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(54) HEAT-SENSITIVE RECORDING BODY

(57) [Problem] To provide a thermosensitive recording medium having an excellent corrosion resistance of a thermal head when printing, as well as good for the environment using kraft lignin as a color developing agent.

[Means to solve the Problem] 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, wherein the thermosensitive recording layer contains a kraft lignin as the electron accepting color developing agent, and the kraft lignin contains almost no hydrogen sulfide or contains only 400 ppm at most.

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Description

[Field of the Invention]

[0001] The present invention relates to a thermosensitive recording medium by utilizing a coloring reaction between a colorless or pale colored electron donating leuco dye (referred to as "leuco dye") and an electron accepting color developing agent (referred to as "color developing agent"), using a kraft lignin as the color developing agent.

[Background of the Invention]

[0002] Thermosensitive recording media are ordinarily prepared by applying a coating solution containing a colorless or pale colored leuco dye and a color developing agent onto a substrate such as paper, synthetic paper, film, plastic and the like. 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 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] Bisphenols, alkylphenols, novolac-type phenolic resin, derivative or metal salt of aromatic carboxylic acid, hydroxybenzoate, sulfonylurea compound, and activated clay are generally used as the color developing agent.

[0004] In addition, to obtain a thermosensitive recording medium using an environmentally friendly color developing agent, it is known to use isolated lignin as the color developing agent (Patent Document 1, etc.).

[0005] Further, several measures are known to prevent corrosion of the thermal head used in printing on thermosensitive recording medium (Patent Document 2-4, etc.).

[Prior Art Document]

[Patent Document]

[0006]

Patent Document 1: Japanese Patent Application Laid-Open (kokai) 2020-104274
Patent Document 2: Japanese Patent Application Laid-Open (kokai) S62-087362
Patent Document 3: Japanese Patent Application Laid-Open (kokai) H10-264425
Patent Document 4: Japanese Patent Application Laid-Open (kokai) 2000-079715

[Summary of the Invention]

[Problems to be solved by the Invention]

[0007] In a printer of thermosensitive recording paper, a thermal head is configured to have a glaze layer, a heating element, electrodes, and a protective film on a base. Aluminum is generally used for the electrodes, but it is known that aluminum is corroded by ionic materials such as sodium ion, chloride ion, and sulfide ion, and if the electrodes corrode, proper printing will not be possible.

[0008] On the other hand, it has been found that when a kraft lignin is used as the color developing agent to provide an environmentally friendly thermosensitive recording medium, depending on the conditions of use, there is a problem of corrosion of the thermal head used for printing on the thermosensitive recording medium (see Comparative Example 1 described below, etc.). However, only measures on the printing device side have been known regarding the corrosion of the thermal head (Patent Documents 2 to 4, etc.).

[0009] Therefore, an object of the present invention is to provide a thermosensitive recording medium having an excellent corrosion resistance of a thermal head when printing, as well as good for the environment using kraft lignin as a color developing agent.

[Means For Solving the Problem]

[0010] As a result of intensive studies in order to solve the above problem, the present inventors have found that by using kraft lignin, which is produced by adding an oxidation step to the production process unlike a conventional method, and as a result has a reduced hydrogen sulfide content, above problems can be solved, and then completed the present invention.

[0011] 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, wherein the thermosensitive recording layer contains a kraft lignin as the electron accepting color developing agent, and the kraft lignin contains almost no hydrogen sulfide or contains 400ppm or less of the hydrogen sulfide.

[0012] Also, the present invention provides a method for reducing corrosion of a thermal head when printing on a thermosensitive recording medium which has a thermosensitive recording layer containing a kraft lignin, the method comprising the step of printing on the above thermosensitive recording medium.

[Effect of the Invention]

[0013] According to the present invention, there can be obtained a thermosensitive recording medium having an excellent corrosion resistance of a thermal head when printing, using kraft lignin as a color developing agent.

[Modes For Carrying out the Invention]

[0014] Since a natural lignin is contained in the cell wall of a plant cell and the natural lignin is complexed with polysaccharides such as cellulose, it is difficult to isolate the natural lignin. Therefore, the lignin is usually isolated by chemical denaturation. Isolated lignin is also called industrial lignin, and includes lignosulfonates, kraft lignin, soda lignin, soda-anthraquinone lignin, organolignin, exploded lignin, sulfuric acid lignin, etc.

[0015] Kraft lignin is used as a color developing agent in the thermosensitive recording medium of the present invention.

