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(54) Heat-sensitive recording material

(57) A heat-sensitive recording material comprises a support having formed thereon one or more heat-sensitive recording layers, wherein the one or more heat-sensitive recording layers include an electron donative colorless dye, an electron acceptive compound and an ultraviolet ray absorbing agent, and a distribution of the ultraviolet ray absorbing agent is such that an amount of the agent increases in a film thickness direction away from the support.

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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 an improvement of a heat-sensitive recording material comprising a support having formed thereon at least one of heat-sensitive recording layer comprising an electron donative colorless dye, an electron acceptive compound and an ultraviolet ray absorbing compound.

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. However, with respect to heat-sensitive materials of this kind using heat-sensitive recording layers using electron donating dye precursors and electron acceptive compounds, there are problems in light fastness of image portions and background portions thereof, i.e., when the heat-sensitive materials are exposed to fluorescent light, sunlight or the like for a long period of time, lowered density of image portions and discoloring of background portions tend to occur.

[0004] To prevent these problems, a method for adding an ultraviolet ray absorbing agent into a heat-sensitive recording layer, a method for adding an ultraviolet ray absorbing agent into a protective layer provided on a heat-sensitive recording layer and the like have been proposed. However, when an ultraviolet ray absorbing agent is simply added into a heat-sensitive recording layer, fogging tends to occur, and when an ultraviolet ray absorbing agent is added into a protective layer, sticking or trash deposition on a thermal head tends to occur when printing is carried out with the thermal head.

SUMMARY OF THE INVENTION

[0005] An object of the present invention is to provide a heat-sensitive recording material which overcomes the above-mentioned problems and has improved light fastness of background portions thereof without decreasing color developing density thereof.

[0006] Accordingly, it is an object of the present invention to provide a heat-sensitive recording material comprising a support having formed thereon one or more heat-sensitive recording layers, wherein at least one of the one or more heat-sensitive recording layers comprise an electron donative colorless dye, an electron acceptive compound and an ultraviolet ray absorbing agent, and a distribution of the ultraviolet ray absorbing agent is such that an amount of the ultraviolet ray absorbing agent increases in a film thickness direction away from the support.

DETAILED DESCRIPTION OF THE INVENTION

[0007] A preferred embodiment of the present invention is explained in the following.

[0008] A heat-sensitive recording material of the present invention comprises a support having formed thereon one or more heat-sensitive recording layers comprising an electron donative colorless dye, an electron acceptive compound and an ultraviolet ray absorbing material. Distribution of the ultraviolet ray absorbing agent in the heat-sensitive recording layer or layers in a direction of the film thickness of the heat-sensitive recording layer or layers is such that the amount of the agent increases in a direction away from the support.

[0009] However, the form of the above distribution in the direction of the film thickness of the heat-sensitive recording layer or layers may be such that the amount of the ultraviolet ray absorbing agent increases sequentially in a direction away from the support, or the ultraviolet ray absorbing agent may be contained only in the heat-sensitive recording layer, of a plurality of laminated heat-sensitive recording layers, which heat-sensitive layer is furthest from the support.

[0010] For example, such forms of distribution are possible in which a plurality of heat-sensitive recording layers are formed on the support and, of these heat-sensitive recording layers, the layer furthest from the support contains the highest amount of the ultraviolet ray absorbing agent and amounts of the agent contained in the layers sequentially decrease in a film thickness direction toward the support, or in which a plurality of heat-sensitive recording layers are formed on the support and the ultraviolet ray absorbing agent is contained only in the layer among these layers furthest from the support and the remaining layers do not contain the ultraviolet ray absorbing agent.

