

(19)



(11)

EP 3 103 649 B2

(12)

NEW EUROPEAN PATENT SPECIFICATION

After opposition procedure

(45) Date of publication and mention
of the opposition decision:
22.01.2025 Bulletin 2025/04

(45) Mention of the grant of the patent:
03.01.2018 Bulletin 2018/01

(21) Application number: **15766003.6**

(22) Date of filing: **06.03.2015**

(51) International Patent Classification (IPC):
B41M 5/42^(2006.01)

(52) Cooperative Patent Classification (CPC):
B41M 5/426; B41M 2205/04; B41M 2205/38

(86) International application number:
PCT/JP2015/056651

(87) International publication number:
WO 2015/141497 (24.09.2015 Gazette 2015/38)

(54) **THERMOSENSITIVE RECORDING MEDIUM**

WÄRMEEMPFLINDLICHES AUFZEICHNUNGSMEDIUM

SUPPORT D'ENREGISTREMENT THERMOSENSIBLE

(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**

(30) Priority: **17.03.2014 JP 2014052924**

(43) Date of publication of application:
14.12.2016 Bulletin 2016/50

(73) Proprietor: **Nippon Paper Industries Co., Ltd.**
Tokyo 114-0002 (JP)

(72) Inventors:
• **NAGAHARA Dai**
Tokyo 114-0002 (JP)
• **ITO Kotaro**
Tokyo 114-0002 (JP)

• **MIDORIKAWA Yoshimi**
Tokyo 114-0002 (JP)

(74) Representative: **Prüfer & Partner mbB**
Patentanwälte · Rechtsanwälte
Sohnckestraße 12
81479 München (DE)

(56) References cited:
EP-B1- 1 910 281 DE-A1- 102008 057 270
JP-A- 2008 194 843 JP-A- 2012 076 230
JP-A- H05 162 446 JP-A- H05 162 446

• **No further relevant documents disclosed**
• **Datasheet "ALBACAR® 5970", Specialty Minerals, 1998**
• **SOCAL® GEFALLTES CALCIUMCARBONAT HERSTELLUNG,EIGENSCHAFTEN, ANWENDUNGEN", SOLVAY, 2005, pages 1-54**

EP 3 103 649 B2

DescriptionField of the Invention

[0001] The present invention relates to a thermosensitive recording medium for recording image by utilizing a color formation reaction between a colorless or pale colored electron donating leuco dye (henceforth referred to as "leuco dye") and an electron accepting color developing agent (henceforth referred to as "color developing agent"), which has an excellent heat discoloration resistance, especially an excellent heat discoloration resistance in the blank portions.

Background of the Invention

[0002] Thermosensitive recording media are ordinarily prepared by mixing together a colorless or pale-colored leuco dye and a color developing agent, such as a phenolic compound and the like, after grinding them into fine particles, preparing a coating solution by adding a binder, a filler, a sensitivity enhancing agent, a slipping agent and other aids to the mixture and applying the coating solution onto a substrate such as paper, synthetic paper, film, plastic and the like. Thermosensitive recording media are widely used as various recording media.

[0003] In recent years, 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. Furthermore the use of thermosensitive recording media is expanding, such as its use for various ticket, receipts, labels, ATM of Bank, meter reading of gas and electricity, cash vouchers, such as car racing or horseracing betting. For the thermosensitive recording medium, the storage stability of the image portion and the blank portion has been required in more severe conditions, for example, in a high temperature condition in a car in midsummer. To solve such a problem, the color developing agent and the leuco dye and the configuration of the protective layer have been studied (see References 1-3).

[0004] Further, it is proposed to improve the recording sensitivity and the printing (recording) run-ability by installing an undercoat layer between the support and the thermosensitive recording layer, which contains inorganic pigments or plastic particles (see References 4,5, etc.).

References**[0005]**

Reference 1: Japanese Patent Application Public Disclosure H10-86529

Reference 2: Japanese Patent Application Public Disclosure 2008-6739

Reference 3: Japanese Patent Application Public Disclosure 2010-94986

Reference 4: Japanese Patent Application Public Disclosure H5-162446

Reference 5: Japanese Patent Application Public Disclosure 2012-076228

Problems to be solved by the Invention

[0006] The color developing agent and the leuco dye and the composition of the protective layer have, conventionally, been mainly studied in order to improve the heat discoloration resistance, especially the heat discoloration resistance in the blank portions of the thermosensitive recording medium, as described above (References 1-3), while the present inventors have examined the composition of the undercoat layer in the structure having an undercoat layer between the support and the thermosensitive recording layer, in order to improve the heat discoloration resistance.

[0007] Accordingly, the objective of the present invention is to provide a thermosensitive recording medium having an excellent heat discoloration resistance, especially an excellent heat discoloration resistance in the blank portions.

Means to solve the Problems

[0008] As a result of intensive studies, the inventors have discovered that the heat discoloration resistance of a thermosensitive recording medium, especially the heat discoloration resistance in the blank portions, can be improved by installing an undercoat layer between the support and the thermosensitive recording layer, incorporating a precipitated calcium carbonate as a pigment in the undercoat layer, and limiting its bulk density to a specific bulk density, in which the precipitated calcium carbonate comprises spindle-shaped primary particles aggregated radially to form secondary particles with a characteristic rosette type shape.

[0009] As the rosette type precipitated calcium carbonate for use in the present invention has a specific shape and a specific bulk density (see Figures 1 and 2), the undercoat layer containing such a pigment hampers the heat transfer from

the support to the thermosensitive recording layer effectively, which is considered to improve the heat discoloration resistance of the thermosensitive recording medium by reducing the heat transfer even when the thermosensitive recording medium is stored at a high temperature condition.

[0010] Further, the undercoat layer containing such a pigment is considered to have a specific absorbing property for the materials contained in the undercoat layer and the adjacent thermosensitive recording layer. For example, the undercoat layer is considered to absorb the color developing material contained in the thermosensitive recording layer, especially the excess color developing agents that are not involved in the chemical reaction with the leuco dye (i.e. cannot participate in the color developing) after the color developing agent melts by being heated by a thermal head during printing. As a result, less debris remains on the thermal head and the printing (recording) run-ability (i.e. prevention of head debris) is considered to be improved. It is also believed that this may have an influence on the expression of binders contained in the undercoat layer.

[0011] That is, the present invention provides a thermosensitive recording medium comprising (i) a support, (ii) an undercoat layer installed on the support, comprising a pigment and a binder as main components, and (iii) a thermosensitive recording layer installed on the undercoat layer, comprising a colorless or pale colored electron donating leuco dye and an electron accepting color developing agent as main components, wherein the pigment contained in the undercoat layer is a rosette type precipitated calcium carbonate comprising spindle-shaped primary particles aggregated radially to form secondary particles, and the bulk density of the rosette type precipitated calcium carbonate is 240 g/L or less, wherein the bulk density is measured according to Japanese Industrial Standard JIS-K-5101-12-1.

Brief Description of the Drawings

[0012]

Figure 1 shows a photograph of the rosette type precipitated calcium carbonate (Albacar (R) LO, product of Specialty Minerals Inc.).

