(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 858 633 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
04.08.2021 Bulletin 2021/31

(21) Application number: **19864836.2**

(22) Date of filing: **24.09.2019**

(51) Int Cl.:
B41M 5/42 *(2006.01)* ***B41M 5/323*** *(2006.01)*
B41M 5/44 *(2006.01)*

(86) International application number:
PCT/JP2019/037329

(87) International publication number:
WO 2020/067045 (02.04.2020 Gazette 2020/14)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **26.09.2018 JP 2018180816**

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

(57) The present disclosure provides a heat-sensitive recording material comprising an intermediate layer, an undercoat layer, and a heat-sensitive recording layer in this order on a support, the undercoat layer containing hollow particles and a polyvinyl alcohol resin, the heat-sensitive recording layer containing a leuco dye and a developer, wherein the intermediate layer contains a cross-linking agent capable of cross-linking to the polyvinyl alcohol resin, and the hollow particles have a hollow ratio of 60% or more; and a method for producing a heat-sensitive recording material comprising the following steps (A) to (C):

(A) applying, to a support, a coating liquid containing a cross-linking agent capable of cross-linking to a polyvinyl alcohol resin;

(B) applying, to the coating liquid applied in step (A), a coating liquid for an undercoat layer containing hollow particles having a hollow ratio of 60% or more and a polyvinyl alcohol resin, followed by drying; and

(C) applying a coating liquid for a heat-sensitive layer containing a leuco dye and a developer to the undercoat layer, followed by drying.

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Description

Technical Field

[0001] The present invention relates to a heat-sensitive recording material using a color-forming reaction of a leuco dye and a developer.

Background Art

[0002] Heat-sensitive recording materials that make use of a color-forming reaction of a leuco dye with a developer, which comes into contact with the leuco dye when heated to develop the color of the leuco dye, so that both coloring materials are melted and brought into contact with each other by heating, thus producing a color image, are widely known. Such heat-sensitive recording materials are relatively inexpensive, and recording devices for these materials are compact and easy to maintain. Therefore, such heat-sensitive recording materials are used as recording media for fax machines, printers, and other applications in a wide variety of fields.

[0003] However, with the expansion of applications, the required performance and quality are diversifying. For example, there is demand for a heat-sensitive recording material that has high image quality and excellent medium energy development density.

[0004] As a method for obtaining a heat-sensitive recording material with high sensitivity, high whiteness, and high print pixel reproducibility, there has been proposed a method comprising providing an intermediate layer containing an inorganic pigment or an organic pigment between a support and a heat-sensitive recording layer, and using a latex having the property of gelation at a certain temperature (temperature-sensitive gelation property) as the binder of the intermediate layer (PTL 1). It is considered that because of having a gelation property by applying heat, gelation occurs before the formation of the layer upon drying; this prevents pigments from dense filling, thus making the coating layer bulky, and exhibiting a heat insulation effect.

Citation List

Patent Literature

[0005] PTL 1: Japanese Patent No. 3565564

Summary of Invention

Technical Problem

[0006] An object of the present invention is to provide a heat-sensitive recording material that provides high image quality and excellent medium energy development density.

Solution to Problem

[0007] With respect to an undercoat layer containing hollow particles with a high hollow ratio, a coating liquid is gelatinized using a cross-linking reaction of a polyvinyl alcohol resin before the undercoat layer is dried, and the movement of the hollow particles with a high buoyancy and a high hollow ratio to the surface layer is suppressed. By suppressing the movement of highly hollow particles to the surface layer, the hollow particles are uniformly distributed in the undercoat layer to improve the smoothness, thereby solving the above problem, and thus accomplishing the present invention. Specifically, the present invention relates to the following heat-sensitive recording materials.

Item 1. A heat-sensitive recording material comprising an intermediate layer, an undercoat layer, and a heat-sensitive recording layer in this order on a support,
the undercoat layer containing hollow particles and a polyvinyl alcohol resin,
the heat-sensitive recording layer containing a leuco dye and a developer,
wherein the intermediate layer contains a cross-linking agent capable of cross-linking to the polyvinyl alcohol resin, and the hollow particles have a hollow ratio of 60% or more.

Item 2. The heat-sensitive recording material according to Item 1, wherein the cross-linking agent contains a boron compound.

Item 3. The heat-sensitive recording material according to Item 1, wherein the cross-linking agent contains at least one compound selected from the group consisting of zirconium nitrate, zirconium chloride, and zirconium hydroxychloride.

Item 4. The heat-sensitive recording material according to any one of Items 1 to 3, wherein the hollow particles have a hollow ratio of 70% or more.

Item. 5 The heat-sensitive recording material according to any one of Items 1 to 4, wherein the polyvinyl alcohol resin is crosslinked.

Item 6. A method for producing a heat-sensitive recording material comprising the following steps (A) to (C):

(A) applying, to a support, a coating liquid containing a cross-linking agent capable of cross-linking to a polyvinyl alcohol resin;
(B) applying, to the coating liquid applied in step (A), a coating liquid for an undercoat layer containing hollow particles having a hollow ratio of 60% or more and a polyvinyl alcohol resin, followed by drying; and
(C) applying a coating liquid for a heat-sensitive layer containing a leuco dye and a developer to the undercoat layer, followed by drying.

Item. 7 A method for producing a heat-sensitive recording material comprising the following steps (a) and (b):

(a) applying, to a support, a coating liquid containing a cross-linking agent capable of cross-linking to a polyvinyl alcohol resin; and
(b) simultaneously applying, to the coating liquid applied in step (a), a coating liquid for an undercoat layer containing hollow particles having a hollow ratio of 60% or more and a polyvinyl alcohol resin, and a coating liquid for a heat-sensitive recording layer containing a leuco dye and a developer, followed by drying.

Item 8. The production method according to Item 6, wherein the coating liquid for an undercoat layer is applied by a curtain coating method.

Advantageous Effects of Invention

[0008] The heat-sensitive recording material according to the present invention provides high image quality and excellent medium energy development density.

Description of Embodiments

[0009] In the present specification, the expression "comprise" or "contain" includes the concepts of "comprising," "consisting essentially of," and "consisting of."

[0010] The "average particle diameter" in the present invention refers to a median diameter based on volume, as measured by laser diffractometry. More simply, the average particle diameter may be shown according to the average value of particle diameters of 10 particles, the particle diameters being measured from the image of each particle with an electron microscope (SEM image).

