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(54) **Heat-sensitive recording material**

Wärmeempfindliches Aufzeichnungsmaterial

Matériau d'enregistrement sensible à la chaleur

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- **PATENT ABSTRACTS OF JAPAN vol. 016, no. 339 (M-1284), 22 July 1992 (1992-07-22) & JP 04 101883 A (OJI PAPER CO LTD), 3 April 1992 (1992-04-03)**
- **PATENT ABSTRACTS OF JAPAN vol. 015, no. 215 (M-1119), 31 May 1991 (1991-05-31) & JP 03 061078 A (KANZAKI PAPER MFG CO LTD), 15 March 1991 (1991-03-15)**
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- **PATENT ABSTRACTS OF JAPAN vol. 33 (M-638), 4 November 1987 (1987-11-04) & JP 62 117787 A (RICOH CO LTD), 29 May 1987 (1987-05-29)**

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EP 0 992 364 B1

Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a heat-sensitive recording material. More particularly, the present invention relates to a heat-sensitive recording material comprising intermediate layers between a support and a heat-sensitive color developing layer thereof, which heat-sensitive recording material is excellent in color developing density.

Description of the Related Art

[0002] Recording materials using electron donative colorless dyes and electron acceptive compounds as color developing components are well known in the form 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 in detail, for example, in GB Patent No. 2,140,449, US Patent Nos. 4,480,052 and 4,436,920, Japanese Patent Application Publication (JP-B) No. 60-23992, Japanese Patent Application Laid-Open (JP-A) Nos. 57-179836, 60-123556, and 60-123557. Regarding heat-sensitive recording, for example, heat-sensitive recording materials using electron donating dye precursors and electron acceptive compounds are disclosed in JP-B Nos. 45-14039 and 43-4160.

[0003] 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. In order to accommodate demand for increasing diversity and higher functions of these devices, particularly demand for higher-speed facsimile machines, improvement of color developing sensitivity is highly desired and various techniques have been proposed. For example, providing a foam layer with high adiathermancy between a support and a heat-sensitive color developing layer and effectively utilizing energy from a thermal head has been proposed in JP-A No. 55-164192 and the like.

[0004] However, in attempts to obtain a foam layer with a sufficient thermal insulation effect there has been a problem in which smoothness of the foam layer is lowered and uniformity of a color developed image is reduced. There also is a problem that when a foam layer is calendered to improve smoothness of the foam layer, adiathermancy of the foam layer is reduced, and the like.

SUMMARY OF THE INVENTION

[0005] An object of the present invention is to provide a heat-sensitive recording material which has high color developing density and is excellent in dot reproducibility.

[0006] The present invention provides heat-sensitive recording material comprising a support having formed thereon at least one heat-sensitive color developing layer comprising an electron donative colorless dye and an electron acceptive compound, wherein

a first intermediate layer and a second intermediate layer are sequentially laminated between the support and the heat-sensitive color developing layer,

the first intermediate layer and the second intermediate layer comprise an inorganic pigment and a binder as main components,

the first intermediate layer is formed by a blade-coating method and has an Oken type smoothness of not less than 700 seconds, and

the second intermediate layer is formed by a free-fall-curtain method and has a density (coating amount in g/m^2 divided by coating thickness in μm) of not more than 1.0.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007]

Fig. 1 is a vertical sectional view of a construction of an Oken type smoothness tester.

DETAILED DESCRIPTION OF THE INVENTION

[0008] A preferred embodiment of the present invention is explained in the following.

[0009] Intermediate layers of the present invention comprise a first intermediate layer formed on a support and a

second intermediate layer laminated on the first intermediate layer. Main components of the first intermediate layer are an inorganic pigment and a binder, and likewise, main components of the second intermediate layer are an inorganic pigment and a binder. Examples of the inorganic pigment contained in these first and second intermediate layers include, for example, kaolin, calcined kaolin, talc, agalmatolite, diatomaceous earth, calcium carbonate, aluminum hydroxide, magnesium hydroxide, magnesium carbonate, titanium oxide, barium carbonate, and the like. A desirable mean particle diameter of these inorganic pigments is 0.1-5μm, preferably 0.5-3μm.

[0010] The inorganic pigment contained in the second intermediate layer particularly desirably is an inorganic pigment having an oil absorption of 70 ml/100 g or more by a measuring method defined by JIS-5101. An inorganic pigment having an oil absorption of 70 ml/100 g or less may be used in combination with the inorganic pigment having an oil absorption of 70 ml/100 g or more so far as the effect of the present invention is not impaired.

[0011] As the binder contained in the first and the second intermediate layers, a water soluble polymer such as a starch derivative, polyvinyl alcohol and styrene-maleic anhydride, and a hydrophobic polymer emulsion such as styrene-butadiene latex and acrylic resin emulsion, and the like can be used.

[0012] The mixing ratio of the inorganic pigment and the binder in the first intermediate layer preferably is that, for 100 parts by weight of the inorganic pigment, the binder is 3-30 parts by weight, preferably 5-20 parts by weight. The mixing ratio of the inorganic pigment and the binder in the second intermediate layer may be same as that of the first intermediate layer.

[0013] The first intermediate layer is formed by coating a coating solution obtained by adding together the inorganic pigment and the binder and additionally adding as required, a dispersing agent, a wax, a thickener, a surfactant, an ultraviolet ray absorbing agent, an antioxidant, a water-and-oil-repellent agent, organic hollow particles, and the like. The first intermediate layer is formed by coating the solution on the support by a blade-coating method. A preferable amount coated of the first intermediate layer is 3-30 g/m^2, desirably 5-15 g/m^2 in solid weight.