Figure 2 shows a photograph of the rosette type precipitated calcium carbonate (TP221BM, product of Okutama Kogyo Co., Ltd.).

Detailed Description of the Invention

[0013] The thermosensitive recording medium of the present invention comprises (i) a support, (ii) an undercoat layer installed on the support, and (iii) a thermosensitive recording layer installed on the undercoat layer.

[0014] The undercoat layer comprises a pigment and a binder as main components, wherein the pigment is a rosette type precipitated calcium carbonate comprising spindle-shaped primary particles aggregated radially to form secondary particles.

[0015] And the bulk density of the precipitated calcium carbonate is 240 g/L or less, preferably 150 - 220g/L. The bulk density is measured according to Japanese Industrial Standard JIS-K-5101-12-1 (a test method for pigments - Part 12: Apparent density or apparent specific volume - Section 1: standing method).

[0016] The rosette type precipitated calcium carbonate for use in the present invention comprises spindle-shaped primary particles aggregated radially to form secondary particles. The "aggregated radially" is referred to those of each primary particle extending to longitudinal direction from the approximate center of the secondary particles.

[0017] The rosette type precipitated calcium carbonate for use in the present invention is available as Albacar (R) LO (Bulk density: 210g/L), a product of Specialty Minerals Inc., and TP211BM (Bulk density: 220g/L), a product of Okutama Kogyo Co., Ltd., etc.

[0018] The rosette type precipitated calcium carbonate may be ground before use by using a publicly known grinder such as a ball mill, attritor, sand grinder and the like.

[0019] The undercoat layer of the present invention may contain other pigments than the rosette type precipitated calcium carbonate of the present invention. As a pigment other than the rosette type precipitated calcium carbonate, for example, precipitated calcium carbonate formed by secondary particles with irregular shape, precipitated calcium carbonate comprising needle-shaped primary particles aggregated radially to form secondary particles with a chestnuts in burrs type shape, precipitated calcium carbonate comprising spindle-shaped, needle-like, columnar, square-shaped, or spherical primary particles without forming secondary particles, heavy calcium carbonate, (calcined) kaolin, clay, talc, silica, aluminum oxide, zinc oxide, titanium oxide, magnesium carbonate, aluminum hydroxide, magnesium hydroxide, aluminum silicate, magnesium silicate, calcium silicate and the like may be used. These pigments may be used alone or in combination.

[0020] When the undercoat layer contains other pigments than the rosette type precipitated calcium carbonate of the present invention, the amount of the rosette type precipitated calcium carbonate is preferably 50 weight % or more, more preferably 70 weight % or more, most preferably 90 weight % or more of the total pigments contained in the undercoat layer,

which contains the rosette type precipitated calcium carbonate.

[0021] The undercoat layer of the present invention preferably contains organic hollow particles, which further improve the heat discoloration resistance in the blank portions and the heat insulating property of the undercoat layer as well, therefore a thermosensitive recording material with an excellent color developing sensitivity can be obtained.

[0022] The organic hollow particle used in the present invention is a fine hollow particle, comprising a thermoplastic resin as its shell and air or other gases inside, which is actually in a foamed state.

[0023] Examples of the thermoplastic resin may include polystyrene, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyacrylic acid ester, polyacrylonitrile, polybutadiene, or copolymers thereof. Especially, styrene resins such as polystyrene, acrylic resins such as polyacrylic acid esters and polyacrylonitriles, copolymers thereof, a copolymer resin composed mainly of polyvinylidene chloride and polyacrylonitriles are preferable. Such organic hollow particles are available as SX8782 (JSR Corporation), MH5055 and MH8103K (Nippon Zeon Co., Ltd.), Ropaque (R) HP-91 (Rohm and Haas Japan Co.) and the like.

[0024] The hollow ratio of the organic hollow particle is preferably from 40 to 90%, more preferably 45 to 90%. If the hollow ratio is less than 40%, the heat discoloration resistance and color developing sensitivity of the blank portion may not be sufficient, since the heat insulation is not sufficient and the thermal energy from a thermal head or the like is easily discharged to outside of the thermosensitive recording medium through the support.

[0025] Here, the hollow ratio is calculated from the outer diameter and the inner diameter of the hollow particles according to the following equation:

Hollow ratio = (the inner diameter of the hollow particles/the outer diameter of the hollow particles)³ × 100 (%).

[0026] The average particle diameter of the organic hollow particles is preferably from 0.5 to 10 μm, more preferably from 1 to 5 μm. If the average particle diameter is larger than 10 μm, a sufficient effect cannot be obtained since the smoothness of the thermosensitive recording layer surface formed on the undercoat layer is reduced and the thermal head or the like cannot closely contact the thermosensitive recording medium. And if the average particle diameter is less than 0.5 μm, the amount of the gas contained in the hollow particles is not sufficient to yield the effect.

[0027] The average particle diameter is represented by the median size d₅₀, which can be measured by a laser diffraction type particle size distribution measuring apparatus. When the particles are divided to two groups according to the diameter, the median size d₅₀ is the diameter in which the amount of one group with larger diameter than the diameter and the amount of another group with smaller diameter than the diameter are equivalent by volume.

[0028] The binders used in the undercoat layer include water-soluble resins and water-insoluble resins. As the water-soluble resin, polyvinyl alcohols such as completely saponified polyvinyl alcohol, partially saponified polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, silanol-modified polyvinyl alcohol, cation-modified polyvinyl alcohol, terminal alkyl-modified polyvinyl alcohol and the like; cellulose ethers and derivatives thereof such as hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, acetyl cellulose and the like; starches such as starch, enzyme modified starch, thermochemically modified starch, oxidized starch, esterified starch, etherified starch (for example, such as hydroxyethyl starch), cationic starch and the like; polyacrylamides such as polyacrylamide, cationic polyacrylamides, anionic polyacrylamides, amphoteric polyacrylamides and the like may be listed. As the water-insoluble resin, urethane resins such as polyester polyurethane resins, polyether polyurethane resins, polyurethane-based ionomer resin and the like; styrene-butadiene resins such as styrene-butadiene copolymer, styrene-butadiene-acrylonitrile copolymer, styrene-butadiene-acrylic copolymer and the like; acrylic resins such as those comprising a (meth) acrylic acid and a monomer component that is copolymerizable with (meth) acrylic acid, such as (meth) acrylonitrile; polyolefin-based resins such as those comprising an olefin, such as ethylene, propylene, butylene, and a monomer component that is copolymerizable with an olefin, such as an unsaturated carboxylic acid such as (meth) acrylic acid, maleic acid, itaconic acid, fumaric acid and the like; polyvinyl acetate; vinyl chloride- vinyl acetate copolymer; polyvinyl chloride; polyvinylidene chloride; polyacrylic ester resin; polystyrene and copolymers thereof; silicone resins; petroleum resins; terpene resins; ketone resins; cumaron resins and the like may be listed.

[0029] Among these, as the water-soluble resin, polyvinyl alcohols, cellulose ethers and their derivatives, and starches are preferable, and polyvinyl alcohols are more preferable. The water-soluble resins can be used by dissolving in a solvent such as water.