[0011] The present invention is directed to a heat-sensitive recording material comprising, in this order, an intermediate layer, an undercoat layer containing hollow particles and a polyvinyl alcohol resin, and a heat-sensitive recording layer containing a leuco dye and a developer on a support, wherein the intermediate layer contains a cross-linking agent capable of cross-linking to the polyvinyl alcohol resin, and the hollow particles have a hollow ratio of 60% or more.

Support

[0012] The support in the present invention is not particularly limited in type, shape, dimension, or the like. For example, high-quality paper (acid paper, neutral paper), medium-quality paper, coated paper, art paper, cast-coated paper, glassine paper, resin laminate paper, polyolefin synthetic paper, synthetic fiber paper, nonwoven fabrics, synthetic resin films, various transparent supports, or the like can be appropriately selected and used. The thickness of the support is not particularly limited, and is usually about 20 to 200 μm. The density of the support is not particularly limited, and is preferably about 0.60 to 0.85 g/cm^3.

Intermediate Layer

[0013] The heat-sensitive recording material of the present invention comprises, between the support and the undercoat layer, an intermediate layer containing a cross-linking agent that is cross-linkable with a polyvinyl alcohol resin. Having this intermediate layer allows the gelation of the coating liquid by the cross-linking reaction of the polyvinyl alcohol resin before the undercoat layer dries, thereby inhibiting the movement of the hollow particles having a high hollow ratio and high buoyancy to the surface layer. As a result, the hollow particles are uniformly distributed in the undercoat layer to improve the smoothness, thus improving the image quality and the medium energy development density.

[0014] Examples of cross-linking agents include aldehyde compounds such as glyoxal; polyamine compounds such as polyethyleneimine; epoxy compounds, polyamide resins, melamine resins, glyoxylic acid salts, dimethylolurea compounds, aziridine compounds, and block isocyanate compounds; inorganic compounds such as ammonium persulfate, ferric chloride, magnesium chloride, soda tetraborate, and potassium tetraborate; boron compounds such as borax, boric acid, boric acid triesters, and boron polymers; zirconium compounds such as zirconium nitrate, zirconium chloride, and zirconium hydroxychloride; hydrazide compounds; glyoxylates; and the like. In the present invention, of the cross-linking agents, it is preferable to use boron compounds, zirconium nitrate, zirconium chloride, and zirconium hydroxychloride. These cross-linking agents can be used alone, or in a combination of two or more types. The amount of the cross-linking agent used is preferably in the range of about 2.0 to 15.0 parts by mass, per 100 parts by mass of the total solids content of the polyvinyl alcohol resin.

[0015] The intermediate layer is formed by mixing and stirring a cross-linking agent or the like, typically using water as a medium to prepare a coating liquid for an intermediate layer, and applying the coating liquid to a support. The amount of the coating liquid for an intermediate layer to be applied is not particularly limited, and is preferably about 0.05 to 2.0 g/m^2, and more preferably 0.1 to 1.0 g/m^2 in terms of dry weight.

Undercoat Layer

[0016] The heat-sensitive recording material of the present invention comprises an undercoat layer between an intermediate layer and a heat-sensitive recording layer, and the undercoat layer contains a polyvinyl alcohol resin and hollow particles having a hollow ratio of 60% or more. Having this undercoat layer can increase recording sensitivity. Further, the presence of the hollow particles improves cushioning properties, which makes printed images clearer, and increases the medium energy development density.

[0017] Examples of the hollow particles include hollow plastic particles. Examples of the hollow plastic particles include conventionally known hollow plastic particles comprising, as a film material, a polymer having a crosslinked structure, such as an acrylic resin (e.g., an acrylic resin containing acrylonitrile as a component), a styrene resin, a vinylidene chloride resin, or the like. The hollow ratio of the hollow particles is preferably 65% or more, and more preferably 70% or more.

[0018] The hollow ratio of the hollow particles is determined by measuring the true specific gravity according to the IPA method, and using the true specific gravity value as follows.

(1) Sample Pretreatment

[0019] A sample was dried at 60°C around the clock.

(2) Reagent

[0020] Isopropyl alcohol (IPA: extra pure reagent)

(3) Measurement method

[0021]

- A volumetric flask was weighed (W1).
- About 0.5 g of the dried sample was weighed in the volumetric flask (W2).
- About 50 mg of IPA was added thereto, and the volumetric flask was fully shaken to completely remove air outside the capsule.
- IPA was added to the marked line, and the volumetric flask was weighed (W3).
- As a blank, IPA alone was added to the marked line of the volumetric flask (W4).

(4) Calculation of true specific gravity

[0022]

$$\text{True specific gravity} = (W2-W1)\times((W4-W1)/100)\}/\{(W4-W1)-(W3-W2)\}$$

(5) Calculation of hollow ratio

[0023]

$$\text{Hollow ratio}(\%)=\{1-1/(1.1/\text{true specific gravity})\}\times 100$$

[0024] The hollow ratio is a value that can be obtained according to the following formula: (d^3/D^3) X100. In the formula, d represents the inner diameter of the hollow plastic particles, and D represents the outer diameter of the hollow plastic particles. The hollow plastic particles preferably have an average particle diameter of about 0.5 to 10 μm. The amount of hollow plastic particles can be selected from a broad range, and is typically preferably about 2 to 90 mass%, and more preferably about 5 to 70 mass%, based on the total solids content of the undercoat layer.

[0025] The undercoat layer can also contain an oil-absorbing pigment with an oil absorption of 70 ml/100 g or more, and particularly about 80 to 150 ml/100 g; and/or thermal expansion particles. In particular, containing an oil-absorbing pigment can enhance the effect of inhibiting the adhesion of the residue to a thermal head, and is thus preferable. The oil absorption referred to herein is a value determined in accordance with JIS K 5101.

[0026] The oil-absorbing pigment may be any of various types of oil-absorbing pigments. Specific examples include inorganic pigments such as calcined kaolin, amorphous silica, light calcium carbonate, and talc. Such oil-absorbing pigments preferably have an average primary particle diameter of about 0.01 to 5 μm, and particularly about 0.02 to 3 μm. The amount of the oil-absorbing pigment can be selected from a broad range. In general, the amount is preferably about 2 to 95 mass%, and more preferably about 5 to 90 mass%, based on the total solids content of the undercoat layer.