[0011] In a case of forming a plurality of heat-sensitive recording layers, a heat-sensitive recording material comprising a first heat-sensitive recording layer and a second heat-sensitive recording layer laminated on the first layer is desirable for practical use. In this case, in view of minimizing the influence of light on the heat-sensitive recording layer, it is desirable to have the second heat-sensitive recording layer contain a desired amount of the ultraviolet ray absorbing agent. In a case of having only the second heat-sensitive recording layer contain the ultraviolet ray absorbing agent, including a higher amount of the ultraviolet ray absorbing agent is preferred in view of preventing fogging of the heat-sensitive recording material. However, in view of coating stability or the like of a heat-sensitive recording layer coating solution, the amount of the ultraviolet ray absorbing agent contained in the second heat-sensitive recording layer is desirably not more than 50% by weight based on the total weight of the solid components. Therefore, considering coating stability of the heat-sensitive recording layer coating solution, fogging prevention of the heat-sensitive recording material and the like, the amount of the ultraviolet ray absorbing agent contained in the second heat-sensitive recording layer is desirably, for example, 20-50% by weight based on the total weight of the solid components, and the amount of the agent contained in the first heat-sensitive recording layer is desirably 0-30% by weight based on the total weight of the solid components.

[0012] That is, when the amount of the ultraviolet ray absorbing agent contained in the second heat-sensitive recording layer is less than 20% by weight, the amount of the agent added to the second heat-sensitive recording layer is small and the amount of the ultraviolet ray absorbing agent contained in the first heat-sensitive recording layer is relatively large, so that a blocking effect of the ultraviolet ray absorbing agent contained in the second layer is lowered and undesirable fogging tends to occur on the heat-sensitive recording material. When the amount of the ultraviolet ray absorbing agent contained in the second heat-sensitive recording layer is increased to over 50% by weight based on the total weight of the solid components, the amount of the agent added to the second heat-sensitive recording layer is large and the amount of the agent contained in the first heat-sensitive recording layer can be decreased; however, coating stability of the second heat-sensitive recording layer coating solution tends to be lowered.

[0013] Any of known ultraviolet ray absorbing agents such as a benzophenone-based ultraviolet ray absorbing agent, a benzotriazole-based ultraviolet ray absorbing agent, a salicylic acid-based ultraviolet ray absorbing agent, a cyanoacrylate -based ultraviolet ray absorbing agent, an oxalic acid anilide-based ultraviolet ray absorbing agent or the like can be used, and the benzotriazole-based compound is particularly suitable. A conventional known benzotriazole-based compound can be used. Benzotriazole-based compounds include, for example, 2-(2'-hydroxy-5'-methylphenyl) benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl) benzotriazole, 2-(2'-hydroxy-5'-t-octylphenyl) benzotriazole, 2-(2'-hydroxy-3', 5'-di-t-aminophenyl) benzotriazole, 2-(2'-hydroxy-3', 5-di-t-butylphenyl) benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3', 5'-di-t-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3', 5-diphenylphenyl) benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl) benzotriazole and the like.

[0014] When the ultraviolet ray absorbing agent is contained in the heat-sensitive recording layer, water soluble resin can be used as a binder for the heat-sensitive recording layer. Polyvinyl alcohol or modified polyvinyl alcohol is preferable as the water soluble resin. It is preferable that the ultraviolet ray absorbing agent and the polyvinyl alcohol or the modified polyvinyl alcohol are contained in the second heat-sensitive recording layer. Particularly, when the benzotriazole-based compound is contained in the heat-sensitive recording layer, the polyvinyl alcohol or the modified polyvinyl alcohol is desirable as the binder to form the heat-sensitive recording layer in view of coating stability of the heat-sensitive recording layer coating solution. As the polyvinyl alcohol, polyvinyl alcohol having a degree of polymerization from 700 to 3000 is desirable.

[0015] When the polymerization degree of the polyvinyl alcohol is less than 700, chemical resistance, plasticizer resistance and the like of the heat-sensitive recording layer tend to decrease. When the polymerization degree is more than 3000, much water is required to adjust viscosity of the coating solution appropriately, therefore, the brightness degree of the heat-sensitive recording material tends to lower due to the burden of drying. Examples of particularly suitable modified polyvinyl alcohols in the present invention include carboxy modified polyvinyl alcohol, silicon modified polyvinyl alcohol, acetoacetyl group modified polyvinyl alcohol, ethylene modified polyvinyl alcohol, polyvinyl alcohol-polyacrylic acid block polymer and the like.

