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(54) **Optimized undercoat for thermal recording material**

(57) The present invention relates to a thermal recording material comprising:
- a base layer;
- one or more undercoat layers which is/are laid down on the base layer, wherein the undercoat layer(s) contain(s) a water-soluble resin and hollow particles;
- a thermo-sensitive coloring layer which is laid down on the uppermost undercoat layer, on the opposite side with respect to the base layer; and

- one or more protective layers which is/are laid down on the thermo-sensitive coloring layer, on the opposite side with respect to the undercoat layer(s);
wherein the water soluble resin is a polyvinyl alcohol with a degree of the polymerisation which is at least 400 and at most 1000, and wherein the ratio by mass of the water-soluble resin in the dried state to the hollow particles in the dried state is at least 50% and at most 200%.

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DescriptionField of the Invention

5 **[0001]** The present invention relates to a thermal (thermosensitive) recording material and an image forming method using the same.

Technical background to the invention

10 **[0002]** Thermosensitive recording materials are known which use a colorant system wherein a dye, such as a leuco dye, in one layer of the material reacts, upon the application of heat, with another component, a so-called "developer" in order to give rise to a coloured product.

[0003] In a typical thermosensitive recording material layer assembly, the following layers are present, constructed in the following order:

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- a support (base) layer is provided e.g. a paper support;
 - on top of the support (base) layer, there may optionally be one or more "undercoat" layers which do not contain the (dye + developer) couple;
 - on top of the support (base) layer, or on top of the uppermost undercoat layer if one or more undercoat layers is/are present, is the thermal layer (thermosensitive coloring layer) containing the (dye + developer) couple; and
 - on top of the thermosensitive coloring layer, there may be one or more "protective" layers. The protective layer or layers separate(s) the thermosensitive coloring layer from the outside environment and the uppermost "protective" layer is, like the lowermost support (base) layer (unless the latter has itself a backing layer), in contact with the outside environment.
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[0004] Thermosensitive recording materials are in common daily use, for example, in the transport industry for train, aeroplane and city underground railway tickets. They are also used in other ticketing applications such as parking, museum, cinema and concert tickets, as well as for displaying information on industrially prepared perishable foods, and also for facsimile machines.

30 **[0005]** A number of properties are sought after for such thermosensitive recording materials. For example, high image resolution and uniformity is required. At the same time light resistance is important. Simultaneously achieving good performance in more than one area is often difficult.

[0006] In EP 2 345 541, a thermosensitive recording material is disclosed having excellent light and water resistance.

35 Summary of the Invention

[0007] It is an object of the present invention is to provide a thermal (thermosensitive) recording material having both high image resolution and uniformity, as well as good light resistance.

40 **[0008]** As a result of investigations, the present inventors have determined that these different requirements can be simultaneously achieved using an undercoat whose composition has been optimized. In particular, the use of one or more undercoat layers which, collectively or in one and the same layer, contain both a polyvinyl alcohol as water-soluble resin having a certain degree of polymerization, as well as hollow particles, has been surprisingly found to successfully allow the preparation of a thermal (thermosensitive) recording material having the required properties.

[0009] In one aspect, the present invention thus relates to a thermal recording material comprising:

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- a base layer;
 - one or more undercoat layers which is/are laid down on the base layer, wherein the undercoat layer(s) contain(s) a water-soluble resin and hollow particles;
 - a thermo-sensitive coloring layer which is laid down on the uppermost undercoat layer, on the opposite side with respect to the base layer; and
 - one or more protective layers which is/are laid down on the thermo-sensitive coloring layer, on the opposite side with respect to the undercoat layer(s);
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55 wherein the water soluble resin is a polyvinyl alcohol with a degree of the polymerisation which is at least 400 and at most 1000, and wherein the ratio by mass of the water-soluble resin in the dried state to the hollow particles in the dried state is at least 50% and at most 200%.

[0010] In a preferred embodiment, there is only one undercoat layer, containing both the polyvinyl alcohol used as the water-soluble resin and the hollow particles.

[0011] In a preferred embodiment, the polyvinyl alcohol used as the water-soluble resin in the undercoat layer (or, potentially, layers) has a degree of the polymerisation which is at least 500 and at most 900, preferably at least 600 and at most 800.

[0012] Most typically, in the thermal recording material of the invention, the thermo-sensitive layer will contain a leuco dye and a developer. In generally appropriate embodiments, the thermal recording material of the invention will show protective layer(s) that contain(s) a water-soluble resin and a fluorescent whitening agent. In one embodiment, the protective layers contain a first protective layer containing a water-soluble resin and a fluorescent whitening agent and a second protective layer containing a water-soluble resin but no fluorescent whitening agent, and wherein the first protective layer and the second protective layer are formed in this order over the thermosensitive coloring layer.

[0013] In another aspect, the present invention relates to an image forming method including recording an image on the thermal recording material as previously defined hereinabove, using an image recording unit, which is any one of a thermal head and a laser. In an appropriate embodiment of the image forming, the laser is a CO₂ laser which emits light having a wavelength of 9.3 μm to 10.6 μm.

Detailed Description of the Invention

Base (support) layer

[0014] The support is suitably selected depending on the intended purpose without any restriction. As the support, any of supports made of woodfree paper, recycled pulp (containing 50% or more of recycled pulp), synthetic paper, polyethylene films, and laminated paper, etc. may be used.

Undercoat layer(s)

[0015] There may be a single undercoat layer or the undercoat may be formed of two or more layers.

[0016] In the present invention, polyvinyl alcohol is used as a water-soluble resin in the undercoat.

