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(54) **HEAT-SENSITIVE RECORDING BODY**

(57) A thermosensitive recording medium, comprising: a thermosensitive recording layer containing a colorless or pale colored electron donating leuco dye and an electron accepting color developing agent on a substrate,

and a back-coating layer on the opposite side of the thermosensitive recording layer of the substrate, wherein the back-coating layer contains an ethylene-vinyl alcohol copolymer and an ethylene-acrylic copolymer.

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Description

[Field of the Invention]

- 5 **[0001]** The present invention relates to a thermosensitive recording medium having water vapor barrier property in its back side.

[Background of the Invention]

- 10 **[0002]** Thermosensitive recording media are ordinarily prepared by applying a coating solution containing an electron donating (hereinafter also referred to as "leuco dye") and an electron accepting color developing agent (hereinafter also referred to as "color developing agent") onto a substrate such as paper, synthetic paper, film, plastic and the like to form a thermosensitive recording layer. Thermosensitive recording medium develops color through an instantaneous chemical reaction when heated by a thermal head, hot stamp, hot pen, laser light or the like to yield a recorded image. Such
15 thermosensitive recording media are used extensively in recording media such as facsimile devices, computer terminal printers, automatic ticket dispensers, recorders for meters, receipts at super markets and convenience stores and the like.
[0003] To obtain good water resistance, a thermosensitive recording material having a back-coating layer containing an adhesive such as polyvinyl alcohol is known (Patent Document 1, etc.). It is also known that a paper substrate containing an ethylene copolymerized polyvinyl alcohol or an ethylene-acrylic copolymer has water vapor barrier property (Patent
20 Document 2-4, etc.).

[Prior Art Document]

Patent Document

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[0004]

Patent Document 1: Japanese Patent Application Laid-Open (kokai) No. 2003-175671

Patent Document 2: Japanese Patent Application Laid-Open (kokai) No. 2013-169988

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Patent Document 3: Japanese Patent Application Laid-Open (kokai) No. 2014-173201

Patent Document 4: Japanese Patent Application Laid-Open (kokai) No. 2020-190063

[Summary of the Invention]

- 35 [Problems to be solved by the Invention]

- [0005]** A printer for medical use or so requires high sensitivity and prints with high energy. This causes the thermal head to reach high temperature, and if printing continues at high temperature for a long period of time, the moisture in the thermosensitive recording medium vaporizes, causing water droplets to form on a back side which is not in contact with the
40 thermal head, resulting in equipment failure.

[0006] Therefore, the present invention provides a thermosensitive recording medium having water vapor barrier property against the moisture in the thermosensitive recording medium.

[Means For Solving the Problem]

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[0007] As a result of intensive studies, the present inventors have found that by having a thermosensitive recording layer on a substrate of a thermosensitive recording medium, and having a back-coating layer on the opposite side of the thermosensitive recording layer of the substrate, further containing an ethylene-vinyl alcohol copolymer and an ethylene-acrylic copolymer in the back-coating layer, above problems can be solved, and then completed the present invention.

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[0008] The present invention provides a thermosensitive recording medium, comprising a thermosensitive recording layer containing a colorless or pale colored electron donating leuco dye and an electron accepting color developing agent on a substrate, and a back-coating layer on the opposite side of the thermosensitive recording layer of the substrate, wherein the back-coating layer contains an ethylene-vinyl alcohol copolymer and an ethylene-acrylic copolymer.

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[Effect of the Invention]

[0009] According to the present invention, there can be obtained a thermosensitive recording medium in which excellent water vapor barrier property on a back side (that is, the opposite side of the thermosensitive recording layer of the

substrate) can be obtained, and almost no water vapor is generated from the back side even when printing for a long time.

[Modes For Carrying out the Invention]

- 5 **[0010]** A thermosensitive recording medium of the present invention is a thermosensitive recording medium, comprising a thermosensitive recording layer containing a leuco dye and a color developing agent on a substrate, and a back-coating layer on the opposite side of the thermosensitive recording layer of the substrate.
- [0011]** The back-coating layer of the present invention contains an ethylene-vinyl alcohol copolymer and an ethylene-acrylic copolymer.
- 10 **[0012]** The ethylene-vinyl alcohol copolymer used in the present invention is a polymer having an ethylene unit and a vinyl alcohol unit.
- [0013]** The ethylene-vinyl alcohol copolymer is usually obtained by saponifying an ethylene-vinyl ester copolymer obtained by polymerizing ethylene and a vinyl ester.
- [0014]** From the viewpoint of using a water-based coating material, an ethylene content of 3 to 20 mol% is preferable. To
- 15 **[0015]** impart barrier property, a saponification degree of 80 to 100 mol% is preferable. If the saponification degree is less than 80 mol%, sufficient barrier property and moisture resistance can not be obtained.
- [0015]** The ethylene-acrylic copolymer used in the present invention is a copolymer obtained by emulsion polymerization of ethylene and an acrylic monomer. As the acrylic monomer, acrylic acid and methacrylic acid are preferred, and acrylic acid is more preferred.
- 20 **[0016]** The ethylene-acrylic copolymer is preferably one or more of ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, ethylene-methyl acrylate copolymer, ethylene-methyl methacrylate copolymer, ethylene-ethyl acrylate copolymer, ethylene-ethyl methacrylate copolymer, ethylene-butyl acrylate copolymer, and ethylene-butyl methacrylate copolymer. The copolymer may contain a small amount of a monomer consisting of other compound which is copolymerizable with ethylene and acrylic monomer.
- 25 **[0017]** Among these, ethylene-acrylic acid copolymer and ethylene-methacrylic acid copolymer are more preferable, and ethylene-acrylic acid copolymer is even more preferable.
- [0018]** As a specific example of the ethylene-acrylic copolymer, for example, an aqueous dispersion of an ethylene-acrylic acid copolymer ammonium salt is available as ZAIKTHENE (registered trademark) AC (copolymerization ratio of acrylic acid: 20%, manufactured by Sumitomo Seika Chemicals Co., Ltd.).
- 30 **[0019]** In addition, the back-coating layer of the present invention may contain water-soluble polymer, water-dispersed resin, pigment, etc., to the extent that the water vapor barrier property is not affected.
- [0020]** Examples of the water-soluble polymer include polyvinyl alcohol other than ethylene-vinyl alcohol copolymer, such as fully saponified polyvinyl alcohol and partially saponified polyvinyl alcohol; proteins such as casein, soy protein, and synthetic protein; starches such as oxidized starch, cationic starch, urea phosphate esterified starch, and hydroxyethyl etherified starch; cellulose derivatives such as carboxymethyl cellulose, hydroxymethyl cellulose, and hydroxyethyl cellulose; polyvinylpyrrolidone; and sodium alginate.
- 35 **[0021]** Examples of the water-dispersed resin include natural rubber, diene rubber, non-diene rubber, and thermoplastic elastomer.
- [0022]** Any pigment that can be used in the thermosensitive recording layer can be used as the pigment, as appropriate, but aluminum hydroxide, silica, kaolin, and calcined kaolin are preferred, and aluminum hydroxide is more preferred.
- 40 **[0023]** This back-coating layer may also contain, as necessary, lubricants, crosslinking agents, UV absorbing agents, dispersants, defoaming agents, fluorescent dyes, etc. that can be used in the thermosensitive recording layer, within the range that does not impair the desired advantages on the above-mentioned problems.
- [0024]** A content(in solid) of the ethylene-vinyl alcohol copolymer in the back-coating layer is preferably 10 to 80 weight %
- 45 **[0025]** %, more preferably 10 to 50 weight %.
- [0025]** A content(in solid) of the ethylene-acrylic copolymer in the back-coating layer is preferably 10 to 80 weight %, more preferably 50 to 80 weight %.
- [0026]** However, a combined amount(in solid) of the ethylene-vinyl alcohol copolymer and the ethylene-acrylic copolymer in the back-coating layer is preferably 50 to 100 weight %, more preferably 50 to 90 weight %, even more
- 50 **[0027]** preferably 70 to 90 weight %.
- [0027]** Further, a content ratio (in solid) of the ethylene-acrylic copolymer is preferably 2.5 to 40 weight parts, more preferably 10 to 40 weight parts per 10 weight parts of the ethylene-vinyl alcohol copolymer.
- [0028]** A content(in solid) of the pigment in the back-coating layer is preferably 50 to 10 weight %, more preferably 30 to 10 weight %.
- 55 **[0029]** The coating amount of the back-coating layer is not limited in particular, but may be determined according to the required performance and the recording suitability. The typical coating amount (in solid) of the back-coating layer is ordinarily in the range of from 0.1 to 5g/m². The coating amount of 2.5 to 4.5g/m is preferable since excellent water vapor barrier property and excellent quality as the thermosensitive recording medium can be obtained.