[0027] The undercoat layer is formed by mixing and stirring hollow plastic particles, an oil-absorbing pigment, a binder, auxiliary agents, and the like typically using water as a medium to prepare a coating liquid for an undercoat layer, applying the coating liquid to a support, and drying. The amount of the coating liquid for an undercoat layer to be applied is not particularly limited, and is preferably about 3 to 20 g/m^2, and more preferably about 5 to 12 g/m^2, in terms of dry weight.

[0028] The polyvinyl alcohol resin is used as a binder. Examples of the polyvinyl alcohol resin include polyvinyl alcohol, fully saponified polyvinyl alcohol, partially saponified polyvinyl alcohol, diacetone modified polyvinyl alcohol, acetoacetyl modified polyvinyl alcohol, carboxy modified polyvinyl alcohol, silicon modified polyvinyl alcohol, and the like. The polyvinyl alcohol resin is present in a crosslinked state due to the cross-linking reaction by the cross-linking agent contained in the intermediate layer. The amount of polyvinyl alcohol resin can be selected from a broad range, and is typically preferably about 0.5 to 20 mass%, and more preferably about 1.0 to 15 mass% of the total solids content of the undercoat layer.

[0029] In the present invention, the polyvinyl alcohol resin is used as a binder in the undercoat layer; however, various known binders may be used in combination as needed in a range that does not cause an impairment. Such a binder can be suitably selected from binders that can be used in the heat-sensitive recording layer. Preferable examples of binders include oxidized starch, starch-vinyl acetate graft copolymers, styrene-butadiene latexes, and the like.

Heat-Sensitive Recording Layer

[0030] The heat-sensitive recording layer of the heat-sensitive recording material of the present invention may contain any of various colorless or pale-colored known leuco dyes. Specific examples of such leuco dyes are described below.

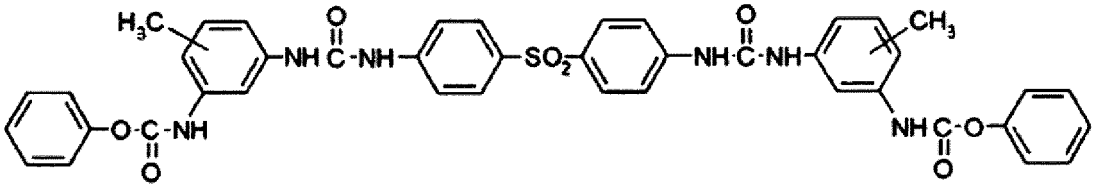
[0031] Specific examples of leuco dyes include dyes capable of developing blue color, such as 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3-(4-diethylamino-2-methylphenyl)-3-(4-dimethylaminophenyl)-6-dimethylaminophthalide, and fluoran; dyes capable of developing green color, such as 3-(N-ethyl-N-p-tolyl)amino-7-N-methylanilinofluoran, 3-diethylamino-7-anilinofluoran, 3-diethylamino-7-dibenzylaminofluoran, and rhodamine B-anilinolactam; dyes capable of developing red color, such as 3,6-bis(diethylamino)fluoran-γ-anilinolactam, 3-cyclohexylamino-6-chlorofluoran, 3-diethylamino-6-methyl-7-chlorofluoran, and 3-diethylamino-7-chlorofluoran; dyes capable of developing black color, such as 3-(N-ethyl-N-isoamyl)amino-6-methyl-7-anilinofluoran, 3-(N-methyl-N-cyclohexyl)amino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-di(n-butyl)amino-6-methyl-7-anilinofluoran, 3-di(n-pentyl)amino-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isoamylamino)-6-methyl-7-alininofluoran, 3-diethylamino-7-(m-trifluoromethylanilino)fluoran, 3-(N-isoamyl-N-ethylamino)-7-(o-chloroanilino)fluoran, 3-(N-ethyl-N-2-tetrahydrofurfur-

ylamino)-6-methyl-7-anilinofluoran, 3-(N-n-hexyl-N-ethylamino)-6-methyl-7-anilinofluoran, 3-[N-(3-ethoxypropyl)-N-ethylamino]-6-methyl-7-anilinofluoran, 3-[N-(3-ethoxypropyl)-N-methylamino]-6-methyl-7-anilinofluoran, 3-diethylamino-7-(2-chloroanilino)fluoran, 3-di(n-butylamino)-7-(2-chloroanilino)fluoran, 4,4'-bis-dimethylaminobenzhydrinbenzyl ether, N-2,4,5-trichlorophenylleucooramine, 3-diethylamino-7-butylaminofluoran, 3-ethyl-tolylamino-6-methyl-7-anilinofluoran, 3-cyclohexyl-methylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-chloro-7-(β-ethoxyethyl)aminofluoran, 3-diethylamino-6-chloro-7-(γ-chloropropyl)aminofluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-(N-isoamyl-N-ethylamino)-6-methyl-7-anilinofluoran, 3-dibutylamino-7-chloroanilinofluoran, 3-diethylamino-7-(o-chlorophenylamino)fluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-(p-toluidino)fluoran, 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilinofluoran, 3-diethylamino-6-chloro-7-anilinofluoran, 3-dimethylamino-6-methyl-7-anilinofluoran, 3-pyrrolidino-6-methyl-7-anilinofluoran, 3-piperidino-6-methyl-7-anilinofluoran, 2,2-bis{(4-[6'-(N-cyclohexyl-N-methylamino)-3'-methylspiro[phthalide-3,9'-xanthen-2'-ylamino]phenyl)}propane, and 3-diethylamino-7-(3'-trifluoromethylphenyl)aminofluoran; dyes having absorption wavelengths in the near-infrared region, such as 3,3-bis[1-(4-methoxyphenyl)-1-(4-dimethylaminophenyl)ethylen-2-yl]-4,5,6,7-tetrachlorophthalide, 3,3-bis[1-(4-methoxyphenyl)-1-(4-pyrrolidinophenyl)ethylen-2-yl]-4,5,6,7-tetrachlorophthalide, 3-p-(p-dimethylaminoanilino)anilino-6-methyl-7-chlorofluoran, 3-p-(p-chloroanilino)anilino-6-methyl-7-chlorofluoran, and 3,6-bis(dimethylamino)fluorene-9-spiro-3'-(6'-dimethylamino)phthalide; and the like. Usable leuco dyes are, of course, not limited to these compounds, and two or more of such compounds can be used in combination as necessary.