[0017] In the present invention, "polyvinyl alcohol" is taken to encompass modified polyvinyl alcohols as commonly used by persons skilled in the art. Polyvinyl alcohol is often prepared industrially by polymerisation of vinyl acetate followed by saponification, so that a certain percentage of (-CH₂-CHO-CO-Me) groups are present, in addition to the main monomer residue of (-CH₂-CHOH-). In typical commercially available polyvinyl alcohols, and which can appropriately be used in the practice of the present invention, the saponification range is normally from 70% to 99%, i.e. the polymer chain contains 70% to 99% of (-CH₂-CHOH-) units. In the context of the present invention, it is possible to use polyvinyl alcohol products which result from copolymerization of vinyl acetate with other monomers, such as itaconic acid, which gives rise to (-CH₂-C(CO₂M)(CH₂CO₂M)-) monomer residues in the polymer chain (M = H or a metal ion such as Na according to the pH / degree of neutralization). Other modified PVAs that can be used in the present invention include sulfonic modified PVAs, diacetic modified PVAs, and acetoacetyl modified PVAs.

[0018] In preferred embodiments of the present invention, the undercoat layer(s) contain(s) substantially only or only PVAs, including modified PVAs, as water-soluble resin. However, provided that the sought-after properties of thermal recording materials of the invention are not compromised, and in particular gas barrier ability as measured by undercoat air permeability, other water-soluble polymers can be used in conjunction with the PVAs used in undercoat layers of the present invention. Other water-soluble polymers that can be used conjointly with PVAs include: starch and derivatives thereof, cellulose derivatives such as methoxy cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, methyl cellulose and ethyl cellulose, polyacrylate soda, polyvinyl pyrrolidone, acryl amide-acrylate copolymers, acryl amide-acrylate-methacrylic acid terpolymers, alkali salts of styrene-maleic anhydride copolymers, alkali salts of isobutylene-maleic anhydride copolymers, polyacrylamide, modified polyacrylamide, methyl vinyl ether-maleic anhydride copolymers, carboxyl-modified polyethylene, polyvinyl alcohol-acryl amide block copolymers, melamine-formaldehyde resin, urea-formaldehyde resin, alginate soda, gelatin and casein.

[0019] In the present invention, the degree of polymerization of the polyvinyl alcohol is between 400 and 1000, i.e. there are between 400 and 1000 monomer units in the polymer chain on average. As explained above, for a perfect PVA homopolymer, all such monomer units would be (-CH₂-CHOH-). However, typically PVA materials sold commercially and used by persons skilled in the art contain a certain degree of residual ester groups and/or other main chain or side-chain modifications as discussed above.

[0020] Commonly used polyvinyl alcohol resin products in the field of thermal recording materials have a degree of polymerisation of 1500 to 2000, in order to ensure good barrier properties. However, lower molecular sizes than this are used in the present invention.

[0021] The amount of the polyvinyl alcohol as water-soluble resin in the undercoat, consisting of the one or more undercoat layers present, is preferably at least 30% by mass, more preferably at least 40% by mass, even more preferably at least 50% by mass. When the amount of the water-soluble resin in the undercoat is too low, it is difficult to reduce air

permeance, which is believed to be correlated with reduced light resistance since oxygen participates together with light in reactions that degrade the thermal recording material. When it is too high, in the case where an image is formed using a thermal head, sufficient coloring sensitivity may not be easily obtained.

[0022] The undercoat layer(s) is (are) formed by applying a water dispersion of the water-soluble resin, followed by drying. As the components added to the water dispersion and contained in the undercoat layer, hollow particles are used.

[0023] The hollow particles preferably have a hollow ratio of 80% or more, more preferably 90% or more, wherein the hollow ratio (in %) is the (inner diameter of a hollow particle / outer diameter of the hollow particle) x 100. When the hollow ratio is less than 80%, thermal insulating properties and cushioning properties are insufficient. In the case where image formation is performed using a thermal head, heat energy from the thermal head is emitted to the outside of the thermosensitive recording material via the support, and the adhesion properties between the thermal head and the thermosensitive recording material becomes poor, causing less effect on improving sensitivity and fineness. The practically obtainable hollow particles each have a hollow ratio of 98% or less.

[0024] Each of the hollow particles has a shell made of a thermoplastic resin and contains therein air or other gas. They are fine hollow particles already in a foamed state, and those having a volume average particle diameter of 2 μm to 10 μm are preferably used. When the volume average particle diameter (outer particle diameter) is less than 2 μm , there is a production problem of difficulty in obtaining given hollow ratio. When the volume average particle diameter is more than 10 μm , the smoothness of the dried coated surface decreases, causing decrease in adhesion properties between the thermal head and the thermosensitive recording material, and less effect on improving sensitivity. Accordingly, the hollow particles preferably have a sharp distribution peak with little variation as well as a volume average particle diameter falling within the aforementioned range.

[0025] The hollow particles are particles each having a thermoplastic resin as a shell, and examples of the thermoplastic resin include polystyrene, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyacrylic ester, polyacrylonitrile, and polybutadiene, and copolymer resins thereof. Among these, the copolymer resins which contain vinylidene chloride and acrylonitrile as main constituents are particularly preferable.

[0026] The amount of the hollow particles after the undercoat (i.e. the undercoat layer or layers) is dried is preferably 0.2 g or more, more preferably 0.4 g to 5 g, per square meter of the support. In any event, the ratio by mass of polyvinyl alcohol as water-soluble resin to the hollow particles, expressed as dry weight, ranges from 50% to 200%.

[0027] In the undercoat, an inorganic filler may also be used. Such an inorganic filler is suitably selected depending on the intended purpose without any restriction. Examples thereof include aluminum hydroxide, calcium carbonate, aluminum oxide, zinc oxide, titanium dioxide, silica, barium sulfate, talc, kaolin, alumina and clay. These may be used alone or in combination. Among these, aluminum hydroxide, calcium carbonate, kaolin and clay are preferable in terms of liquid properties in a coating liquid, stability of dispersed particles, and water solubility.

[0028] An aqueous emulsion resin may also be used in the undercoat, such as latexes of, for example, styrene-butadiene copolymers, and styrene-butadiene-acryl copolymers; and emulsions of, for example, vinyl acetate resins, vinyl acetate-acrylate copolymers, styrene-acrylate copolymers, acrylate resins, and polyurethane resins. These may be used alone or in combination.