[0030] The thermosensitive recording layer of the present invention contains a leuco dye and a color developing agent, and optionally may further contains sensitizer, binder, pigment, crosslinking agent, stabilizer, and other ingredients.

[0031] All of the leuco dyes well known in the conventional field of pressure sensitive and thermosensitive recording media may be used as the electron donating leuco dye in the present invention. Although the leuco dye is not particularly restricted, triphenylmethane type compounds, fluorane type compounds, fluorene type compounds, divinyl type compounds and the like are preferred as the leuco dye. Specific examples of the typical colorless to pale colored basic colorless leuco dye (leuco dye precursors) are shown below. In addition, these leuco dye precursors may be used individually and also in mixtures of at least two of them.

<Triphenylmethane type leuco dyes>

[0032] 3,3-bis(p-Dimethyl aminophenyl)-6-dimethylaminophthalide [alternate name: crystal violet lactone] and 3,3-bis(p-Dimethyl aminophenyl) phthalide [alternate name: malachite green lactone]

<Fluorane type leuco dyes>

[0033] 3-Diethylamino-6-methylfluorane, 3-diethylamino-6-methyl-7-anilino-6-methyl-7-(o,p-dimethylanilino)fluorane, 3-diethylamino-6-methyl-7-chloro-6-methyl-7-(m-trifluoromethylanilino) fluorane, 3-diethylamino-6-methyl-7-(o-chloroanilino) fluorane, 3-diethylamino-6-methyl-7-(p-chloroanilino) fluorane, 3-diethylamino-6-methyl-7-(o-fluoroanilino) fluorane, 3-diethylamino-6-methyl-7-(m-methylanilino) fluorane, 3-diethylamino-6-methyl-7-n-octylanilino fluorane, 3-diethylamino-6-methyl-7-n-octylamino fluorane, 3-diethylamino-6-methyl-7-benzylamino fluorane, 3-diethylamino-6-methyl-7-dibenzylamino fluorane, 3-diethylamino-6-chloro-7-methyl fluorane, 3-diethylamino-6-chloro-7-anilino fluorane, 3-diethylamino-6-chloro-7-p-methylanilino fluorane, 3-diethylamino-6-ethoxyethyl-7-anilino fluorane, 3-diethylamino-7-methyl fluorane, 3-diethylamino-7-chloro fluorane, 3-diethylamino-7-(m-trifluoromethylanilino) fluorane, 3-diethylamino-7-(o-chloroanilino) fluorane, 3-diethylamino-7-(p-chloroanilino) fluorane, 3-diethylamino-7-(o-fluoroanilino) fluorane, 3-diethylamino-benz[a] fluorane, 3-diethylamino-benz[c] fluorane, 3-dibutylamino-6-methyl-fluorane, 3-dibutylamino-6-methyl-7-anilino fluorane, 3-dibutylamino-6-methyl-7-(o,p-dimethylanilino) fluorane, 3-dibutylamino-7-(o-chloroanilino) fluorane, 3-butylamino-6-methyl-7-(p-chloroanilino) fluorane, 3-dibutylamino-6-methyl-7-(o-fluoroanilino) fluorane, 3-dibutylamino-6-methyl-7-(m-fluoroanilino) fluorane, 3-dibutylamino-6-methyl-chloro fluorane, 3-dibutylamino-6-ethoxyethyl-7-anilino fluorane, 3-dibutylamino-6-chloro-7-anilino fluorane, 3-dibutylamino-6-methyl-7-p-methylanilino fluorane, 3-dibutylamino-7-(o-chloroanilino) fluorane, 3-dibutylamino-7-(o-fluoroanilino) fluorane, 3-di-n-pentylamino-6-methyl-7-anilino fluorane, 3-di-n-pentylamino-6-methyl-7-(p-chloroanilino) fluorane, 3-di-n-pentylamino-7-(m-trifluoromethylanilino) fluorane, 3-di-n-pentylamino-6-chloro-7-anilino fluorane, 3-di-n-pentylamino-7-(p-chloroanilino) fluorane, 3-pyrrolidino-6-methyl-7-anilino fluorane, 3-piperidino-6-methyl-7-anilino fluorane, 3-(N-methyl-N-propylamino)-6-methyl-7-anilino fluorane, 3-(N-methyl-N-cyclohexylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-cyclohexylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-xylylamino)-6-methyl-7-(p-chloroanilino) fluorane, 3-(N-ethyl-p-toluidino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-isoamylamino)-6-chloro-7-anilino fluorane, 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-isobutylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-ethoxypropylamino)-6-methyl-7-anilino fluorane, 3-cyclohexylamino-6-chloro fluorane, 2-(4-oxahexyl)-3-dimethylamino-6-methyl-7-anilino fluorane, 2-(4-oxahexyl)-3-diethylamino-6-methyl-7-anilino fluorane, 2-(4-oxahexyl)-3-dipropylamino-6-methyl-7-anilino fluorane, 2-methyl-6-o-(p-dimethylaminophenyl) aminoanilino fluorane, 2-methoxy-6-p-(p-dimethylaminophenyl) aminoanilino fluorane, 2-chloro-3-methyl-6-p-(p-phenylaminophenyl) aminoanilino fluorane, 2-chloro-6-p-(p-dimethylaminophenyl) aminoanilino fluorane, 2-nitro-6-p-(p-diethylaminophenyl) aminoanilino fluorane, 2-amino-6-p-(p-diethylaminophenyl) aminoanilino fluorane, 2-diethylamino-6-p-(p-diethylaminophenyl) aminoanilino fluorane, 2-phenyl-6-methyl-6-p-(p-phenylaminophenyl) aminoanilino fluorane, 2-benzyl-6-p-(p-phenylaminophenyl) aminoanilino fluorane, 2-hydroxy-6-p-(p-phenylaminophenyl) aminoanilino fluorane, 3-methyl-6-p-(p-dimethylaminophenyl) aminoanilino fluorane, 3-diethylamino-6-p-(p-diethylaminophenyl) aminoanilino fluorane, 3-diethylamino-6-p-(p-dibutylaminophenyl) aminoanilino fluorane and 2,4-dimethyl-6-[(4-dimethylamino) anilino] fluorane.