[0016] Kraft lignin is also called thiolignin or sulfate lignin. Kraft lignin is a compound having hydroxyphenyl propane as a base unit and containing functional groups such as phenolic hydroxyl group, alcoholic hydroxyl group, and thiol group. Kraft lignin is usually obtained by reacting wood with a mixed aqueous solution of sodium hydroxide and sodium sulfide, and is insoluble in water. Kraft lignin can be used in the form of an alkaline solution of kraft lignin, powdered kraft lignin obtained by spray-drying an alkaline solution of kraft lignin to produce a powder, or acid-precipitated kraft lignin obtained by precipitating an alkaline solution of kraft lignin with an acid.

[0017] The kraft lignin of the present invention is produced, for example, as described in JPA 2013-527339, and is obtained by an oxidation process of black liquor. When refining the kraft lignin, the black liquor is usually neutralized with carbon dioxide and filtered to purify and redisperse the carbonic acid-neutralized lignin, and then extracted with sulfuric acid, filtered and washed, and purified. The kraft lignin used in the present invention has an extremely low hydrogen sulfide content by adding an oxidation process with oxygen before the carbonic acid neutralization process.

[0018] Such kraft lignin contains almost no hydrogen sulfide or contains only 400 ppm at most. And even if the kraft lignin contains the hydrogen sulfide, preferably it contains 200 ppm or less, more preferably 100 ppm or less of the hydrogen sulfide. The lower limit of hydrogen sulfide content is usually 50 ppm or less, for example about 10 ppm.

[0019] The hydrogen sulfide content in the kraft lignin is measured, for example, by heating kraft lignin (200°C) and measuring the amount of generated hydrogen sulfide with a hydrogen sulfide concentration meter. The melting point of a kraft lignin is about 170°C, and can be measured by heating at 200°C.

[0020] Furthermore, a lignin content in such kraft lignin is preferably 90% by weight or more, more preferably 92 to 100% by weight.

[0021] A density of such kraft lignin at a concentration of 60% is preferably 0.4 to 0.5 g/cm^3.

[0022] When the lignin content becomes within the above range, the content of impurities such as sulfides is reduced, which reduces the impact on the corrosion of the thermal head. In addition, when the lignin content becomes within the above range, the work efficiency during reagent dispersion is improved, and the amount of kraft lignin required to achieve the same dispersion concentration can be reduced compared with the density below the above range.

[0023] An example of such kraft lignin is Amallin A, a product name, manufactured by West Fraser.

[0024] In the present invention, the above-mentioned kraft lignin is used as a color developing agent, but a color developing agent other than the kraft lignin may be used in combination. This can provide more excellent effects in terms of color development (print density) and other performances.

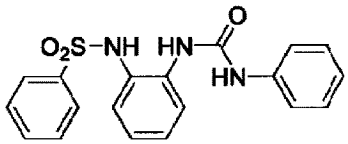
[0025] As such color developing agents, for example, inorganic acidic substances such as activated clay, attapulgite, colloidal silica, aluminum silicate and the like, 4,4'-isopropylidene diphenol, 1,1-bis(4-hydroxyphenyl) cyclohexane, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, 4,4'-dihydroxydiphenyl 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'-methyldiphenyl 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), 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, N-[2-(3-phenylureido)phenyl]benzenesulfonamide, 3-(3-tosyl ureido) phenyl-p-toluene sulfonate, urea urethane compound, 3-{[(phenylamino) carbonyl] amino} benzenesulfonamide, thiourea compounds such as N,N'-di-m-chlorophenyl thiourea and the like, p-chlorobenzoic acid, stearyl gallate, bis[zinc 4-(n-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. In addition, metal chelate type coloring component, such as metal double salt of higher-fatty-acid described in JP H10 - 258577A and multivalent hydroxy aromatic compound, can also be contained.

[0026] Among these color developing agents, 4,4'-dihydroxy diphenylsulfone, 4-hydroxy-4'-isopropoxy diphenyl sulfone or a color developing agent having urea structure(-NHCONH-) is preferable as a color developing agent used in combination with the kraft lignin because the balance of performances, such as coloring development (print density) and preservability becomes good. As the color developing agent having urea structure, following color developing agents are mentioned, for example.

