used preferably in an amount of 0.1 to 200 parts by weight with respect to 100 parts by weight of acetoacetyl-modified polyvinyl alcohol, more preferably 50 to 150 parts by weight. If the amount of the compounds is less than 0.1 parts by weight, the strength of coating

will become insufficient, and thus the water resistance of a recording material decreases, resulting in an increased likelihood of smudge on a recording head and sticking. By contrast, if the amount of the compounds is in excess of 200 parts by weight, it is more likely that thermal fog and a reduction of degree of whiteness will occur.

In the present invention, aldehyde compounds may be used as hardeners. Examples of aldehyde compounds include monoaldehydes such as formaldehyde and acetaldehyde and polyvalent aldehydes such as glyoxal, glutaraldehyde, and dialdehyde. When used as a hardener, an aldehyde compound must be added in an amount of 40 to 200 parts by weight inclusive with respect to 100 parts by weight of acetoacetyl-modified polyvinyl alcohol.

If the amount of an aldehyde compound is less than 40 parts by weight, the strength of coating will become insufficient, and thus the water resistance of a recording material decreases, resulting in an increased likelihood of smudge on a recording head and sticking. By contrast, if the amount of an aldehyde compound is in excess of 200 parts by weight, it is more likely that thermal fog and a reduction of degree of whiteness will occur.

A heat-sensitive color generating layer may contain any of ordinary organic or inorganic pigments. Specific examples of pigments include calcium carbonate, aluminum hydroxide, barium sulfate, titanium oxide, talc, agalmatolite, kaolin, baked kaolin, amorphous silica, amorphous silica calcium, urea-formalin resin powder, polyethylene resin powder, and benzoguanamine resin powder. These pigments may be used singly or in combination. Among these pigments, aluminum hydroxide, amorphous silica, and amorphous silica calcium effectively provide water resistance. Particularly, aluminum hydroxide is effective for water resistance (friction resistance). Amorphous silica and amorphous silica calcium effectively provide appropriate feed performance. Particularly, amorphous silica effectively stabilizes a coating solution after hardeners are added thereto.

When these pigments are used, the weight ratio between amorphous silica or amorphous silica calcium and aluminum hydroxide is particularly preferably 3:7 to 9:1. When this range of weight ratio is not observed, water resistance (friction resistance), feed performance, coating strength (printability), and stability of a coating solution are impaired.

In the present invention, a heat-sensitive color generating layer contains at least a substantially colorless color generation component A and a substantially colorless color generation component B which reacts with the color generation component A to generate color. The color generation components A and B used in the present invention initiate a color generation reaction upon contact with each other. Examples of such a combination include the following combinations (a) to (m).

(a) Photolyzable diazo compounds and couplers.

(b) Electron donating dye precursors and electron accepting compounds.

(c) Organic metal salts such as silver behenate and silver stearate and reducing agents such as protocatechuic acid, spiroindane and hydroquinone.

(d) Long-chain aliphatic salts such as ferric stearate and ferric myristate and phenols such as gallic acid and ammonium salicylate.

(e) Combination of heavy metal salts of organic acids such as nickel, cobalt, lead, copper, iron, mercury, and silver salts of acetic acid, stearic acid, and palmitic acid, and sulfides of alkaline earth metal such as calcium sulfide, strontium sulfide, and potassium sulfide; or combination of those heavy metal salts of organic acids and organic chelating agents such as s-diphenylcarbazide and diphenylcarbazone.

(f) Sulfates of heavy metal such as sulfates of silver, lead, mercury, and sodium and sulfur compounds such as Na-tetrathionate, sodium thiosulfate, and thiourea.

(g) Aliphatic ferric salts such as ferric stearate and aromatic polyhydroxy compounds such as 3,4-hydroxytetraphenylmethane.

(h) Organic rare metal salts such as oxalate and mercury oxalate and organic polyhydroxy compounds such as polyhydroxyalcohol, glycerol, and glycol.

(i) Aliphatic ferric salts such as ferric pelargonate and ferric laurate and derivatives of thiocetylcarbamide and isothiocetylcarbamide.

(j) Lead salts of organic acids such as lead caproate, lead pelargonate, and lead behenate and thiourea derivatives such as ethylene thiourea and N-dodecylthiourea.

(k) Heavy metal salts of higher fatty acids such as ferric stearate and copper stearate and zinc dialkyldithiocarbamate.

(l) A combination to form an oxazine dye such as a combination of resorcin and a nitroso compound.

(m) Formazan compounds and reducing agents and/or metal salts

Among these combinations, the combination (a) (photolyzable diazo compounds and couplers), the combination (b) (electron donating dye precursors and electron accepting compounds), and the combination (c) (organic metal salts and reducing agents) are preferred. Particularly preferred are the combinations (a) and (b).

A photolyzable diazo compound in the combination (a) reacts with a color developer called a coupling component, which will be described later, to thereby develop a desired hue. Upon exposure to light having a specific wavelength

before the reaction, such a photolyzable diazo compound degrades and generates no color even when a coupling component acts thereon.

Hue to be developed in this color generation system is determined by a diazo dye generated by the reaction between a diazo compound and a coupling component. Accordingly, as well known, hue to be generated can be readily changed through modification of the chemical structure of a diazo compound or a coupling compound.

Photolyzable diazo compounds in the present invention refer primarily to aromatic diazo compounds. Specific examples include aromatic diazonium salts, diazosulfonate compounds, and diazoamino compounds.