[0030] As the water-insoluble resin, styrene-butadiene resins, acrylic resins, polyolefin-based resins are preferable, and styrene-butadiene resins are more preferable. The water-insoluble resin can be used as an emulsion or a dispersed emulsion as a paste in water or other media.

[0031] These binders may be used in combination of two or more depending on the required quality.

[0032] As the binder used in the undercoat layer of the present invention, it is preferable to use a water-soluble resin and a water-insoluble resin at a specific ratio.

[0033] The weight ratio (in solid content) of water-soluble resin / water-insoluble resin is preferably 35/100 or less, more

preferably from 3/100 to 30/100, further preferably from 3/100 to 20/100.

[0034] If the weight ratio of the water-soluble resin / non-water-soluble resin is larger than 35/100, the heat discoloration resistance, printing image quality, prevention of head debris tend to be lowered (see Examples below). Further, if the amount of water-soluble resin is less than 3/100, the prevention of migration (described later) is not sufficient, then the strength of the coating layer may decrease.

[0035] Water-soluble resins such as polyvinyl alcohols are generally viscous and retain water. Therefore the water-soluble resins penetrate into the voids in the undercoat layer that contains the pigments of the present invention with a specific shape and a specific bulk density, and the water-soluble resins tend to remain there. Accordingly, the water-soluble resins may fill the voids in the undercoat layer, which will deteriorate the heat discoloration resistance, the print quality, and the prevention of head debris.

[0036] On the other hand, the water-insoluble resins, such as styrene-butadiene resins, are generally less viscous and retain less water. Therefore the water-insoluble resins may pass through the undercoat layer that contains the pigments of the present invention with a specific shape and a specific bulk density, and penetrate into the support. This problem is called as "migration".

[0037] By using both the water-soluble resins and the water-insoluble resins at a moderately adjusted ratio, it is possible to reduce the migration while maintaining the bulky (i.e. low density) state of the undercoat layer so that moderate heat discoloration resistance, print quality and prevention of head debris can be achieved.

[0038] In the present invention, various aids such as a dispersion agent, plasticizer, thickeners, surfactants, activator, pH controlling agent, de-foaming agent, water retention agent, preservative, coloring dye, UV light inhibiting agent, antioxidants, water and oil repellants and the like may be added to the undercoat layer in the range that does not adversely affect the desired effects for the problems described above.

[0039] The amounts of the pigment, the organic hollow particle and the binder used in the undercoat layer are determined according to the required performance and recording properties and are not particularly restricted. The amount (in solid) of the pigment in the undercoat layer is ordinarily from 50 to 95 weight parts, preferably from 70 to 90 weight parts per 100 weight parts of the total solid content of the undercoat layer. The amount (in solid) of the organic hollow particle in the undercoat layer is preferably from 1 to 18 weight parts, more preferably from 3 to 15 weight parts per 100 weight parts of the total solid content of the undercoat layer. The color developing sensitivity will increase as the amount of the organic hollow particles increases, while the printing (recording) run-ability (i.e. prevention of head debris) may decrease, if the amount exceeds 18 weight parts, since debris may remain on the thermal head. The amount (in solid) of the binder is preferably from 7 to 30 weight parts, more preferably from 10 to 25 weight parts per 100 weight parts of the total solid content of the undercoat layer.

[0040] In the present invention, the method for coating the undercoat layer is not limited in particular, but any well-known conventional techniques may be used to coat on a support of suitable material, such as paper, recycled paper, plastic film, synthetic paper or the like. The method for coating may be appropriately selected and used among, for example, off-machine coater and on-machine coater, which is equipped with coaters such as air knife coater, rod blade coater, bent blade coater, bevel blade coater, roll coater, curtain coater and the like. Preferred among these is a blade coater such as rod blade coater, bent blade coater, bevel blade coater and the like, since a coating solution can be coated with higher concentration, then undercoat solution is unlikely to penetrate into the support, and then a uniform undercoat layer can be formed.

[0041] The coating amount of the undercoat layer is not limited in particular, but the typical dried coating amount of the undercoat layer is ordinarily in the range of from 1 to 15g/m².

[0042] The various materials used in the thermosensitive recording layer of the thermosensitive recording medium of the present invention are shown below. However, a binder, a cross linking agent, a pigment etc. can be used also for other coating layer(s) in the range which does not inhibit the desired effect for the problems described above.

[0043] All of the color developing agents well known in the conventional field of pressure sensitive and thermosensitive recording media may be used as the color developing agent in a thermosensitive recording material of the present invention. Although the color developing agent is not particularly restricted, activated clay, attapulgite, colloidal silica, inorganic acidic substances such as aluminum silicate and the like, 4,4'-isopropylidene diphenol, 1,1-bis(4-hydroxyphenyl) cyclohexane, 2,2-bis(4-hydroxyphenyl)-4-methylpentane, 4,4'-dihydroxydiphenyl sulfide, hydroquinone monobenzyl ether, benzyl 4-hydroxybenzoate, 4,4'-dihydroxy diphenyl sulfone, 2,4'-dihydroxy diphenyl sulfone, 4-hydroxy-4'-isopropoxy diphenyl sulfone, 4-hydroxy-4'-n-propoxy diphenyl sulfone, bis(3-allyl-4-hydroxyphenyl) sulfone, 4-hydroxy-4'-methyl diphenyl sulfone, 4-hydroxyphenyl-4'-benzyloxyphenyl 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 compounds such as diphenyl sulfone crosslinked compounds and the like described in International Publication WO97/16420, phenolic compounds described in International Publication WO02/081229 or Japanese Patent Application Public Disclosure No. 2002-301873, thiourea compounds such as N,N'-di-m-chlorophenyl thiourea and the like, p-chlorobenzoic acid, stearyl gallate, bis [zinc 4-octyloxy carbonylamino] salicylate dihydrate, 4-[2-(p-methoxyphenoxy) ethyloxy] salicylic acid, 4-[3-(p-trisulfonyl) 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 and the like of terephthal aldehyde acid with other aromatic carboxylic acids, for example, may be cited as the color developing agent.

[0044] These color developing agents may be used individually and in mixtures of at least two.

[0045] 1-[4-(4-hydroxyphenyl-sulfonyl) phenoxy]-4-[4-(4-isopropoxyphenyl sulfonyl) phenoxy] butane is available under the trade name of JKY-214 produced by API Corporation. The phenol condensate composition described in Japanese Patent Application Public Disclosure No. 2003-154760 is available under the trade name of JKY-224 produced by API Corporation. The diphenylsulfone crosslinked type compound described in International Publication WO97/16420 is available under the trade name of D-90 produced by Nippon Soda Co., Ltd.. The compound described in International Publication WO02/081229 is also available under the trade names of NKK-395 and D-100 produced by Japan Soda K.K. In addition, high molecular weight aliphatic acid metal complex salts described in Japanese Patent Application Public Disclosure No. H10-258577 and metal chelate type color developing components such as polyvalent hydroxy aromatic compounds and the like may also be present.