[0016] The percentage content of the polyvinyl alcohol or the modified polyvinyl alcohol in the second heat-sensitive recording layer is desirably not less than 40% by weight based on the total weight of the solid components. If the percentage content of the polyvinyl alcohol or the modified polyvinyl alcohol in the second heat-sensitive recording layer is less than 40% by weight, coating strength of the second heat-sensitive recording layer is decreased and chemical resistance, plasticizer resistance and water resistance (waterproof) of the heat-sensitive recording material are impaired; therefore it is not preferable.

[0017] In view of improving water resistance of the heat-sensitive recording material and pot life of the heat-sensitive recording layer coating solution, it is desirable that the first heat-sensitive recording layer contains a water-proofing agent which reacts with the polyvinyl alcohol contained in the second heat-sensitive recording layer.

[0018] The heat-sensitive recording layer of the present invention comprises an electron donative colorless dye and an electron acceptive compound as heat-sensitive color developing components. 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.

[0019] 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, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-7-octylaminofluoran, 3-diethylamino-7-phenylfluoran, 3-diethylamino-7-(3,4-dichlor)anilinofluoran, 3-diethylamino-7-(2-chloroanilino)fluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-piperidino-6-methyl-7-anilinofluoran, 3-ethyl-tolylamino-6-methyl-7-anilinofluoran, 3-ethyltolylamino-6-methyl-7-phenylfluoran, 3-diethylamino-7-(4-nitoroanilino)fluoran, 3-N-dibutylamino-6-methyl-7-fluoran, 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.

[0020] Examples of the electron acceptive compound include a phenol derivative, a salicylic acid derivative, hydroxybenzoate, and the like. Bisphenols and hydroxybenzoates are particularly preferred.

[0021] 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. 2,4'-dihydroxydiphenylsulfone is particularly suitable.

[0022] 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 low-melting-point organic compound containing an appropriate amount of an aromatic group and a polar group in the molecule is preferred, and examples thereof include 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 and the like.

[0023] An antioxidant, a metallic soap or a wax and the like may be added into the heat-sensitive recording layers as required. Examples of the antioxidant include a hindered amine light stabilizer, a hindered phenol-based antioxidant, an aniline-based antioxidant, a quinoline-based antioxidant and the like, and a hindered amine light stabilizer such as 1,1,3-tris-(2-methyl-4-hydroxy-5-t-butylphenyl)butane is especially suitable. Examples of the metallic soap include a polyvalent metal salt of higher fatty acid such as zinc stearate, aluminum stearate, and calcium stearate, and the like. Examples of the wax include paraffin wax, carnauba wax, microcrystalline wax, polyethylene bisstearoamide, higher fatty acid ester, and the like.

[0024] The first and the second heat-sensitive recording layers can be applied simultaneously using methods such as those described in specifications of US Patent Nos. 2,761,791, 3,508,947, 2,941,898, and 3,526,528, in Yuji HARASAKI, "Coating Technology", page 253 (Asakura Shoten, 1973) and the like.

[0025] In a method for forming heat-sensitive recording layers, for example, in forming of the first and the second heat-sensitive recording layers, the coating amount of the first heat-sensitive recording layer is 1-10 g/m^2, preferably 2-7 g/m^2 in dry weight, and the coating amount of the second heat-sensitive recording layer is 0.5-7 g/m^2, preferably 1-5 g/m^2 in dry weight. After the heat-sensitive recording layer is coated with the coating solution by any coating method, the layer may be calendered to improve smoothness of the coated surface as required.

[0026] A protective layer may be provided on the heat-sensitive recording layer of the present invention as required. 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 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; however, an inorganic pigment is particularly preferable.

[0027] 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.

[0028] A waterproofing agent can be added thereto to further improve storage stability of the heat-sensitive recording material by cross-linking the binder components in the protective layer. Examples of the water-resistence 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.