Diazonium salts are compounds represented by the formula, ArN_2^+X^- (Ar: substituted or unsubstituted aromatic portion; N_2^+ : diazonium group; X^- : acid anion).

Generally, the wavelength which causes photolysis of a diazonium salt is said to be an absorption maximum wavelength of the diazonium salt. An absorption maximum wavelength of a diazonium salt is known to range from about 200 nm to about 700 nm in accordance with the chemical structure of the diazonium salt (Takahiro TUNODA, Tuguo YAMAOKA, "Photolysis and Chemical Structure of Photosensitive Diazonium Salts," Journal of The Society of Photographic Science and Technology of Japan, Vol. 29 (4), pp. 197-205 (1965)). That is, being used as a photolyzable compound, a diazonium salt photolyzes upon exposure to light having a specific wavelength corresponding to the chemical structure thereof. Also, the different chemical structures of diazonium salts, result in different hues of dyes obtained from a coupling reaction with the respective diazonium salts and a coupler even if the coupler used are the same.

Many diazosulfonate compounds which can be used in the present invention are known and obtained through treatment of corresponding diazonium salts with sulfite.

Diazo amino compounds usable in the present invention are obtained through coupling of a diazo group with dicyandiamide, sarcosine, methyl taurine, N-ethyl anthranilic acid-5-sulfonic acid, monoethanolamine, diethanolamine, or guanidine.

These diazo compounds are described in detail in, for example, JP-A No. 2-136286.

A light source for photolysis of a diazo compound may be of any type which generates light having a desired wavelength. Examples of such a light source include fluorescent lamps, xenon lamps, xenon flash lamps, mercury lamps having various pressures, photographic flashes, and stroboscopic lights. In order to make a fixing zone compact, a light source unit and an exposure unit may be separately installed and connected through optical fibers.

Examples of coupling components which couple with diazo compounds used in the present invention to generate dyes include 2-hydroxy-3-naphthoanilide, resorcin, and those described in JP-A No. 62-146678.

Further, through use of coupling components in combination, an image in any color tone can be obtained. Accordingly, the present invention is not limited to monochromatic heat-sensitive recording materials.

Since these diazo compounds and coupling components couple more readily with each other in a basic atmosphere, a basic substance may be added into a heat-sensitive layer.

As basic substances intended for this purpose, slightly-water-soluble or water-insoluble basic substances and substances to generate alkali upon heating are used. Examples of these substances include nitrogen-containing compounds such as inorganic and organic ammonium salts, organic amine, amide, urea and thiourea and their derivatives, thiazoles, pyrroles, pyrimidines, piperazines, guanidines, indoles, imidazoles, imidazolines, triazoles, morpholines, piperidines, amidines, formazines, and pyridines. Specific examples are described in, for example, JP-A No. 61-291183. Basic substances may be used in combination.

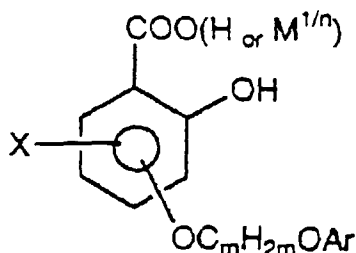
Electron donating dye precursors in the aforementioned combination (b) are not particularly limited, but are those compounds which donate electrons or accept protons from acids or the like to generate color and which are usually substantially colorless and have as part of skeleton thereof lactone, lactam, sultone, spiropyran, ester, amide, and the like, which partial skeletons open or break when the electron donating dye precursors contact electron accepting compounds serving as color developer.

Specifically, examples of the electron donating dye precursors include Crystal Violet Lactone, Benzoyl Leucomethylene Blue, Malachite Green Lactone, Rhodamine B Lactam, and 1,3,3-trimethyl-6'-ethyl-8'-butoxyindolinobenzospiropyran.

As electron accepting compounds for these color-generating agents, there may be employed acidic substances such as phenol compounds, organic phosphoric acid compounds, and aliphatic carboxylic compounds.

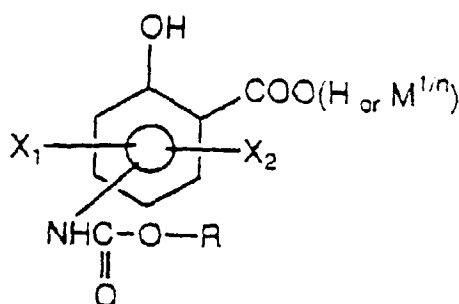
In the present invention, particularly preferred electron accepting compounds include the following compounds of formulas (6) through (9).

formula (6)



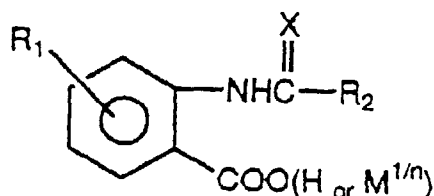
wherein Ar is an aryl group, X is a hydrogen atom, an alkyl group, an alkoxy group, or a halogen atom, m is an integer between 1 and 4 inclusive, n is an integer between 1 and 3 inclusive, and M is a metal atom having a valence n.

formula (7)



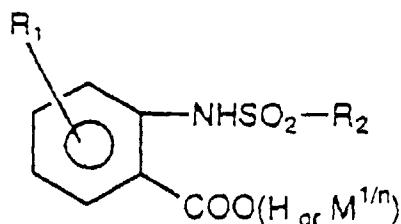
wherein each of X^1 and X^2 is a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, or a halogen atom, R is an alkyl group, an alkenyl group, an aralkyl group, or an aryl group, n is an integer between 1 and 3 inclusive, and M is a metal atom having a valence n.