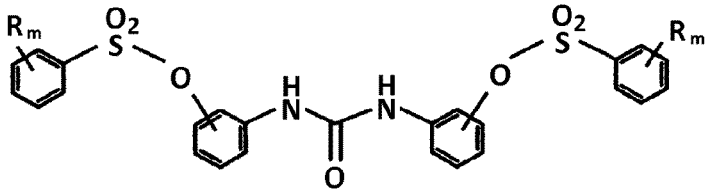
i) N-(2-(3-phenyl ureido) phenyl) benzenesulfonamide (Nippon Soda Co.,Ltd. NKK1304, following general formula)

[Formula 1]



ii)Urea compound represented by the following general formula (Formula 2)

[Formula 2]



[0027] In the general formula (Formula 2), R represents an alkyl group or a alkoxy group, preferably an alkyl group and m represents an integer of 0 to 3, preferably 0 to 2, and more preferably 0 to 1. The number of carbon atoms of the alkyl group is, for example, 1 to 12, preferably 1 to 8, and more preferably 1 to 4.

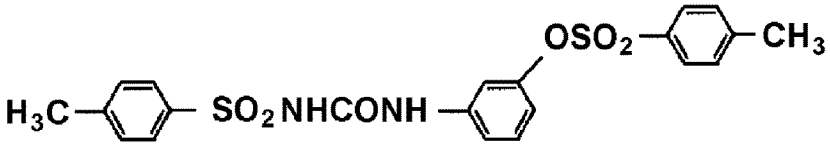
[0028] The position of R in the benzene ring in the general formula (Formula 2) may be the same or different, and is preferably 3-position, 4-position or 5-position, more preferably 4-position.

[0029] The example of the urea compound includes N, N'-di- [3- (p-toluenesulfonyloxy) phenyl] urea.

[0030]

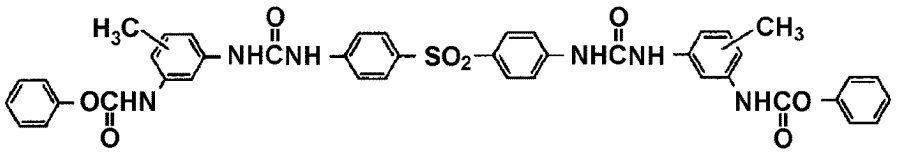
iii)3-(3-tosyl ureido) phenyl-p-toluene sulfonate (manufactured by BASF, DP201, following general formula)

[Formula 3]



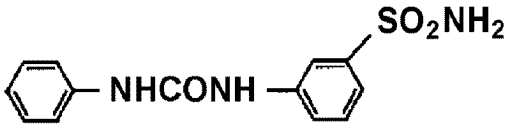
iv) Urea urethane compound (manufactured by Chemipro Kasei Kaisha, Ltd. UU, following general formula)

[Formula 4]



v)3-{[(phenylamino) Carbonyl] Amino} benzenesulfonamide (manufactured by Mitsubishi Chemical Corporation, SU727, following general formula)

[Formula 5]



[0031] In the present invention, a content (in solid) of the kraft lignin in the thermosensitive recording layer is preferably 0.5 to 20 weight %, more preferably 1 to 15 weight %, even more preferably 2 to 12 weight %.

[0032] When a color developing agent other than the kraft lignin is used in combination with the kraft lignin in the present invention, a weight ratio of the kraft lignin to the color developing agent other than the kraft lignin (the kraft lignin / the color developing agent other than the kraft lignin) is preferably 90 / 10 - 10/90, more preferably 80 / 20 - 20/80, still more preferably 60 / 40 - 25/75.

[0033] The thermosensitive recording medium of the present invention can use a conventional composition except for using the kraft lignin as the color developing agent.

[0034] That is, the thermosensitive recording medium of the present invention indispensably has a thermosensitive recording layer on a substrate, and optionally may further have a protective layer on the thermosensitive recording layer, and may have an undercoat layer between the substrate and the thermosensitive recording layer. Also the present invention may have a back-coating layer on the opposite side of the thermosensitive recording layer of the substrate. In addition, coating layer(s), appropriately configured according to the intended use, may be provided among these layers.

[0035] The substrate can be appropriately selected from conventionally known substrates, such as paper, recycled paper, synthetic paper, film, plastic film, foamed plastic film, and nonwoven fabric depending on the desired quality of the thermosensitive recording medium, and is not particularly limited. Further, a composite sheet obtained by combining these sheets may be used as the substrate.

[0036] The thermosensitive recording layer of the present invention essentially contains a leuco dye in addition to the above color developing agent, and optionally may further contain sensitizer, binder, pigment, crosslinking agent, stabilizer, and other ingredients.