[0046] 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>

[0047] 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>

[0048] 3-Diethylamino-6-methylfluorane, 3-diethylamino-6-methyl-7-anilino fluorane, 3-diethylamino-6-methyl-7-(o,p-dimethylanilino) fluorane, 3-diethylamino-6-methyl-7-chloro fluorane, 3-diethylamino-6-methyl-7-(m-trifluoromethylanilino) fluorane, 3-diethylamino-6-methyl-7-(o-chloroanilino) fluorane, 3-diethylamino-6-methyl-7-(p-chloroanilino) fluorane, 3-diethylamino-6-methyl-7-(o-fluoroanilino) fluorane, 3-diethylamino-6-methyl-7-(m-methylanilino) fluorane, 3-diethylamino-6-methyl-7-n-octylanilino fluorane, 3-diethylamino-6-methyl-7-n-octylamino fluorane, 3-diethylamino-6-methyl-7-benzylamino fluorane, 3-diethylamino-6-methyl-7-dibenzylamino fluorane, 3-diethylamino-6-chloro-7-methyl fluorane, 3-diethylamino-6-chloro-7-anilino fluorane, 3-diethylamino-6-chloro-7-p-methylanilino fluorane, 3-diethylamino-6-ethoxyethyl-7-anilino fluorane, 3-diethylamino-7-methyl fluorane, 3-diethylamino-7-chloro fluorane, 3-diethylamino-7-(m-trifluoromethylanilino) fluorane, 3-diethylamino-7-(o-chloroanilino) fluorane, 3-diethylamino-7-(p-chloroanilino) fluorane, 3-diethylamino-7-(o-fluoroanilino) fluorane, 3-diethylamino-benz[a] fluorane, 3-diethylamino-benz[c] fluorane, 3-dibutylamino-6-methyl-fluorane, 3-dibutylamino-6-methyl-7-anilino fluorane, 3-dibutylamino-6-methyl-7-(o,p-dimethylanilino) fluorane, 3-dibutylamino-7-(o-chloroanilino) fluorane, 3-butylamino-6-methyl-7-(p-chloroanilino) fluorane, 3-dibutylamino-6-methyl-7-(o-fluoroanilino) fluorane, 3-dibutylamino-6-methyl-7-(m-fluoroanilino) fluorane, 3-dibutylamino-6-methyl-chloro fluorane, 3-dibutylamino-6-ethoxyethyl-7-anilino fluorane, 3-dibutylamino-6-chloro-7-anilino fluorane, 3-dibutylamino-6-methyl-7-p-methylanilino fluorane, 3-dibutylamino-7-(o-chloroanilino) fluorane, 3-dibutylamino-7-(o-fluoroanilino) fluorane, 3-di-n-pentylamino-6-methyl-7-anilino fluorane, 3-di-n-pentylamino-6-methyl-7-(p-chloroanilino) fluorane, 3-di-n-pentylamino-7-(m-trifluoromethylanilino) fluorane, 3-di-n-pentylamino-6-chloro-7-anilino fluorane, 3-di-n-pentylamino-7-(p-chloroanilino) fluorane, 3-pyrrolidino-6-methyl-7-anilino fluorane, 3-piperidino-6-methyl-7-anilino fluorane, 3-(N-methyl-N-propylamino)-6-methyl-7-anilino fluorane, 3-(N-methyl-N-cyclohexylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-cyclohexylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-xylylamino)-6-methyl-7-(p-chloroanilino) fluorane, 3-(N-ethyl-p-toluidino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-isoamylamino)-6-chloro-7-anilino fluorane, 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-isobutylamino)-6-methyl-7-anilino fluorane, 3-(N-ethyl-N-ethoxypropylamino)-6-methyl-7-anilino fluorane, 3-cyclohexylamino-6-chloro fluorane, 2-(4-oxahexyl)-3-dimethylamino-6-methyl-7-anilino fluorane, 2-(4-oxahexyl)-3-diethylamino-6-methyl-7-anilino fluorane, 2-(4-oxahexyl)-3-dipropylamino-6-methyl-7-anilino fluorane, 2-methyl-6-

o-(p-dimethylaminophenyl) aminoanilino fluorane, 2-methoxy-6-p-(p-dimethylaminophenyl) aminoanilino fluorane, 2-chloro-3-methyl-6-p-(p-phenylaminophenyl) aminoanilino fluorane, 2-chloro-6-p-(p-dimethylaminophenyl) aminoanilino fluorane, 2-nitro-6-p-(p-diethylaminophenyl) aminoanilino fluorane, 2-amino-6-p-(p-diethylaminophenyl) aminoanilino fluorane, 2-diethylamino-6-p-(p-diethylaminophenyl) aminoanilino fluorane, 2-phenyl-6-methyl-6-p-(p-phenylaminophenyl) aminoanilino fluorane, 2-benzyl-6-p-(p-phenylaminophenyl) aminoanilino fluorane, 2-hydroxy-6-p-(p-phenylaminophenyl) aminoanilino fluorane, 3-methyl-6-p-(p-dimethylaminophenyl) aminoanilino fluorane, 3-diethylamino-6-p-(p-diethylaminophenyl) aminoanilino fluorane, 3-diethylamino-6-p-(p-dibutylaminophenyl) aminoanilino fluorane and 2,4-dimethyl-6-[(4-dimethylamino) anilino] fluorane.

<Fluorene type leuco dye>

[0049] 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>

[0050] 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>

[0051] 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-B-naphthoylethane, 1,1-bis-[2',2',2",2"-tetrakis-(p-dimethylaminophenyl)-ethenyl]-2,2-diacetylene and bis-[2,2,2',2'-tetrakis-(p-dimethylaminophenyl)-ethenyl]-methylmalonic acid dimethyl ester.

[0052] The previously well known sensitizers may be used as the sensitizer in the thermosensitive recording medium of the present invention. As such sensitizers, aliphatic acid amides such as stearic acid amide, palmitic acid amide and the like, ethylene bis-amide, montan acid wax, polyethylene wax, 1,2-di-(3-methylphenoxy) ethane, p-benzyl biphenyl, β -benzyloxy naphthalene, 4-biphenyl-p-tolyl ether, m-terphenyl, 1,2-diphenoxyethane, dibenzyl oxalate, di(p-chlorobenzyl) oxalate, di(p-methylbenzyl) oxalate, dibenzyl terephthalate, benzyl p-benzyloxy benzoate, di-p-tolyl carbonate, phenyl- α -naphthyl carbonate, 1,4-diethoxynaphthalene, 1-hydroxy-2-naphthoic acid phenyl ester, o-xylene-bis-(phenyl ether), 4-(m-methyl phenoxy)methyl biphenyl, 4,4'-ethylene dioxy-bis-benzoic acid dibenzyl ester, dibenzoyloxy methane, 1,2-di(3-methylphenoxy) ethylene, bis[2-(4-methoxy-phenoxy) ethyl] ether, methyl p-nitrobenzoate, phenyl p-toluene sulfonate, o-toluenesulfonamide, p-toluenesulfonamide, and the like may be listed as examples. These sensitizers may be used individually and as mixtures of at least two of them.

