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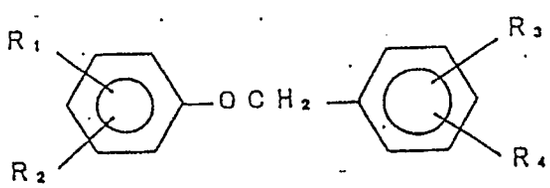
(54) Heat-sensitive recording material.

(57) A heat-sensitive recording material has on a support e.g. of paper, in order:
(1) a heat-sensitive coloring layer containing, usually in a water-soluble polymer binder, at least an electron-donating colorless dye, an electron-accepting compound, an ether represented by



(I)

wherein R_1 to R_4 each represents a hydrogen or halogen (e.g. C1) atom or an alkyl or alkoxy group, as pigment calcium carbonate having an oil absorption by a specified JIS method of not more than 60 ml/100 g and optionally an aliphatic amide or ureide or an aromatic ester or another aromatic ether,and
(2) a layer of a water-soluble polymer containing at least an inorganic pigment having an oil absorption by the JIS method of at least 50 ml/100 g, a wax (e.g., paraffin wax) and a metal soap (e.g. a stearate).

The coating dispersions may be coated simultaneously or separately. A back-coat layer may be present. The upper layer (2) components may diffuse into layer (1).

The material has good coloring density and running properties under a thermal head e.g., in a facsimile machine.

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HEAT-SENSITIVE RECORDING MATERIAL

This invention relates to a heat-sensitive recording material, and more particularly to a heat-sensitive recording material having on a support a coloring layer containing an electron donating colorless dye and an electron accepting compound.

Recording material using an electron - donating colorless dye and an electron-accepting compound is already well known, e.g., as pressure-sensitive recording papers, heat-sensitive recording papers, light- and pressure-sensitive recording papers, electro heat-sensitive recording papers, heat-sensitive transfer papers, etc., as described in British Patent 2,140,449, U.S. Patents 4,480,052, 4,436,920, JP-B-60-23992 (the term "JP-B" as used herein means an "examined published Japanese patent application"), and JP-A-57-179836, 60-123556, and 60-123557, (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), and particularly in terms of heat-sensitive recording materials in JP-B-43-4160 and 45-14039.

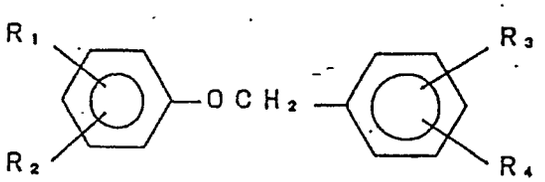
Recently, active investigations have been made to increase the recording speed and reduce the energy required for a heat-sensitive recording system, and, as a result of various investigations on electron donating colorless dyes and sensitizers, the present inventors previously found that the sensitivity of a heat-sensitive recording material could be improved by using a compound shown by formula (I) described below as a sensitizer (see U.S. Patent 4,480,052 and U.S. Patent application serial No. 07/385,508). However, a heat-sensitive recording material having an even higher sensitivity has now been required, and the requirements for running properties of such a heat-sensitive recording material (such as less head staining, less sticking to head, etc.) have also become severer.

The object of this invention is, therefore, to provide a heat-sensitive recording material having a high sensitivity and excellent running property.

The aforesaid object can be attained by the present invention as set forth hereinbelow.

That is, according to this invention, there is provided a heat-sensitive recording material having, on a support

(1) a heat-sensitive coloring layer containing at least an electron-donating colorless dye, and an electron-accepting compound, a compound represented by formula (I),



(I)

wherein R_1, R_2, R_3 and R_4 each represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, or a halogen atom, preferably chlorine, bromine or fluorine, more preferably chlorine, and a pigment, wherein the pigment is calcium carbonate having an oil absorption by JIS method K-5101 of not more than 60 ml/100 g, and (2) a water-soluble polymer layer containing at least an inorganic pigment having an oil absorption by JIS method K-5101 of at least 50 ml/100 g, a wax, and a metal soap formed on the heat-sensitive coloring layer.