[0029] The deposition amount of a first undercoat layer in the thermosensitive recording material is suitably selected depending on the intended purpose without any restriction. It is preferably 0.4 g/m² to 10 g/m², more preferably 0.6 g/m² to 7 g/m². When the deposition amount of the first undercoat layer is less than 0.4 g/m², it is difficult to appropriate air permeance. When the deposition amount is more than 10 g/m², the binding properties of the first undercoat layer may decrease.

[0030] In a preferred embodiment, the undercoat of the present invention has an air permeance of 150 mL/min or less. When the air permeance is more than 150 mL/min, the performance of the undercoat layer required for light resistance, i.e. performance for blocking the oxygen ingress from a surface of the undercoat layer facing the support, is insufficient, and a desired light resistance cannot be attained. From this standpoint, the air permeance of the undercoat layer is more preferably 50 mL/min or less, ideally 0 mL/min. Here, the air permeance can be measured using BENDTSEN TESTER (manufactured by Messmer Instruments Ltd.) in accordance with ISO5636 (Bendtsen method).

Thermosensitive Coloring Layer

[0031] The thermosensitive coloring layer contains a colorant system wherein a dye, such as a leuco dye, in one layer of the material reacts, upon the application of heat, with another component, a so-called "developer" in order to give rise to a coloured product.

[0032] The leuco dye is a compound exhibiting electron donation properties, and may be used singly or in combination of two or more species. However, the leuco dye itself is a colorless or light-colored dye precursor, and commonly known leuco compounds can be used. Examples of the leuco compounds include triphenylmethane phthalide compounds, triarylmethane compounds, fluoran compounds, phenothiazine compounds, thiofluoran compounds, xanthen compounds, indophthalyl compounds, spiropyran compounds, azaphthalide compounds, chlormenopirazole compounds,

methyne compounds, rhodamine anilinolactum compounds, rhodamine lactum compounds, quinazoline compounds, diazaxanthen compounds, bislactone compounds. In consideration of coloring property, fogging of the background, and color fading of the image due to moisture, heat or light radiation, specific examples of such compounds are as follows.

2-anilino-3-methyl-6-diethyl amino fluoran, 2-anilino-3-methyl-6-(di-n-butyl amino) fluoran, 2-anilino-3-methyl-6-(di-n-pentyl amino) fluoran, 2-anilino-3-methyl-6-(N-n-propyl-N-methyl amino) fluoran, 2-anilino-3-methyl-6-(N-isopropyl-N-methyl amino) fluoran, 2-anilino-3-methyl-6-(N-isobutyl-N-methyl amino) fluoran, 2-anilino-3-methyl-6-(N-n-amyl-N-methyl amino) fluoran, 2-anilino-3-methyl-6-(N-sec-butyl-N-ethyl amino) fluoran, 2-anilino-3-methyl-6-(N-n-amyl-N-ethyl amino) fluoran, 2-anilino-3-methyl-6-(N-iso-amyl-N-ethyl amino) fluoran, 2-anilino-3-methyl-6-(N-cyclohexyl-N-methyl amino) fluoran, 2-anilino-3-methyl-6-(N-ethyl-p-toluidino) fluoran, 2-anilino-3-methyl-6-(N-methyl-p-toluidino) fluoran, 2-(m-trichloro methyl anilino)-3-methyl-6-diethyl amino fluoran, 2-(m-trifluoro methyl anilino)-3-methyl-6-diethyl amino fluoran, 2-(m-trifluoro methyl anilino)-3-methyl-6-(N-cyclohexyl-N-methyl amino) fluoran, 2-(2,4-dimethyl anilino)-3-methyl-6-diethyl amino fluoran, 2-(N-ethyl-p-toluidino)-3-methyl-6-(N-ethyl anilino) fluoran, 2-(N-methyl-p-toluidino)-3-methyl-6-(N-propyl-p-toluidino) fluoran, 2-anilino-6-(N-n-hexyl-N-ethyl amino) fluoran, 2-(o-chloranilino)-6-diethyl amino fluoran, 2-(o-bromoanilino)-6-diethyl amino fluoran, 2-(o-chloranilino)-6-dibutyl amino fluoran, 2-(o-fluoroanilino)-6-dibutyl amino fluoran, 2-(m-trifluoro methyl anilino)-6-diethyl amino fluoran, 2-(p-acetyl anilino)-6-(N-n-amyl-N-n-butyl amino) fluoran, 2-benzyl amino-6-(N-ethyl-p-toluidino) fluoran, 2-benzyl amino-6-(N-methyl-2,4-dimethyl anilino) fluoran, 2-benzyl amino-6-(N-ethyl-2,4-dimethyl anilino) fluoran, 2-dibenzyl amino-6-(N-methyl-p-toluidino) fluoran, 2-dibenzyl amino-6-(N-ethyl-p-toluidino) fluoran, 2-(di-p-methyl benzyl amino)-6-(N-ethyl-p-toluidino) fluoran, 2-([alpha]-phenyl ethyl amino)-6-(N-ethyl-p-toluidino) fluoran, 2-methyl amino-6-(N-methyl anilino) fluoran, 2-methyl amino-6-(N-ethyl anilino) fluoran, 2-methyl amino-6-(N-propyl anilino) fluoran, 2-ethyl amino-6-(N-methyl-p-toluidino) fluoran, 2-methyl amino-6-(N-methyl-2,4-dimethyl anilino) fluoran, 2-ethyl amino-6-(N-methyl-2,4-dimethyl anilino) fluoran, 2-dimethyl amino-6-(N-methyl anilino) fluoran, 2-dimethyl amino-6-(N-ethyl anilino) fluoran, 2-diethyl amino-6-(N-methyl-p-toluidino) fluoran, benzo leuco methylene blue, 2-[3,6-bis(diethyl amino)]-6-(o-chloranilino) xanthyl benzoic acid lactum, 2-[3,6-bis(diethyl amino)]-9-(o-chloranilino) xanthyl benzoic acid lactum, 3,3-bis(p-dimethyl amino phenyl) phthalide, 3,3-bis(p-dimethyl amino phenyl)-6-dimethyl amino phthalide, 3,3-bis(p-dimethyl amino phenyl)-6-diethyl amino phthalide, 3,3-bis(p-dimethyl amino phenyl)-6-chlorophthalide, 3,3-bis(p-dibutyl amino phenyl) phthalide, 3-(2-methoxy-4-dimethyl amino phenyl)-3-(2-hydroxy-4,5-dichlorophenyl) phthalide, 3-(2-hydroxy-4-dimethyl amino phenyl)-3-(2-methoxy-5-chlorophenyl) phthalide, 3-(2-hydroxy-4-dimethoxy amino phenyl)-3-(2-methoxy-5-chlorophenyl) phthalide, 3-(2-hydroxy-4-dimethoxy amino phenyl)-3-(2-methoxy-5-nitrophenyl) phthalide, 3-(2-hydroxy-4-diethyl amino phenyl)-3-(2-methoxy-5-methyl phenyl) phthalide, 3,6-bis(dimethyl amino) fluorenespiro (9,3')-6'-dimethyl amino phthalide, 6'-chloro-8'-methoxybenzoindolino spiropyran, and 6'-bromo-2'-methoxy benzoindolino spiropyran. These may be used alone or in combination.