[0014] Oken type smoothness of the first intermediate layer formed by a blade-coating method is required to be not less than 700 seconds, desirably not less than 800 seconds, and more desirably not less than 900 seconds. When Oken type smoothness of the first intermediate layer is less than 700 seconds, the smoothness of the layer is too low so that the smoothness of the first intermediate layer negatively influences smoothness of the second intermediate layer, and smoothness of a heat-sensitive color developing layer formed on the second intermediate layer tends be reduced, and thus uniformity of color developing density (dot reproducibility) decreases. Therefore, it is not preferable.

[0015] In the present application, the Oken type smoothness is measured using a pressure type smoothness-and-air-permeability tester, manufactured by Kumagai Riki-Kogyo Co., Ltd., which is used in smoothness tests for paper and paperboard. As shown in Fig. 1, the pressure type smoothness-and-air-permeability tester consists of a measuring section 1, an air compressor 2, a pressure reducing valve 3, a filter 4, a regulating valve 5, a water column type air pressure governor 6 (height of the water column: 500 mm), a measurment air inlet orifice 7 (0.3ϕ $\times$ 50 mm), a water column manometer 8, and a scale plate 9. The air pressure is regulated to be 5-7 kg/cm^2 at the air compressor 2, to be about 1 kg/cm^2 at the pressure reducing valve 3, and to be about 0.1 kg/cm^2 at the regulating valve 5. The water column type air pressure governor 6 comprises a tank (inner diameter: 100 mm, height: 700 mm) and an air chamber having an opening at 500 mm under the water surface. The air is regulated again at this air pressure governor 6, then passes through the orifice 7 and reaches the measuring section.

[0016] Ten test strips having a size of 60 $\times$ 60 mm square or more, which are clean and have no problems such as folds or creases, are prepared. The test strips are left for four hours under conditions in which the temperature is 20 °C and the relative humidity is 65 %, and thereafter, are measured under the same environmental conditions.

[0017] Measurement of the smoothness is performed as follows: fill the water column type air pressure governor 6 with air having a pressure regulated to be about 0.1 kg/cm^2; adjust the tester so that the water column manometer 8 indicates 500 mm on the scale when a weight 10 having a pressure plate 11 made of rubber attached thereto is placed on a smoothness measuring head 13, and the water column manometer 8 indicates 0 mm on the scale when the weight 10 is removed; place a test strip 12 on the measuring head 13 with a measurement surface of the test strip 12 facing downward, then, apply a fixed load by a lever; read a value indicated by the water column manometer 8 ten seconds after the start of the measurement. This is repeated ten times. An average of the ten values obtained thereby is the value for Oken type smoothness in the present application.

[0018] The second intermediate layer laminated on the first intermediate layer is also formed by coating a coating solution obtained by adding together the inorganic pigment and the binder and additionally adding as required, a dispersing agent, a wax, a thickener, a surfactant, an ultraviolet ray absorbing agent, an antioxidant, a water-and-oil-repellent agent, organic hollow particles, and the like. The second intermediate layer is formed by coating the solution on the first intermediate layer on the support by a free-fall-curtain method. A preferable amount coated of the second intermediate layer is 3-20 g/m^2, desirably 4-10 g/m^2 in solid weight. Density of the second intermediate layer is required to be not more than 1.0, desirably not more than 0.85, and more desirably, not more than 0.70.

[0019] It is not desirable that density of the second intermediate layer is over 1.0, because image density tends to be insufficient. This phenomenon is caused because thermal energy obtained from a thermal head or the like does not

effectively affect on a heat-sensitive recording layer during image formation.

[0020] The density of the second intermediate layer is defined as follows:

$$\text{coating density} = \text{coating amount } (g/m^2) \,/\, \text{coating thickness } (\mu m).$$

[0021] The above coating amount (g/m^2) can be obtained from a calculation based on the two basic weights as follows:

$$\text{coating amount } (g/m^2) = \text{basic weight after coating the second intermediate layer } (g/m^2) - \text{basic weight before coating the second intermediate layer } (g/m^2).$$

[0022] These two basic weights can be found through a method in JIS P8124.

[0023] The above coating thickness (μm) can be obtained from by a calculation based on the two basic weights as follows:

$$\text{coating thickness } (\mu m) = \text{basic thickness after coating the second intermediate layer}(\mu m) - \text{basic thickness before coating the second intermediate layer}(\mu m).$$

[0024] These two basic thickness weights can be found through a method in JIS P8124.

[0025] In the present invention, the heat-sensitive color developing layer formed on these intermediate layers comprises an electron donative colorless dye and an electron acceptive compound as heat-sensitive color developing components.

[0026] A plurality of heat-sensitive color developing layers comprising a diazonium salt compound and a coupler may be provided as required on the heat-sensitive color developing layer comprising an electron donative colorless dye and an electron acceptive compound.

[0027] In a case of a heat-sensitive recording layer comprising the electron donative colorless dye and an acidic material as heat-sensitive color developing components, one of the components melts with heating and then both react with each other to develop a color. A third meltable component (generally a low-melting-point organic material) may also be added to the heat-sensitive recording layer as required.