"JIS" refers to Japanese Industrial Standard.

The water-soluble polymer layer to be formed on the heat-sensitive coloring layer may be coated separately from the coloring layer or immediately after coating the composition (solution) for the coloring layer. The components of the upper layer may diffuse into the heat-sensitive coloring layer or mix with the components of the heat-sensitive coloring layer, but at least 50% of the components of the upper layer remain in the upper layer.

Specific examples of the compound of formula (I) for use in this invention include 4′-methoxyphenyl-4-methyl-benzyl ether, 4′-methylphenyl-4-methoxybenzyl ether, 4′-methoxyphenyl-4-chlorobenzyl ether, 4′-ethoxyphenyl-4-chlorobenzyl ether, 4′-chlorophenyl-4-methoxybenzyl ether and 3′-methyl-4′-chlorophenyl-4-methoxybenzyl ether.

The aforesaid compound can be used with a compound disclosed, for example, in JP-A-58-57989 or 58-87094. Typical examples of such a compound are aromatic ethers, aromatic esters, aliphatic amides, and aliphatic ureides.

Examples of the water-soluble polymer binder used for the coloring and upper layers in this invention include polyvinyl alcohol (including carboxy-denatured, itaconic acid-denatured, maleic acid-denatured, and

silica-denatured polyvinyl alcohols), methyl cellulose, carboxymethyl cellulose, starches (including denatured starches), gelatin, gum arabic, casein, the hydrolyzed product of a styrene-maleic acid copolymer, polyacrylamide and saponification product of a vinyl acetate-polyacrylic acid copolymer.

The binder is used not only for dispersing, but also for improving the strength of the coated layer. For the latter purpose, a latex series binder of a synthetic polymer can be used together therewith, such as a styrene-butadiene copolymer, a vinyl acetate copolymer, an acrylonitrile-butadiene copolymer, a methyl acrylate-butadiene copolymer or polyvinylidene chloride, in an amount of not more than 200 % by weight of the water-soluble polymer. Also, if necessary, according to the kind of the binder, a suitable crosslinking agent for the binder may be used.

As the pigment used for the heat-sensitive coloring layer in this invention, calcium carbonate having an oil absorption by JIS method K-5101 of not more than 60 ml/100 g is used, and the amount of the pigment is generally in the range of 0.02 to 1.0% by weight, and preferably 0.05 to 0.6% by weight based on the weight of the solid component of the compound represented by formula (I) being used. The compound of formula (I) has a high selectivity for pigment and the compound does not show a high sensitivity effect with pigments other than the aforesaid pigment.

However, in the case of only using the aforesaid pigment and the aforesaid amount thereof for the heat-sensitive coloring layer in this invention, good running properties can not be maintained, and the layer is liable to fog. Thus, in this invention a water-soluble polymer layer containing an inorganic pigment having an oil absorption by JIS method K-5101 of at least 50 ml/100 g, a wax, and a metal soap is formed on the heat-sensitive coloring layer, whereby the running property of the heat-sensitive recording material can be improved with the high sensitivity effect by the compound of formula (I).

Examples of the metal soap used in this invention include higher fatty acid metal salts such as zinc stearate, calcium stearate, and aluminum stearate.

Examples of the wax for use in this invention include paraffin wax, microcrystalline wax, carnauba wax, methylol stearoamide, polyethylene wax, polystyrene wax, methylol stearoamide, polyethylene wax, polystyrene wax, and a fatty acid series wax. They can be used singly or as a mixture thereof.

As the inorganic pigment used for the upper layer in this invention, there are inorganic pigments which have hitherto been used for heat-sensitive recording materials, such as calcium carbonate, aluminum hydroxide, talc, kaolin, burned kaolin. or silica, each having an oil absorption by JIS method K-5101 of at least 50 ml/100 g.

A method of preparing the heat-sensitive recording material is explained below.