[0037] 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>

[0038] 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>

[0039] 3-Diethylamino-6-methylfluorane, 3-diethylamino-6-methyl-7-anilinofluorane, 3-diethylamino-6-methyl-7-(o,p-dimethylanilino)fluorane, 3-diethylamino-6-methyl- 7-chlorofluoran, 3-diethylamino-6-methyl-7-(m-trifluoromethylanilino) fluorane, 3- diethylamino-6-methyl-7-(o-chloroanilino) fluorane, 3-diethylamino-6-methyl-7-(p- chloroanilino) fluor-

ane, 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-6-methyl-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-trifluoroanilino) 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-pyrolidino-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-xylamino)-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-p-(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>

[0040] 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>

[0041] 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>

[0042] 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'-nitroanilinolactam, 3,6-bis(diethylamino)fluorane-γ-(4'-nitro) anilinolactam, 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] -2-6-naphthoylethane, 1,1-bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-diacetylethane and bis-[2,2,2',2'-tetrakis-(p-dimethylaminophenyl)-ethenyl]-methylmalonic acid dimethyl ester.

[0043] As the sensitizer being usable for the present invention, diphenylsulfone, aliphatic acid amides such as stearic acid amide, palmitic acid amide and the like, benzyloxy naphthalene, 1,2-di-(3-methylphenoxy) ethane, di(p-methylbenzyl) oxalate agent, and the like may be listed as examples. These sensitizers may be used individually and as mixtures of at least two of them.

[0044] Among these sensitizers, diphenylsulfone is preferable in order to compensate for the color development (print density) when the kraft lignin is used as the color developing agent.

[0045] 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, pyrolidone-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, enzyme-modified 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.

[0046] 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.

[0047] 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.

[0048] 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.

[0049] In addition, UV absorption agents, such as benzophenone type and triazole type UV absorption agents, dispersion agents, defoaming agents, oxidation inhibitors, fluorescent dye and the like may also be used.

[0050] In the present invention, the color developing agent is used at a ratio of preferably 0.05 to 4.0 part by weight, more preferably 0.1 to 3.0 part by weight per 1 part by weight of the leuco dye.

[0051] The types and amounts of the sensitizer, the binder, the pigment, the crosslinking agent, the stabilizer, and the other optional ingredients may be determined according to the required performance and printability. Although the amounts of those are not particularly restricted, approximately, from 0.1 to 10 parts by weight of the sensitizer, from 0.5 to 50 parts by weight of the pigment, from 0.01 to 10 parts by weight of the stabilizer, and from 0.01 to 10 parts by weight of the other ingredients is ordinarily used. From 5 parts to 50 parts by weight in solid of the binder is appropriate per 100 part by weight of the thermosensitive recording layer(in solid). From 5 parts to 10 parts by weight in solid of a lubricant is appropriate per 100 part by weight of the thermosensitive recording layer(in solid).

[0052] The leuco dye, the color developing agent and the other materials added as needed are finely ground into particles with several microns or smaller in size, by using a grinder or a suitable emulsification device such as a ball mill, an attritor, a sand grinder and the like. The coating solutions are prepared by adding a binder and various additives thereto depending on the objective. Water, alcohol and the like can be used as the solvent for the coating solution and the content in solid of the coating solution is about from 20 to 40 weight %.

[0053] A protective layer can include the binder, the pigment, the crosslinking agent, and the other ingredients usable for above-mentioned thermosensitive recording layer within the range that does not impair the desired advantages. Preferably, the protective layer includes the binder and the pigment, and may also contain other ingredients such as a surfactant and a viscosity modifier, if needed.

[0054] As the binder used for the protective layer, the polyvinyl alcohols and the acrylic resin are preferable among the binders usable for above-mentioned thermosensitive recording layer

[0055] As the polyvinyl alcohols, completely saponified polyvinyl alcohol, carboxy-modified polyvinyl alcohol, diacetone-modified polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol are preferable.

[0056] As an element (excluding olefin) that can be copolymerized with (meth)acrylic acid of the acrylic resin includes alkyl acrylic acid resin, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, iso-butyl(meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate, octyl (meth)acrylate and the like, modified alkyl acrylic acid resin, such as alkyl acrylic acid resin that is modified with epoxy resin, silicone resin, styrene or these derivatives, (meth)acrylonitrile, acrylic ester and hydroxy-alkyl acrylic ester. Among these, alkyl acrylic acid resin, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, iso-butyl(meth)

acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate, octyl (meth)acrylate and the like, modified alkyl acrylic acid resin, such as alkyl acrylic acid resin that is modified with epoxy resin, silicone resin, styrene or these derivatives, (meth)acrylonitrile, acrylic ester and hydroxy-alkyl acrylic ester are preferred. Especially, (meth) acrylonitrile and/or methyl (meth)acrylate are preferred. The acrylic resin is preferably a non-core shell type acrylic resin.