formula (8)



wherein R^1 is a hydrogen atom, an alkyl group, or an aryl group, R^2 is an alkyl group, a cycloalkyl group, an aryl group, an alkylamino group, an alkoxy group, an aryloxy group, or an arylamino group, X is an oxygen atom or a sulfur atom, n is an integer between 1 and 3 inclusive, and M is a metal atom having a valence n.

formula (9)



wherein R^1 is a hydrogen atom, an alkyl group, or an aryl group, R^2 is an alkyl group, a cycloalkyl group, an aryl group, an alkylamino group, an alkoxy group, an aryloxy group, or an arylamino group, X is an oxygen atom or a sulfur atom, n is an integer between 1 and 3 inclusive, and M is a metal atom having a valence n.

Specific examples of the phenol compounds include p-(dodecylthio)phenol, p-(tetradecylthio)phenol, p-(hexadecylthio)phenol, p-(octadecylthio)phenol, p-(eicosylthio)phenol, p-(docosylthio)phenol, p-(tetracosylthio)phenol, p-(dodecyloxy)phenol, p-(tetradecyloxy)phenol, p-(hexadecyloxy)phenol, p-(octadecyloxy)phenol, p-(eicosyloxy)phenol,

p-(docosyloxy)phenol, p-(tetracosyloxy)phenol, p-dodecylcarbamoylphenol, p-tetradecylcarbamoylphenol, p-hexadecylcarbamoylphenol, p-octadecylcarbamoylphenol, p-eicosylcarbamoylphenol, p-docosylcarbamoylphenol, p-tetracosylcarbamoylphenol, hexadecyl gallate, octadecyl gallate, eicosyl gallate, docosyl gallate, and tetracosyl gallate.

Specific examples of the organic acid Ophosphoric compounds include dodecylphosphonic acid, tetradecylphosphonic acid, hexadecylphosphonic acid, octadecylphosphonic acid, eicosylphosphonic acid, docosylphosphonic acid, tetracosylphosphonic acid, hexacosylphosphonic acid, and octacosylphosphonic acid.

Examples of the aliphatic carboxylic acids include α -hydroxydecanoic acid, α -hydroxytridecanoic acid, α -hydroxytetradecanoic acid, α -hydroxyhexadecanoic acid, α -hydroxyoctadecanoic acid, α -hydroxypentadecanoic acid, α -hydroxyeicosanoic acid, α -hydroxydocosanoic acid, α -hydroxytetracosanoic acid, α -hydroxyhexacosanoic acid, α -hydroxyoctacosanoic acid, 2-bromohexadecanoic acid, 2-bromoheptadecanoic acid, 2-bromooctadecanoic acid, 2-bromoeicosanoic acid, 2-bromotetracosanoic acid, 3-bromooctadecanoic acid, 3-bromoeicosanoic acid, 2,3-dibromooctadecanoic acid, 2-fluorodecanoic acid, 2-fluorotetradecanoic acid, 2-fluorohexadecanoic acid, 2-fluorooctadecanoic acid, 2-fluoroeicosanoic acid, 2-fluorodocosanoic acid, 2-iodooctadecanoic acid, 3-iodohexadecanoic acid, 3-iodooctadecanoic acid, perfluorooctadecanoic acid, 2-oxodecanoic acid, 2-oxotetradecanoic acid, 2-oxohexadecanoic acid, 2-oxooctadecanoic acid, 2-oxoeicosanoic acid, 2-oxotetracosanoic acid, 3-oxodecanoic acid, 3-oxotetradecanoic acid, 3-oxohexadecanoic acid, 3-oxooctadecanoic acid, 3-oxoeicosanoic acid, 3-oxotetracosanoic acid, 4-oxohexadecanoic acid, 4-oxooctadecanoic acid, 4-oxodocosanoic acid, dodecylmalic acid, tetradecylmalic acid, hexadecylmalic acid, octadecylmalic acid, eicosylmalic acid, docosylmalic acid, tetracosylmalic acid, dodecylthiomalic acid, tetradecylthiomalic acid, hexadecylthiomalic acid, octadecylthiomalic acid, eicosylthiomalic acid, docosylthiomalic acid, tetracosylthiomalic acid, dodecylthiomalic acid, tetradecylthiomalic acid, hexadecylthiomalic acid, octadecylthiomalic acid, eicosylthiomalic acid, docosylthiomalic acid, tetracosylthiomalic acid, dodecylthiomalic acid, tetradecylthiomalic acid, hexadecylthiomalic acid, octadecylthiomalic acid, eicosylthiomalic acid, docosylthiomalic acid, tetracosylthiomalic acid, dodecylbutanedioic acid, tridecylbutanedioic acid, tetradecylbutanedioic acid, pentadecylbutanedioic acid, octadecylbutanedioic acid, eicosylbutanedioic acid, docosylbutanedioic acid, 2,3-dihexadecylbutanedioic acid, 2,3-dioctadecylbutanedioic acid, 2-methyl-3-dodecylbutanedioic acid, 2-methyl-3-tetradecylbutanedioic acid, 2-methyl-3-hexadecylbutanedioic acid, 2-ethyl-3-dodecylbutanedioic acid, 2-propyl-3-decylbutanedioic acid, 2-octyl-3-hexadecylbutanedioic acid, 2-tetradecyl-3-octadecylbutanedioic acid, dodecylmalonic acid, tetradecylmalonic acid, hexadecylmalonic acid, octadecylmalonic acid, eicosylmalonic acid, docosylmalonic acid, tetracosylmalonic acid, didodecylmalonic acid, ditetradecylmalonic acid, dihexadecylmalonic acid, dioctadecylmalonic acid, dieicosylmalonic acid, didocosylmalonic acid, methyl octadecylmalonic acid, methyleicosylmalonic acid, methyl docosylmalonic acid, methyl tetracosylmalonic acid, ethyl octadecylmalonic acid, ethyleicosylmalonic acid, ethyldocosylmalonic acid, ethyltetracosylmalonic acid, 2-dodecylpentanedioic acid, 2-hexadecylpentanedioic acid, 2-octadecylpentanedioic acid, 2-eicosylpentanedioic acid, 2-docosylpentanedioic acid, 2-dodecylhexanedioic acid, 2-pentadecylhexanedioic acid, 2-octadecylhexanedioic acid, 2-eicosylhexanedioic acid, and 2-docosylhexanedioic acid.