The electron donating colorless dye, the electron accepting compound, and the compound represented by formula (I) are dispersed in a ball mill, a sand mill, etc., together with an aqueous solution (generally 0.2 to 15 wt%) of a water-soluble polymer such as polyvinyl alcohol, to sizes of less than 3 microns in diameter. In this case, the compound of formula (I) may be dispersed alone or together with the electron donating colorless dye and/or the electron accepting compound after adding the compound of formula (I) thereto or formed into an eutectic mixture with each followed by dispersing.

Also, if desired, the calcium carbonate used for the heat-sensitive recording layer may be dispersed in a ball mill, a sand mill, a kady mill, a homogenizer, etc., together with a surface active agent, a dispersing agent, a water-soluble polymer, etc.

The aforesaid dispersions and calcium carbonate (or the dispersion thereof) are mixed with each other, and, if desired, a surface active agent, a binder, a metal soap, a wax, an antioxidant, a ultraviolet absorbent, etc., may be added to the mixture to provide a coating composition for the heat-sensitive recording layer.

Also, the inorganic pigment having an oil absorption by JIS method K-5101 of at least 50 ml/100 g used for the upper layer in this invention may be dispersed similarly to the case of dispersing calcium carbonate for the coating composition of the heat-sensitive recording layer described above. After mixing the inorganic pigment or the dispersion thereof with a wax, a metal soap, and a water-soluble polymer, to the mixture may be added a surface active agent, an additional binder, an additional metal soap, an additional wax, an antioxidant, a ultraviolet absorbent, etc. to provide the coating composition for the upper layer.

The coating composition for the heat-sensitive recording layer and the coating composition for the upper layer thus obtained may be simultaneously or separately coated on a wood-free paper, a wood-free paper having a subbing layer, a synthetic paper, a plastic film, etc., followed by drying, and it is preferred that they are coated on a wood-free paper having a subbing layer, followed by drying. Thus, the heat-sensitive recording material is obtained.

Practical examples of the electron-donating colorless dye for use in this invention are triarylmethane series compounds, diphenylmethane series compounds, xanthene series compounds, thiazine series compounds, and spiropyran series compounds, as described e.8., in JP-A-55-227253.

Specific examples of the aforesaid compounds include triarylmethane series compounds such as 3,3-

bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,3-dimethylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl)-phthalide, etc.; diphenylmethane series compounds such as 4,4′-bis-dimethylaminobenzhydrin benzyl ether, N-halophenyl-leucoauramine, N-2,4,5-trichlorophenyl-leucoauramine; xanthene series compounds such as rhodamine-B-anilinolactam, rhodamine(p-nitrino)lactam, 2-(dibenzylamino)fluoran, 2-anilino-3-methyl-6-diethylaminofluoran,2-anilino-3-methyl-6-dibutylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-isoamylaminofluoran,2-anilino-3-methyl-6-N-methyl-N-cyclohexylaminofluoran, 2-anilino-3-chloro-6-diethylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-iso-butylaminofluoran, 2-anilino-6-dibutylaminofluoran, 2-anilino-3-methyl-6-N-methyl-N-tetrahydrofurfirylmethylaminofluoran, 2-anilino-3-methyl-6-piperidinoaminofluoran, 2-(o-chloroanilino)-6-diethylaminofluoran, 2-(3,4-dichloroanilino)-6-diethylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-n-hexylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-γ-ethoxypropylaminofluoran, 2-anilino-3-methyl-6-N-methyl-N-γ-ethoxypropylaminofluoran, 2-anilino-3-methyl-6-N-ethyl-N-γ-methoxypropylaminofluoran, 2-anilino-3-methyl-6- dipentylaminofluoran; thiazine series compounds such as benzoylleucomethylene blue, p-nitrobenzylleucomethylene blue, and spiropyran series compounds such as 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3,3′-dichloro-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methyl-naphtho-(3-methoxy-benzo)-spiropyran, 3-propyl-spiro-dibenzopyran .