<Fluorene type leuco dye>

[0034] 3,6,6-Tris(dimethylamino) spiro[fluorane-9,3'-phthalide] and 3,6,6'-tris (diethylamino) spiro[fluorane-9,3'-phthalide].

<Divinyl type leuco dyes>

[0035] 3,3-bis-[2-(p-dimethylaminophenyl)-2-(p-methoxyphenyl) ethenyl] -4,5,6,7-tetrabromophthalide, 3,3-bis-[2-(p-

dimethylaminophenyl)-2-(p-methoxyphenyl) ethenyl]-4,5,6,7-tetrachlorophthalide, 3,3-bis-[1,1-bis(4-pyrrolidinophenyl) ethylene-2-yl] 4,5,6,7-tetra-bromophthalide, 3,3-bis-[1-(4-methoxyphenyl)-1-(4-pyrrolidinophenyl) ethylene-2-yl]-4,5,6,7-tetrachlorophthalide

<Others>

[0036] 3-(4-Diethylamino-2-ethoxyphenyl)-3-(1-ethyl-2-methylindol-3-yl)-4-azaphthalide, 3-(4-diethylamino-2-ethoxyphenyl)-3-(1-octyl-2-methylindol-3-yl)-4-azaphthalide, 3-(4-cyclohexyl ethylamino-2-methoxyphenyl)-3-(1-ethyl-2-methylindol-3-yl)-4-azaphthalide, 3,3-bis(1-ethyl-2-methylindol-3-yl)phthalide, 3,6-bis(diethylamino)fluorane- γ -(3'-nitroanilino)lactam, 3,6-bis(diethylamino)fluorane- γ -(4'-nitro) anilino)lactam, 1,1-bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-dinitrilethane, 1,1-bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2- β -naphthoylethane, 1,1-bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-diacetylene and bis-[2,2,2',2'-tetrakis-(p-dimethylaminophenyl)-ethenyl]-methylmalonic acid dimethyl ester.

[0037] All of the color developing agent(s) well known in the conventional field of pressure sensitive and thermosensitive recording media may be used as the electron donating leuco dye in the thermosensitive recording medium of the present invention. Although the color developing agent is not particularly restricted, as such color developing agents, for example, activated clay, attapulgite, colloidal silica, inorganic acidic substances such as aluminum silicate and the like, 4,4'-isopropylidene diphenol, 1,1-bis(4-hydroxyphenyl) cyclohexane, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, 4,4'-dihydroxydiphenyl sulfide, hydroquinone monobenzyl ether, benzyl 4-hydroxybenzoate, 4,4'-dihydroxy diphenyl sulfone, 2,4'-dihydroxy diphenyl sulfone, 4-hydroxy-4'-isopropoxy diphenyl sulfone, 4-hydroxy-4'-n-propoxy diphenyl sulfone, bis(3-allyl-4-hydroxyphenyl) sulfone, 4-hydroxy-4'-methyl diphenyl sulfone, 4-hydroxyphenyl-4'-benzyloxy phenyl sulfone, 3,4-dihydroxyphenyl-4'-methyl phenyl sulfone, 1-[4-(4-hydroxyphenyl-sulfonyl) phenoxy]-4-[4-(4-isopropoxyphenyl sulfonyl) phenoxy] butane, phenol condensate composition described in Japanese Patent Application Public Disclosure No. 2003-154760, aminobenzene sulfonamide derivatives described in Japanese Patent Application Public Disclosure No. H08-59603, bis(4-hydroxyphenyl thioethoxy) methane, 1,5-di(4-hydroxyphenyl thio)-3-oxapentane, butyl bis(p-hydroxyphenyl) acetate, methyl bis(p-hydroxyphenyl) acetate, 1,1-bis(4-hydroxyphenyl)-1-phenyl ethane, 1,4-bis[α -methyl- α -(4'-hydroxyphenyl)ethyl] benzene, 1,3-bis[α -methyl- α -(4'-hydroxyphenyl)ethyl] benzene, di(4-hydroxy-3-methylphenyl) sulfide, 2,2'-thiobis(3-tert-octylphenol), 2,2'-thiobis(4-tert-octylphenol), N-[2-(3-phenylureido)phenyl]benzenesulfonamide, N, N'-di-[3-(p-toluenesulfonyloxy) phenyl] urea, phenolic compound such as diphenylsulfone crosslinked compound described in International Publication WO97/16420, compounds described in International Publication WO02/081229 or Japanese Patent Application Public Disclosure No. 2002-301873, thiourea compounds such as N,N'-di-m-chlorophenyl thiourea and the like, p-chlorobenzoic acid, stearyl gallate, bis[zinc 4-octyloxy carbonylamino salicylate] dihydrate, 4-[2-(p-methoxyphenoxy) ethyloxy] salicylic acid, 4-[3-(p-tolylsulfonyl) propyloxy] salicylic acid, aromatic carboxylic acids such as 5-[p-(2-p-methoxyphenoxyethoxy) cumyl] salicylic acid, and salts of these aromatic carboxylic acids and polyvalent metals such as zinc, magnesium, aluminum, calcium, titanium, manganese, tin, nickel and the like, and, furthermore, antipirin complexes of zinc thiocyanate and complex zinc salts of terephthal aldehyde acid with other aromatic carboxylic acids and the like may be cited. These color developing agents may be used individually or as a mixture of at least two of them.