[0028] Examples of the electron donative colorless dye include a triarylmethane-based compound, a diphenylmethane-based compound, a thiazine-based compound, a xanthene-based compound, a spiropyrane-based compound and the like, and a triarylmethane-based compound and a xanthene-based compound are especially useful due to their high color developing density. A portion thereof may be exemplified by 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide (namely, crystal violet lactone), 3,3-bis(p-dimethylamino)phthalide, 3-(p-dimethylaminophenyl)-3-(1,3-dimethylindole-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindole-3-yl)phthalide, 3-(o-methyl-p-dimethylaminophenyl)-3-(2-methylindole-3-yl)phthalide, 4,4'-bis(dimethylamino)benzhydrinbenzyl ether, N-halophenylleucoauramine, N-2,4,5-trichlorophenylleucoauramine, rhodamine-B-anilinolactam, rhodamine(p-nitroanilino) lactam, rhodamine-B-(p-chloroanilino)lactam, 2-benzylamino-6-disthylaminofluoran, 2-anilino-6-diethilaminofluoran, 2-anilino-3-methyl-6-diethilaminofluoran, 2-anilino-3-methyl-6-cyclohexylmethylaminofluoran, 2-anilino-3-methyl-6-isoamylethylaminofluoran, 2-(o-chloroanilino)-6-diethylaminofluoran, 2-octylamino-6-diethylaminofluoran, 2-ethoxyethylamino-3-chloro-2-diethylaminofluoran, 2-anilino-3-chloro-6-diethylaminofluoran, benzoylleucomethylene blue, p-nitrobenzylleucomethylene blue, 3-methyl- spiro-dinaphthopyran, 3-ethyl- spiro-dinaphthopyran, 3,3'-dichloro-spiro-dinaphthopyran, 3-benzylspirodinaphthopyran, 3-propyl-spiro-dibenzopyran and the like.

[0029] Examples of the electron acceptive compound include a phenol derivative, a salicylic acid derivative, hydroxybenzoate, and the like. Bisphenols and hydroxybenzoates are particularly preferred.

[0030] A portion thereof may be exemplified by 2,4'-dihydroxydiphenylsulfone, 2,2'-dihydroxydiphenylsulfone, 2,2-bis (p-hydroxyphenyl)propane (namely, bisphenol A), 2,2-bis(p-hydroxyphenyl)pentane, 2,2-bis(p-hydroxyphenyl)ethane,

2,2-bis(p-hydroxyphenyl)butane, 2,2-bis(4'-hydroxy-3',5'-dichlorophenyl)propane, 1,1-(p-hydroxyphenyl)cyclohexane, 1,1-(p-hydroxyphenyl)propane, 1,1-(p-hydroxyphenyl)pentane, 1,1-(p-hydroxyphenyl)-2-ethylhexane, 3,5-di(α-methylbenzyl)salicylic acid and polyvalent metal salts thereof, 3,5-di(tert-butyl)salicylic acid and polyvalent metal salts thereof, 3-α,α-dimethylbenzylsalicylic acid and polyvalent metal salts thereof, butyl p-hydroxybenzoate, benzyl p-hydroxybenzoate, 2-ethylhexyl p-hydroxybenzoate, p-phenylphenol, p-cumylphenol, and the like.

[0031] The low-melting-point organic compounds are called sensitizers because color developing reactions start at lower temperatures with addition of these low-melting-point organic compounds. As the sensitizer, a known material can be used, for example, benzyl p-benzyloxybenzoate, α-naphthylbenzyl ether, β-naphthylbenzyl ether, phenyl β-naphtoate, phenyl α-hydroxy- β-naphtoate, β-naphtol-(p-chlorobenzyl)ether, 1,4-butane diol phenyl ether, 1,4-butane diol-p-methylphenyl ether, 1,4-butane diol-p-ethylphenyl ether, 1,4-butane diol-m-methylphenylether, 1-phenoxy-2-(p-tolyloxy)ethane, 1-phenoxy-2-(p-ethylphenoxy)ethane, 1-phenoxy-2-(p-chlorophenoxy)ethane, p-benzylbiphenyl, ethylene bisstearic acid amide and the like.

[0032] In the case of a heat-sensitive color developing layer comprising a diazonium salt compound and a coupler which develops color by reacting with the diazonium salt compound under heat, the reaction between the diazonium salt compound and the coupler takes place due to heating. A dye is thus formed and color develops. In this case, the color image can be fixed by light exposure after the above development. This is because the light exposure decomposes unreacted diazonium salt in the heat-sensitive color developing layer. Thus, a reheating processing will not result in color development in the light-fixed layer.

[0033] In case of the heat-sensitive recording layer comprising the diazonium salt compound and the coupler, further an organic or inorganic basic material is often added for the purpose of accelerating the reaction between the diazonium salt compound and the coupler under heat. These are used in conventional diazo copy papers and many of them are well known.

[0034] Diazonium salt compounds are compounds represented by the formula

$$Ar\text{-}N_2^+X^-$$

(in which Ar represents an aromatic ring, N_2^+ represents a diazonium group, and X^- represents an acid anion), and the maximum absorption wavelengths of these are controlled depending on types and positions of the substituents in the Ar portion.