As the electron accepting compound, phenolic compounds, or salicylic acid compounds and the polyvalent metal salts thereof are preferred.

Specific examples of the aforesaid preferred electron accepting compounds include phenolic compounds such as 2,2′-bis(4-hydroxyphenyl)propane(bisphenol A), 4-t-butylphenol, 4-phenylphenol, 4-hydroxydiphenoxide, 1,1′-bis(3-chloro-4-hydroxyphenyl)cyclohexane, 4,4′-sec-butylidenediphenol, 4-p-methylphenylphenol, 4,4′-methylcyclohexylidenephenol, 1,1′-bis(3-chloro-4-hydroxyphenyl)-2-ethylbutane, 1,1′-bis-(4-hydroxyphenyl)-cyclohexane, 4,4′-sec-isooctylidenediphenol, 4,4′-isopentylidenephenol, benzyl p-hydroxybenzoate, etc.; salicylic acid derivatives such as 4-pentadecylsalicylic acid, 3,5-di(α-methylbenzyl)salicylic acid, 3,5-di(teroctyl)salicylic acid, 5-octadecylsalicylic acid, 5-α-(p-α-methylbenzylphenyl)ethylsalicylic acid, 3-α-methylbenzyl-5-teroctylsalicylic acid, 5-tetradecylsalicylic acid, 4-hexyloxysalicylic acid, 4-cyclohexyloxysalicylic acid, 4-decyloxysalicylic acid, 4-dodecyloxysalicylic acid, 4- pentadecyloxysalicylic acid, 4-octadecyloxysalicylic acid, etc.; and polyvalent metal salts thereof such as zinc salts, aluminum salts, calcium salts, copper salts and lead salts.

The amount of the electron-accepting compound being used is preferably from 50 to 800% by weight, and more preferably from 100 to 500% by weight of the amount of the electron donating colorless dye.

If the amount is less than 50% by weight, coloring may be insufficient, and if the amount is over 800% by weight, a further effect is not obtained.

In this invention, the compounds disclosed in JP-A-58-57989, 58-87094, etc. can be further used as a sensitizer in addition to the compound represented by formula (I).

Also, if desired, the heat-sensitive recording material may further contain a surface active agent, an antistatic agent, a ultraviolet absorbent, an anti-oxidant, a deforming agent, an electric conductive agent, a fluorescent dye, a coloring dye, etc.

Also, for inhibiting the decolorization of image printout portions and fastening the formed images, a decolorization inhibitor may be added to the heat-sensitive coloring layer. As the decolorization inhibitor, phenol compounds, and in particular hindered phenol compounds, are effectively used. The amount of the phenolic compound is preferably from 1 to 200% by weight, and more preferably from 5 to 50% by weight based on the amount of the electron accepting compound.

Also if desired, a back coat layer may be formed on the surface of the support of the heat-sensitive recording material opposite to the side carrying the heat-sensitive recording layer.

For the back coat layer, any materials which are conventionally used for back coat layers of heat-sensitive recording materials can be used.

The following examples are intended to illustrate this invention in greater detail, but not to limit it in any way.

EXAMPLE 1

Preparation of Heat-Sensitive Coloring Layer:

Each of 20 g of 2-anilino-3-methyl-6-dibutylaminofluoran as an electron donating colorless dye, 20 g of bisphenol A as electron accepting compound, and 20 g of 4′-ethoxyphenyl-4-chlorobenzyl ether as a sensitizer was dispersed for about 24 hours in a ball mill together with 100 g of an aqueous solution of 5% polyvinyl alcohol (PVA-105, trademark for product made by Kuraray Co., Ltd.) to a mean grain size of less than 1.5 μm in each case to provide each dispersion. Also, 80 g of calcium carbonate (Unibur 70, oil absorption 40 ml/100 g, trademark for product made by Shiraishi Kogyo K.K.) was dispersed in a homogenizer together with 160 g of an aqueous solution of 0.5% sodium hexamethaphosphoric acid to provide a pigment dispersion.