A heat-sensitive recording material which contains the above described electron donating dye precursors and electron accepting compounds in combination may be a rewritable one which permit coloring and decoloring reversibly and repeatedly (JP-A No. 5-124360). Moreover, di- and tri-arylmethane dye precursors (thiolactone) and organic silver salts are advantageously used in combination (JP-A No. 63-501941).

Specific examples of the organic metal salts used in combination with the reducing agents include silver salts of long-chain aliphatic carboxylic acids such as silver laurate, silver myristate, silver palmitate, silver stearate, silver arachate, and silver behenate; silver salts of imino group-containing organic compounds such as silver salts of benzotriazole, benzimidazole, carbazole, and phthalazinone; silver salts of sulfur-containing organic compounds such as silver s-alkyl thioglycolate; silver salts of aromatic carboxylic acids such as silver benzoate and silver phthalate; silver sulfonates such as silver ethanesulfonate; silver sulfinates such as silver o-toluenesulfinate; silver phosphates such as silver phenylphosphate; silver barbiturate; silver saccharinate; silver salt of salicylaldehyde; and mixtures thereof. Among these compounds, silver salts of long-chain aliphatic carboxylic acids are preferable, particularly silver behenate. Also behenic acid may be used in combination with silver behenate.

The reducing agents which can be used in the present invention are suitably incorporated according to the description in Japanese Patent Application Laid Open (JP-A) No. 53-1020 (from page 227, line 14 in the left column to page 229, line 11 in the right column). Examples of the reducing agents include mono-, bis-, tris-, or tetrakis-phenols, mono- or bis-naphthols, di- or poly-hydroxynaphthalenes, di- or poly-hydroxybenzenes, hydroxy monoethers, ascorbic acids, 3-pyrazolidones, pyrazolines, pyrazolones, reducing sugars, phenylenediamines, hydroxylamines, reductones, hydroxamines, hydrazides, amidoximes, and N-hydroxyureas. Among them, aromatic organic reducing agents such as polyphenols, sulfonamide phenols, and naphthols are particularly preferred.

Conventionally, color generating components are individually dispersed in an aqueous polymer solution, such as acetoacetyl-modified polyvinyl alcohol solution, prepared with a ball mill, a sand mill or the like, so that their grain sizes are less than several microns. After these dispersions are prepared, they are mixed together and further mixed with optional additives such as oil-absorbing pigments, binders, waxes, metallic soaps, antioxidants, UV-absorbers, surfactants, antistatic agents, defoaming agents, conductive agents, fluorescent dyes, and coloring dyes to provide a coat-

ing solution for heat-sensitive color-generating layer. The heat-sensitive recording materials are manufactured by applying the resultant coating solution support such as wood free paper, wood free paper having an undercoat layer, synthetic paper, or plastic film; drying the applied film; and calendering the resultant material to make the surface thereof smooth. In this case, the support preferably has a smoothness, as defined by JIS-8119, of at least 500 seconds, particularly preferably at least 800 seconds, in view of favorable dot reproducibility. The support having the smoothness of at least 500 seconds can be manufactured by, for example, (1) use of a material having high smoothness such as synthetic paper or plastic films; (2) provision of an undercoat layer mainly containing a pigment on a support; or (3) enhancement of the smoothness of a support by use of a calender, such as a supercalender.

The heat-sensitive recording materials of the present invention may contain thermally meltable substances (hereinafter referred to as sensitizers) in any layers that constitute the recording material in order to enhance the thermal response. Examples of the sensitizers include benzyl p-benzyloxybenzoate, β -naphthyl-benzyl ether, stearic amide, stearylurea, p-benzylbiphenyl, di(2-methylphenoxy)ethane, di(2-methoxyphenoxy)ethane, β -naphthol-(p-methylbenzyl) ether, α -naphthyl-benzyl ether, 1,4-butanediol-p-methylphenyl ether, 1,4-butanediol-p-isopropylphenyl ether, 1,4-butanediol-p-tertiary-octylphenyl ether, 1-phenoxy-2-(4-ethylphenoxy)ethane, 1-phenoxy-2-(4-chlorophenoxy)ethane, 1,4-butanediol phenyl ether, diethylene glycol-bis(4-methoxyphenyl) ether, 4-ethoxyphenyl-p-chlorobenzyl ether, 1-(4-methoxy-phenoxy)-2-phenoxypropane, 1,3-bis(4-methoxyphenoxy)propane, 3-methyl-4-chlorophenyl-p-methoxybenzyl ether, 3,5-dimethyl-4-chlorophenyl-p-methoxybenzyl ether, 4-chlorophenyl-p-methoxybenzyl ether, 1-phenoxy-2-(4-methoxy-phenoxy)propane, dibenzyl oxalate, and di(p-methylbenzyl) oxalate. These sensitizers are incorporated singly or as a mixture. In order to obtain sufficient thermal response, the sensitizer may be added to and dispersed with one or both color-generating components in an aqueous polymer solution. Alternatively, the sensitizer may be dispersed by preparing a thermally eutectic mixture of the color-generating component and the sensitizer, and cooling dispersing the mixture.