[0035] Specific examples of the diazonium salt compound used in the present invention include 4-(N-(2-(2,4-di-tert-amylphenoxy)butyryl)piperazino)benzene diazonium, 4-dioctylaminobenzene diazonium, 4-(N-(2-ethylhexanoyl) piperazino)benzene diazonium, 4-dihexylamino-2-hexyloxybenzene diazonium, 4-N-ethyl-N-hexadecylamino-2-ethoxybenzodiazonium, 3-chloro-4-dioctylamino-2-octyloxybenzene diazonium, 2,5-dibutoxy-4-morpholinobenzene diazonium, 2,5-octoxy-4-morpholinobenzene diazonium, 2,5-dibutoxy-4-(N-(2-ethylhexanoyl)piperazino)benzene diazonium, 2,5-diethoxy-4-(N-(2-(2,4-di-tert-amylphenoxy)butyryl)piperazino)benzene diazonium, 2,5-dibutoxy-4-tolylthiobenzene diazonium, 3-(2-octyloxyethoxy)-4-morpholinobenzene diazonium and the like.

[0036] For the acid anion, salts of hexafluorophosphoric acid, salts of tetrafluoroboric acid, salts of 1,5-naphthalenesulfonic acid and the like can be useful.

[0037] Examples of the coupler which develops color by reacting under heat with above-described diazonium salt used in the present invention include resorcin, phloroglucin, sodium 2,3-dihydroxynaphthalene-6-sulfonate, 1-hydroxy-2-naphthoic acid morpholinopropylamide, 1,5-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,3-dihydroxy-6-sulfanylnaphthalene, 2-hydroxy-3-naphthoic acid anilide, 2-hydroxy-3-naphthoic acid ethanolamide, 2-hydroxy-3-naphthoic acid octylamide, 2-hydroxy-3-naphthoic acid-N-dodecyloxypropylamide, 2-hydroxy-3-naphthoic acid tetradecylamide, acetanilide, acetacetoanilide, benzoylacetanilide, 2-chloro-5-octylacetacetoanilide, 1-phenyl-3-methyl-5-pyrazolone, 1-(2'-octylphenyl)-3 methyl-5-pyrazolone, 1-(2',4',6'-trichlorophenyl)-3-benzamide-5-pyrazolone, 1-(2',4',6'-trichlorophenyl)-3-anilino-5-pyrazolone, 1-phenyl-3-phenylacetamide-5-pyrazolone and the like. These couplers can also be used in combination of two or more to obtain an intended hue in color development.

[0038] In addition to inorganic or organic compounds, examples of the basic material include compounds which cause decomposition and the like under heat to release an alkaline material. Representative examples thereof include nitrogen-containing compounds such as an organic ammonium salt, organic amine, amide, urea and thiourea and derivatives thereof, thiazoles, pyrroles, pyrimidines, piperazines, guanidines, indoles, imidazoles, imidazolines, triazoles, morpholines, piperidines, amidines, formazines, pyridines, and the like. Specific examples thereof include tricyclohexylamine, tribenzylamine, octadecylbenzylamine, stearylamine, allylurea, thiourea, methylthiourea, allylthiourea, ethylenethiourea, 2-benzylimidazole, 4-phenylimidazole, 2-phenyl-4-methylimidazole, 2-undecylimidazoline, 2,4,5-trifuryl-2-imidazoline, 1,2-diphenyl-4,4-dimethyl-2-imidazoline, 2-phenyl-2-imidazoline, 1,2,3-triphenylguanidine, 1,2-dicyclohexylguanidine, 1,2,3-tricyclohexylguanidine, guanidinetrichloro acetate, N,N'-dibenzylpiperazine, 4,4'-dithiomorpholine, morpholiniumtrichloroacetate, 2-aminobenzothiazole, 2-benzoylhydrazinobenzothiazole, and the like. These

can be used in combination of two or more.

[0039] A protective layer can be provided on these heat-sensitive color developing layers as required. In the present invention, it is particularly desirable to provide a protective layer whose main components are a water soluble polymer and inorganic or organic powder. The protective layer can comprise organic or inorganic powder, a binder, a surfactant, a thermally fusible material, and the like. Examples of the powder include inorganic powder such as kaolin, calcium carbonate, silica, zinc oxide, titanium oxide, aluminum hydroxide, zinc hydroxide, barium sulfate, clay, talc, surface-treated calcium and silica and the like, and organic powder such as urea-formalin resin, stylen/methacrylic acid copolymer, polystyrene, and the like.

[0040] As a binder in the protective layer, polyvinyl alcohol, carboxy modified polyvinyl alcohol, vinyl acetate- acrylic amide copolymer, silicon modified polyvinyl alcohol, starch, modified starch, methylcellulose, carboxymethylcellulose, hydroxymethylcellulose, gelatins, gum arabic, casein, styrene-maleic anhydride copolymer hydrolyzate, a polyacrylic amide derivative, polyvinyl pyrolidone, and latex such as styrene-butadiene gum latex, acrylonitrile-butadiene gum latex, methyl acrylate-butadiene gum latex, vinyl acetate emulsion, and the like can be used.

[0041] By cross-linking the binder components in the protective layer, storage stability of the heat-sensitive recording material can be further improved. Examples of the cross-linking agent include water soluble primary condensates such as N-methylolurea, N-methylolmelamine and urea-formalin, dialdehyde compounds such as glyoxal and glutaraldehyde, inorganic crosslinking agents such as boric acid, borax and colloidal silica, and polyamide epichlorohydrine. The protective layer may further comprise a known ultraviolet ray absorbing agent or a precursor thereof.