[0033] The amount of the leuco dye contained in the thermosensitive coloring layer is preferably 5% by mass to 20% by mass, more preferably 10% by mass to 15% by mass.

[0034] As the developer, various electron accepting materials are suitably used to react with the aforementioned leuco dye at the time of heating so as to develop colors. Examples thereof include phenolic compounds, organic or inorganic acidic compounds and esters or salts thereof. Specific examples thereof include bisphenol A, tetrabromobisphenol A, gallic acid, salicylic acid, 3-isopropyl salicylate, 3-cyclohexyl salicylate, 3-5-di-tert-butyl salicylate, 3,5-di-[alpha]-methyl benzyl salicylate, 4,4'-isopropylidenediphenol, 1,1'-isopropylidene bis (2-chlorophenol), 4,4'-isopropylidene bis (2,6-dibromophenol), 4,4'-isopropylidene bis (2,6-dichlorophenol), 4,4'-isopropylidene bis (2-methyl phenol), 4,4'-isopropylidene bis (2,6-dimethyl phenol), 4,4'-isopropylidene bis (2-tert-butyl phenol), 4,4'-sec-butylidene diphenol, 4,4'-cyclohexylidene bisphenol, 4,4'-cyclohexylidene bis (2-methyl phenol), 4-tert-butyl phenol, 4-phenyl phenol, 4-hydroxy diphenoxide, α -naphthol, p-naphthol, 3,5-xenol, thymol, methyl-4-hydroxybenzoate, 4-hydroxyacetophenone, novolak phenol resins, 2,2'-thio bis (4,6-dichloro phenol), catechol, resorcin, hydroquinone, pyrogallol, fluoroglycine, fluoroglycine carboxylate, 4-tert-octyl catechol, 2,2'-methylene bis (4-chlorophenol), 2,2'-methylene bis (4-methyl-6-tert-butyl phenol), 2,2'-dihydroxy diphenyl, ethyl p-hydroxybenzoate, propyl p-hydroxybenzoate, butyl p-hydroxybenzoate, benzyl p-hydroxybenzoate, p-hydroxybenzoate-p-chlorobenzyl, p-hydroxybenzoate-o-chlorobenzyl, / p-hydroxybenzoate-p-methylbenzyl, p-hydroxybenzoate-n-octyl, benzoic acid, zinc salicylate, 1-hydroxy-2-naphthoic acid, 2-hydroxy-6-naphthoic acid, 2-hydroxy-6-zinc naphthoate, 4-hydroxy diphenyl sulphone, 4-hydroxy-4'-chloro diphenyl sulfone, bis (4-hydroxy phenyl) sulfide, 2-hydroxy-p-toluic acid, 3, 5-di-tert-zinc butyl salicylate, 3,5-di-tert-tin butyl salicylate, tartaric acid, oxalic acid, maleic acid, citric acid, succinic acid, stearic acid, 4-hydroxyphthalic acid, boric acid, thiourea derivatives, 4-hydroxy thiophenol derivatives, bis (4-hydroxyphenyl) acetate, bis (4-hydroxyphenyl) ethyl acetate, bis (4-hydroxyphenyl) acetate-n-propyl, bis (4-hydroxyphenyl) acetate-n-butyl, bis (4-hydroxyphenyl) phenyl acetate, bis (4-hydroxyphenyl) benzyl acetate, bis (4-hydroxyphenyl) phenethyl acetate, bis (3-methyl-4-hydroxyphenyl) acetate, bis (3-methyl-4-hydroxyphenyl) methyl acetate, bis (3-methyl-4-hydroxyphenyl) acetate-n-propyl, 1,7-bis (4-hydroxyphenylthio) 3,5-dioxahexane, 1,5-bis (4-hydroxyphenylthio) 3-oxahexane, 4-hydroxy phthalate dimethyl, 4-hydroxy-4'-methoxy diphenyl sulfone, 4-hydroxy-4'-ethoxy diphenyl sulfone, 4-hydroxy-4'-isopropoxy diphenyl sulfone, 4-hydroxy-4'-propoxy diphenyl sulfone, 4-hydroxy-4'-butoxy diphenyl sulfone, 4-hydroxy-4'-isopropoxy diphenyl sulfone, 4-hydroxy-4'-sec-butoxy diphenyl sul-

fone, 4-hydroxy-4'-tert-butoxy diphenyl sulfone, 4-hydroxy-4'-benzyloxy diphenyl sulfone, 4-hydroxy-4'-phenoxy diphenyl sulfone, 4-hydroxy-4'-(m-methyl benzoxy) diphenyl sulfone, 4-hydroxy-4'-(p-methyl benzoxy) diphenyl sulfone, 4-hydroxy-4'-(o-methyl benzoxy) diphenyl sulfone, 4-hydroxy-4'-(p-chloro benzoxy) diphenyl sulfone and 4-hydroxy-4'-oxyaryl diphenyl sulfone. These may be used alone or in combination.