[0038] 1-[4-(4-hydroxyphenyl-sulfonyl) phenoxy]-4-[4-(4-isopropoxyphenyl sulfonyl) phenoxy] butane is available, for example, under the trade name of TOMILAC 214 produced by Mitsubishi Chemical Group Corporation. The phenol condensate composition described in Japanese Patent Application Public Disclosure No. 2003-154760 is available, for example, under the trade name of TOMILAC 224 produced by Mitsubishi Chemical Group Corporation. The diphenylsulfone crosslinked compound described in International Publication WO97/16420 is available, for example, under the trade names of D-90 produced by Nippon Soda Co., Ltd. The compound described in International Publication WO02/081229 is available, for example, under the trade names of NKK-395 and D-100 produced by Nippon Soda Co., Ltd.

[0039] The previously wellknown sensitizers may be used as the sensitizer in the thermosensitive recording medium of the present invention. As such sensitizers, aliphatic acid amides such as stearic acid amide, palmitic acid amide and the like, ethylene bis-amide, montan acid wax, polyethylene wax, 1,2-di-(3-methylphenoxy) ethane, p-benzyl biphenyl, β -benzyloxy naphthalene, 4-biphenyl-p-tolyl ether, m-terphenyl, 1,2-diphenoxyethane, dibenzyl oxalate, di(p-chlorobenzyl) oxalate, di(p-methylbenzyl) oxalate, dibenzyl terephthalate, benzyl p-benzyloxy benzoate, di-p-tolyl carbonate, phenyl- α -naphthyl carbonate, 1,4-diethoxynaphthalene, 1-hydroxy-2-naphthoic acid phenyl ester, o-xylene-bis-(phenyl ether), 4-(m-methyl phenoxyethyl) biphenyl, 4,4'-ethylene dioxy-bis-benzoic acid dibenzyl ester, dibenzoyloxy methane, 1,2-di(3-methylphenoxy) ethylene, bis[2-(4-methoxyphenoxy) ethyl] ether, methyl p-nitrobenzoate, phenyl p-toluene sulfonate, and the like may be listed as examples. However, the sensitizer is not limited to these. These sensitizers may be used individually and as mixtures of at least two of them.

[0040] As the binder being usable for the present invention, polyvinyl alcohols such as completely saponified polyvinyl alcohol, partially saponified polyvinyl alcohol, carboxy-modified polyvinyl alcohol, diacetone-modified polyvinyl alcohol,

acetoacetyl-modified polyvinyl alcohol, amide-modified polyvinyl alcohol, sulfonic acid-modified polyvinyl alcohol, butyral-modified polyvinyl alcohol, olefin-modified polyvinyl alcohol, nitrile-modified polyvinyl alcohol, pyrrolidone-modified polyvinyl alcohol, silanol-modified polyvinyl alcohol, cation-modified polyvinyl alcohol, terminal-alkyl-modified polyvinyl alcohol, cellulose ethers and derivatives thereof such as hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, acetylcellulose, starches such as starch, enzymemodified starch, thermochemically-modified starch, oxidized starch, esterified starch, etherified starch (such as hydroxy-ethylated starch), cationic starch, polyacrylamides such as polyacrylamide, cationic polyacrylamide, anionic polyacrylamide, amphoteric polyacrylamide, urethane resins such as polyester polyurethane resin, polyether polyurethane resin, polyurethane ionomer resin, acrylic resin contains (meth) acrylic acid and a monomer component (excluding olefin) copolymerizable with (meth) acrylic acid, styrene-butadiene resins such as styrene-butadiene copolymer, styrene-butadiene -acrylonitrile copolymer, styrene-butadiene -acryl copolymer, polyolefin resins such as polyvinyl acetate, vinyl chloride-vinyl acetate copolymer, ethylene-vinyl acetate copolymer, polyvinyl chloride, polyvinylidene chloride, polyacrylic acid ester, gum Arabic, polyvinyl butylal, polystyrol and their copolymers, silicone resins, petroleum resins, terpene resins, ketone resins, cumaron resins and the like may be listed as examples. These may be used individually and as mixtures of at least two of them.

[0041] As a pigment usable for the present invention, inorganic or organic fillers such as silica, calcium carbonate, kaolin, calcined kaolin, diatomaceous earth, talc, titanium oxide, aluminum hydroxide and the like may be listed as examples. These may be used individually and as mixtures of at least two of them.

[0042] As a crosslinking agent usable for the present invention, glyoxal, methylol melamine, melamine formaldehyde resin, melamine urea resin, poly(amine epichlorohydrin) resin, poly(amide epichlorohydrin) resin, potassium persulfate, ammonium persulfate, sodium persulfate, ferric chloride, magnesium chloride, borax, boric acid, alums (aluminum potassium sulfate), ammonium chloride, and the like may be listed as examples.

[0043] As stabilizers in the present invention that impart oil resistance and the like to recorded images, 4,4'-butylidene (6-t-butyl-3-methylphenol), 2,2'-di-t-butyl-5,5'-dimethyl-4,4'-sulfonyl diphenol, 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl) butane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, 4-benzyloxy-4'-(2,3-epoxy-2-methyl propoxy)diphenylsulfone and the like may be used, unless the desired effects for the problems described above are not hampered.

[0044] In addition, UV absorption agents, such as benzophenone type and triazole type UV absorption agents, lubricants, dispersion agents, defoaming agents, oxidation inhibitors, fluorescent dye and the like may also be used.

[0045] The types and amounts of the electron donating leuco dye, electron accepting color developing agent, and other various ingredients used in the thermosensitive recording medium of the present invention may be determined according to the required performance and printability. Although the amounts of those are not particularly restricted, approximately, from 0.5 parts to 10 parts by weight of the electron accepting color developing agent, from 0.5 parts to 10 parts by weight of the sensitizer are ordinarily used per 1 part by weight of the electron donating leuco dye.