[0032] The amount of the leuco dye is not particularly limited, and is preferably about 3 to 30 mass%, more preferably about 5 to 25 mass%, and even more preferably about 7 to 20 mass%, based on the total solids content of the heat-sensitive recording layer. A leuco dye content of 3 mass% or more can enhance color development ability, and thus improve print density; whereas a leuco dye content of 30 mass% or less can enhance heat resistance.

[0033] Specific examples of developers include phenolic compounds such as 4-tert-butylphenol, 4-acetylphenol, 4-tert-octylphenol, 4,4'-sec-butylidenediphenol, 4-phenylphenol, 4,4'-dihydroxydiphenylmethane, 4,4'-isopropylidenediphenol, 4,4'-cyclohexylidenediphenyl, 4,4'-cyclohexylidenediphenol, 1,1-bis(4-hydroxyphenyl)-ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 4,4'-bis(p-tolylsulfonylaminocarbonylamino)diphenylmethane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 2,2'-bis[4-(4-hydroxyphenyl)phenoxy]diethyl ether, 4,4'-dihydroxydiphenylsulfide, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 4,4'-dihydroxydiphenylsulfone, 2,4'-dihydroxydiphenylsulfone, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, 2,4'-dihydroxydiphenylsulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, 4-hydroxy-4'-n-propoxydiphenylsulfone, 4-hydroxy-4'-allyloxydiphenylsulfone, 4-hydroxy-4'-benzyloxydiphenylsulfone, 3,3'-diallyl-4,4'-dihydroxydiphenylsulfone, butyl bis(p-hydroxyphenyl)acetate, methyl bis(p-hydroxyphenyl)acetate, hydroquinone monobenzyl ether, bis(3-allyl-4-hydroxyphenyl)sulfone, 4-hydroxy-4'-methyldiphenylsulfone, 4-allyloxy-4'-hydroxydiphenylsulfone, 3,4-dihydroxyphenyl-4'-methylphenylsulfone, 4-hydroxybenzophenone, dimethyl 4-hydroxyphthalate, methyl 4-hydroxybenzoate, propyl 4-hydroxybenzoate, sec-butyl 4-hydroxybenzoate, phenyl 4-hydroxybenzoate, benzyl 4-hydroxybenzoate, 4-hydroxybenzoic acid benzyl ester, tolyl 4-hydroxybenzoate, chlorophenyl 4-hydroxybenzoate, and 4,4'-dihydroxydiphenyl ether; aromatic carboxylic acids such as benzoic acid, p-chlorobenzoic acid, p-tert-butylbenzoic acid, tolylchlorobenzoic acid, terephthalic acid, salicylic acid, 3-tert-butylsalicylic acid, 3-isopropylsalicylic acid, 3-benzylsalicylic acid, 3-(α-methylbenzyl)salicylic acid, 3,5-di-tert-butylsalicylic acid, 4-[2-(p-methoxyphenoxy)ethyloxy]salicylic acid, 4-[3-(p-tolylsulfonyl)propyloxy]salicylic acid, 5-[p-(2-p-methoxyphenoxyethoxy)cumyl]salicylic acid, and zinc 4-{3-(p-tolylsulfonyl)propyloxy]salicylate; salts of these phenolic compounds or aromatic carboxylic acids with, for example, polyvalent metals such as zinc, magnesium, aluminum, calcium, titanium, manganese, tin, and nickel; antipyrine complex of zinc thiocyanate; organic acidic substances such as composite zinc salts of terephthalic aldehyde acid and other aromatic carboxylic acids; urea compounds such as N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea, N-p-toluenesulfonyl-N'-p-butoxycarbonylphenylurea, N-p-tolylsulfonyl-N'-phenylurea, 4,4'-bis(p-toluenesulfonylaminocarbonylamino)diphenylmethane, and 4,4'-bis[(4-methyl-3-phenoxycarbonylaminophenyl)ureido]diphenylsulfone; thiourea compounds such as N,N'-di-m-chlorophenylthiourea; organic compounds having an -SO_2NH-bond in the molecule, such as N-(p-toluenesulfonyl)carbamic acid p-cumylphenyl ester, N-(p-toluenesulfonyl)carbamic acid p-benzyloxyphenyl ester, N-[2-(3-phenylureido)phenyl]benzenesulfonamide, and N-(o-toluoyl)-p-toluenesulfoamide; inorganic acidic substances such as activated clay, attapulgite, colloidal silica, and aluminum silicate; and the like.

[0034] Examples of the developer include urea urethane derivatives represented by formula (1) below, such as 4,4'-bis[(4-methyl-3-phenoxycarbonylaminophenyl)ureido]diphenylsulfone, 4,4'-bis[(2-methyl-5-phenoxycarbonylaminophenyl)ureido]diphenylsulfone, and 4-(2-methyl-3-phenoxycarbonylaminophenyl)ureido-4'-(4-methyl-5-phenoxycarbonylaminophenyl)ureidodiphenylsulfone; diphenylsulfone derivatives represented by formula (2) below; and the like.



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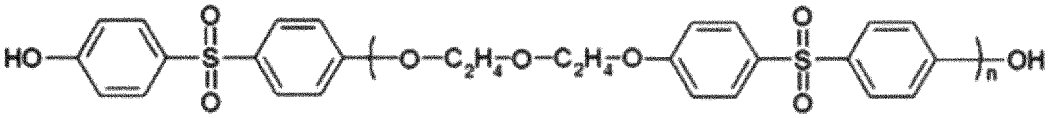

(2)

wherein n is an integer of 1 to 6.

[0035] The developer is, of course, not limited thereto. If necessary, two or more types of the compounds can be used.

[0036] The amount of the developer is not particularly limited, and can be adjusted according to the leuco dye used. The amount of the developer is typically preferably 0.5 parts by mass or more, more preferably 0.8 parts by mass or more, further preferably 1 part by mass or more, even more preferably 1.2 part by mass or more, and particularly preferably 1.5 part by mass or more, per part by mass of the leuco dye. The amount of the developer is preferably 10 parts by mass or less, more preferably 5 parts by mass or less, even more preferably 4 parts by mass or less, and particularly preferably 3.5 parts by mass or less, per part by mass of the leuco dye. A developer content of 0.5 parts by mass or more can enhance recording performance, whereas a developer content of 10 parts by mass or more can effectively suppress background fogging in a high-temperature environment.