The dispersions thus prepared were mixed with each other in mixing ratio of 5 g of the dispersion of the electron donating colorless dye, 10 g of the dispersion of the electron accepting compound, 10 g of the dispersion of the sensitizer, and 5 g of the dispersion of calcium carbonate, to provide a coating composition for a heat-sensitive coloring layer.

The coating composition was coated on a wood-free paper by a coating bar at a dry weight of 5 g/m^2 and dried for one minute at 50° C to form a heat-sensitive colorless layer.

Preparation of Coating Composition For Upper Layer:

By dispersing 40 g of calcium carbonate (KARURAITO SA, oil absorption 60 ml/100 g, trademark for product made by Shiraishi Chuo Kenkyu Sho) in a homogenizer together with 60 g of an aqueous solution of 1% sodium hexametaphosphate, a pigment dispersion was obtained. To 10 g of the pigment dispersion were added 20 g of an aqueous solution of 10% polyvinyl alcohol (PVA-117, trademark for product made by Kuraray Co., Ltd.), 10 g of an emulsion of 21% zinc stearate, 17 g of an emulsion of 30% paraffin wax, and 300 g of water, to provide a coating composition for the upper layer.

Preparation of Heat-Sensitive Recording Paper:

The coating composition for the upper layer was coated on the heat-sensitive coloring layer using a coating bar at a dry weight of 0.5 g/m^2, and dried for one minute at 50° C to provide a heat-sensitive recording paper.

EXAMPLE 2

By following the same procedure as in Example 1 except that the amount (10 g) of the dispersion of calcium carbonate which was used in the coating composition for the heat-sensitive coloring layer was reduced to 5 g, a heat-sensitive recording material was prepared.

EXAMPLE 3

By following the same procedure as in Example 1 except that burned kaolin (Ansilex 93, oil absorption 90 ml/100 g, trademark for product made by Engerhard Co.) was used in place of calcium carbonate (KARURAITO SA) in the coating composition for upper layer, a heat-sensitive recording material was prepared.

COMPARISON EXAMPLE 1

By following the same procedure as in Example 1, except that the upper layer was not formed, a heat-sensitive recording paper was prepared.

COMPARISON EXAMPLE 2

By following the same procedure as in Example 1, except that the amount (10 g) of the dispersion of calcium carbonate which was used in the coating composition for the heat-sensitive coloring layer was increased to 20 g, a heat-sensitive recording paper was prepared.

COMPARISON EXAMPLE 3

By following the same procedure as in Example 1, except that aluminum hydroxide (HAIJIRAITO H42, oil absorption 30 ml/100 g, trademark for product made by Showa Denko K.K.) was used in place of the calcium carbonate (Unibur 70) which was used in the coating composition for the heat-sensitive coloring layer, a heat-sensitive recording paper was prepared.

COMPARISON EXAMPLE 4

By following the same procedure as in Example 1, except that calcium carbonate (KURURITO KT, oil absorption 70 ml/100 g, trademark for product made by Shiraishi Chuo Kenkyu Sho) was used in place of calcium carbonate (Unibur 70) which was used in the coating composition for the heat-sensitive coloring layer, a heat-sensitive recording paper was prepared.

COMPARISON EXAMPLE 5

By following the same procedure as in Example 1, except that the paraffin wax emulsion in the coating composition for the upper layer was omitted, a heat-sensitive recording paper was prepared.

COMPARISON EXAMPLE 6

By following the same procedure as in Example 1, except that the emulsion of zinc stearate in the coating composition for the upper layer was omitted, a heat-sensitive recording paper was prepared.

COMPARISON EXAMPLE 7

By following the same procedure as in Example 1, except that calcium carbonate (Brilliant-15, oil absorption 40 ml/100 g, trademark for product made by Shiraishi Kogyo K.K.) was used in place of calcium carbonate (KARURAITO SA) used in the coating composition for the upper layer, a heat-sensitive recording material was prepared.