[0042] As the support in the present invention, a conventional known support can be used. Examples of the support include woodfree paper, neutral paper, acidic paper, regenerated paper, coated paper, polyolefine resin laminated paper, synthetic paper, polyester film, cellulose derivative film such as cellulose triacetate film and the like, polystyrene film, polyolefine film such as polypropylene film and polyethylene film, and the like.

EXAMPLES

[0043] Examples of the present invention are described in the following. All "parts" are by weight in the following examples unless indicated as otherwise.

Example 1

[Coating of the first and the second intermediate layers]

[0044]

calcined kaolin (Ansilex 90, oil absorption 78 ml/100 g)	40 parts
sodium hexametaphosphate	4 parts
water	56 parts

These were mixed and stirred by a homogenizer for three minutes to obtain Solution A.

10% polyvinyl alcohol aqueous solution	40 parts
48% SBR latex (SN-307 manufactured by Sumitomo Chemical Co., Ltd.)	10 parts
solution A	100 parts

These were mixed by being stirred to obtain a coating solution for the intermediate layers.

[0045] To provide the first intermediate layer, the coating solution for the intermediate layers was coated in a dry coating amount of 10 g/m^2 using a blade coating method onto a woodfree paper having a basic weight of 50 g/m^2, then was dried in an oven and subjected to a calender treatment. Oken type smoothness of the coated surface thereof was 800 seconds. (Measuring time of Oken type smoothness was 10 seconds.)

[0046] Further, to provide the second intermediate layer, the same coating solution for the intermediate layers was coated in a dry coating amount of 10 g/m^2 on the coated surface of the first intermediate layer by a free-fall-curtain method, then was dried in an oven and subjected to a calender treatment.

[0047] Density of the coating of the second intermediate layer was 0.67.

[0048] In order to enable the second intermediate layer to be coated by a free-fall-curtain method, the following surfactant was added to the coating solution for the intermediate layers:

coating solution for the intermediate layers	100 parts
30% sodium dodecylbenzene sulfate aqueous solution	1 part

[Coating of a heat-sensitive color developing layer]

[0049]

(Preparation of solution B)	
3-N-dibutylamino-6-methyl-7-anilinofluoran	10 parts
10% polyvinyl alcohol aqueous solution	10 parts
water	30 parts

These were mixed and milled by a ball mill to obtain a mean particle diameter of 0.6 μm, thus preparing solution B.

(Preparation of solution C)	
2,4'-dihydroxydiphenylsulfone	20 parts
10% polyvinyl alcohol aqueous solution	20 parts
water	50 parts

[0050] These were mixed and milled by a ball mill to obtain a mean particle diameter of 0.6 μm, thus preparing solution C.

(Preparation of solution D)	
calcium carbonate (Univer) 70 manufactured by Shiraishi Kogyo)	35 parts
sodium hexametaphosphate	0.5 parts
water	70 parts

These were mixed and milled by a ball mill to obtain a mean particle diameter of 1.8 μm, thus preparing solution D.

(Preparation of a coating solution for a heat-sensitive recording layer)

[0051] A coating solution for the heat-sensitive recording layer was obtained by mixing and stirring 10 parts of 30% zinc stearate dispersed solution into the mixture of solutions A, B and C after mixing and stirring them.

[0052] This coating solution for the heat-sensitive recording layer was coated on the intermediate-layer-side of the woodfree paper, previously coated with the first and the second intermediate layers, in dry coating amount of 5 g/m^2 by a hand-coating bar method, then was dried in an oven and subjected to a calender treatment. Thus, the heat-sensitive recording layer was coated.

[Coating of a protective layer]

[0053]

kaolin (Kaobright) manufactured by Shiraishi Kogyo)	10 parts
sodium hexametaphosphate	0.1 parts
water	20 parts

These were stirred and mixed for three minutes by a homogenizer to obtain solution E.

10% polyvinyl alcohol aqueous solution	100 parts
solution E	30 parts

These were mixed and stirred to obtain a coating solution for the protective layer.

This coating solution for the protective layer was coated on the previously obtained heat-sensitive recording layer in a dry coating amount of 2 g/m^2 by a hand-coating bar method, thus obtaining a heat-sensitive recording paper.

Comparative Example 1

[0054] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the first intermediate layer was coated by a free-fall-curtain method and the second intermediate layer was coated by a blade-coating method. Oken type smoothness of the first intermediate layer was 650 seconds, and density of the second intermediate layer was 1.05 at that time.

Comparative Example 2

[0055] A heat-sensitive recording paper was obtained in the same way as Example 1, except that both of the first and the second intermediate layers were coated by a blade-coating method. Oken type smoothness of the first intermediate layer was 800 seconds, and density of the second intermediate layer was 1.04 at that time.

Comparative Example 3

[0056] A heat-sensitive recording paper was obtained in the same way as Example 1, except that both of the first and the second intermediate layers were coated by a free-fall-curtain method. Oken type smoothness of the first intermediate layer was 650 seconds, and density of the second intermediate layer was 0.94 at that time.

Comparative Example 4

[0057] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the first intermediate layer was coated with a blade-coating method in a dry coating amount of 20 g/m^2, and the second intermediate layer was not provided. Oken type smoothness of the intermediate layer was 850 seconds, and density thereof was 1.03 at that time.

Comparative Example 5

[0058] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the first intermediate layer was coated with a free-fall-curtain method in a dry coating amount of 20 g/m^2, and the second intermediate layer was not provided. Oken type smoothness of the intermediate layer was 680 seconds, and density thereof was 0.68 at that time.