[0037] In the present invention, the heat-sensitive recording layer may further contain a stabilizer, mainly in order to enhance the preservation of the developed color image. As such a stabilizer, it is possible to use, for example, at least one member selected from the group consisting of phenol compounds such as 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl)butane, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,1-bis(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 4,4'-[1,4-phenylenebis(1-methylethylidene)]bisphenol, and 4,4'-[1,3-phenylenebis(1-methylethylidene)]bisphenol; epoxy compounds such as 4-benzyloxyphenyl-4'-(2-methyl-2,3-epoxypropyloxy)phenylsulfone, 4-(2-methyl-1,2-epoxyethyl)diphenylsulfone, and 4-(2-ethyl-1,2-epoxyethyl)diphenylsulfone; and isocyanuric acid compounds such as 1,3,5-tris(2,6-dimethylbenzyl-3-hydroxy-4-tert-butyl)isocyanuric acid. Usable stabilizers are, of course, not limited to these compounds, and two or more of such compounds can be used in combination as necessary.

[0038] When a stabilizer is used, the amount thereof may be an effective amount for improving image preservation. The stabilizer is typically preferably used in an amount of about 1 to 30 mass%, and more preferably about 5 to 20 mass%, based on the total solids content of the heat-sensitive recording layer.

[0039] In the present invention, the heat-sensitive recording layer may further contain a sensitizer. Use of the sensitizer enhances the recording sensitivity. Examples of usable sensitizers include stearic acid amide, methoxycarbonyl-N-stearic acid benzamide, N-benzoyl stearic acid amide, N-eicosanoic acid amide, ethylenebisstearic acid amide, behenic acid amide, methylenebisstearic acid amide, N-methylol stearic acid amide, dibenzyl terephthalate, dimethyl terephthalate, dioctyl terephthalate, diphenylsulfone, benzyl p-benzyloxybenzoate, phenyl 1-hydroxy-2-naphthoate, 2-naphthyl benzyl ether, m-terphenyl, p-benzylbiphenyl, oxalic acid-di-p-chlorobenzyl ester, oxalic acid-di-p-methylbenzyl ester, oxalic acid-dibenzyl ester, p-tolyl biphenyl ether, di(p-methoxyphenoxyethyl)ether, 1,2-di(3-methylphenoxy)ethane, 1,2-di(4-methylphenoxy)ethane, 1,2-di(4-methoxyphenoxy)ethane, 1,2-di(4-chlorophenoxy)ethane, 1,2-diphenoxyethane, 1-(4-methoxyphenoxy)-2-(3-methylphenoxy)ethane, p-methylthiophenylbenzylether, 1,4-di(phenylthio)butane, p-acetotoluidide, p-acetophenetidide, N-acetoacetyl-p-toluidine, 1,2-diphenoxymethylbenzene, di(β-biphenylethoxy)benzene, p-di(vinyloxyethoxy)benzene, 1-isopropylphenyl-2-phenylethane, di-o-chlorobenzyl adipate, 1,2-bis(3,4-dimethylphenyl)ethane, 1,3-bis(2-naphthoxy)propane, diphenyl, benzophenone, and the like. These sensitizers can be used in combination, as long as the combined use does not impair the effect of the present invention. The sensitizer content may be an effective amount for sensitization; and is typically preferably about 2 to 40 mass%, and more preferably about 5 to 25 mass%, based on the total solids content of the heat-sensitive recording layer.

[0040] The heat-sensitive recording layer may contain a fine particle pigment having high whiteness and an average particle diameter of 10 μm or less, in order to enhance the whiteness of the heat-sensitive recording layer and improve the uniformity of the obtained image. Examples of usable fine particle pigments include inorganic pigments such as calcium carbonate, magnesium carbonate, kaolin, clay, talc, calcined clay, silica, diatomaceous earth, synthetic aluminum silicate, zinc oxide, titanium oxide, aluminium hydroxide, barium sulfate, surface-treated calcium carbonate, and surface-treated silica; and organic pigments such as urea-formalin resin, styrene-methacrylic acid copolymer resin, and polystyrene resin. The pigment content is preferably an amount that does not reduce the color development density, that is, 50 mass% or less, based on the total solids content of the heat-sensitive color development layer.

[0041] As other components that constitute the heat-sensitive recording layer, a binder can be used. Further, if necessary, cross-linking agents, waxes, metal soaps, water resistance improving agents, dispersants, colored dyes, fluorescent dyes, and the like can be used.

[0042] The binder that is used in the coating liquid for a heat-sensitive recording layer can be an aqueous binder selected from water-soluble binders and water-dispersible binders. Examples of water-soluble binders include polyvinyl alcohol, modified polyvinyl alcohols such as carboxy-modified polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol, diacetone-modified polyvinyl alcohol, and silicon-modified polyvinyl alcohol; starch and derivatives thereof; cellulose derivatives such as methoxy cellulose, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropylmethyl cellulose, methyl cellulose, and ethyl cellulose; sodium polyacrylate, polyvinylpyrrolidone, polyamide, diisobutylene-maleic anhydride copolymer salts, styrene-acrylic acid copolymer salts, styrene-maleic anhydride copolymer salts, ethylene-maleic anhydride copolymer salts, acrylic acid amide-acrylic acid ester copolymers, acrylic acid amide-acrylic acid ester-methacrylic acid copolymers, polyacrylamide, sodium alginate, gelatin, casein, gum arabic, and the like. Examples of water-dispersible binders include latexes of water-insoluble polymers such as polyvinyl acetate, polyurethane, styrene-butadiene copolymers, styrene-butadiene-acrylonitrile copolymers, acrylonitrile-butadiene copolymers, polyacrylic acid, polyacrylic acid esters, vinylchloride-vinylacetate copolymers, polybutyl methacrylate, ethylene-vinylacetate copolymers, silylated urethane, acrylic-silicone composites, acrylic-silicone-urethane composites, urea resins, melamine resins, amide resins, and polyurethane resins. These binders can be used singly, or in a combination of two or more. The heat-sensitive recording layer preferably contains at least one of these binders in an amount of about 5 to 50 mass%, and more preferably about 10 to 40 mass%, based on the total solids content of the heat-sensitive recording layer.