[0053] As a pigment, kaolin, calcined kaolin, calcium carbonate, aluminum oxide, titanium oxide, magnesium carbonate, aluminum silicate, magnesium silicate, calcium silicate, aluminum hydroxide, silica and the like may be used. These pigments may be used in combinations depending on the required quality.

[0054] As the binder used in the present invention, completely saponified polyvinyl alcohol, partially saponified polyvinyl alcohol, acetoacetylated polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, amide-modified polyvinyl alcohol, sulfonic acid-modified polyvinyl alcohol, butyral-modified polyvinyl alcohol, olefin-modified polyvinyl alcohol, nitrile-modified polyvinyl alcohol, pyrrolidone-modified polyvinyl alcohol, silicone-modified polyvinyl alcohol, other modified polyvinyl alcohol; cellulose derivatives such as hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, acetyl cellulose and the like; styrene-maleic anhydride copolymer, styrene-butadiene copolymer; casein, gum arabic, oxidized starch, etherified starch, dialdehyde starch, esterified starch, polyvinyl chloride, polyvinyl acetate, polyacrylamide, polyacrylic acid esters, polyvinyl butyral, polystyrene, and copolymers thereof, polyamide resin, silicone resins, petroleum resins, terpene resins, ketone resins, cumaron resins and the like may be listed as examples.

[0055] These polymeric substances may be used upon dissolving them in a solvent such as water, alcohol, ketones, esters, hydrocarbons and the like or upon emulsifying or dispersing into a paste in water or other media. The polymeric materials may also be used in combinations according to the qualities demanded.

[0056] As the crosslinking agent used in the present invention, epichlorohydrin-based resins such as polyamine-epichlorohydrin resin, polyamide-epichlorohydrin resin; polyamine/polyamide type resin such as polyamide-urea resin, polyalkylene polyamine resin, polyalkylene polyamide resin, polyamine polyurea resin, modified polyamine resin,

modified polyamide resin, polyalkylene polyamine urea formalin resin, polyalkylene polyamine polyamide polyurea resin; glyoxal, methylol melamine, melamine formaldehyde resins, melamine urea resins, potassium persulfate, ammonium persulfate, sodium persulfate, ferric chloride, magnesium chloride, borate sand, boric acid, alum, ammonium chloride and the like may be listed as examples.

[0057] As the slipping agent used in the present invention, fatty acid metal salts such as zinc stearate, calcium stearate, and the like; waxes; silicone resins, and the like may be cited.

[0058] In addition, a stabilizing agent that improves oil resistance in recorded images and the like, such as 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 and the like may also be added in the range that does not adversely affect the desired effects for the problems described above.

[0059] In addition, a benzophenone type and triazole type UV light absorption agent, dispersion agent, de-foaming agent, antioxidant, fluorescent dye and the like may also be used.

[0060] The types and amounts of the leuco dye, color developing agent, sensitizer and other various ingredients used in the thermosensitive recording medium of the present invention are determined according to the required performance and printability and are not particularly restricted. However, from 0.5 to 10 parts of the color developing agent, from 0.5 to 20 parts of the pigment, from 0.5 to 10 parts of the sensitizer, from 0.01 to 10 parts of the stabilizing agent and from 0.01 to 10 parts of the other ingredients are ordinarily used per 1 part of the leuco dye. The appropriate amount (in solid) of the binder in the thermosensitive recording layer is from 5 to 25 weight %.

[0061] The leuco dye, the color developing agent and materials added when needed are finely ground into particles, several microns or smaller in size, using a grinder or a suitable emulsification device such as a ball mill, attritor, sand grinder and the like, and a coating solution is prepared by adding a binder and various additive materials depending on the objective. Water, alcohol and the like can be used as the solvent for the coating solution and the solid content of the coating solution is about from 20 to 40 weight %.

[0062] As the thermosensitive recording medium of the present invention has the undercoat layer installed on the support and the thermosensitive recording layer installed on the undercoat layer, the thermosensitive recording medium may further have other layer other than the undercoat layer and the thermosensitive recording layer appropriately.

[0063] For example, the thermosensitive recording medium may further have a protective layer on the thermosensitive recording layer, and a back coat layer on the surface of the support opposite to the thermosensitive recording layer.

[0064] In the present invention, the method for coating the coating layer other than the undercoat layer, such as the thermosensitive recording layer, the protective layer, the back coat layer and the like, is not limited in particular, but any well-known conventional techniques may be used. The method for coating may be appropriately selected and used among, for example, off-machine coater and on-machine coater, which is equipped with coaters such as air knife coater, rod blade coater, bent blade coater, bevel blade coater, roll coater, curtain coater.

[0065] The coating amount of the coating layer other than the undercoat layer is determined according to the required performance and recording suitability, but is not limited in particular.

[0066] The dried coating amount of the thermosensitive recording layer is ordinarily in the range of from 2 to 12g/m², and the dried coating amount of the protective layer is preferably in the range of from 0.5 to 5.0 g/m².

[0067] Furthermore, various technologies known in the thermosensitive recording medium field may be used as needed, for example, a flattening treatment such as super calendaring and the like can be conducted after coating individual coating layers.

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. The coatings and dispersions were prepared as described below.

[Example 1]

[Undercoat layer coating solution 1]

[0069] Undercoat layer coating solution was prepared by dispersing and stirring the following formulation:

Rosette type precipitated calcium carbonate (Specialty Minerals Inc., Albacar (R) LO, Bulk density: 210g/L, Figure 1)	100.0 parts
Styrene-butadiene copolymer latex (Zeon Corporation, ST5526, solid content: 48%)	40.0 parts

EP 3 103 649 B2

(continued)

Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117, solid content: 10%)	30.0 parts
Water	100.0 parts

[0070] This undercoat layer coating solution was applied on one side of a support (i.e. groundwood free paper with a basis weight of 60g/m²) by using a bent blade coater with a coating amount (in solid) of 10.0 g/m², and was dried to prepare an undercoated paper.

[0071] A color developing agent dispersion (solution A) and a leuco dye dispersion (solution B) with the following formulation were separately wet ground using sand grinders until the average particle size was about 0.5 μm.

Color developing agent dispersion (Solution A)

4-hydroxy-4'-isopropoxy diphenyl sulfone (API Corporation, NYDS)	6.0 parts
Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117, solid content: 10%)	18.8 parts
Water	11.2 parts

Leuco dye dispersion (Solution B)

3-Dibutylamino-6-methyl-7-anilino fluorane (Yamamoto Chemicals Inc., ODB-2)	6.0 parts
Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117, solid content: 10%)	4.6 parts
Water	2.6 parts

[0072] Next these dispersions were blended in the proportion described below to prepare the thermosensitive recording layer coating solution.