Example 2

[0059] A heat-sensitive recording paper was obtained in the same way as Example 1, except that a protective layer was not provided.

Example 3

[0060] A heat-sensitive recording paper was obtained in the same way as Example 1, except that kaolin (oil absorption, 37 ml/100 g) was used in the second intermediate layer instead of calcined kaolin. Oken type smoothness of the first intermediate layer was 800 seconds, and density of the second intermediate layer was 0.90.

Comparative Example 6

[0061] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the amount of 48% SBR latex (SN-307 manufactured by Sumitomo Chemical Co., Ltd.) in the second intermediate layer was increased to 60 parts. Density of the second intermediate layer was 1.03.

[Evaluation of the resulting heat-sensitive recording papers]

(1) Sensitivity (recording density)

[0062] Printing was performed on the resulting heat-sensitive recording papers using a Kyocera KJT head (resistance

value 2964 Ω) at a platen pressure of 1 kg/cm^2, head surface temperature of 30 °C, applied voltage of 23.8 V, pulse cycle of 10 ms, pulse duration of 1.5 ms and print density of 7.7 dot/mm. The recording density for each example was measured by a Macbeth reflection densitometer RD 918. Recorded image density of not less than 1.1 is preferable for practical use.

(2) Chemical resistance

[0063] Color tone of each example was observed when the resulting heat-sensitive recording papers were marked by a fluorescent marker (pink) manufactured by Mitsubishi Pencil Co., Ltd.

Pink was not darkened : ○
Pink changed to a darkened color : ×

(3) Plasticizer resistance

[0064] Printing (recording) was performed on the resulting heat-sensitive recording papers using a Kyocera KJT head (resistance value 2964 Ω) at a platen pressure of 1 kg/cm^2, head surface temperature of 30 °C, applied voltage of 23.8 V, pulse cycle of 10 ms, pulse duration of 1.5 ms and print density of 7.7 dot/mm. Then, the papers were put in contact with a vinyl chloride tube having a diameter of 76 mm (3 inches) with the printed surface thereof being outside and wrapped three times by a vinyl chloride wrap (Polymer Wrap 300 manufactured by Shin-Etsu Chemical Co., Ltd.), and left for 24 hours at room temperature. Then the residual image density was measured for each example by a Macbeth reflection densitometer RD 918. Residual density of not less than 1.0 is preferable for practical use.

(4) Bar code dot reproducibility

[0065] A bar code pattern produced by CODESOFT manufactured by Nippon Brady K. K. was printed using a Zebra printer 140 XiII at a set energy level of +20, then reproducibility of the bar code portion was observed and sensory evaluation was performed.

[0066] Each of the examples was evaluated with the following criteria with the focus upon blurring and thickening of the printed bar code pattern:

(blurring) ○ ··· not blurred
Δ ··· partially blurred
× ··· very blurred
(thickening) ○ ··· normal
Δ ··· lines thickened and spaces between lines narrowed
× ... lines thickened so that no spaces between lines

[0067] The results are shown in Table 1.

Table 1

	Recording Density	Chemical Resistance	Plasticizer Resistance	Blurring	Thickening
Example 1	1.20	○	1.14	○	○
Comp. Ex. 1	1.07	○	1.06	Δ	○
Comp. Ex. 2	1.06	○	1.04	Δ	○
Comp. Ex. 3	1.08	○	1.05	Δ	○
Comp. Ex. 4	1.07	○	1.06	Δ	○
Comp. Ex. 5	1.06	○	1.05	Δ	○
Example 2	1.35	×	0.15	○	Δ
Comp. Ex. 6	1.05	○	1.03	Δ	○
Example 3	1.12	○	1.10	○	○
*Blurring and thickening are those of bar codes.					

[0068] As shown in Table 1, in comparative examples which do not meet any one of requirements that Oken type smoothness of the first intermediate layer is not less than 700 seconds or that density of the second intermediate layer is not more than 1.0, recording density is low and bar code pattern is partially blurred, and therefore, there is a problem in dot reproducibility. However, in examples which meet both of the requirements, recording density is high and dot reproducibility is excellent. In example 2, which is the same as example 1 except that a protective layer is not provided thereto, recording density is high but chemical resistance and plasticizer resistance are low. Therefore, it is desirable to provide a protective layer to improve chemical resistance and plasticizer resistance as well as recording density.

[0069] As described above, in accordance with the present invention, a heat-sensitive recording material can be provided which has high recording density and is excellent in dot reproducibility.

Claims

1. A heat-sensitive recording material comprising a support having formed thereon at least one heat-sensitive color developing layer comprising an electron donative colorless dye and an electron acceptive compound, wherein
   a first intermediate layer and a second intermediate layer are sequentially laminated between the support and the heat-sensitive color developing layer,
   the first intermediate layer and the second intermediate layer comprise an inorganic pigment and a binder as main components,
   the first intermediate layer is formed by a blade-coating method and has an Oken type smoothness of not less than 700 seconds, and
   the second intermediate layer is formed by a free-fall-curtain method
   and has a density (coating amount in g/m^2 divided by coating thickness in μm) of not more than 1.0.

2. A heat-sensitive recording material according to claim 1, wherein a protective layer whose main components are a water soluble polymer and inorganic or organic powder is provided on the heat-sensitive color developing layer.