Examples of the metallic salts include metal salts of higher fatty acids, such as zinc stearate, zinc myristate, calcium stearate, and aluminum stearate.

Examples of the waxes include montan wax, paraffin wax, carnauba wax, microcrystalline wax, and polyethylene wax. Moreover, the recording material may have an optional back coat layer on the side opposite the color generating layer. Any material can be used for the back-coat layers, so long as it is known to serve as a back-coat layer of recording materials. Incorporation of the aforementioned acetoacetyl-modified polyvinyl alcohol and a film-hardening agent in the back-coat layer improves various properties such as water resistance.

EXAMPLES

The present invention will next be described by way of examples, which should not be construed as limiting the invention thereto. Concentrations in the examples are expressed as wt. %.

Example 1

20 gram of 2-anilino-3-methyl-6-N-n-propylaminofluoran as an electron donating colorless dye were dispersed in 100 grams of 2.5% aqueous solution of polyvinyl alcohol (PVA-105 available from Kuraray Co., Ltd.) by a ball mill for one day to prepare an electron donating colorless dye dispersion having an average grain size of not more than 1.5 μ m. An electron accepting compound dispersion was prepared in the above-described manner except that 20 grams of zinc 4- β -p-methoxyphenoxyethoxysalicylate as an electron accepting compound were substituted for 20 grams of 2-amino-3-methyl-6-N-n-propylaminofluoran. Moreover, a sensitizer dispersion was prepared in the above described manner except that 20 grams of 2-benzyloxynaphthalene as a sensitizer were substituted for 20 grams of 2-amino-3-methyl-6-N-n-propylaminofluoran.

40 grams of an amorphous silica (Mizukasil P-527 available from Mizusawa Industrial Chemicals, Ltd.), 40 grams of an aluminum hydroxide (Higilite H-42 available from Showa Denko, K.K.) were dispersed in 160 grams of a 0.5% aqueous solution of sodium hexametaphosphate with a homogenizer to thereby obtain a dye dispersion.

5 grams of an electron donating colorless dye dispersion, 10 grams of an electron accepting compound dispersion, 10 grams of a sensitizer dispersion, and 8 grams of a pigment dispersion were mixed together. Moreover, 2 grams of a 31.5% zinc stearate emulsion, 15 grams of a 5% aqueous solution of acetoacetyl-modified polyvinyl alcohol (Gohsefimer Z-200 available from The Nippon synthetic Chemical Industry Co., Ltd.) and 1.5 grams of a 50% aqueous solution of 2,3-dihydroxy-5-methyl-1,4-dioxazine were added to the resultant mixture, to obtain a heat-sensitive coating solution. By use of a wire bar, the heat-sensitive coating solution was applied to a support described below so that the dry weight of the coat layer was 5 g/m². Immediately after application, the coat layer was exposed to hot air (100°C) for 3 seconds and dried at 50°C for 1 minute.

Preparation of the support

80 grams of a baked kaolin (Ansilex 90 available from Engelhart Co.) were dispersed in 160 grams of a 0.5% aqueous solution of sodium hexametaphosphate with a homogenizer. 100 grams of a 2.5% aqueous polyvinyl alcohol (PVA-105 available from Kuraray Co., Ltd.) solution were added to the resultant dispersion to obtain an undercoat layer coating solution. By use of a wire bar, the dispersion was applied to the surface of wood free paper having a basis weight of 50 g/m², so that the dry weight of the undercoat layer was 7.0 g/m². The undercoat layer was subjected to heat for 1 minute at 50°C. The support having the undercoat layer was calendered to a Beck smoothness of 300 ± 100 seconds.

Example 2:

The procedure of Example 1 was repeated to obtain heat-sensitive recording paper, except that, in place of zinc 4-β-p-methoxyphenoxyethoxysalicylate (20 g), zinc 4-β-p-methoxyphenoxyethoxysalicylate (10 g) and 1,4-bis (4'-hydroxycumyl)benzene (10 g) were used in a heat-sensitive coating solution.

Examples 3 to 6:

The procedure of Example 2 was repeated to obtain heat-sensitive recording paper, except that, in place of 2,3-dihydroxy-5-methyl-1,4-dioxazine, 2,3-dihydroxy-1,4-dioxazine (Example 3), 2,3-dihydroxy-5,6-dimethyl-1,4-dioxazine (Example 4), 2,3-dihydroxy-2,5,6-trimethyl-1,4-dioxazine (Example 5), and 2,3-dihydroxy-2-methyl-1,4-dioxazine (Example 6) were used respectively in heat-sensitive coating solutions.