COMPARISON EXAMPLE 8

By following the same procedure as in Example 1, except that the dispersion of calcium carbonate (KARURAITO SA) used in the coating composition for the upper layer was omitted, a heat-sensitive recording material was prepared.

Each of the heat-sensitive recording papers (materials) thus prepared was printed at a pulse width of 1.0 ms. by means of a heat-sensitive printout experimental apparatus manufactured by Kyocera Corporation using a press roll at a head potential of 24 V and pulse cycle of 10 ms., and the printout density thereof was measured by a Macbeth reflection densitomer RD-918.

Also, printout of 50% in black ratio was performed on each sample using a Facsimile UF-22 machine, manufactured by Matsushita Graphic Communication Systems, Inc., after which head staining and sticking were evaluated.

The head staining and sticking were evaluated by the following standard.

A: Did not occur

B: Occurred, but not to an extent of causing printout hindrance and making reading of print impossible.

X: Occurred to an extent hindering printout.

The results are shown in Table 1 below.

Table 1

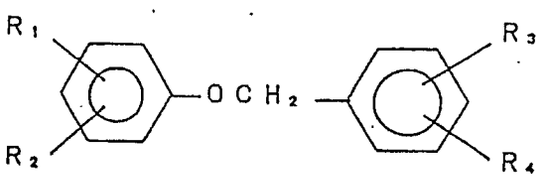
Example	Coloring Density	Head Stain	Sticking
Example 1	1.38	A	A
Example 2	1.42	B	A
Example 3	1.37	A	A
Comparison Example 1	1.40	X	X
Comparison Example 2	1.20	B	A
Comparison Example 3	1.18	B	B
Comparison Example 4	1.25	B	B
Comparison Example 5	1.20	X	A
Comparison Example 6	1.40	A	X
Comparison Example 7	1.40	X	B
Comparison Example 8	1.40	X	X

As shown in the above table, it can be seen that the heat-sensitive recording papers of this invention show a good coloring density even using low energy and are excellent in running properties.

Claims

1. A heat-sensitive recording material having on a support

(1) a heat-sensitive coloring layer containing at least an electron-donating colorless dye, and an electron-accepting compound, a compound represented by formula (I),



(I)

wherein R_1, R_2, R_3, and R_4 each represents a hydrogen atom, an alkyl group, an alkoxy group or a halogen atom,

and a pigment, wherein said pigment is calcium carbonate having an oil absorption by JIS method K-5101 of not more than 60 ml/100 g, and

(2) a water-soluble polymer layer containing at least an inorganic pigment having an oil absorption by JIS method K-5101 of at least 50 ml/100 g, a wax and a metal soap formed on said heat-sensitive coloring layer.

2. A heat-sensitive recording material as in claim 1, wherein said inorganic pigment having an oil absorption by said JIS method of at least 50 ml/100 g is calcium carbonate, aluminum hydroxide, talc, kaolin, burned kaolin, or silica each having the oil absorption of at least 50 ml/100 g.

3. A heat-sensitive recording material as in Claim 1 or 2, wherein the electron-donating colorless dye is a triarylmethane series compound, a diphenylmethane series compound, a xanthene series compound, a thiazine series compound or a spiropyran series compound.

4. A heat-sensitive recording material as in Claim 1,2 or 3, wherein the electron-accepting compound is a

phenolic compound, a salicylic acid compound, or a polyvalent metal salt of a salicyclic acid compound.

5. A heat-sensitive recording material as in any of claims 1 to 4, wherein the calcium carbonate having an oil absorption of not more than 60 ml/100 g is present in an amount of 0.05 to 0.6% by weight based on the weight of the solid component of the compound present represented by formula (I).

6. A heat-sensitive recording material as in any of claims 1 to 5, wherein the amount of electron-accepting compound is from 100 to 500% by weight of the amount of the electron-donating colorless dye.

7. A heat-sensitive recording material as in any of claims 1 to 6, wherein the heat-sensitive coloring layer additionally comprises a hindered phenol compound in an amount of from 5 to 50% by weight based on the amount of the accepting compound.