3. A heat-sensitive recording material according to claim 1 or claim 2, wherein the inorganic pigment in the second intermediate layer has an oil absorption of 70 ml/100 g or more by a measuring method defined by JIS-5101.

4. A heat-sensitive recording material according to any one of claims 1 to 3, wherein a mixing ratio of the inorganic pigment and the binder in the first intermediate layer and/or in the second intermediate layer is that the binder is 3-30 parts by weight for 100 parts by weight of the inorganic pigment.

5. A heat-sensitive recording material according to any one of claims 1 to 4, wherein the mixing ratio of the inorganic pigment and the binder in the first intermediate layer and/or in the second intermediate layer is that the binder is 5-20 parts by weight for 100 parts by weight of the inorganic pigment.

6. A heat-sensitive recording material according to any one of claims 1 to 5, wherein the Oken type smoothness of the first intermediate layer is not less than 800 seconds.

7. A heat-sensitive recording material according to any one of claims 1 to 6, wherein the Oken type smoothness of the first intermediate layer is not less than 900 seconds.

8. A heat-sensitive recording material according to any one of claims 1 to 7, wherein an amount coated of the second intermediate layer is 3-20 g/m^2 in solid weight.

9. A heat-sensitive recording material according to any one of claims 1 to 8, wherein the amount coated of the second intermediate layer is 4-10 g/m^2 in solid weight.

10. A heat-sensitive recording material according to any one of claims 1 to 9, wherein density of the second intermediate layer is not more than 0.85.

11. A heat-sensitive recording material according to any one of claims 1 to 10, wherein the density of the second intermediate layer is not more than 0.70.

12. A heat-sensitive recording material according to any one of claims 1 to 11. wherein the inorganic pigment in the first and second intermediate layers is at least one inorganic pigment selected from the group consisting of kaolin,

calcined kaolin, talc, agalmatolite, diatomaceous earth, calcium carbonate, aluminum hydroxide, magnesium hydroxide, magnesium carbonate, titanium oxide, and barium carbonate.

13. A heat-sensitive recording material according to any one of claims 1 to 12, wherein the binder contained in the first and second intermediate layers is at least one binder selected from the group consisting of a water soluble polymer selected from a starch derivative, polyvinyl alcohol and styrene-maleic anhydride, and a hydrophobic polymer selected from styrene-butadiene resin and acrylic resin.

14. A heat-sensitive recording material according to any one of claims 1 to 13, wherein a plurality of heat-sensitive color developing layers comprising a diazonium compound and a coupler are further provided on the heat-sensitive color developing layer comprising the electron donative colorless dye and the electron acceptive compound.

Patentansprüche

1. Wärmeempfindliches Aufzeichnungsmaterial, das einen Träger umfasst, der mindestens eine wärmeempfindliche Farbentwicklungsschicht, die einen elektronenabgebenden farblosen Farbstoff und eine elektronenaufnehmende Verbindung umfasst, darauf ausgebildet aufweist, worin
eine erste Zwischenschicht und eine zweite Zwischenschicht nacheinander zwischen dem Träger und der wärmeempfindlichen Farbentwicklungsschicht laminiert sind,
die erste Zwischenschicht und die zweite Zwischenschicht umfassen ein organisches Pigment und ein Bindemittel als Hauptkomponenten,
die erste Zwischenschicht wird erzeugt nach einem Klingenbeschichtungsverfahren und weist eine Oken-Glätte von nicht weniger als 700 Sekunden auf, und
die zweite Zwischenschicht wird erzeugt nach einem frei fallenden Vorhangverfahren und besitzt eine Dichte (Beschichtungsmenge in g/m^2 geteilt durch die Beschichtungsdicke in μm) von nicht mehr als 1,0.

2. Wärmeempfindliches Aufzeichnungsmaterial gemäss Anspruch 1, worin eine Schutzschicht, deren Hauptkomponenten ein wasserlösliches Polymer und ein anorganisches oder organisches Pulver sind, auf der wärmeempfindlichen Farbentwicklungsschicht bereitgestellt ist.

3. Wärmeempfindliches Aufzeichnungsmaterial gemäss Anspruch 1 oder 2, worin das organische Pigment in der zweiten Zwischenschicht eine Ölabsorption von 70 ml/100 g oder mehr nach einem Messverfahren, wie in JIS-5101 definiert, aufweist.

4. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 3, worin das Mischungsverhältnis des organischen Pigments und des Bindemittels in der ersten Zwischenschicht und/oder in der zweiten Zwischenschicht so ist, dass das Bindemittel 3-30 Gew.-Teile auf 100 Gew.-Teile anorganisches Pigment beträgt.

5. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 4, worin das Mischungsverhältnis des organischen Pigments und des Bindemittels in der ersten Zwischenschicht und/oder in der zweiten Zwischenschicht so ist, dass das Bindemittel 5-20 Gew.-Teile auf 100 Gew.-Teile anorganisches Pigment beträgt.

6. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 5, worin die Oken-Glätte der ersten Zwischenschicht nicht weniger als 800 Sekunden beträgt.

7. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 6, worin die Oken-Glätte der ersten Zwischenschicht nicht weniger als 900 Sekunden beträgt.

8. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 7, worin die Beschichtungsmenge der zweiten Zwischenschicht 3-20 g/m^2 Feststoffgewicht beträgt.

9. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 8, worin die Beschichtungsmenge der zweiten Zwischenschicht 4-10 g/m^2 Feststoffgewicht beträgt.

10. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 9, worin die Dichte

der zweiten Zwischenschicht nicht mehr als 0,85 beträgt.

11. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 10, worin die Dichte der zweiten Zwischenschicht nicht mehr als 0,70 beträgt.

12. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 11, worin das anorganische Pigment in der ersten und zweiten Zwischenschicht mindestens ein anorganisches Pigment ist, ausgewählt aus Kaolin, calciniertem Kaolin, Talk, Agalmatolit, Diatomeenerde, Calciumcarbonat, Aluminiumhydroxid, Magnesiumhydroxid, Magnesiumcarbonat, Titanoxid und Bariumcarbonat.

13. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 12, worin das Bindemittel, das in der ersten und zweiten Zwischenschicht enthalten ist, mindestens ein Bindemittel ist, das ausgewählt ist aus einem wasserlöslichen Polymer, ausgewählt aus einem Stärkederivat, Polyvinylalkohol und Styrol-Maleinsäureanhydrid, und einem hydrophoben Polymer, das ausgewählt ist aus Styrol-Butadien-Harz und Acrylharz.

14. Wärmeempfindliches Aufzeichnungsmaterial gemäss mindestens einem der Ansprüche 1 bis 13, worin ferner mehrere wärmeempfindliche Farbentwicklungsschichten, die eine Diazoniumverbindung und einen Kuppler umfassen, auf der wärmeempfindlichen Farbentwicklungsschicht, die den elektronenabgebenden farblosen Farbstoff und die elektronenaufnehmende Verbindung umfasst, bereitgestellt sind.

Revendications

1. Matériau d'enregistrement sensible à la chaleur comprenant un support sur lequel est formée au moins une couche révélateur de couleur sensible à la chaleur comprenant un colorant incolore donneur d'électrons et un composé accepteur d'électrons, dans lequel

une première couche intermédiaire et une seconde couche intermédiaire sont séquentiellement laminées entre le support et la couche révélateur de couleur sensible à la chaleur,

la première couche intermédiaire et la seconde couche intermédiaire comprennent un pigment inorganique et un liant en tant que les principaux composants,

la première couche intermédiaire est formée par un procédé de revêtement à la lame et a un lissé de type Oken n'étant pas inférieur à 700 secondes, et

la seconde couche intermédiaire est formée par un procédé au rideau par gravité et a une densité (quantité de revêtement en g/m^2 divisée par l'épaisseur du revêtement en μm) n'étant pas supérieure à 1,0.

2. Matériau d'enregistrement sensible à la chaleur selon la revendication 1, dans lequel une couche de protection dont les principaux composants sont un polymère hydrosoluble et une poudre inorganique ou organique est prévue sur la couche révélateur de couleur sensible à la chaleur.

3. Matériau d'enregistrement sensible à la chaleur selon la revendication 1 ou la revendication 2, dans lequel le pigment inorganique dans la seconde couche intermédiaire a une absorption d'huile de 70 mL/100 g ou plus par un procédé de mesure défini par JIS-5101.

4. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 3, dans lequel un rapport de mélange du pigment inorganique et du liant dans la première couche intermédiaire et/ou dans la seconde couche intermédiaire est tel que le liant représente de 3 à 30 parties en poids pour 100 parties en poids du pigment inorganique.

5. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 4, dans lequel le rapport de mélange du pigment inorganique et du liant dans la première couche intermédiaire et/ou dans la seconde couche intermédiaire est tel que le liant représente de 5 à 20 parties en poids pour 100 parties en poids du pigment inorganique.

6. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 5, dans lequel le lissé de type Oken de la première couche intermédiaire n'est pas inférieur à 800 secondes.

7. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 6, dans lequel le

lissé de type Oken de la première couche intermédiaire n'est pas inférieur à 900 secondes.

8. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 7, dans lequel une quantité enduite de la seconde couche intermédiaire est de 3 à 20 g/m^2 en poids solide.

9. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 8, dans lequel une quantité enduite de la seconde couche intermédiaire est de 4 à 10 g/m^2 en poids solide.

10. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 9, dans lequel la densité de la seconde couche intermédiaire n'est pas supérieure à 0,85.

11. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 10, dans lequel la densité de la seconde couche intermédiaire n'est pas supérieure à 0,70.

12. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 11, dans lequel le pigment inorganique dans les première et seconde couches intermédiaires est au moins un pigment inorganique choisi dans le groupe constitué par le kaolin, le kaolin calciné, le talc, l'agalmatolite, la terre de diatomées, le carbonate de calcium, l'hydroxyde d'aluminium, l'hydroxyde de magnésium, le carbonate de magnésium, l'oxyde de titane, et le carbonate de baryum.

13. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 12, dans lequel le liant contenu dans les première et seconde couches intermédiaires est au moins un liant choisi dans le groupe constitué par un polymère hydrosoluble choisi parmi un dérivé d'amidon, un alcool polyvinylique et un anhydride styrène-maléique, et un polymère hydrophobe choisi parmi une résine styrène-butadiène et une résine acrylique.

14. Matériau d'enregistrement sensible à la chaleur selon l'une quelconque des revendications 1 à 13, dans lequel une pluralité de couches révélateurs de couleur sensibles à la chaleur comprenant un composé diazonium et un copulant sont en outre prévues sur la couche révélateur de couleur sensible à la chaleur comprenant le colorant incolore donneur d'électrons et le composé accepteur d'électrons.

FIG. 1