[0035] In the thermosensitive coloring layer, the mixing ratio of the developer to the leuco dye is such that the developer is preferably 0.5 parts by mass to 10 parts by mass, more preferably 1 part by mass to 5 parts by mass, relative to 1 part by mass of the leuco dye.

[0036] Besides the above-described leuco dye and developer, it is possible to appropriately add, to the thermosensitive coloring layer, other materials customarily used in thermosensitive recording materials, such as a binder, a filler, a hot-melttable material, a crosslinking agent, a pigment, a surfactant, a fluorescent whitening agent and a lubricant.

[0037] The binder may be used if necessary in order to improve the adhesiveness and coatability of the layer. The binder is suitably selected depending on the intended purpose without any restriction. Specific examples of the binder resin include starches, hydroxyethyl cellulose, methyl cellulose, carboxy methyl cellulose, gelatin, casein, gum arabic, polyvinyl alcohols, salts of diisobutylene-maleic anhydride copolymers, salts of styrene-maleic anhydride copolymers, salts of ethylene-acrylic acid copolymers, salts of styrene-acryl copolymers and salt emulsions of styrene-butadiene copolymers.

[0038] The filler is suitably selected depending on the intended purpose without any restriction. Examples thereof include inorganic pigments such as calcium carbonate, aluminum oxide, zinc oxide, titanium dioxide, silica, aluminum hydroxide, barium sulfate, talc, kaolin, alumina and clay, and commonly known organic pigments. Among these, acidic pigments (those which exhibit acidity in aqueous solutions) such as silica, alumina and kaolin are preferable, with silica being particularly preferable from the viewpoint of developed color density.

[0039] The hot-melttable material is suitably selected depending on the intended purpose without any restriction. Examples thereof include fatty acids such as stearic acid and behenic acid; fatty acid amides such as stearic acid amide, erucic acid amide, palmitic acid amide, behenic acid amide and palmitic acid amide; N-substituted amides such as N-lauryl lauric acid amide, N-stearyl stearic acid amide and N-oleyl stearic acid amide; bis fatty acid amides such as methylene bis stearic acid amide, ethylene bis stearic acid amide, ethylene bis lauric acid amide, ethylene bis capric acid amide and ethylene bis behenic acid amide; hydroxyl fatty acid amides such as hydroxyl stearic acid amide, methylene bis hydroxyl stearic acid amide, ethylene bis hydroxyl stearic acid amide and hexamethylene bis hydroxy stearic acid amide; metal salts of fatty acids, such as zinc stearate, aluminum stearate, calcium stearate, zinc palmitate and zinc behenate; p-benzyl biphenyl, terphenyl, triphenyl methane, benzyl p-benzyloxybenzoate, [beta]-benzyloxy naphthalene, phenyl [beta]-naphthoate, 1-hydroxy-2-phenyl naphthoate, methyl 1-hydroxy-2-naphthoate, diphenyl carbonate, benzyl terephthalate, 1,4-dimethoxy naphthalene, 1,4-diethoxy naphthalene, 1,4-dibenzyloxy naphthalene, 1,2-diphenoxy ethane, 1,2-bis (4-methyl phenoxy ethane), 1,4-diphenoxy-2-butene, 1,2-bis (4-methoxy phenyl thio) ethane, dibenzoyl methane, 1,4-diphenylthio butane, 1,4-diphenylthio-2-butene, 1,3-bis (2-vinyloxy ethoxy) benzene, 1,4-bis (2-vinyloxy ethoxy) benzene, p-(2-vinyloxy ethoxy) biphenyl, p-aryloxy biphenyl, dibenzoyloxymethane, dibenzoyloxypropane, dibenzyl sulfide, 1,1-diphenyl ethanol, 1,1-diphenyl propanol, p-benzyloxy benzyl alcohol, 1,3-phenoxy-2-propanol, N-octadecyl carbamoyl-p-methoxy carbonyl benzene, N-octadecyl carbamoyl benzene, 1,2-bis (4-methoxyphenoxy) propane, 1,5-bis (4-methoxyphenoxy)-3-oxapentane, dibenzyl oxalate, bis (4-methyl benzyl) oxalate and bis (4-chlorobenzyl) oxalate. These may be used alone or in combination.

[0040] Further, it is preferred that diacetone-modified polyvinyl alcohol be incorporated into the thermosensitive coloring layer, when N-aminopolyacryl amide serving as a crosslinking agent is added to the thermosensitive coloring layer and the protective layer, a crosslinking reaction readily occurs, and water resistance can be improved without adding another crosslinking agent that could impede color development.

[0041] The thermosensitive coloring layer can be formed by commonly known methods. For example, a leuco dye and a developer have been pulverized and dispersed together with a binder and other components so as to have a particle diameter of 1 μm to 3 μm by a disperser such as a ball mill, an Attriter and a sand mill. The resultant dispersion is mixed, if necessary, together with a filler and a hot-melttable material (sensitizer) dispersion liquid in accordance with a predetermined formulation, to thereby prepare a coating liquid of a thermosensitive coloring layer, followed by applying the thus-prepared coating liquid onto a support.

[0042] The thickness of the thermosensitive coloring layer varies depending on the composition of the thermosensitive coloring layer and intended use of the thermosensitive recording materials and cannot be specified flatly, but it is preferably 1 μm to 50 μm , more preferably 3 μm to 20 μm .

Protective Layer

[0043] The protective layer(s) contain(s) at least a water-soluble resin and a fluorescent whitening agent, and further contains other components as necessary. By providing the protective layer, it is expected to further improve the light resistance while the background whiteness is maintained.