[0046] The types and amounts of other optional components, namely the binder, the pigment, the stabilizer and the other ingredients, may be determined according to the required performance and printability. Although the amounts of those are not particularly restricted, approximately, from 5 parts to 50 parts by weight in solid of the binder is ordinarily appropriate per 100 part by weight of the thermosensitive recording layer (in solid), and from 0 parts to 50 parts by weight in solid of the pigment is ordinarily appropriate per 100 part by weight of the thermosensitive recording layer (in solid). And when the lubricant is used, approximately, from 5 parts to 10 parts by weight in solid of the lubricant is ordinarily appropriate per 100 part by weight of the thermosensitive recording layer (in solid).

[0047] The thermosensitive recording medium of the present invention may further have a protective layer on the thermosensitive recording layer. The protective layer comprises mainly a binder and a pigment, and the binder, the pigment, the cross-linking agent or the like described as being usable for the thermosensitive recording layer can be used.

[0048] Any binder that can be used in the thermosensitive recording layer described above can be used as the binder, but carboxy-modified polyvinyl alcohol and non-core-shell type acrylic resin are preferably used. These binders may be used solely or in combination of two or more.

[0049] Any cross-linking agent that can be used in the thermosensitive recording layer described above can be used as the cross-linking agent, and epichlorohydrin-based resin and polyamine/polyamide-based resin (excluding those categorized as epichlorohydrin-based resin) are preferably used.

[0050] It is more preferable that the protective layer contains an epichlorohydrin-based resin and a polyamine/polyamide-based resin together with a carboxy-modified polyvinyl alcohol, which further improves the color developing property.

[0051] The carboxy modified poly(vinyl alcohol) is, for example, obtained in the form of a reaction product of poly(vinyl alcohol) and a polyvalent carboxylic acid such as fumaric acid, phthalic anhydride, mellitic anhydride, itaconic anhydride and the like or as esterified materials of these reaction products or, furthermore, in the form of saponified materials of the copolymers of vinyl acetate with an ethylenic unsaturated dicarboxylic acid such as maleic acid, fumaric acid, itaconic acid, crotonic acid, acrylic acid, methacrylic acid and the like. More specifically, the production processes listed as examples in Example 1 or Example 4 in, for example, Japanese Patent Application Public Disclosure S53-91995 may be cited. In

addition, a degree of saponification of from 72 to 100 mole % is preferred for the carboxy-modified poly(vinyl alcohol). A degree of polymerization is preferably from 500 to 2400, more preferably 1000 to 2000.

[0052] The glass transition point (T_g) of the non-core-shell type acrylic resin is preferably 95 degree C or lower, and further preferably 50 degree C or higher. The T_g is measured by differential scanning calorimetry (DSC).

[0053] The non-core shell type acrylic resin contains (meth) acrylic acid and a monomer component copolymerizable with (meth) acrylic acid, and the content of the (meth) acrylic acid is preferably from 1 to 10 parts by weight per 100 parts by weight of the non-core shell type acrylic resin. (Meta) acrylic acid is alkali-soluble and has the property of making a non-core shell type acrylic resin water-soluble by adding a neutralizing agent. By making the non-core-shell type acrylic resin water-soluble, the bondability to pigments is remarkably increased, when the protective layer contains a pigment, and the protective layer with excellent strength can be formed, even when a large amount of pigment is contained. As the monomer component copolymerizable with (meth) acrylic acid, for example, alkyl acrylate resins, such as methyl (meth) acrylate, ethyl (meth) acrylate, propyl (meth) acrylate, butyl (meth) acrylate, isobutyl (meth) acrylate, pentyl (meth) acrylate, hexyl (meth) acrylate, 2-ethyl hexyl (meth)acrylate, octyl (meth) acrylate, and the like; epoxy resins; silicone resins; modified alkyl acrylate resins, such as alkyl acrylate resin modified with styrene or its derivative; (meth) acrylonitrile; acrylic acid ester; hydroxyalkyl acrylic acid ester and the like may be listed. The monomer is preferably (meta) acrylonitrile and/or methyl methacrylate. It is preferable to formulate from 15 to 70 parts of (meth) acrylonitrile per 100 parts of the non-core shell type acrylic resin. Further, it is preferable to formulate from 20 to 80 parts of methyl methacrylate per 100 parts of a non-core shell type acrylic resin. When both (meth) acrylonitrile and methyl methacrylate are contained, it is preferable to formulate from 15 to 18 parts of (meth) acrylonitrile and from 20 to 80 parts of methyl methacrylate per 100 parts of a non-core shell type acrylic resin.

[0054] The epichlorohydrin resin is a resin characterized by containing an epoxy group in the molecule, and examples thereof include, poly(amide epichlorohydrin) resins, poly(amine epichlorohydrin) resins and the like and these can be used individually or in combinations. In addition, primary to quaternary amines may be used as the amine that is present in the main chain of an epichlorohydrin resin, and no particular restrictions apply. Furthermore, a degree of cationization of no greater than 5 meq/g solid (measured at pH 7) and a molecular weight of at least 500,000 are preferred from the view point of good water resistance. Sumirez Resin 650 (30), Sumirez Resin 675A, Sumirez Resin 6615 (the above, Sumitomo Chemical Co., Ltd.), WS4002, WS 4020, WS4024, WS4030, WS4046, WS4010, CP8970 (the above, Seiko PMC Corporation) may be cited as specific examples of the epichlorohydrin resin.

[0055] The polyamine/amide resin does not contain epoxy group in the molecule, and examples of the polyamine/amide resin include polyamide urea resins, polyalkylene polyamine resins, polyalkylene polyamide resins, polyamine polyurea resins, modified polyamine resins, modified polyamide resins, polyalkylene polyamine urea formalin resins, and polyalkylene polyamine polyamide polyurea resins. These may be used individually or as mixtures of at least two of them. Specific examples of the polyamine/amide resin include Sumirez resin 302 (polyamine polyurea resin produced by Sumitomo Chemical Co., Ltd.), Sumirez resin 712 (polyamine polyurea resin produced by Sumitomo Chemical Co., Ltd.), Sumirez resin 703 (polyamine polyurea resin produced by Sumitomo Chemical Co., Ltd.), Sumirez resin 636 (polyamine polyurea resin produced by Sumitomo Chemical Co., Ltd.), Sumirez resin SPI-100 (modified polyamine resin produced by Sumitomo Chemical Co., Ltd.), Sumirez resin SPI-102A (modified polyamine resin produced by Sumitomo Chemical Co., Ltd.), Sumirez resin SPI-106N (modified polyamide resin produced by Sumitomo Chemical Co., Ltd.), Sumirez resin SPI-203(50)(Sumitomo Chemical Co., Ltd.), Sumirez resin SPI-198 (Sumitomo Chemical Co., Ltd.), PrintiveA-700 (Asahi Kasei Corporation), PrintiveA-600 (Asahi Kasei Corporation), PA6500, PA6504, PA6634, PA6638, PA6640, PA6644, PS6646, PA6654, PA6702, PA 6704 (the above, polyalkylene polyamine polyamide polyurea resins produced by Seiko PMC Corporation), and CP8994 (polyethyleneimine resin produced by Seiko PMC Corporation). From the viewpoint of print intensity (recording intensity), polyamine resins (polyalkylene polyamine resins, polyamine polyurea resins, modified polyamine resins, polyalkylene polyamine urea formalin resins, and polyalkylene polyamine polyamide polyurea resins) are preferable.