[0029] In these waterproofing agents, for example, colloidal silica, glyoxal or the like may be added into the first heat-sensitive recording layer and the polyvinyl alcohol or the like in the second heat-sensitive recording layer may be cross-linked, to form a film with high water resistance at the interface between the first and the second heat-sensitive recording layers.

[0030] 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

[0031] 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

[Preparation of a coating solution for the first heat-sensitive recording layer]

(Preparation of solution A)

[0032]

3-N-dibutylamino-6-methyl-7-anilinofluoran	10 parts
10% polyvinyl alcohol aqueous solution	10 parts
water	30 parts

[0033] These were mixed and milled by a ball mill to obtain a median particle diameter of 0.6 µm, thus preparing Solution A. The median particle diameter was measured using a Microtrac FRA.

(Preparation of solution B)

[0034]

2,4-dihydroxybenzilsulfone	20 parts
1,1,3-tris-(2-methyl-4-hydroxy-5-t-butylphenyl)butane	5 parts
ethylene bisstearic acid amide	10 parts
10% polyvinyl alcohol aqueous solution	35 parts
water	45 parts

[0035] These were mixed and milled by a ball mill to have a median particle diameter of 0.6 µm, thus preparing Solution B.

(Preparation of solution C)

[0036]

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

[0037] These were mixed and milled by a ball mill to obtain a median particle diameter of 1.8 µm, thus preparing Solution C. The coating solution for the first 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.

[Preparation of a coating solution for the second heat-sensitive recording layer]

[0038]

ultraviolet ray absorbing agent 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole, Tinuvin 326 manufactured by Ciba-Geigy Co., Ltd.	10 parts
10% polyvinyl alcohol aqueous solution	10 parts
water	30 parts

[0039] These were mixed and milled by a ball mill to obtain a median particle diameter of 0.6 µm, thus preparing Solution D.

solution A	10 parts
solution B	20 parts
solution C	10 parts
10% polyvinyl alcohol (PVA 117 manufactured by Kuraray Co., Ltd.) aqueous solution	200 parts

(continued)

water	50 parts

[0040] These were mixed and stirred to obtain a coating solution for the second heat-sensitive recording layer.

[Preparation of a coating solution for the protective layer]

[0041]

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

[0042] These were mixed for three minutes by a homogenizer to obtain Solution E.

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

[0043] These were mixed and stirred to obtain a coating solution for the protective layer.

[Preparation of heat-sensitive recording papers]

[0044] The obtained coating solution for the first heat-sensitive recording layer was coated onto a woodfree paper having a basic weight of 50 g/m^2 in a dry coating-amount of 5 g/m^2 by a hand-coating bar, and then was dried in an oven and subjected to a calender treatment. Thus, the first heat-sensitive recording layer was provided with coating. The obtained coating solution for the second heat-sensitive recording layer was coated onto the first heat-sensitive recording layer in a dry coating amount of 3 g/m^2 by a hand-coating bar, and then was dried in an oven and subjected to a calender treatment. Thus, the second heat-sensitive recording layer was provided by coating. The obtained coating solution for the protective layer was coated onto the second heat-sensitive recording layer in a dry coating amount of 2 g/m^2 by a hand-coating bar, and then was dried in an oven and subjected to a calender treatment. Thus, a heat-sensitive recording paper was obtained.

Example 2

[0045] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the polyvinyl alcohol (PVA 117, having polymerization degree of 1700) in the solution D was substituted to silicon modified polyvinyl alcohol (R-1130 manufactured by Kuraray Co., Ltd., polymerization degree 1700).

Example 3

[0046] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the amount of the 10% polyvinyl alcohol aqueous solution used in the coating solution for the second heat-sensitive recording layer was reduced to 100 parts.

Example 4

[0047] A heat-sensitive recording paper was obtained in the same way as Example 2, except that 10 parts of colloidal silica (Snowtex O manufactured by Nissan Chemical Kogyo Co., Ltd.) was added to the coating solution of the first heat-sensitive recording layer.