[0043] The heat-sensitive recording layer may contain a cross-linking agent that cures a binder in the heat-sensitive recording layer or other layers. This can improve the water resistance of the heat-sensitive recording layer. Examples of cross-linking agents include aldehyde compounds such as glyoxal; polyamine compounds such as polyethyleneimine; epoxy compounds, polyamide resins, melamine resins, glyoxylic acid salts, dimethylolurea compounds, aziridine compounds, block isocyanate compounds; and inorganic compounds such as ammonium persulfate, ferric chloride, magnesium chloride, soda tetraborate, and potassium tetraborate; and boric acid, boric acid triesters, boron polymers, hydrazide compounds, glyoxylic acid salts, and the like. These may be used singly, or in a combination of two or more. The amount of the cross-linking agent used is preferably in the range of about 1 to 10 parts by mass per 100 parts by mass of the total solids content of the heat-sensitive recording layer. This can enhance the water resistance of the heat-sensitive recording layer.

[0044] Examples of waxes include waxes such as paraffin wax, carnauba wax, microcrystalline wax, polyolefin wax, and polyethylene wax; higher fatty acid amides such as stearic acid amide and ethylene-bis-stearic acid amide; higher fatty acid esters, and derivatives thereof; and the like.

[0045] Examples of metal soaps include higher fatty acid polyvalent metal salts, such as zinc stearate, aluminum stearate, calcium stearate, and zinc oleate. If necessary, various auxiliary agents such as oil repellents, defoaming agents, and viscosity control agents may be added to the heat-sensitive recording layer within a range that does not impair the effect of the present invention.

[0046] The heat-sensitive recording layer is formed on the undercoat layer by dispersing a leuco dye and a developer, and if necessary, further a sensitizer and a stabilizer, together or separately, typically using water as a dispersion medium and using at least one of various stirrers or wet pulverizers, such as a ball mill, a co-ball mill, an attritor, or a vertical or horizontal sand mill together with a water-soluble synthetic polymer compound, such as polyacrylamide, polyvinyl pyrrolidone, polyvinyl alcohol, methylcellulose, or a styrene-maleic anhydride copolymer salt, and other additives such as a surfactant to form a dispersion; then using the resulting dispersion having an average particle size of 2 μm or less and optionally further mixing therewith a pigment, a binder, an auxiliary agent, and the like to prepare a coating liquid for a heat-sensitive recording layer; applying the coating liquid for a heat-sensitive recording layer to the undercoat layer; and then drying. The coating amount of the heat-sensitive recording layer is not particularly limited and is preferably about 1 to 12 g/m^2, more preferably about 2 to 10 g/m^2, even more preferably about 2.5 to 8 g/m^2, and particularly preferably about 3 to 5.5 g/m^2, in terms of the coated amount after drying. Note that the heat-sensitive recording layer may be formed as two or more separate layers if necessary, and the composition and coated amount of each layer may be the same or different.

Protective Layer

[0047] The heat-sensitive recording material can comprise a protective layer formed on the heat-sensitive recording layer, as necessary. The protective layer preferably contains a pigment and a binder. The protective layer preferably further contains a lubricant, such as polyolefin wax or zinc stearate, for the purpose of preventing the layer from sticking to the thermal head. The protective layer can also contain a UV absorber. When a glossy protective layer is formed, the obtained product can have increased added value.

[0048] The binder contained in the protective layer is not particularly limited, and any aqueous binder selected from water-soluble binders and water-dispersible binders can be used. The binder can be appropriately selected from those that can be used for the heat-sensitive recording layer.

[0049] The protective layer is formed on the heat-sensitive recording layer by mixing a pigment and a binder optionally with an auxiliary agent and the like, typically using water as a dispersion medium, to prepare a coating liquid for a protective layer; applying the obtained coating liquid to the heat-sensitive recording layer; and then drying. The amount of the coating liquid for a protective layer to be applied is not particularly limited, and is preferably about 0.3 to 15 g/m^2, more preferably about 0.3 to 10 g/m^2, even more preferably about 0.5 to 8 g/m^2, particularly preferably about 1 to 8 g/m^2, and still even more preferably about 1 to 5 g/m^2 in terms of dry weight. The protective layer may be formed as two or more separate layers if necessary, and the composition and coated amount of each layer may be the same or different.

Other Layers

[0050] In the present invention, in order to increase the added value of the heat-sensitive recording material, the obtained heat-sensitive recording material may be further processed to form a heat-sensitive recording material having higher functionality. For example, adhesive paper, remoistening adhesive paper, or delayed tack paper can be formed by subjecting the back surface of the obtained heat-sensitive recording material to coating with, for example, an adhesive, such as an adhesive, a remoistening adhesive, or a delayed tack adhesive. Recording paper capable of two-sided recording can also be formed by imparting to the back surface of the heat-sensitive recording material a function as heat transfer paper, ink jet recording paper, carbon-free paper, electrostatic recording paper, or xerography paper. Of course, the heat-sensitive recording material can be formed into a two-sided, heat-sensitive recording material. A back layer can also be provided to inhibit oil and plasticizer permeation from the back side of the heat-sensitive recording material, or for curl control and antistatic purposes.

[0051] The heat-sensitive recording material can also be formed into linerless labels that do not require release paper, by forming a silicone-containing release layer on the protective layer and applying an adhesive to the back side.

Heat-Sensitive Recording Material

[0052] Any known coating method, such as an air knife method, a blade method, a gravure method, a roll coater method, a spray method, a dip method, a bar method, a curtain method, a slot-die method, a slide die method, and an extrusion method, can be used as the method for forming each layer described above on the support. The individual coating liquids may be applied in such a manner that a first coating liquid is applied and dried, and then a second coating liquid is applied and dried to form one layer after another; or the same coating liquid may be applied separately to form two or more layers. Further, simultaneous multilayer coating may also be performed in which individual coating liquids are applied all at once to form two or more layers simultaneously. In any stage after each layer is formed or after all of the layers are formed, the layers may be subjected to a smoothing treatment by a known method, such as supercalendering or soft calendering.

[0053] The undercoat layer is preferably a layer formed by a curtain coating method. This allows the formation of a layer with a uniform thickness, which enhances recording sensitivity and barrier properties against oil, plasticizers, alcohol, and the like. Curtain coating is a method by which the coating liquid is channeled down and dropped freely to coat the intermediate layer without direct contact. Any publicly known curtain coating method, such as a slide curtain method, couple curtain method, and twin curtain method, can be employed without particular limitation.