[0056] When the protective layer contains epichlorohydrin resins and polyamine/amide resins together with carboxy-modified poly(vinyl alcohol), each content of epichlorohydrin resins and polyamine/amide resins is preferably from 1 to 100 parts, more preferably from 5 to 50 parts, further preferably from 10 to 40 parts per 100 parts of carboxy-modified poly(vinyl alcohol) by weight.

[0057] As a pigment used in the protective layer, the pigments described as usable for the thermosensitive recording layer can be used, and preferably kaolin, calcined kaolin, aluminum hydroxide, silica are used. These may be used individually and as mixtures of at least two of them.

[0058] The content (in solid) of the binder in the protective layer is preferably 20 weight % or higher, more preferably from 20 to 80 weight %. When the protective layer contains pigments, the content (in solid) of binder is from 30 parts to 300 parts per 100 part of pigments by weight.

[0059] If necessary, the coating solution for the protective layer may further contain cross-linking agents, slipping agents, stabilizers, and various auxiliary agents such as UV absorbing agents, dispersants, defoaming agents, anti-oxidants, fluorescent dyes, etc. that can be used for the above-mentioned thermosensitive recording layer.

[0060] The thermosensitive recording medium of the present invention may further have an undercoat layer between the substrate and the thermosensitive recording layer. The undercoat layer comprises mainly a binder and a pigment.

[0061] As the binder used for the undercoat layer, the various binders used in the above-mentioned thermosensitive recording layer can be used. These binders may be used individually and as mixtures of at least two of them.

[0062] As the pigment used for the undercoat layer, the various pigments used in the above-mentioned thermosensitive recording layer can be used. These pigments may be used individually and as mixtures of at least two of them.

[0063] The amount of the pigments in the undercoat layer is ordinarily from 50 to 95 weight parts, preferably from 70 to 90 weight parts per 100 parts by weight of the total solid of the undercoat layer.

[0064] Various aids such as a dispersion agent, plasticizer, pH controlling agent, de-foaming agent, water retention agent, preservative, coloring dye, UV absorber and the like may be added to the coating solution for the undercoat layer, as required.

[0065] The thermosensitive recording medium to be intended is obtained by coating any substrate such as paper, recycled paper, synthetic paper, film, plastic film, foamed plastic film and non-woven fabric with a coating liquid formulated for each coating layer described above. Combined sheets combining these may be used as the substrate.

[0066] Electron donating leuco dye, an electron accepting color developing agent, an electron acceptor, an electronic donor, and materials added as necessary are pulverized to a particle size of a few microns or less by a pulverizer such as a ball mill, an attritor, a sand grinder, or other appropriate emulsifying device. Various additives are added thereto depending on the purpose to make the coating liquid.

[0067] The method for coating above individual coating layers are not limited in particular, but any known conventional techniques may be used. The method for coating may be appropriately selected from off-machine coating machines and on-machine coating machines, which are equipped with coaters such as air knife coater, rod blade coater, bent blade coater, bevel blade coater, roll coater, curtain coater, spray coater and the like. The coating amounts of the thermosensitive recording layer is not limited in particular, but may be determined according to the required performance and the recording suitability. The typical coating amount (in solid) of the thermosensitive recording layer is ordinarily in the range of from 2 to 12g/m².

[0068] Furthermore, various technologies known in the thermosensitive recording medium field, such as a flattening treatment such as super calendaring and the like can be applied as needed after coating individual coating layers.

[Examples]

[0069] The following Examples illustrate the present invention, but the Examples are not intended to limit the scope of the present invention. In the following description, the terms parts and % indicate parts by weight and weight %, respectively.

[Preparation of each coating solution]

[0070] Undercoat layer coating solution was prepared by dispersing and stirring the following formulation:

[Undercoat layer coating solution]

[0071]

Calcined kaolin (Imeris Minerals Japan.: Alpha-Tex HP)	50.0 parts
Plastic hollow particle (Zeon Corporation, MH8109)	50.0 parts
Styrene-butadiene copolymer latex (Zeon Corporation, ST55226, solid content: 48%)	10.0 parts
Water	50.0 parts

[0072] Back-coating layer coating solution 1-6 were prepared by mixing the following formulation:

[Back-coating layer coating solution 1]

[0073]

kaolin (Imeris Minerals Japan.: trade name contour 1500)	20.0 parts
ethylene-vinyl alcohol copolymer (KURARAY CO., LTD., trade name exceval RS4104)	10.0 parts

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(continued)

ethylene-acrylic copolymer(Sumitomo Seika Chemicals Co., Ltd. trade name ZAIKTHENE AC, melting point:80-95 degree C) 40.0 parts

5 [Back-coating layer coating solution 2]

[0074]

10	kaolin (Imeris Minerals Japan.: trade name contour 1500)	20.0 parts
	ethylene-vinyl alcohol copolymer (RS4104)	10.0 parts
	ethylene-acrylic copolymer(ZAIKTHENE AC)	20.0 parts
	Styrene-butadiene copolymer latex (ST5526)	20.0 parts

15 [Back-coating layer coating solution 3]

[0075]

20	kaolin (contour 1500)	20.0 parts
	ethylene-acrylic copolymer(ZAIKTHENE AC)	50.0 parts

25 [Back-coating layer coating solution 4]

[0076]

30	kaolin (contour 1500)	20.0 parts
	ethylene-vinyl alcohol copolymer (RS4104)	50.0 parts

[Back-coating layer coating solution 5]

[0077]

35	kaolin (contour 1500)	20.0 parts
	Fully saponified polyvinyl alcohol aqueous solution (PVA117)	10.0 parts
	ethylene-acrylic copolymer(ZAIKTHENE AC)	40.0 parts

40 [Back-coating layer coating solution 6]

[0078]

45	kaolin (contour 1500)	20.0 parts
	ethylene-vinyl alcohol copolymer (RS4104)	10.0 parts
	Styrene-butadiene copolymer latex (ST5526)	40.0 parts

50 [0079] Each of color developing agent dispersion, leuco dye dispersion, and sensitizer dispersion having the following blend was wet ground separately by a sand grinder to an average particle size of 0.5 μ m.