[0044] There may be a single protective layer or more than one protective layer, such as two protective layers. It is preferred that a first protective layer containing the water-soluble resin and the fluorescent whitening agent, and a second protective layer containing the water-soluble resin but no fluorescent whitening agent be formed in this order over the thermosensitive coloring layer. In this case, even though the amount of the fluorescent whitening agent is increased in the entire protective layer, background whiteness can be maintained while the background is suppressed from being turned into yellow color. Moreover, it can be expected to further improve the light resistance due to the fluorescent whitening agent, as well as improving the water resistance.

[0045] A first protective layer may contain the fluorescent whitening agent and the water-soluble resin, and further contain a crosslinking agent.

[0046] The fluorescent whitening agent is suitably selected depending on the intended purpose without any restriction. A stilbene compound is preferable from the standpoint of exhibiting excellent light resistance.

[0047] The stilbene compound is suitably selected depending on the intended purpose without any restriction. Examples thereof include 4,4'-bis(2-amino-4-anilino-1, 3, 5-triazinyl-6-amino) stilbene-2, 2'-disulfonic acid, disodium 4,4'-bis(2,4-dianilino-1,3,5-triazin-6-yl-amino)stilbene-2,2'-disulfonic acid, 4,4'-bis(2-anilino-4-hydroxyethylamino-1,3,5-triazinyl-6-amino)stilbene disulfonic acid, sodium 4,4'-bis[2-(2-methylanilino)-4-bis(hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid, sodium 4,4'-bis[2-(2-methylanilino)-4-bis(hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid, sodium 4,4'-bis[2-(m-sulfoanilino)-4-(2-hydroxypropyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid, sodium 4-[2-p-sulfoanilino-4-bis(hydroxyethyl)amino-1, 3, 5-triazinyl-6-amino]-4'-[2-m-sulfoanilino-4-bis(hydroxyethyl)amino-1, 3, 5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid, sodium 4,4'-bis[2-sodiumsulfanyl-4-di(hydroxyethyl)amino-1,3,5-triazinyl-6-amino]stilbene-2,2'-disulfonic acid, 4,4'-bis[4-[3-acetylaminol-4-(4,8-disulfo-2-naphthylazo)]anilino-6-(3-carboxypyridinio)-1,3, 5-triazin-2-ylamino]-2,2'-disulfostilbene dihydroxide hexasodium salt, 4,4'-bis[4-[3-acetylaminol-4-(4,8-disulfo-2-naphthylazo)]anilino-6-chloro-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid hexasodium salt, 4,4'-bis[4-[3-[3-carboxy-5-hydroxy-1-(p-sulfoanilino)-4-pyrazolylazo]-4-sulfoanilino]-6-chloro-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid octasodium salt, 4,4'-bis[4-chloro-6-[3-[1-(2-chloro-5-sulfoanilino)-5-hydroxy-3-methyl-4-pyrazolylazo]-4-sulfoanilino]-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid hexasodium salt, 4,4'-bis[6-[N-(2-cyanoethyl)-N-[2-(2-hydroxyethoxy)ethyl]amino]-4-(2,5-disulfoanilino)-1, 3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid hexasodium salt, 4,4'-bis[4-bis(2-hydroxypropyl)amino-6-(4-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid tetrasodium salt, 4-(4-amino-6-anilino-1,3,5-triazin-2-ylamino)-4'-(4,6-diamino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, calcium 4-(2,4-diamino-1,3,5-triazin-6-yl)amino-4'-(4-amino-2-chloro-6-yl)amino-2, 2'-stilbene disulfonic acid, 4,4'-bis(4-amino-6-anilino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis(4-amino-6-anilino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, potassium hydrogen 4,4'-bis(4-amino-6-anilino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulphonic acid, 4,4'-bis(4-amino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis(4-amino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, calcium 4,4'-bis(6-amino-4-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, potassium hydrogen 4,4'-bis(4-amino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, sodium hydrogen 4,4'-bis(4-amino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, disodium 4,4'-bis(4-amino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4,4'-bis[4-anilino-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid potassium salt (primary salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-anilino-6-(2-hydroxyethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis[4-anilino-6-(2-hydroxyethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, potassium hydrogen 4,4'-bis[4-anilino-6-(2-hydroxyethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, disodium 4,4'-bis(4-anilino-6-methylamino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4,4'-bis[4-(2,5-disulfoanilino)-6-(2-hydroxypropylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[6-(m-sulfoanilino)-4-(2-hydroxydiethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[6-(m-sulfoanilino)-4-(2-hydroxypropylamino)-1,3,5-triazin-2-ylaminol-2,2'-stilbene disulfonic acid, 4,4'-bis[6-(2-hydroxyethylamino)-4-anilino-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, sodium hydrogen 4,4'-bis[4-bis(2-hydroxyethyl)amino-6-chloro-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis(4-methylamino-6-phenylamino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4-[4-chloro-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-ylamino]-4'-[4,6-bis[bis(2-hydroxyethyl)amino]-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-ylaminol-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis[4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-ylaminol-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis[4-anilino-6-[N-(2-hydroxyethyl)-N-methylaminol-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, potassium hydrogen 4,4'-bis[4-anilino-6-[N-(2-hydroxyethyl)-N-methylamino]-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[4-(diethylamino)-6-(2,5-disulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid sodium salt (primary salt, secondary salt, tertiary salt, quaternary salt, quinary salt, or senary salt), 4,4'-bis[6-(p-sulfamoylphenylamino)-4-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[4-bis(2-hydroxyethyl)amino-6-(p-sulfamoylanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, disodium 4,4'-bis[4-bis(2-hydroxyethyl)amino-6-chloro-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[6-bis(2-hydroxyethyl)amino-4-(2,5-disulfoanilino)-1, 3, 5-triazin-2-ylaminol-2,2'-stilbene disulfonic ac-