Examples 7 to 10:

The procedure of Example 2 was repeated to obtain heat-sensitive recording paper, except that, in place of 1.5 g of 50% aqueous solution of 2,3-dihydroxy-5-methyl-1,4-dioxazine, 3 g (Example 7), 2 g (Example 8), 0.7 g (Example 9), and 0.4 g (Example 10) of the same solution were used respectively in heat-sensitive coating solutions.

Example 11:

The procedure of Example 2 was repeated to obtain heat-sensitive recording paper, except that, in place of 2.5% aqueous solution of polyvinyl alcohol serving as a binder respectively for an electron donating colorless dye dispersion, an electron accepting compound dispersion, and a sensitizer dispersion, 2.5% aqueous solution of acetoacetyl-modified polyvinyl alcohol (The Nippon Synthetic Chemical Industry Co., Ltd., Gohsefimer Z-210) was used in a heat-sensitive coating solution.

Examples 12 to 14:

The procedure of Example 11 was repeated to obtain heat-sensitive recording paper, except that, in place of 1.5 g of 50% aqueous solution of 2,3-dihydroxy-5-methyl-1,4-dioxazine, 0.4 g (Example 12), 0.1 g (Example 13), and 0.05 g (Example 14) of the same solution were used respectively in heat-sensitive coating solutions.

Examples 15 and 16:

The procedure of Example 2 was repeated to obtain heat-sensitive recording paper, except that, in place of 1.5 g of 50% aqueous solution of 2,3-dihydroxy-5-methyl-1,4-dioxazine, 0.75 g (Example 15) and 3.5 g (Example 16) of 40% aqueous solution of glyoxal were used respectively in heat-sensitive coating solutions.

Example 17:

The procedure of Example 2 was repeated to obtain heat-sensitive recording paper, except that, in place of amorphous silica (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-527), amorphous silica calcium (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-832) was used in a heat-sensitive coating solution.

Example 18:

The procedure of Example 11 was repeated to obtain heat-sensitive recording paper, except that, in place of amorphous silica (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-527, 40 g) and aluminum hydroxide (Showa Denko, K.K.,

Higilite H-42, 40 g), amorphous silica (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-527, 72 g) and aluminum hydroxide (8 g) were respectively used in a heat-sensitive coating solution.

Example 19:

The procedure of Example 11 was repeated to obtain heat-sensitive recording paper, except that, in place of amorphous silica (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-527, 40 g) and aluminum hydroxide (Showa Denko, K.K., Higilite H-42, 40 g), amorphous silica (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-527, 24 g) and aluminum hydroxide (56 g) were respectively used in a heat-sensitive coating solution.

Examples 20 to 22

The procedure of Example 1 was repeated to obtain heat-sensitive recording paper, except that, in place of zinc 4- β -p-methoxyphenoxyethoxysalicylate, zinc 4-n-octyloxycarbonylamino salicylate (Example 20), zinc N-benzoylanthranilate (example 21), and zinc N-(phenylacetyl)anthranilate (Example 22) were used respectively in heat-sensitive coating solutions.

Example 23:

The procedure of Example 19 was repeated to obtain heat-sensitive recording paper, except that, in place of zinc 4- β -p-methoxyphenoxyethoxysalicylic acid, bisphenol A was used in a heat-sensitive coating solution.

Comparative example 1:

The procedure of Example 2 was repeated to obtain heat-sensitive recording paper, except that, 50% aqueous solution of 2,3-dihydroxy-5-methyl-1,4-dioxazine (1.5 g) was not used in a heat-sensitive coating solution.

Comparative example 2:

The procedure of Example 2 was repeated to obtain heat-sensitive recording paper, except that, in place of acetoacetyl-modified polyvinyl alcohol (The Nippon Synthetic Chemical Industry Co., Ltd., Gohsefimer Z-200), polyvinyl alcohol (Kuraray Co., PVA-117) was used in a heat-sensitive coating solution.

Comparative example 3:

The procedure of Example 2 was repeated to obtain heat-sensitive recording paper, except that, in place of 50% aqueous solution of 2,3-dihydroxy-5-methyl-1,4-dioxazine (1.5 g), 40% aqueous solution of glyoxal (0.2 g) was used in a heat-sensitive coating solution.

Comparative example 4:

The procedure of Example 11 was repeated to obtain heat-sensitive recording paper, except that, in place of amorphous silica (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-527, 40 g) and aluminum hydroxide (Showa Denko, K.K., Higilite H-42, 40 g), amorphous silica (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-527, 80 g) was used in a heat-sensitive coating solution.

Comparative example 5:

The procedure of Example 11 was repeated so as to obtain a heat-sensitive recording paper, except that, in place of amorphous silica (Mizusawa Industrial Chemicals, Ltd., Mizukasil P-527, 40 g) and aluminum hydroxide (Showa Denko, K.K., Higilite H-42, 40 g), aluminum hydroxide (80 g) was used in a heat-sensitive coating solution.

[Evaluation method]

Water-resistance (Blocking):

A droplet of water (1 ml) was placed on the surface of the recording material which had undergone a printing procedure by use of a printer, Canon HT-950. The material was folded so that two recorded surfaces adhered to each other.

A weight (50 g) was placed on the resultant folded sample, and the sample was allowed to dry for 24 hours. Subsequently, the two surfaces were separated for visual inspection.

⊙: The two recording surfaces were not adhered to each other, and the surfaces were maintained intact.

○: The two recording surfaces were adhered to each other, but the surfaces were not exfoliated.

△: The recording surfaces were slightly exfoliated but practically acceptable.

X: The recording surfaces were exfoliated, raising problems in practice.