Color developing agent dispersion (A1 liquid)

55 [0080]

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N-[2-(3-phenylureido)phenyl]benzenesulfonamide(Nippon Soda Co., Ltd. NKK1304, hereinafter referred to as "urea compound") 6.0 parts

Fully saponified polyvinyl alcohol aqueous solution (KURARAY CO., LTD., PVA117, solid content 10 %) 5.0 parts

Water 1.5 parts

Color developing agent dispersion (A2 liquid)

[0081]

4-benzyloxy-4'-dihydroxy diphenyl sulfone (Nikka Chemical Co., Ltd. BPS-MA3) 6.0 parts

Fully saponified polyvinyl alcohol aqueous solution (PVA117) 5.0 parts

Water 1.5 parts

Leuco dye dispersion (B liquid)

[0082]

3-di buthylamino-6-methyl-7-anilino fluoran (Yamamoto Chemicals, Inc., ODB-2) 6.0 parts

Fully saponified polyvinyl alcohol aqueous solution (PVA117) 5.0 parts

Water 1.5 parts

Sensitizer dispersion (C liquid)

[0083]

1,2-bis(3-Methylphenoxy) ethane (Sanko Co. Ltd, KS232) 6.0 parts

Fully saponified polyvinyl alcohol aqueous solution (PVA117) 5.0 parts

Water 1.5 parts

[0084] Next, each dispersion was mixed in the following percentage to prepare a coating material for the thermosensitive recording layer.

<Coating material for thermosensitive recording layer 1>

[0085]

Color developing agent dispersion (A1 liquid) 18.0 parts

Leuco dye dispersion (B liquid) 18.0 parts

Sensitizer dispersion (C liquid) 36.0 parts

Silica dispersion(Mizusawa Industrial Chemicals, Ltd. MIZUKASIL P-537, solid content 25%) 17.5 parts

Fully saponified polyvinyl alcohol aqueous solution (PVA117) 30.0 parts

<Coating material for thermosensitive recording layer 2>

[0086]

Color developing agent dispersion (A2 liquid) 18.0 parts

Leuco dye dispersion (B liquid) 18.0 parts

Sensitizer dispersion (C liquid) 36.0 parts

Silica dispersion(MIZUKASIL P-537) 17.5 parts

(continued)

Fully saponified polyvinyl alcohol aqueous solution (PVA117) 30.0 parts

5 **[0087]** Next, protective layer coating solution was prepared by mixing the following formulations:

<Protective layer coating solution>

[0088]

10	Aluminum hydroxide dispersion (Martinsberg: Martifin OL, solid content: 50%)	9.0 parts
	Carboxy-modified polyvinyl alcohol solution (Kuraray Co., Ltd., trade name: KL318, degree of polymerization: about 1700, degree of saponification: 95 to 99 mol%, solid content 10%)	30.0 parts
15	Poly(amide epichlorohydrin) resin (Seiko PMC Corporation, trade name: WS4030, solid content 25%)	4.0 parts
	Modified polyamine resin (Sumitomo Chemical Co., Ltd. trade name: Sumirez Resin SPI-102A, solid content 45%)	2.2 parts
	Zinc stearate (Chukyo Yushi Co., Ltd.: HydrinZ-7-30, solid content: 30%)	2.0 parts
20	Water	22.8 parts

[Example 1]

25 **[0089]** The undercoat layer coating solution was applied on one side of a substrate (groundwood free paper with a basis weight of 60 g/m²) by using a bent blade coater with a coating amount (in solid) of 6.0 g/m², and was dried to prepare an undercoated paper.

[0090] The thermosensitive recording layer coating solution 1 was applied on the undercoat layer of the undercoated paper by using a rod blade coater with a coating amount (in solid) of 3.0 g/m² and was dried and super calendared so that the smoothness was 500-1000 seconds to prepare a thermosensitive recording layer coated paper.

30 **[0091]** Then the protective layer coating solution was applied on the thermosensitive recording layer of the thermosensitive recording layer coated paper by using a rod blade coater with a coating amount (in solid) of 3.0 g/m² and was dried to prepare a protective layer coated paper.

[0092] Next the back-coating layer coating solution 1 was applied on the opposite side of the protective layer of the protective layer coated paper by using a rod blade coater with a coating amount (in solid) of 3.5 g/m² and was dried to prepare a thermosensitive recording medium.

[Example 2]

40 **[0093]** A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the coating amount of the back-coating layer coating solution to 2.0 g/m².

[Example 3]

45 **[0094]** A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the coating amount of the back-coating layer coating solution to 2.5 g/m².

[Example 4]

50 **[0095]** A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the coating amount of the back-coating layer coating solution to 4.5 g/m².

[Example 5]

55 **[0096]** A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the formulated amount of the ethylene-vinyl alcohol copolymer to 30 parts and the ethylene-acrylic copolymer to 20 parts of the back-coating layer coating solution.

[Example 6]

[0097] A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the formulated amount of the ethylene-vinyl alcohol copolymer to 40 parts and the ethylene-acrylic copolymer to 10 parts of the back-coating layer coating solution.

[Example 7]

[0098] A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the thermosensitive recording layer coating solution 1 to the thermosensitive recording layer coating solution 2.

[Example 8]

[0099] A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the back-coating layer coating solution 1 to the back-coating layer coating solution 2.

[Comparative Example 1]

[0100] A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the back-coating layer coating solution 1 to the back-coating layer coating solution 3.

[Comparative Example 2]

[0101] A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the back-coating layer coating solution 1 to the back-coating layer coating solution 4.

[Comparative Example 3]

[0102] A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the back-coating layer coating solution 1 to the back-coating layer coating solution 5.

[Comparative Example 4]

[0103] A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the back-coating layer coating solution 1 to the back-coating layer coating solution 6.

[Comparative Example 5]

[0104] A thermosensitive recording medium was prepared in the same manner as described in Example 1 except that any back-coating layer coating solution was not coated.

[0105] The prepared thermosensitive recording media were evaluated as below.

<Color developing property (Recorded density)>

[0106] A checkerboard pattern was printed on the prepared thermosensitive recording medium by using a thermosensitive recording medium print tester (Okura Engineering Co., Ltd. TH-PMD equipped with a thermal head by Kyocera Co.) at applied energy of 0.35 mJ/dot and printing speed of 50mm/sec. The density of the printed portion was measured by using Macbeth Densitometer (RD-914, with Amber filter) to evaluate the color developing property (recorded density).

<Moisture-proof property of the back side>

[0107] The performance of the prepared thermosensitive recording medium was evaluated under the following two conditions.