Thermosensitive recording layer coating solution 1

Color developing agent dispersion (Solution A)	36.0 parts
Leuco dye dispersion (Solution B)	13.2 parts
Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117, solid content: 10%)	25.0 parts
Aluminum hydroxide (Showa Denko K.K, Higilite (R) H-32, 50% dispersion)	12.0 parts

[0073] This thermosensitive recording layer coating solution 1 was applied on the undercoat layer of the above undercoated paper by using a rod blade coater with a coating amount (in solid) of 2.5 g/m² and was dried and super calendared so that the smoothness was 500-1,000 seconds to yield a thermosensitive recording medium.

[Example 2]

[0074] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of changing the amount of the styrene-butadiene copolymer latex in the undercoat layer coating solution 1 from 40.0 parts to 45.0 parts and the amount of the aqueous solution of completely saponified polyvinyl alcohol in the undercoat layer coating solution 1 from 30.0 parts to 7.0 parts.

[Example 3]

[0075] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of changing the amount of the styrene-butadiene copolymer latex in the undercoat layer coating solution 1 from 40.0 parts to 44.0 parts and the amount of the aqueous solution of completely saponified polyvinyl alcohol in the undercoat layer coating solution 1 from 30.0 parts to 11.0 parts.

[Example 4]

[0076] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of changing the amount of the styrene-butadiene copolymer latex in the undercoat layer coating solution 1 from 40.0 parts to 39.0 parts and the amount of the aqueous solution of completely saponified polyvinyl alcohol in the undercoat layer coating solution 1 from 30.0 parts to 37.0 parts.

[Example 5]

[0077] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of changing the amount of the styrene-butadiene copolymer latex in the undercoat layer coating solution 1 from 40.0 parts to 36.0 parts and the amount of the aqueous solution of completely saponified polyvinyl alcohol in the undercoat layer coating solution 1 from 30.0 parts to 50.0 parts.

[Example 6]

[0078] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of changing the amount of the styrene-butadiene copolymer latex in the undercoat layer coating solution 1 from 40.0 parts to 35.0 parts and the amount of the aqueous solution of completely saponified polyvinyl alcohol in the undercoat layer coating solution 1 from 30.0 parts to 55.0 parts.

[Example 7]

[0079] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of changing the amount of the styrene-butadiene copolymer latex in the undercoat layer coating solution 1 from 40.0 parts to 23.5 parts and the amount of the aqueous solution of completely saponified polyvinyl alcohol in the undercoat layer coating solution 1 from 30.0 parts to 111.0 parts.

[Example 8]

[0080] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of changing the amount of the styrene-butadiene copolymer latex in the undercoat layer coating solution 1 from 40.0 parts to 15.5 parts and the amount of the aqueous solution of completely saponified polyvinyl alcohol in the undercoat layer coating solution 1 from 30.0 parts to 148.0 parts.

[Example 9]

[0081] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of using the rosette type precipitated calcium carbonate (Okutama Kogyo Co., Ltd., TP221BM, Bulk density: 230g/L, Figure 2) in place of the rosette type precipitated calcium carbonate (Albacar (R) LO).

[Example 10]

[0082] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of using the undercoat layer coating solution 2 in place of the undercoat layer coating solution 1.

[Undercoat layer coating solution 2]

Rosette type precipitated calcium carbonate (Albacar (R) LO)	100.0 parts
Organic hollow particles (Rohm and Haas, HP1055, Average particle diameter (d_{50}): 1.0 μ m, Hollow ratio: 50%)	20.0 parts
Styrene-butadiene copolymer latex (Zeon Corporation, ST5526)	40.0 parts
Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117)	30.0 parts
Water	100.0 parts

[Example 11]

[0083] A thermosensitive recording medium was prepared in the same manner described in Example 1 with the

EP 3 103 649 B2

exception of using the undercoat layer coating solution 3 in place of the undercoat layer coating solution 1.

[Undercoat layer coating solution 3]

5	Rosette type precipitated calcium carbonate (Albacar (R) LO)	80.0 parts
	Calcined clay (BASF Co., Ansilex (R) 93, Bulk density: 195g/L)	12.0 parts
	Styrene-butadiene copolymer latex (Zeon Corporation, ST5526)	40.0 parts
	Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117)	30.0 parts
	Water	100.0 parts

[Comparative Example 1]

15 **[0084]** A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of using the rosette type precipitated calcium carbonate (Specialty Minerals Inc., Albacar (R) 5970, Bulk density: 250g/L) in place of the rosette type precipitated calcium carbonate (Albacar (R) LO) in the undercoat layer coating solution 1.

[Comparative Example 2]

20 **[0085]** A thermosensitive recording medium was prepared in the same manner described in Example 10 with the exception of using the rosette type precipitated calcium carbonate (Albacar (R) 5970) in place of the rosette type precipitated calcium carbonate (Albacar (R) LO) in the undercoat layer coating solution 2.

[Comparative Example 3]

25 **[0086]** A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of using the undercoat layer coating solution 4 in place of the undercoat layer coating solution 1.

[Undercoat layer coating solution 4]

30	Rosette type precipitated calcium carbonate (Albacar (R) 5970)	80.0 parts
	Calcined clay (BASF Co., Ansilex (R) 93)	20.0 parts
	Styrene-butadiene copolymer latex (Zeon Corporation, ST5526)	40.0 parts
	Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117)	30.0 parts
35	Water	100.0 parts

[Comparative Example 4]

40 **[0087]** A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of using the undercoat layer coating solution 5 in place of the undercoat layer coating solution 1.

[Undercoat layer coating solution 5]

45	Calcined clay (BASF Co., Ansilex (R) 93)	100.0 parts
	Styrene-butadiene copolymer latex (Zeon Corporation, ST5526)	40.0 parts
	Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117)	30.0 parts
	Water	100.0 parts

[Comparative Example 5]

50 **[0088]** A thermosensitive recording medium was prepared in the same manner described in Example 1 with the exception of using the undercoat layer coating solution 6 in place of the undercoat layer coating solution 1.

[Undercoat layer coating solution 6]

55	Organic hollow particles (Rohm and Haas, HP1055)	20.0 parts
	Styrene-butadiene copolymer latex (Zeon Corporation, ST5526)	40.0 parts

EP 3 103 649 B2

(continued)

Aqueous solution of completely saponified polyvinyl alcohol (Kuraray Co., Ltd., PVA117)	30.0 parts
Water	100.0 parts

5 **[0089]** The thermosensitive recording media obtained were evaluated as described below.

<Color developing sensitivity (Recorded density)>

10 **[0090]** A thermosensitive recording medium print tester (Ohkura Engineering Co., Ltd. TH-PMD equipped with a thermal head by Kyocera Co.) was used to print a solid pattern on the obtained thermosensitive recording media at applied energy of 0.27 mJ/dot and printing speed of 50mm/sec. The density of the solid pattern was measured by using Macbeth Densitometer (RD-914, with Amber filter) to evaluate the color developing sensitivity.

15 <Heat discoloration resistance in blank portion>

20 **[0091]** The obtained thermosensitive recording medium was treated in an environment of 80 degree C for one hour and stored in an environment of 23 degree C, 50% RH for three hours. The color density of non-printed portion (i.e. blank portion) was measured by using Macbeth Densitometer (RD-914, with Amber filter) to calculate the background color value from the difference between the color densities before and after the treatment. The heat discoloration resistance in the blank portion was evaluated on the following criteria. If the evaluation is rated as Good or Fair, no problem happens in the practical use..