[0057] In order to improve water resisting etc., the protective layer may contain a carboxyl group-containing resin as a binder, and may further contain a polyamine/polyamide resin.

[0058] Examples of this carboxyl group-containing resin include the above-mentioned carboxy-modified polyvinyl alcohol, acrylic resin, oxidized starch, carboxymethyl cellulose, etc.

[0059] 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.

[0060] In the present invention, when the protective layer contains a pigment, the water resistance and thermal printing run-ability of the thermosensitive recording medium are improved. For this reason, silica, kaolin, calcined kaolin, and aluminum hydroxide are preferable as the pigment, further, kaolin and aluminum hydroxide are more preferable.

[0061] When the protective layer of the present invention does not contain a pigment, the amount of the binder in the protective layer is usually 70 to 100% by weight, preferably 85 to 100% by weight, in terms of solid content.

[0062] On the other hand, when the protective layer contains a pigment, the total amount of the binder and the pigment in the protective layer is usually 80 to 100% by weight, and preferably 90 to 100% by weight, in solids content. And the amount of the binder is preferably about 30 to 300 parts by weight per 100 parts by weight of the pigment.

[0063] The amount of each component other than the binder, the crosslinking agent, and the pigment does not exceed 15% by weight respectively, and preferably 10% by weight respectively, in the protective layer.

[0064] Each coating layer provided arbitrarily other than the thermosensitive recording layer and the protective layer may contain the above-mentioned binders, pigments, crosslinking agents and other ingredients within the range that does not impair the desired advantages.

[0065] The coating method for the thermosensitive recording layer, protective layer, and other coating layers is not particularly limited, and any conventionally known method can be used, such as curtain coating, air knife coating, bar blade coating, rod blade coating, bent blade coating, bevel blade coating, roll coating, or spray coating.

[0066] The coating amounts of the thermosensitive recording layer, the protective layer and other coating layers are 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/m^2 and the coating amount in solid of the protective layer is in the range of from 1 to 5 g/m^2.

[0067] Furthermore, various technologies known in the thermosensitive recording medium field, such as a flattening treatment such as super calendaring and the like

[Examples]

[0068] 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.

[0069] Each dispersion and coating solution were prepared as follows.

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

[Undercoat layer coating solution]

[0071]

Calcined kaolin (BASF Co.: Ansilex 90)	100.0 parts
Styrene-butadiene copolymer latex (Zeon Corporation, ST5526, solid content: 48%)	10.0 parts
Water	50.0 parts

[0072] Kraft lignin dispersions (liquids A and B) were prepared by wet grinding with a sand grinder until the average particle size was 3.0 μm. Note that the kraft lignin used in liquid A of the kraft lignin dispersion had undergone a black liquor oxidation process in the manufacturing process, while liquid B had not undergone an oxidation process.

Kraft lignin dispersion-liquid (liquid A)

[0073]

Kraft lignin (manufactured by West Fraser, Amallin A, a product name,), hydrogen sulfide content: 68 ppm, lignin content: 93%, density: 0.45 g/cm^3, hereinafter referred to as "Kraft Lignin 1".	6.0 parts
Completely saponified polyvinyl alcohol aqueous solution (KURARAY CO., LTD., product name :PVA117, solid content 10 %)	5.0 parts
Water	1.5 parts

Kraft lignin dispersion-liquid (liquid B)

[0074]

Kraft lignin (manufactured by Meadwestbaco, Indulin AT, a product name,), hydrogen sulfide content: 1100 ppm, lignin content: 87%, density: 0.35 g/cm^3, hereinafter referred to as "Kraft Lignin 2".	6.0 parts
Completely saponified polyvinyl alcohol aqueous solution (KURARAY CO., LTD., PVA117, solid content 10 %)	5.0 parts
Water	1.5 parts

[0075] Next, each of color developing agent dispersion (A1-A4 liquid), leuco dye dispersion (B liquid), and sensitizer dispersion (C liquid) having the following blend was wet ground separately by a sand grinder to an average particle size of 0.5 μm.