Examples

[0054] The present invention is described below in more detail with reference to Examples. However, the present invention is not limited to these Examples. In the Examples, "parts" and "%" represent "parts by mass" and "percent by mass," respectively, unless otherwise specified.

Example 1

(1) Preparation of Coating Liquid for Intermediate Layer

[0055] Borax was dissolved in water to give an intermediate layer coating liquid with a concentration of 0.5%.

(2) Preparation of Coating Liquid for Undercoat Layer

[0056] A coating liquid for an undercoat layer was prepared by mixing and stirring a composition comprising 412 parts

of hollow particles A (product name: A-170, produced by Sansuisha Co., Ltd.; solids content: 17.0%, hollow ratio: 72%), 52 parts of styrene-butadiene latex (product name: L-1571, produced by Asahi Kasei Chemicals, solids content: 48%), 10 parts of a 10% aqueous solution of polyvinyl alcohol (degree of polymerization: 1700, degree of saponification: 88%), and 2.5 parts of carboxymethyl cellulose (product name: Cellogen 7A, produced by Daiichi Kogyo Seiyaku Co., Ltd.).

(3) Preparation of Leuco Dye Dispersion (Liquid A)

[0057] 40 parts of 3-di-(n-butyl)amino-6-methyl-7-anilinofluoran, 40 parts of a 10% aqueous solution of polyvinyl alcohol (degree of polymerization: 500, degree of saponification: 88%), and 20 parts of water were mixed. The resulting mixture was pulverized with a sand mill (produced by Imex Co., Ltd., a sand grinder) to a median diameter of 0.5 μm as measured with a SALD2200 laser diffraction particle size distribution analyzer (produced by Shimadzu Corporation), thus obtaining a leuco dye dispersion (Liquid A)

(4) Preparation of Developer Dispersion (Liquid B-1)

[0058] 40 parts of 4-hydroxy-4'-isopropoxydiphenyl sulfone (D8 produced by Nippon Soda Co., Ltd.), 40 parts of a 10% aqueous solution of polyvinyl alcohol (degree of polymerization: 500, degree of saponification: 88%), and 20 parts of water were mixed. The resulting mixture was pulverized with a sand mill (produced by Imex Co., Ltd., a sand grinder) to a median diameter of 0.7 μm as measured with a SALD2200 laser diffraction particle size distribution analyzer (produced by Shimadzu Corporation), thus obtaining a developer dispersion (liquid B).

(5) Preparation of Sensitizer Dispersion (Liquid C)

[0059] 40 parts of oxalic acid di(p-methylbenzyl) ester (product name: HS-3520, produced by DIC Corporation), 40 parts of a 10% aqueous solution of polyvinyl alcohol (degree of polymerization: 500, degree of saponification: 88%), and 20 parts of water were mixed. The resulting mixture was pulverized with a sand mill (produced by Imex Co., Ltd., a sand grinder) to a median diameter of 1.0 μm as measured with a SALD2200 laser diffraction particle size distribution analyzer (produced by Shimadzu Corporation), thus obtaining a sensitizer dispersion (dispersion C).

(6) Preparation of Coating Liquid for Heat-Sensitive Recording Layer

[0060] A coating liquid for a heat-sensitive recording layer was obtained by mixing and stirring a composition comprising 29.5 parts of liquid A, 59.1 parts of liquid B, 45.4 parts of liquid C, 20 parts of a 5% aqueous solution of hydroxymethyl cellulose, 46 parts of a 10% aqueous solution of completely saponificated polyvinyl alcohol (polymerization degree: 1000, degree of saponification: 99 mole%), 9.4 parts of a butadiene copolymer latex (product name: L-1571, produced by Asahi Kasei Corporation, solids content: 48%), 17.1 parts of light calcium carbonate (product name: Brilliant-15, produced by Shiraishi Kogyo Co., Ltd.), 11.7 parts of paraffin wax (product name: Hydrin L-700, produced by Chukyo Yushi Co., Ltd., solids content: 30%), 2 parts of adipic acid dihydrazide (produced by Otsuka Chemical Co., Ltd.), and 120 parts of water.

(7) Preparation of Coating Liquid for Protective Layer

[0061] A coating liquid for a protective layer was obtained by mixing and stirring a composition comprising 300 parts of a 12% aqueous solution of acetoacetyl-modified polyvinyl alcohol (product name: GOHSENX Z-200, degree of saponification: 99.4 mol%, average degree of polymerization: 1000, modification degree: 5 mol%, produced by The Nippon Synthetic Chemical Industry Co., Ltd.), 19 parts of kaolin (product name: Hydragloss 90, produced by KaMin LLC), 35 parts of aluminum hydroxide (product name: Higilite H-42M, produced by Showa Denko K.K.), 4 parts of silica (product name: Mizukasil P-527, produced by Mizusawa Chemical Co., Ltd.), 2.5 parts of polyethylene wax (product name: Chemipearl W-400, produced by Mitsui Chemicals Inc., solids content: 40%), and 114.5 parts of water.

(8) Production of Heat-Sensitive Recording Material

[0062] A coating liquid for an intermediate layer, a coating liquid for an undercoat layer, a coating liquid for a heat-sensitive recording layer, and a coating liquid for a protective layer were applied in amounts after drying of 0.1 g/m^2, 3.0 g/m^2, 4.0 g/m^2, and 2.0 g/m^2, respectively, to one surface of high-quality paper having a basis weight of 60 g/m^2, and dried to form an intermediate layer, an undercoat layer, a heat-sensitive recording layer, and a protective layer in this order. The obtained product was then super-calendered to smooth the surface, thus obtaining a heat-sensitive recording material.

Example 2

[0063] A heat-sensitive recording material was obtained in the same manner as in Example 1, except that 539 parts of hollow particles B (product name: A-380, produced by Sansui Co., Ltd., solids content: 13.0%, hollow ratio: 78%) was used in place of the 412 parts of hollow particles A (product name: A-170, produced by Sansui Co., Ltd., solids content: 17.0%, hollow ratio: 72%) in the preparation of the coating liquid for an undercoat layer according to Example 1.