id, 4,4'-bis[4-bis(2-hydroxyethyl)amino-6-(m-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilben e disulfonic acid, 4,4'-bis[4-bis(2-hydroxyethyl)amino-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilben e disulfonic acid, 4,4'-bis[4-bis(2-hydroxyethyl)amino-6-(m-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilben e disulfonic acid potassium salt (primary salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-bis(2-hydroxyethyl)amino-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-4'-[4-bis(2-hydroxyethyl)amino-6-(m-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4-[4-bis(2-hydroxyethyl)amino-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-4'-[4-bis(2-hydroxyethyl)amino-6-(m-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid sodium salt (primary salt, secondary salt, tertiary salt, or quaternary salt), 4-[4-bis(2-hydroxyethyl)amino-6-methoxy-1,3,5-triazin-2-ylamino]-4'-(4-methoxy-6-morpholino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4-[4-bis(2-hydroxyethyl)amino-6-methoxy-1,3,5-triazin-2-ylamino]-4'-[4-(2-hydroxysulfonyl)ethylamino]-6-methoxy-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, disodium 4-(4-anilino-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4-(4-anilino-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, dipotassium 4-(4-anilino-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, potassi-
um hydrogen 4-(4-anilino-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, sodium hydrogen 4-(4-anilino-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, disodium 4-(4-anilino-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4,4'-bis[6-(1-hydroxy-1-methylethylamino)-4-methoxy-1,3,5-triazin-2-ylamino]-2,2'-stilben e disulfonic acid, 4-(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, dipotassium 4-(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, potassium hydrogen 4-(4-chloro-6-methoxy-1,3,5-triazin-2-ylami-
no)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, sodium hydrogen 4-(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, disodium hydrogen 4-(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4,6-dimethoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4,4'-bis(4-anilino-6-methoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4,4'-bis[4-chloro-6-(p-sulphophenoxy)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid disodium salt (primary salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-chloro-6-phenoxy-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid sodium salt (primary salt, or secondary salt), 4,4'-bis[4-chloro-6-methoxy-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, potassium hydrogen 4,4'-bis(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene di-
sulfonic acid, 4,4'-bis(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid sodium salt (primary salt, or secondary salt), 4,4'-bis[4-(2-hydroxyethylamino)-6-phenoxy-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[4-(2-hydroxyethylamino)-6-methoxy-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis(4-anilino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis(4-anilino-6-chloro-1,3,5-triazin-2-ylami-
no)-2,2'-stilbene disulfonic acid, potassium hydrogen 4,4'-bis(4-anilino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene di-
sulfonic acid, sodium hydrogen 4,4'-bis(4-anilino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, disodium hydrogen 4,4'-bis(4-anilino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, potassium sodium 4,4'-bis(4-anilino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4,4'-bis[4-chloro-6-(p-chloroanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, sodium hydrogen 4,4'-bis [4-chloro-6-(p-chloroanilino)-1,3,5-triazin-2-ylamino] -2,2'-stilbene disulfonic acid, disodium hydrogen 4,4'-bis [4-chloro-6-(p-chloroanilino)-1,3,5-triazin-2-ylamino] -2,2'-stilbene disulfonic acid, 4,4'-bis[4-chloro-6-(2,5-disulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'- stilbene disulfonic acid, 4,4'-bis[4-chloro-6-(2,5-disulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid sodium salt (primary salt, second-
ary salt, tertiary salt, quaternary salt, quinary salt, or senary salt), disodium 4,4'-bis[4-chloro-6-(p-sulfamoylanilino)-1,3,5-triazin-2-ylaminol-2,2'-stilbene disulfonic acid, 4,4'-bis[4-chloro-6-(m-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[4-chloro-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[4-chloro-6-(m-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid potassium salt (primary salt, secondary salt, ter-
tiary salt, or quaternary salt), 4,4'-bis[4-chloro-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid po-
tassium salt (primary salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-chloro-6-(2,5-disulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'- stilbene disulfonic acid hexapotassium salt, 4,4'-bis[4-chloro-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid sodium salt(primary salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-chloro-6-(m-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid sodium salt(primary salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-chloro-6-(2-sulfoethylamino)-1,3,5-triazin-2-ylamino] -2,2'-stilbene disulfonic
acid, 4,4'-bis[4-chloro-6-(2-sulfoethylamino)-1,3,5-triazin-2-ylamino]-2,2'- stilbene disulfonic acid potassium salt (prima-
ry salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-chloro-6-(2-sulfbethylamino)-1,3,5-triazin-2-ylamino]-
2,2'-stilbene disulfonic acid sodium salt (primary salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-chloro-6-(o-toluidino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis[4-chloro-6-(o-toluidino)-1,3,5-triazin-2-ylami-

no]-2,2'-stilbene disulfonic acid, sodium hydrogen 4,4'-bis[4-chloro-6-(o-toluidino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, disodium hydrogen 4,4'-bis[4-chloro-6-(o-toluidino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, sodium hydrogen 4,4'-bis[4-chloro-6-(2-hydroxyethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, disodium 4,4'-bis[4-chloro-6-(2-hydroxyethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[4-chloro-6-(2-hydroxyethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid sodium salt (primary salt, secondary salt, tertiary salt, quaternary salt, quinary salt, or senary salt), 4,4'-bis[4-chloro-6-(7-phenylazo-8-hydroxy-2,5-disulfo-1-naphthylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid sodium salt (primary salt, secondary salt, tertiary salt, quaternary salt, quinary salt, or senary salt), disodium 4,4'-bis[4-chloro-6-(o-methylanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis(4,6-dichloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, calcium 4,4'-bis(4,6-dichloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, sodium hydrogen 4,4'-bis(4,6-dichloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4,4'-bis[4-morpholino-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis[4-morpholino-6-(2-sulfoethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid potassium salt (primary salt, secondary salt, tertiary salt, or quaternary salt), 4,4'-bis[4-morpholino-6-(o-toluidino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, dipotassium 4,4'-bis[4-morpholino-6-(o-toluidino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, potassium hydrogen 4,4'-bis[4-morpholino-6-(o-toluidino)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, disodium 4-(4-chloro-6-methoxy-1,3,5-triazin-2-ylamino)-4'-(4-methoxy-6-morpholino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, 4,4'-bis[4-chloro-6-morpholino-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, sodium hydrogen 4,4'-bis[4-chloro-6-morpholino-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, disodium 4,4'-bis[4-chloro-6-morpholino-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid, 4,4'-bis(4,6-dimorpholino-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic acid, and disodium 4,4'-bis[4,6-dimorpholino-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid. These may be used alone or in combination.