- (1) Stored at 23°C × 50% RH for 24 hours, and then Printed under 23°C × 50% RH condition
- (2) Stored at 35°C × 80% RH for 24 hours, and then Printed under 23°C × 50% RH condition

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[0108] That is, using a Sony UP-X898MD (medical thermal printer), a solid pattern was printed under S mode condition for one roll (20 m), and then the damper part of the printer, opposite to the thermal head, was visually observed to see if there were any water droplets attached thereto, and the moisture-proof property was evaluated by the following criteria.

- 5 Excellent: No water droplets adhered
 Fair: Water droplets adhered but disappeared quickly
 Poor: Water droplets adhered and did not disappear for several minutes
 Very poor: Water droplets adhered and did not disappear for several hours

10 <Blocking after winding >

[0109] The prepared thermosensitive recording medium was rolled into a small roll (110 mm × 20 m) and left to stand for 24 hours under environmental condition of 35°C × 80% RH, after then visually evaluated by the following criteria.

- 15 Excellent: No blocking occurred, and the protective layer and the back-coating layer did not peel off
 Poor: Blocking occurred, and the protective layer or the back-coating layer peeled off

[0110] The results are shown in Table below.

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[Table 1]

	Color developing agent	Resin component(s) in the back-coating layer				Coating amount of the back-coating layer (g/m ²)	Color developing property	Moisture-proof property of the back side		Blocking after winding
		(formulated amount/weight part)	(formulated amount/weight part)	(formulated amount/weight part)	(formulated amount/weight part)			Stored at 23°C × 50% RH for 24 hours	Stored at 23°C × 80% RH for 24 hours	
Example 1	Urea compound	ethylene-PVA copolymer	(10)	ethylene-acrylic copolymer	(40)	-	-	Excellent	Excellent	Excellent
Example 2	Urea compound	ethylene-PVA copolymer	(10)	ethylene-acrylic copolymer	(40)	-	-	Excellent	Fair	Excellent
Example 3	Urea compound	ethylene-PVA copolymer	(10)	ethylene-acrylic copolymer	(40)	-	-	Excellent	Excellent	Excellent
Example 4	Urea compound	ethylene-PVA copolymer	(10)	ethylene-acrylic copolymer	(40)	-	-	Excellent	Excellent	Excellent
Example 5	Urea compound	ethylene-PVA copolymer	(30)	ethylene-acrylic copolymer	(20)	-	-	Excellent	Excellent	Excellent
Example 6	Urea compound	ethylene-PVA copolymer	(40)	ethylene-acrylic copolymer	(10)	-	-	Excellent	Excellent	Excellent
Example 7	BPS-M43	ethylene-PVA copolymer	(10)	ethylene-acrylic copolymer	(40)	-	-	Excellent	Excellent	Excellent
Example 8	Urea compound	ethylene-PVA copolymer	(10)	ethylene-acrylic copolymer	(20)	styrene-butadiene resin	(20)	Excellent	Excellent	Excellent
Comp-Example 1	Urea compound	-	(10)	ethylene-acrylic copolymer	(40)	-	-	Excellent	Poor	Poor

(continued)

	Color developing agent	Resin component(s) in the back-coating layer				Coating amount of the back-coating layer (g/m ²)	Color developing property	Moisture-proof property of the back side		Blocking after winding
		(formulated amount/weight part)	(formulated amount/weight part)	(formulated amount/weight part)	(formulated amount/weight part)			Stored at 23°C × 50% RH for 24 hours	Stored at 23°C × 80% RH for 24 hours	
Comp-Ex-ample 2	Urea compound	ethylene-PVA copolymer	(10)	-	(40)	-	3.5	Poor	Poor	Excellent
Comp-Ex-ample 3	Urea compound	-	-	ethylene-acrylic copolymer	(40)	(10)	3.5	Poor	Poor	Excellent
Comp-Ex-ample 4	Urea compound	ethylene-PVA copolymer	(10)	-	-	styrene-butadiene resin	3.5	Poor	Poor	Poor
Comp-Ex-ample 5	Urea compound	-	(10)	-	(40)	-	No coating	Very poor	Very poor	Excellent

[0111] As shown in Table 1, the thermosensitive recording medium of the present invention prevents adhesion of water droplets to the back side and has excellent water vapor barrier property, without adversely affecting color development sensitivity

Claims

1. A thermosensitive recording medium, comprising:

a thermosensitive recording layer containing a colorless or pale colored electron donating leuco dye and an electron accepting color developing agent on a substrate, and a back-coating layer on the opposite side of the thermosensitive recording layer of the substrate, wherein the back-coating layer contains an ethylene-vinyl alcohol copolymer and an ethylene-acrylic copolymer.

2. The thermosensitive recording medium according to claim 1, wherein a content ratio (in solid) of the ethylene-acrylic copolymer is 2.5 to 40 weight parts per 10 weight parts of the ethylene-vinyl alcohol copolymer.

3. The thermosensitive recording medium according to claim 1 or 2, wherein a combined content(in solid) of the ethylene-vinyl alcohol copolymer and the ethylene-acrylic copolymer in the back-coating layer is 50 to 90 weight %.

4. The thermosensitive recording medium according to any one of claim 1 to 3, wherein a coating amount of the back-coating layer is 2.5 to 4.5 g/m².

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/012159

A. CLASSIFICATION OF SUBJECT MATTER

B41M 5/40(2006.01)i; **B41M 5/323**(2006.01)i
FI: B41M5/40 220; B41M5/323 220

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B41M5/40; B41M5/323

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-208115 A (RICOH CO., LTD.) 03 August 1999 (1999-08-03) claims, examples	1-4
A	JP 2011-008089 A (NIPPON PAPER INDUSTRIES CO., LTD.) 13 January 2011 (2011-01-13) claims, paragraph [0035]	1-4
A	JP 5-032044 A (KANZAKI PAPER MFG. CO., LTD.) 09 February 1993 (1993-02-09) example 2	1-4
A	JP 9-265149 A (FUJI PHOTO FILM CO., LTD.) 07 October 1997 (1997-10-07) claims, paragraph [0069]	1-4
A	JP 2006-084607 A (RICOH CO., LTD.) 30 March 2006 (2006-03-30) examples	1-4
A	JP 2009-255551 A (RICOH CO., LTD.) 05 November 2009 (2009-11-05) paragraphs [0102]-[0108]	1-4

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"P" document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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JP 2011-008089 A	13 January 2011	(Family: none)	
JP 5-032044 A	09 February 1993	(Family: none)	
JP 9-265149 A	07 October 1997	(Family: none)	
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Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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