Color developing agent dispersion (A1 liquid)

[0076]

4-hydroxy-4'-isopropoxy diphenyl sulfone (manufactured by Mitsubishi Chemical Corporation, product name:NYDS)	6.0 parts
Completely saponified polyvinyl alcohol aqueous solution (PVA117)	5.0 parts
Water	1.5 parts

Color developing agent dispersion (A2 liquid)

[0077]

N, N'-di- [3- (p-toluenesulfonyloxy) phenyl] urea (hereinafter referred to as "urea compound 1")	6.0 parts
Completely saponified polyvinyl alcohol aqueous solution (PVA117)	5.0 parts
Water	1.5 parts

Color developing agent dispersion (A3 liquid)

[0078]

4,4'-dihydroxy diphenylsulfone (manufactured by Konishi Chemical Ind. Co., Ltd., product name:44BPS)	6.0 parts
Completely saponified polyvinyl alcohol aqueous solution (PVA117)	5.0 parts
Water	1.5 parts

Color developing agent dispersion (A4 liquid)

[0079]

N-[2-(3-phenylureido)phenyl]benzenesulfonamide(Nippon Soda Co., Ltd. product name: NKK1304)	6.0 parts
Completely saponified polyvinyl alcohol aqueous solution (PVA117)	5.0 parts

(continued)

Water	1.5 parts

Leuco dye dispersion (B liquid)

[0080]

3-di buthylamino-6-methyl-7-anilinofluoran (Yamamoto Chemicals, Inc., product name: ODB-2)	6.0 parts
Completely saponified polyvinyl alcohol aqueous solution (PVA117)	5.0 parts
Water	1.5 parts

Sensitizer dispersion (C liquid)

[0081]

Diphenylsulfone (manufactured by Volant, product name:DPS)	6.0 parts
Completely saponified polyvinyl alcohol aqueous solution (PVA117)	5.0 parts
Water	1.5 parts

[0082] Next, each dispersion was mixed in the following percentage, and stirred thoroughly to prepare a coating material for thermosensitive recording layer 1 and 2.

<Coating material for thermosensitive recording layer 1>

[0083]

Kraft lignin dispersion-liquid (liquid A)	1.5 parts
Leuco dye dispersion (B liquid)	1.05 parts
Sensitizer dispersion (C liquid)	1.2 parts
Silica dispersion(Mizusawa Industrial Chemicals, Ltd. MIZUKASIL P-537, solid content 25%)	5.0 parts
Zinc stearate (Chukyo Yushi Co., Ltd.: Hydrin L536)	5.0 parts
Completely saponified polyvinyl alcohol aqueous solution (PVA117)	20.0 parts

<Coating material for thermosensitive recording layer 2>

[0084]

Kraft lignin dispersion-liquid (liquid A)	0.75 parts
Color developing agent dispersion (A1 liquid)	0.75 parts
Leuco dye dispersion (B liquid)	1.05 parts
Sensitizer dispersion (C liquid)	1.2 parts
Silica dispersion(MIZUKASIL P-537)	5.0 parts
Zinc stearate (Hydrin L536)	5.0 parts
Completely saponified polyvinyl alcohol aqueous solution (PVA117)	20.0 parts

[Example 1]

[0085] The undercoat layer coating solution was applied on one side of a substrate (groundwood free paper with a basis weight of 47 g/m^2) by using a bent blade coater with a coating amount (in solid) of 10.0 g/m^2, and was dried to prepare an undercoated paper.

[0086] The thermosensitive recording layer coating solution 1(kraft lignin in the thermosensitive recording layer: 10.0%, color developing agent /leuco dye: 1.43) was applied on the undercoat layer of the undercoated paper by using a rod blade

coater with a coating amount (in solid) of 6.0 g/m^2 and was dried and super calendared so that the smoothness was 500-1000 seconds to prepare a thermosensitive recording layer coated paper.

[Example 2]

[0087] 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(kraft lignin in the thermosensitive recording layer: 5.0%, color developing agent /leuco dye: 1.43.

[Example 3]

[0088] A thermosensitive recording medium was prepared in the same manner as described in Example 2 with the exception of changing the color developing agent dispersion (A1 liquid) of the thermosensitive recording layer coating solution 2 to the color developing agent dispersion (A2 liquid).

[Example 4]

[0089] A thermosensitive recording medium was prepared in the same manner as described in Example 2 with the exception of changing the color developing agent dispersion (A1 liquid) of the thermosensitive recording layer coating solution 2 to the color developing agent dispersion (A3 liquid).

[Example 5]

[0090] A thermosensitive recording medium was prepared in the same manner as described in Example 2 with the exception of changing the color developing agent dispersion (A1 liquid) of the thermosensitive recording layer coating solution 2 to the color developing agent dispersion (A4 liquid).