Water-resistance (Abrasion):

A droplet of water (1 ml) was placed on the surface of the recording material which had undergone a printing procedure by use of a printer, Canon HT-950. One hour later, the material was abraded with fingers five times and then visually evaluated.

○: Almost no exfoliation was found in the recording surface.

△: The recording surface was slightly exfoliated.

X: The recording surface was exfoliated.

Coating strength (printability):

Printing was performed by use of an RI printer manufactured by Akira Seisakusho (ink: product of Tokashikiso K.K., T=15, ink amount: 0.5 g). The recording surfaces were visually inspected in terms of exfoliation.

⊙: The recording surface was maintained intact and not exfoliated.

○: The recording surface was slightly exfoliated but considered good.

△: The recording surface was slightly exfoliated but practically acceptable.

X: The recording surface was exfoliated, raising problems in practice.

Head smudge:

A 6-m continuous traveling test was performed by use of a Handy Terminal Canon HT-9000, HT-950, NEC HS-40, and Fujitsu Party V⁺⁺. Severity of blur in printed portions due to head smudge was visually evaluated. After the samples were traveled continuously, PPC paper soaked with alcohol was passed through the copier and deposits of head smudge were visually checked.

○: No blurring of image portion, and almost no head smudge.

△: No blurring of image portion, with presence of slight head smudge.

X: Image portion slightly blurred, with presence of slight head smudge.

Vinyl chloride applicability test (Plasticizer resistance):

Print samples were prepared by printing images by use of a print tester manufactured by Kyocera. Image density (D1) was measured with a Macbeth densitometer. Subsequently, the samples were brought into contact with Polymer Wrap (product of Shin'etsu) for 3 days under conditions of 23°C and 65%RH, and the image density (D2) was measured again. The residual ratio (%) was calculated from the following equation:

$$\text{Residual ratio of image density (\%)} = \frac{\{\text{Image density after treatment (D2)}\}}{\{\text{Image density before treatment (D1)}\}} \times 100$$

Higher plasticizer resistance is preferred, because the recording paper bearing printed image does not permit reduction in image density, when it contacts water or a plasticizer.

Table 1-1

5		Water resistance		Coating strength	Head smudge	Plasticizer Resistance(%)
		Blocking	Abrasion			
10	Ex. 1	○	○	○	○	83
	Ex. 2	○	○	○	○	65
15	Ex. 3	○	○	○	○	68
	Ex. 4	○	○	○	○	60
20	Ex. 5	○	○	○	○	58
	Ex. 6	○	○	○	○	61
25	Ex. 7	○	○	○	○	62
	Ex. 8	○	○	○	○	62
30	Ex. 9	○	○	△	○	57
	Ex. 10	△	△	△	○	59
35	Ex. 11	⊙	○	⊙	○	64
	Ex. 12	○	○	○	○	61
40	Ex. 13	△	△	△	○	55
	Ex. 14	△	△	△	○	58

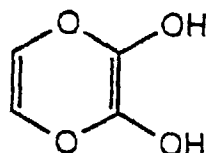
Table 1-2

35		Water resistance		Coating strength	Head smudge	Plasticizer Resistance(%)
		Blocking	Abrasion			
40	Ex. 15	○	○	○	○	59
	Ex. 16	○	○	○	○	57
45	Ex. 17	○	△	△	○	68
	Ex. 18	○	○	△	○	54
50	Ex. 19	○	○	○	○	69
	Ex. 20	○	○	○	○	35
55	Ex. 21	○	○	○	○	64
	Ex. 22	○	○	○	○	61
60	Ex. 23	○	○	○	○	5
	Comp. Ex.1	X	X	X	△	52
65	Comp. Ex.2	X	X or △	○	○	60
	Comp. Ex.3	X or △	△	△	○	51
70	Comp. Ex.4	○	X or △	X	○	31
	Comp. Ex.5	X or △	○	○	△	70

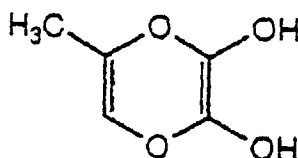
Claims

1. A heat-sensitive recording material comprising a support and a heat-sensitive color generating layer provided on the support, the heat-sensitive color generating layer containing a substantially colorless color-generating component A, a substantially colorless color-generating component B which reacts with the color-generating component A to generate color, acetoacetyl-modified polyvinyl alcohol which serves as a binder, and at least one of the compounds represented by formulas (1) to (5) serving as hardeners.

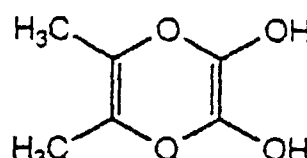
formula (1)



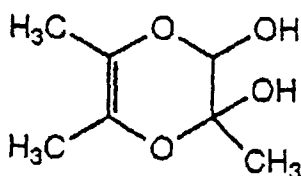
formula (2)



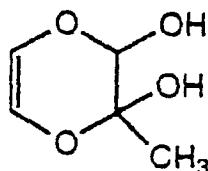
formula (3)



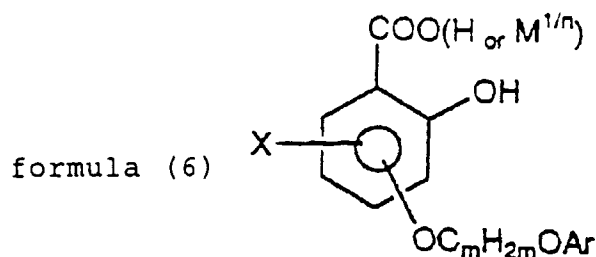
formula (4)