[0092] Background color value = (color density of the non-printing portion after the treatment) - (color density of the non-printing portion before the treatment)

25 Good: The background color value is less than 0.3

Fair: The background color value is 0.3 or higher and less than 0.4

Poor: The background color value is 0.4 or higher

30 <Print image quality>

35 **[0093]** The prepared thermosensitive recording medium was printed a solid pattern by using a thermosensitive recording medium print tester (Ohkura Engineering Co., Ltd. TH-PMD equipped with a thermal head by Kyocera Co.) at applied energy of 0.15 mJ/dot and printing speed of 50mm/sec. Then the print image quality of the solid pattern was visually evaluated on the following criteria. If the evaluation is rated as Excellent, Good or Fair, no problem happens in the practical use..

Excellent: No unrecorded area is observed.

Good: Slight unrecorded area is observed and the printed solid pattern is even.

40 Fair: Although unrecorded area is observed, the printed solid pattern is almost even.

Poor: Much unrecorded area is observed.

<Printing run-ability (prevention of head debris)>

45 **[0094]** The prepared thermosensitive recording medium was printed a solid pattern by using a print tester (Canon Inc., HT180) at applied energy of 0.20 mJ/dot and at -10 degree C. After printing 1m long, the debris on the thermal head of the printer was visually evaluated on the following criteria. If the evaluation is rated as Excellent, Good or Fair, no problem happens in the practical use..

50 Excellent: No head debris is observed.

Good: Almost no head debris is observed.

Fair: Slight head debris is observed.

Poor: Much head debris is observed.

55 **[0095]** The evaluation results are shown in Table 1.

[Table 1]

	Undercoat layer					Evaluation				
	Rosette type precipitated calcium carbonate		Other pigment	Organic hollow particles	Binder	Recorded density	Heat discoloration resistance in blank portion (Background color value/ Evaluation)		Print image quality	Prevention of head debris
	Product name	Bulk density (g/L)	PVA/SBR (%)							
Example 1	Albacar (R) LO	210	-	-	15.6	1.10	0.32	Fair	Excellent	Excellent
Example 2	Albacar (R) LO	210	-	-	3.2	1.06	0.32	Fair	Excellent	Excellent
Example 3	Albacar (R) LO	210	-	-	5.2	1.07	0.32	Fair	Excellent	Excellent
Example 4	Albacar (R) LO	210	-	-	19.8	1.11	0.33	Fair	Excellent	Excellent
Example 5	Albacar (R) LO	210	-	-	28.9	1.12	0.34	Fair	Excellent	Good
Example 6	Albacar (R) LO	210	-	-	32.7	1.13	0.35	Fair	Excellent	Fair
Example 7	Albacar (R) LO	210	-	-	98.4	1.03	0.37	Fair	Good	Fair
Example 8	Albacar (R) LO	210	-	-	198.9	0.99	0.39	Fair	Good	Fair
Example 9	TP221 BM	230	-	-	15.6	1.08	0.38	Fair	Good	Excellent
Example 10	Albacar (R) LO	210	-	contained	15.6	1.17	0.29	Good	Excellent	Good
Example 11	Albacar (R) LO	210	Calcined clay	-	15.6	1.10	0.36	Fair	Good	Good
Comparative Example 1	Albacar (R) 5970	250	-	-	15.6	1.05	0.47	Poor	Good	Good

(continued)

	Undercoat layer					Evaluation			
	Rosette type precipitated calcium carbonate		Other pigment	Organic hollow particles	Binder	Recorded density	Heat discoloration resistance in blank portion (Background color value/ Evaluation)	Print image quality	Prevention of head debris
	Product name	Bulk density (g/L)			PVA/SBR (%)				
Comparative Example 2	Albacar (R) 5970	250	-	contained	15.6	1.12	0.45	Good	Good
Comparative Example 3	Albacar (R) 5970	250	Calcined clay	-	15.6	1.04	0.51	Fair	Good
Comparative Example 4	-	-	Calcined clay	-	15.6	1.03	0.55	Poor	Good
Comparative Example 5	-	-	-	contained	15.6	1.18	0.26	Excellent	Poor
* In the table, PVA/SBR (%) represents the weight ratio (% in solid) of PVA (completely saponified polyvinyl alcohol) to SBR (styrene-butadiene copolymer latex).									

Claims

1. A thermosensitive recording medium comprising (i) a support, (ii) an undercoat layer installed on the support, comprising a pigment and a binder as main components, and (iii) a thermosensitive recording layer installed on the undercoat layer, comprising a colorless or pale colored electron donating leuco dye and an electron accepting color developing agent as main components, **characterised in that** the pigment contained in the undercoat layer is a rosette type precipitated calcium carbonate comprising spindle-shaped primary particles aggregated radially to form secondary particles, and **in that** the bulk density of the rosette type precipitated calcium carbonate is 240 g/L or less, wherein the bulk density is measured according to Japanese Industrial Standard JIS-K-5101-12-1.
2. The thermosensitive recording medium of claim 1, wherein the bulk density of the rosette type precipitated calcium carbonate is from 150 to 220 g/L.
3. The thermosensitive recording medium of claim 1 or 2, wherein the binder contained in the undercoat layer comprises a water-soluble resin and a water-insoluble resin and the weight ratio, in solid content, of water-soluble resin 1 water-insoluble resin is 35/100 or less.
4. The thermosensitive recording medium of claim 1 or 2, wherein the binder contained in the undercoat layer comprises a water-soluble resin and a water-insoluble resin and the weight ratio, in solid content, of water-soluble resin 1 water-insoluble resin is from 3/100 to 30/100.
5. The thermosensitive recording medium of claim 3 or 4, wherein the water-soluble resin is polyvinyl alcohols.
6. The thermosensitive recording medium of any of claims 3-5, wherein the water-insoluble resin is styrene-butadiene resins.
7. The thermosensitive recording medium of any of claims 1-6, wherein the amount of the rosette type precipitated calcium carbonate is 70 weight % or more of the total pigments contained in the undercoat layer.