Example 3

[0064] A heat-sensitive recording material was obtained in the same manner as in Example 1, except that zirconium nitrate was used in place of the borax in the coating liquid for an intermediate layer according to Example 1.

Example 4

[0065] A heat-sensitive recording material was obtained in the same manner as in Example 1, except that zirconium chloride was used in place of the borax in the coating liquid for an intermediate layer according to Example 1.

Comparative Example 1

[0066] A heat-sensitive recording material was obtained in the same manner as in Example 1, except that the intermediate layer coating layer of Example 1 was not provided.

Comparative Example 2

[0067] A heat-sensitive recording material was obtained in the same manner as in Example 1, except that 264 parts of hollow particles C (product name: Ropaque SN-1055, produced by The Dow Chemical Company, solids content: 26.5%, hollow ratio: 55%) was used in place of 412 parts of hollow particles A (product name: A-170, produced by Sansuisha Co., Ltd., solids content: 17.0%, hollow ratio: 72%) in the preparation of the coating liquid for an undercoat layer of Example 1.

[0068] The heat-sensitive recording materials prepared in Examples 1 to 4 and Comparative Examples 1 and 2 above were subjected to the following evaluations. Table 1 shows the results.

Medium Energy Development Density

[0069] An image was recorded on each heat-sensitive recording material at an applied energy of 0.16 mJ/dot in a medium energy range using a thermal recording tester (product name: TH-PMD, produced by Ohkura Electric Co., Ltd.). The obtained printed portion was measured with a Macbeth densitometer (product name: RD-914, produced by Macbeth Co., Ltd.) in visual mode. A greater numerical value indicates a higher print density. The recording density is preferably 1.00 or more for practical use.

Image Quality

[0070] A barcode was recorded using a label printer (product name: L-2000, produced by Ishida Co., Ltd.). The recorded image quality was visually observed, and evaluated according to the following criteria:

A: No white spots in image quality, and no increase in the width of the barcode; there are no problems.
B: Almost no white spots in image quality, and almost no increase in the width of the barcode; there are no problems in practical use.
C: White spots in image quality, and increase in the width of the barcode; there are problems in practical use.

Table 1

	Recording density	Image quality
Example 1	1.11	A
Example 2	1.21	A
Example 3	1.10	A

(continued)

	Recording density	Image quality
Example 4	1.12	A
Comp. Ex. 1	0.95	B
Comp. Ex. 2	0.80	C

Claims

1. A heat-sensitive recording material comprising an intermediate layer, an undercoat layer, and a heat-sensitive recording layer in this order on a support,
the undercoat layer containing hollow particles and a polyvinyl alcohol resin,
the heat-sensitive recording layer containing a leuco dye and a developer,
wherein the intermediate layer contains a cross-linking agent capable of cross-linking to the polyvinyl alcohol resin, and the hollow particles have a hollow ratio of 60% or more.

2. The heat-sensitive recording material according to claim 1, wherein the cross-linking agent contains a boron compound.

3. The heat-sensitive recording material according to claim 1, wherein the cross-linking agent contains at least one compound selected from the group consisting of zirconium nitrate, zirconium chloride, and zirconium hydroxychloride.

4. The heat-sensitive recording material according to any one of claims 1 to 3, wherein the hollow particles have a hollow ratio of 70% or more.

5. The heat-sensitive recording material according to any one of claims 1 to 4, wherein the polyvinyl alcohol resin is crosslinked.

6. A method for producing a heat-sensitive recording material comprising the following steps (A) to (C):

   (A) applying, to a support, a coating liquid containing a cross-linking agent capable of cross-linking to a polyvinyl alcohol resin;
   (B) applying, to the coating liquid applied in step (A), a coating liquid for an undercoat layer containing hollow particles having a hollow ratio of 60% or more and a polyvinyl alcohol resin, followed by drying; and
   (C) applying a coating liquid for a heat-sensitive layer containing a leuco dye and a developer to the undercoat layer, followed by drying.

7. A method for producing a heat-sensitive recording material comprising the following steps (a) and (b):

   (a) applying, to a support, a coating liquid containing a cross-linking agent capable of cross-linking to a polyvinyl alcohol resin; and
   (b) simultaneously applying, to the coating liquid applied in step (a), a coating liquid for an undercoat layer containing hollow particles having a hollow ratio of 60% or more and a polyvinyl alcohol resin, and a coating liquid for a heat-sensitive recording layer containing a leuco dye and a developer, followed by drying.

8. The production method according to claim 6, wherein the coating liquid for an undercoat layer is applied by a curtain coating method.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/037329

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. B41M5/42(2006.01)i, B41M5/323(2006.01)i, B41M5/44(2006.01)i

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)
Int.Cl. B41M5/42, B41M5/323, B41M5/44

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	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

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.
X Y A	JP 2015-193161 A (OJI HOLDINGS CORPORATION) 05 November 2015, paragraphs [0019]-[0028], examples 1-2, 4-8 (Family: none)	1-2, 6 7-8 3-5
Y	JP 2012-245666 A (OJI HOLDINGS CORPORATION) 13 December 2012, example 12 (Family: none)	7

☒ 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
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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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
29 October 2019 (29.10.2019)	26 November 2019 (26.11.2019)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/037329

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2011-178094 A (OJI PAPER CO., LTD.) 15 September 2011, examples 1-10, paragraphs [0093], [0103] (Family: none)	7
Y	JP 2006-175636 A (NIPPON PAPER INDUSTRIES CO., LTD.) 06 July 2006, examples 1-5 (Family: none)	8
A	JP 2014-195995 A (RICOH CO., LTD.) 16 October 2014, examples 13-15, paragraphs [0017]-[0027] & US 2016/0001583 A1, examples 13-15, paragraphs [0036]-[0058] & WO 2014/136988 A1 & EP 3290218 A2 & CN 105026171 A & KR 10-2015-0119351 A	1-8
A	WO 2009/122850 A1 (OJI PAPER CO., LTD.) 08 October 2009, examples 14-20, paragraphs [0045]-[0060] (Family: none)	1-8
A	JP 2009-23237 A (RICOH CO., LTD.) 05 February 2009, examples 1-13, paragraphs [0012]-[0022] (Family: none)	1-8
A	CN 104553433 A (RICOH THERMAL MEDIA (WUXI) CO., LTD.) 29 April 2015, examples 1-8 (Family: none)	1-8

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 3565564 B **[0005]**