[Comparative Example 1]

[0091] A thermosensitive recording medium was prepared in the same manner as described in Example 1 with the exception of changing the Kraft lignin dispersion-liquid (liquid A) of the thermosensitive recording layer coating solution 1 to the Kraft lignin dispersion-liquid (liquid B)

[Comparative Example 2]

[0092] A thermosensitive recording medium was prepared in the same manner as described in Example 2 with the exception of changing the Kraft lignin dispersion-liquid (liquid A) of the thermosensitive recording layer coating solution 2 to the Kraft lignin dispersion-liquid (liquid B)

[Comparative Example 3]

[0093] A thermosensitive recording medium was prepared in the same manner as described in Example 3 with the exception of changing the Kraft lignin dispersion-liquid (liquid A) of the thermosensitive recording layer coating solution 2 to the Kraft lignin dispersion-liquid (liquid B)

[Comparative Example 4]

[0094] A thermosensitive recording medium was prepared in the same manner as described in Example 4 with the exception of changing the Kraft lignin dispersion-liquid (liquid A) of the thermosensitive recording layer coating solution 2 to the Kraft lignin dispersion-liquid (liquid B)

[Comparative Example 5]

[0095] A thermosensitive recording medium was prepared in the same manner as described in Example 5 with the exception of changing the Kraft lignin dispersion-liquid (liquid A) of the thermosensitive recording layer coating solution 2 to the Kraft lignin dispersion-liquid (liquid B)

[0096] The prepared thermosensitive recording media were evaluated as below.

<Color developing property (Recorded density)>

[0097] A checkerboard pattern was printed on the prepared thermosensitive recording medium by using a a thermal printer of Okura Engineering Co., Ltd. (TH-PMD) at applied energy of 0.27 mJ/dot and 0.35 mJ/dot, printing speed of 50mm/sec.

[0098] The density of the printed portion was measured by using Macbeth Densitometer (RD-914, with Amber filter). Table 1 below shows the density of the printed portion at each applied energy.

< Head corrosiveness >

[0099] A checkerboard pattern was printed on the prepared thermosensitive recording medium by using a a thermal printer of Okura Engineering Co., Ltd. (TH-PMD) at applied energy of 0.35 mJ/dot and printing speed of 50mm/sec, under the conditions of 23°C x 50% RH and 40°C x 90% RH.

[0100] After printing for 50 km, it was confirmed whether or not white streaks occurred in the image due to poor heating caused by corrosion of the thermal head, and corrosiveness was evaluated according to the following criteria.

Good: No corrosion occurred
Poor: Corrosion occurred

[0101] The evaluated results are shown in Table below. The content of the color developing agent indicates the content (solid content, % by weight) of the color developing agent in the thermosensitive recording layer.

[Table 1]

			Example 1	Example 2	Example 3	Example 4	Example 5	Comp-Example 1	Comp-Example 2	Comp-Example 3	Comp-Example 4	Comp-Example 5
Thermosensitive recording layer	Kraft lignin		Kraft lignin 1					Kraft lignin 2				
	Properties of Kraft Lignin	Hydrogen sulfide content(ppm)	68					1100				
		Lignin content (weight %)	93					87				
		Density(g/cm3)	0.45					0.35				
	Content of kraft lignin(weight %)		10.0	5.0	5.0	5.0	5.0	10.0	5.0	5.0	5.0	5.0
	Content of other color developing agent (weight %)	4-hydroxy-4'-isopropoxy diphenyl sulfone	–	5.0	–	–	–	–	5.0	–	–	–
		urea compound 1	–	–	5.0	–	–	–	–	5.0	–	–
		4,4BPS	–	–	–	5.0	–	–	–	–	5.0	–
		NKK1304	–	–	–	–	5.0	–	–	–	–	5.0
Color developing property (Recorded density)		0.27 (mJ/dot)	0.25	1.00	0.95	0.97	0.84	0.30	1.01	0.96	0.98	0.84
		0.35 (mJ/dot)	0.30	1.11	1.07	1.08	1.03	0.35	1.13	1.07	1.07	1.04
Head corrosiveness		23℃×50%Rh	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
		40℃×90%Rh	Good	Good	Good	Good	Good	Poor	Poor	Poor	Poor	Poor

[0102] From this table, it is apparent that the thermosensitive recording medium using kraft lignin containing almost no hydrogen sulfide or containing only 400 ppm at most is excellent in head corrosiveness.

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,
wherein the thermosensitive recording layer contains a kraft lignin as the electron accepting color developing agent, and the kraft lignin contains almost no hydrogen sulfide or contains only 400 ppm at most.