Patentansprüche

1. Ein wärmeempfindliches Aufzeichnungsmedium, umfassend
 - (i) einen Träger,
 - (ii) eine auf dem Träger aufgebrachte Grundierungsschicht, umfassend ein Pigment und ein Bindemittel als Hauptkomponenten, und
 - (iii) eine auf der Grundierungsschicht aufgebrachte wärmeempfindliche Aufzeichnungsschicht, die einen farblosen oder blass gefärbten Elektronen spendenden Leukofarbstoff und ein Elektronen-aufnehmende und Farbeentwickelnde Agens als Hauptkomponenten umfasst,

dadurch gekennzeichnet, dass das in der Grundierungsschicht enthaltene Pigment ein ausgefälltes rosettenartiges Calciumcarbonat ist, das spindelförmige Primärteilchen umfasst, die radial zu sekundären Teilchen aggregiert sind, und dass die Schüttdichte des ausgefällten rosettenartigen Calciumcarbonats 240 g/l oder weniger ist, wobei die Schüttdichte gemäß dem japanischen Industriestandard JIS-K-5101-12-1 gemessen ist.
2. Thermosensitives Aufzeichnungsmedium nach Anspruch 1, wobei die Schüttdichte des ausgefällten rosettenartigen Calciumcarbonats von 150 bis 220 g/l beträgt.
3. Thermosensitives Aufzeichnungsmedium nach Anspruch 1 oder 2, wobei das in der Grundierungsschicht enthaltene Bindemittel ein wasserlösliches Harz und ein wasserunlösliches Harz umfasst und das Gewichtsverhältnis, im Feststoffgehalt, von wasserlöslichem Harz / wasserunlöslichem Harz 35/100 oder weniger ist.
4. Thermosensitives Aufzeichnungsmedium nach Anspruch 1 oder 2, wobei das in der Grundierungsschicht enthaltene Bindemittel ein wasserlösliches Harz und ein wasserunlösliches Harz umfasst und das Gewichtsverhältnis, im Feststoffgehalt, von wasserlöslichem Harz / wasserunlöslichem Harz von 3/100 bis 30/100 ist.
5. Thermosensitives Aufzeichnungsmedium nach einem der Ansprüche 3 oder 4, wobei das wasserlösliche Harz

Polyvinylalkohol ist.

6. Thermosensitives Aufzeichnungsmedium nach einem der Ansprüche 3 bis 5, wobei das wasserunlösliche Harz Styrol-Butadien-Harz ist.

7. Thermosensitives Aufzeichnungsmedium nach einem der Ansprüche 1 bis 6, wobei die Menge des ausgefällten rosettenartigen Calciumcarbonats 70 Gew.-% oder mehr der gesamten in der Grundierungsschicht enthaltenen Pigmente beträgt.

Revendications

1. Support d'enregistrement thermosensible comprenant (i) un support, (ii) une sous-couche de revêtement disposée sur le support, comprenant un pigment et un liant comme composants principaux, et (iii) une couche d'enregistrement thermosensible disposée sur la sous-couche de revêtement, comprenant un colorant leuco donneur d'électrons incolore ou de couleur pâle et un agent révélateur de couleur accepteur d'électrons comme composants principaux, **caractérisé en ce que** le pigment contenu dans la sous-couche de revêtement est un carbonate de calcium précipité de type rosette comprenant des particules primaires en forme de broche agrégées radialement pour former des particules secondaires et **en ce que** la densité apparente du carbonate de calcium précipité de type rosette est de 240 g/litre ou moins, dans lequel la densité apparente est mesurée selon la norme industrielle japonaise JIS-K-5101-12-1.
2. Support d'enregistrement thermosensible selon la revendication 1, dans lequel la densité apparente du carbonate de calcium précipité de type rosette est de 150 à 220 g/litre.
3. Support d'enregistrement thermosensible selon la revendication 1 ou 2, dans lequel le liant contenu dans la sous-couche de revêtement comprend une résine soluble dans l'eau et une résine insoluble dans l'eau et le rapport en poids, en teneur en solide, de la résine soluble dans l'eau / la résine insoluble dans l'eau est de 35/100 ou moins.
4. Support d'enregistrement thermosensible selon la revendication 1 ou 2, dans lequel le liant contenu dans la sous-couche de revêtement comprend une résine soluble dans l'eau et une résine insoluble dans l'eau et le rapport en poids, en teneur en solide, de la résine soluble dans l'eau / la résine insoluble dans l'eau est de 3/100 à 30/100.
5. Support d'enregistrement thermosensible selon la revendication 3 ou 4, dans lequel la résine soluble dans l'eau est constituée par les alcools polyvinyliques.
6. Support d'enregistrement thermosensible selon l'une quelconque des revendications 3 à 5, dans lequel la résine insoluble dans l'eau est constituée par les résines de styrène - butadiène.
7. Support d'enregistrement thermosensible selon l'une quelconque des revendications 1 à 6, dans lequel la quantité de carbonate de calcium précipité de type rosette est de 70 % en poids ou plus des pigments totaux contenus dans la sous-couche de revêtement.

Fig. 1

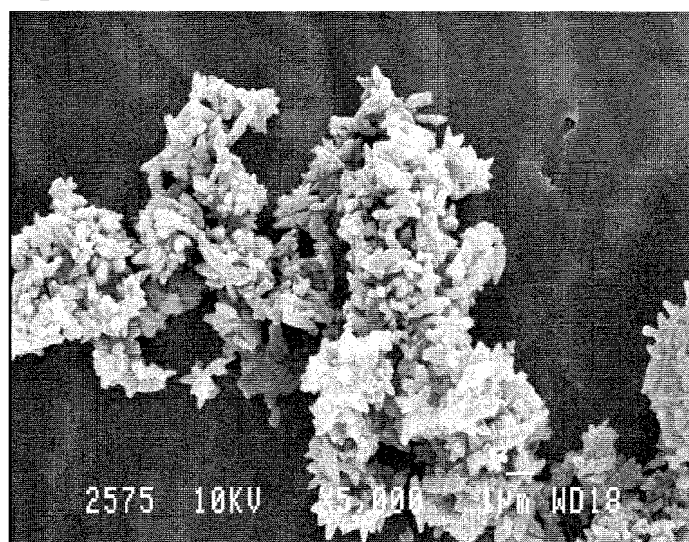
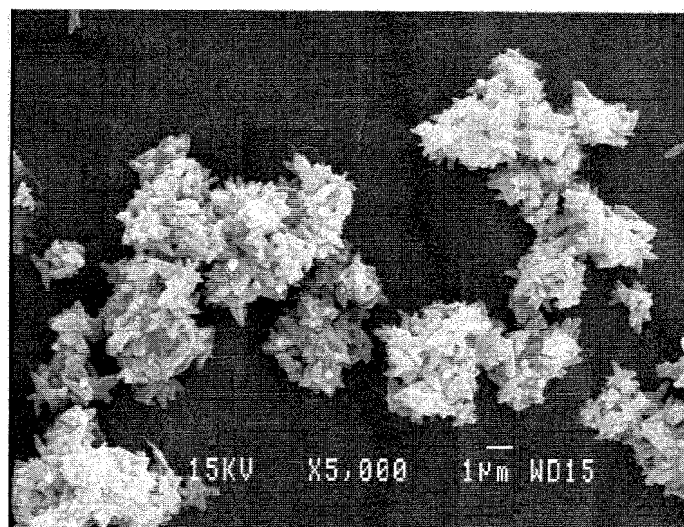


Fig. 2



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP H1086529 B [0005]
- JP 2008006739 A [0005]
- JP 2010094986 A [0005]
- JP H5162446 B [0005]
- JP 2012076228 A [0005]
- JP 2003154760 A [0043] [0045]
- JP H0859603 B [0043]
- WO 9716420 A [0043] [0045]
- WO 02081229 A [0043] [0045]
- JP 2002301873 A [0043]
- JP H10258577 B [0045]