Example 5

[0048] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the polyvinyl alcohol used in the coating solution for the second heat-sensitive recording layer was substituted with PVA 105 (manufactured by Kuraray Co., Ltd., having a polymerization degree of 550).

Example 6

[0049] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the polyvinyl alcohol used in the coating solution for the second heat-sensitive recording layer was substituted with PVA 135 H (manufactured by Kuraray Co., Ltd., having a polymerization degree of 3500).

Comparative Example 1

[0050] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the solution D was not added to the coating solution for the second heat-sensitive recording layer.

Comparative Example 2

[0051] A heat-sensitive recording paper was obtained in the same way as Example 1, except that the mixture of the coating solutions for the first and the second heat-sensitive recording layers were coated on a woodfree paper in a dry coating amount of 8 g/m^2 by a hand-coating bar, and then dried in an oven.

Example 7

[0052] A heat-sensitive recording paper was obtained in the same way as Example 4, except that colloidal silica was added to the second heat-sensitive recording layer, not to the first heat-sensitive recording layer.

[Evaluation of the resulting heat-sensitive recording papers]

(1) Sensitivity (recording density)

[0053] 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 width 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. Recording density of not less than 1.1 is preferable for practical use.

(2) Brightness

[0054] Brightness of 10-sheet-ply of each of the resulting heat-sensitive recording papers was measured by a Hunter brightness meter (manufactured by Kumagai Riki-Kogyo) using a blue filter. Brightness of not less than 80% is preferable for practical use.

(3) Chemical resistance

[0055] 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 was slightly darkened : △
Pink changed to a darkened color : X

(4) Plasticizer resistance

[0056] 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 width 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 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.

(5) Light fastness of background portions

[0057] A light fastness test was performed on the resulting heat-sensitive recording papers for five hours using Weather meter (Ci65A manufactured by Toyo Seiki), and the density of background portions of each example was measured by a Macbeth reflection densitometer RD 918. Background density of not more than 0.10 is preferable for practical use.

(6) Water resistance

[0058] 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 width of 1.5 ms and print density of 7.7 dot/mm. Then, the papers were immersed in tap water of 20 °C for 24 hours and air dried. Then the residual image density was measured for each example by a Macbeth reflection densitometer RD 918. Density of not less than 0.8 is preferable.

[0059] The results of the evaluation are shown in Table 1.

Table 1

	Recording Density	Brightness	Chemical Resistance	Plasticizer Resistance	Light Fastness	Water Resistance	Notes
Example 1	1.25	81	○	1.15	0.08	0.95	
Example 2	1.24	80	○	1.19	0.08	1.05	R1130
Example 3	1.28	82	△	1.01	0.08	0.85	PVA ↓
Example 4	1.22	81	○	1.15	0.08	1.13	colloidal
Example 5	1.29	81	X	0.85	0.08	0.85	PVA105
Example 6	1.08	78	○	1.05	0.08	0.95	PVA135
Comp. Ex. 1	1.29	82	○	1.18	0.15	1.10	no UV
Comp. Ex. 2	1.07	80	X	0.65	0.11	0.75	mixture
Example 7	1.25	82	○	1.15	0.08	1.17	colloidal

[0060] As shown in Table 1, Examples 1-7, having an ultraviolet ray absorbing agent added into the second heat-sensitive recording layer thereof with no ultraviolet ray absorbing agent added into the first heat-sensitive recording layer thereof, have shown a light fastness of 0.08, which is a preferable value for practical use, and a recording density of almost the same value with those of the Comparative Examples 1 and 2.

[0061] However, Example 5, the polymerization degree of the polyvinyl alcohol used in the second heat-sensitive recording layer thereof being 550, had particularly low chemical resistance. Example 6, the polymerization degree of the polyvinyl alcohol used in the second heat-sensitive recording layer thereof being 3500, had low brightness. In light of these points, the polymerization degree of the polyvinyl alcohol used in the second heat-sensitive recording layer is preferably between about 700-3000.