2. The thermosensitive recording medium according to claim 1, wherein a content of a lignin in the kraft lignin is 90% or more.

3. The thermosensitive recording medium according to claim 1, wherein a density of the kraft lignin is 0.4-0.5 g/cm^3.

4. The thermosensitive recording medium according to claim 1, wherein a content (in solid) of the kraft lignin in the thermosensitive recording layer is 0.5 to 20 weight %.

5. The thermosensitive recording medium according to any one of claim 1 to 4, wherein the thermosensitive recording layer contains an electron accepting color developing agent other than the kraft lignin, and the electron accepting color developing agent other than the kraft lignin is 4,4'-dihydroxy diphenyl sulfone, 4-hydroxy-4'-isopropoxy diphenyl sulfone, or a color developing agent having urea structure(- NHCONH-).

6. The thermosensitive recording medium according to claim 5, wherein a weight ratio of the color developing agent to the electron donating leuco dye is 0.05 to 4.0.

7. A method for reducing corrosion of a thermal head when printing on a thermosensitive recording medium which has a thermosensitive recording layer containing a kraft lignin, the method comprising the step of printing on the thermosensitive recording medium according to any one of claims 1 to 4.

8. A method for reducing corrosion of a thermal head when printing on a thermosensitive recording medium which has a thermosensitive recording layer containing a kraft lignin, the method comprising the step of printing on the thermosensitive recording medium according to claim 5.

9. A method for reducing corrosion of a thermal head when printing on a thermosensitive recording medium which has a thermosensitive recording layer containing a kraft lignin, the method comprising the step of printing on the thermosensitive recording medium according to claim 6.

Amended claims under Art. 19.1 PCT

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,
   wherein the thermosensitive recording layer contains a kraft lignin as the electron accepting color developing agent, and the kraft lignin does not contain hydrogen sulfide or contains only 400 ppm at most.

2. The thermosensitive recording medium according to claim 1, wherein a content of a lignin in the kraft lignin is 90% or more.

3. The thermosensitive recording medium according to claim 1, wherein a density of the kraft lignin is 0.4-0.5 g/cm^3.

4. The thermosensitive recording medium according to claim 1, wherein a content (in solid) of the kraft lignin in the thermosensitive recording layer is 0.5 to 20 weight %.

5. The thermosensitive recording medium according to any one of claim 1 to 4, wherein the thermosensitive recording layer contains an electron accepting color developing agent other than the kraft lignin, and the electron accepting color developing agent other than the kraft lignin is 4,4'-dihydroxy diphenyl sulfone, 4-hydroxy-4'-isopropoxy diphenyl sulfone, or a color developing agent having urea structure(-NHCONH-).

6. The thermosensitive recording medium according to claim 5, wherein a weight ratio of the color developing agent to the electron donating leuco dye is 0.05 to 4.0.

7. A method for reducing corrosion of a thermal head when printing on a thermosensitive recording medium which has a thermosensitive recording layer containing a kraft lignin, the method comprising the step of printing on the thermosensitive recording medium according to any one of claims 1 to 4.

8. A method for reducing corrosion of a thermal head when printing on a thermosensitive recording medium which has a thermosensitive recording layer containing a kraft lignin, the method comprising the step of printing on the thermosensitive recording medium according to claim 5.

9. A method for reducing corrosion of a thermal head when printing on a thermosensitive recording medium which has a thermosensitive recording layer containing a kraft lignin, the method comprising the step of printing on the thermo-

sensitive recording medium according to claim 6.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2024/008233

A. CLASSIFICATION OF SUBJECT MATTER

B41M 5/333(2006.01)i; ***B41M 5/337***(2006.01)i
FI: B41M5/333 220; B41M5/337 214

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)

B41M5/333; B41M5/337

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 1971-2024
Registered utility model specifications of Japan 1996-2024
Published registered utility model applications of Japan 1994-2024

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2023/276498 A1 (NICCA CHEMICAL CO., LTD.) 18 January 2023 (2023-01-18) claims, paragraphs [0048]-[0082]	1-9
A	JP 2020-104274 A (NIPPON PAPER INDUSTRIES CO., LTD.) 09 July 2020 (2020-07-09) claims, paragraphs [0031]-[0051]	1-9

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 April 2024	**23 April 2024**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/008233

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2023/276498 A1	18 January 2023	JP 2023-6125 A	
JP 2020-104274 A	09 July 2020	(Family: none)	

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2002301873 A **[0025]**
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