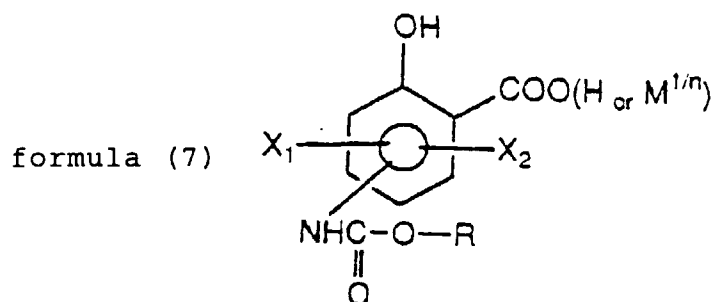
formula (5)



2. The heat-sensitive recording material according to claim 1, wherein the compound represented by formulas (1) to (5) is contained in an amount of between 0.1 and 200 parts by weight inclusive based on 100 parts by weight of the acetoacetyl-modified polyvinyl alcohol.
3. A heat-sensitive recording material comprising a support and a heat-sensitive color generating layer provided on the support, the heat-sensitive color generating layer containing a substantially colorless color-generating component A, a substantially colorless color-generating component B which reacts with the color-generating component A to generate color, acetoacetyl-modified polyvinyl alcohol which serves as a binder, and an aldehyde compound which serves as a hardener, wherein the aldehyde compound is contained in an amount of between 40 to 200 parts by weight inclusive with respect to 100 parts by weight of the acetoacetyl-modified polyvinyl alcohol.
4. The heat-sensitive recording material according to any one of claims 1 through 3, wherein the heat-sensitive color generating layer contains, as a pigment, amorphous silica or amorphous silica calcium and aluminum hydroxide.
5. The heat-sensitive recording material according to claim 4, wherein the ratio by weight of the amorphous silica or amorphous silica calcium to aluminum hydroxide is 3:7 to 9:1.
6. The heat-sensitive recording material according to any one of claims 1 through 5, wherein the color-generating component A is an electron donating colorless dye, and the color-generating component B is an electron accepting compound.
7. The heat-sensitive recording material according to claim 6, wherein the electron accepting compound is at least one of the compounds represented by formulas (6) through (9):

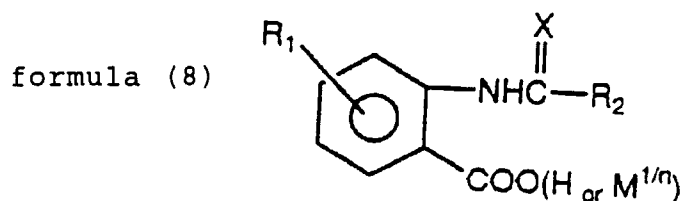


wherein Ar is an aryl group, X is a hydrogen atom, an alkyl group, an alkoxy group, or a halogen atom, m is an integer between 1 and 4 inclusive, n is an integer between 1 and 3 inclusive, and M is a metal atom having a valence n.



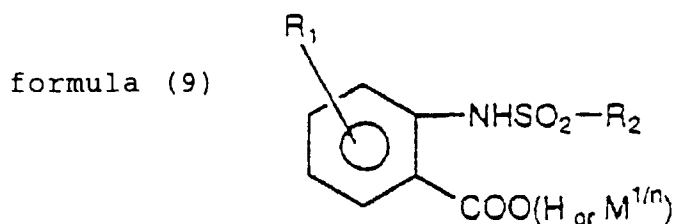
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wherein each of X^1 and X^2 is a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, or a halogen atom, R is an alkyl group, an alkenyl group, an aralkyl group, or an aryl group, n is an integer between 1 and 3 inclusive, and M is a metal atom having a valence n.



40

wherein R^1 is a hydrogen atom, an alkyl group, or an aryl group, R^2 is an alkyl group, a cycloalkyl group, an aryl group, an alkylamino group, an alkoxy group, an aryloxy group, or an arylamino group, X is an oxygen atom or a sulfur atom, n is an integer between 1 and 3 inclusive, and M is a metal atom having a valence n.



55

wherein R^1 is a hydrogen atom, an alkyl group, or an aryl group, R^2 is an alkyl group, a cycloalkyl group, an aryl group, an alkylamino group, an alkoxy group, an aryloxy group, or an arylamino group, X is an oxygen atom or a sulfur atom, n is an integer between 1 and 3 inclusive, and M is a metal atom having a valence n.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 12 0382

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.6)
A	GB 2 180 661 A (FUJI PHOTO FILM CO LTD) * claim 1 * * the whole document * ---	1-7	B41M5/30
A	GB 2 169 299 A (NIPPON SYNTHETIC CHEM IND) * page 2, line 12 - line 13 * * page 2, line 57 - line 60 * * page 3, line 13 - line 14 * * the whole document * ---	3-7	
A	EP 0 440 388 A (KANZAKI PAPER MFG CO LTD) * page 5, line 43 - line 52 * * page 6, line 4 - line 5 * * the whole document * ---	3-7	
A	EP 0 400 485 A (KANZAKI PAPER MFG CO LTD) * page 5, line 10 - line 14 * * example 3 * * the whole document * -----	3-7	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41M
Place of search		Date of completion of the search	Examiner
THE HAGUE		25 February 1998	Martins Lopes, L
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