[0062] As described above, according to the heat-sensitive recording material of the present invention, light fastness of background portions of a heat-sensitive recording paper can be improved without lowering color developing density thereof.

Claims

1. A heat-sensitive recording material comprising a support having formed thereon one or more heat-sensitive recording layers, wherein

at least one of the one or more heat-sensitive recording layers comprise an electron donative colorless dye, an electron acceptive compound and an ultraviolet ray absorbing agent, and

a distribution of the ultraviolet ray absorbing agent is such that an amount of the ultraviolet ray absorbing agent increases in a film thickness direction away from the support.

2. A heat-sensitive recording material according to claim 1, further comprising a protective layer on the one or more heat-sensitive recording layers.

3. A heat-sensitive recording material according to claim 1 or claim 2, wherein the one or more heat-sensitive recording layers are a plurality of laminated heat-sensitive recording layers, and, of these layers, only the heat-sensitive recording layer furthest from the support contains the ultraviolet ray absorbing agent.

4. A heat-sensitive recording material according to claim 1 or claim 2, wherein the one or more heat-sensitive recording layers are a plurality of laminated heat-sensitive recording layers, and, of these layers, the heat-sensitive recording layer furthest from the support contains a highest amount of ultraviolet ray absorbing agent and the amounts of the ultraviolet ray absorbing agent contained in the layers sequentially decrease in a film thickness direction toward the support.

5. A heat-sensitive recording material according to any one of claims 1 to 4, wherein the one or more heat-sensitive recording layers are a first heat-sensitive recording layer and a second heat-sensitive recording layer laminated on the first heat-sensitive recording layer, and the second heat-sensitive recording layer comprises the ultraviolet ray absorbing agent and a polyvinyl alcohol or a modified polyvinyl alcohol.

6. A heat-sensitive recording material according to claim 5, wherein the polyvinyl alcohol is contained in an amount that is 40% or more by weight based on the total weight of the solid components of the second heat-sensitive recording layer.

7. A heat-sensitive recording material according to claim 5 or claim 6, wherein the first heat-sensitive recording layer contains a water-proofing agent which reacts with the polyvinyl alcohol contained in the second heat-sensitive recording layer.

8. A heat-sensitive recording material according to any one of claims 5 to 7, wherein an amount of the ultraviolet ray absorbing agent contained in the second heat-sensitive recording layer is 50% by weight or less based on the total weight of the solid components.

9. A heat-sensitive recording material according to any one of claims 5 to 8, wherein an amount of the ultraviolet ray absorbing agent contained in the second heat-sensitive recording layer is of 20-50% by weight based on the total weight of the solid components.

10. A heat-sensitive recording material according to any one of claims 5 to 9, wherein the first heat-sensitive recording layer contains the ultraviolet ray absorbing agent in an amount of from 0 to 30% by weight based on the total weight of the solid components.

11. A heat-sensitive recording material according to any one of claims 1 to 10, wherein the ultraviolet ray absorbing agent is a benzotriazole-based ultraviolet ray absorbing agent.

12. A heat-sensitive recording material according to any one of claims 5 to 11, wherein the polyvinyl alcohol has a polymerization degree of from 700 to 3000.

13. A heat-sensitive recording material according to any one of claims 1 to 12, wherein at least one of the one or more heat-sensitive recording layers further comprise at least one selected from an antioxidant, a metallic soap and a wax.

14. A heat-sensitive recording material according to any one of claims 5 to 13, wherein a coating amount of the first heat-sensitive recording layer is 1-10 g/m^2 in dry weight and a coating amount of the second heat-sensitive recording layer is 0.5-7 g/m^2 in dry weight.

15. A heat-sensitive recording material according to any one of claims 5 to 14, wherein a coating amount of the first heat-sensitive recording layer is 2-7 g/m^2 in dry weight and a coating amount of the second heat-sensitive recording layer is 1-5 g/m^2 in dry weight.

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 7836

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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