[0048] In the thermosensitive recording material, the dry mass of the fluorescent whitening agent in the first protective layer is preferably 0.5 g/m² to 1.5 g/m², and the amount of the fluorescent whitening agent in the first protective layer is preferably 20% by mass or more relative to the total amount of the first protective layer. When the dry mass of the fluorescent whitening agent is less than 0.5 g/m², the light resistance cannot be sufficiently obtained. When the dry mass is more than 1.5 g/m², the degree of the light resistance is not changed, but the deposition amount of the entire protective layer is required to increase so as to prevent the background of the thermosensitive recording material from turning into yellow color, possibly causing decrease in coloring properties.

[0049] When the amount of the fluorescent whitening agent is less than 20% by mass, it is necessary to increase the deposition amount of the first protective layer in order to obtain a predetermined amount of the fluorescent whitening agent, possibly causing decrease in the coloring properties of the thermosensitive recording material. From these standpoints, the amount is preferably 30% by mass or more.

[0050] The maximum amount is preferably 80% by mass or less in terms of making the thermosensitive recording material water resistance.

[0051] The dry mass and amount of the fluorescent whitening agent in the first protective layer are measured as follows. The first protective layer is separated from the thermosensitive recording material, followed by dissolving the first protective layer in a solvent, and then component analysis is performed on the resulting solution by HPLC analysis, IR analysis, or mass spectrometry, etc.

[0052] The water-soluble resin of the protective layer is suitably selected depending on the intended purpose without any restriction. Examples thereof include polyvinyl alcohol, modified polyvinyl alcohol, starch and derivatives thereof, cellulose derivatives, poly(meth)acrylate and alkali salts thereof, poly(meth)acrylamide and alkali salts thereof, (meth)acrylamide copolymers and alkali salts thereof, alkali salts of styrene-maleic anhydride copolymers, polyvinylpyrrolidone, polyethyleneimine, alginate soda, gelatin and casein.

[0053] As the water-soluble resin, an aqueous emulsion resin may be used. Examples thereof include emulsions of, for example, acryl copolymers, acrylic acid copolymers, (meth)acrylate copolymers, urethane resins, epoxy resins, vinyl acetate (co)polymers, vinylidene chloride (co)polymers, vinyl chloride (co)polymers; latexes of, for example, styrene-butadiene copolymers, and styrene-butadiene-acryl copolymers. Among these, polyvinyl alcohol, and diacetone-modified polyvinyl alcohol are preferable, in term of barrier properties, head matching properties, and mechanical strength.

[0054] The crosslinking agent is suitably selected depending on the intended purpose without any restriction. Examples thereof include polyvalent amine compounds such as ethylene diamine; polyvalent aldehyde compounds such as glyoxal, glutaraldehyde and dialdehyde; dihydrazide compounds such as dihydrazide adipate and dihydrazide phthalate; polyamide-epichlorohydrin compounds; water-soluble methylol compounds (urea, melamine and phenol); multifunctional epoxy compounds; multivalent metal salts (e.g., Al, Ti, Zr and Mg); titanium lactate; and boric acid.

[0055] The amount of the crosslinking agent in the (first) protective layer is suitably selected depending on the intended purpose without any restriction. The amount of the crosslinking agent varies depending on the amounts and types of functional groups of the crosslinking agent, but it is preferably 0.1 parts by mass to 100 parts by mass, more preferably 1 part by mass to 50 parts by mass, relative to 100 parts by mass of the binder resin.

[0056] In one appropriate embodiment, a second protective layer contains the water-soluble resin but no fluorescent whitening agent, and further contains a crosslinking agent, an inorganic filler, and a lubricant, and the like.

[0057] The water-soluble resin is suitably selected depending on the intended purpose without any restriction. For example, the water-soluble resins used in the first protective layer may be used. As the water-soluble resin used in the

[0058] As the water-soluble resin used in the second protective layer, a polyvinyl alcohol resin is preferably used similarly in the first protective layer.

[0059] The crosslinking agent is suitably selected depending on the intended purpose without any restriction. For example, the crosslinking agent used in the first protective layer may be used. It is noted that as the crosslinking agent used in the second protective layer, the same as or different from the crosslinking agent used in the first protective layer may be used.

[0060] The amount of the crosslinking agent in the second protective layer is suitably selected depending on the intended purpose without any restriction. The amount of the crosslinking agent varies depending on the amounts and types of functional groups of the crosslinking agent, but it is preferably 0.1 parts by mass to 100 parts by mass, more preferably 1 part by mass to 50 parts by mass, relative to 100 parts by mass of the binder resin.

[0061] The inorganic filler is suitably selected depending on the intended purpose without any restriction. Examples the inorganic filler include aluminum hydroxide, calcium carbonate, aluminum oxide, zinc oxide, titanium dioxide, silica, barium sulfate, talc, kaolin, alumina and clay. These may be used alone or in combination. Among these, aluminum hydroxide, and calcium carbonate are particularly preferable because the protective layer containing such inorganic filler is provided with excellent abrasion resistance with respect to a thermal head when printing is performed for a long period of time. The amount of the inorganic filler in the second protective layer is suitably selected depending on the intended purpose without any restriction. The amount of the inorganic filler depends on types of the filler, but it is preferably 50 parts by mass to 500 parts by mass, relative to 100 parts by mass of the binder resin.

[0062] The lubricant is suitably selected depending on the intended purpose without any restriction. Examples thereof include higher fatty acids such as zinc stearate, calcium stearate, montanate wax, polyethylene wax, carnauba wax, paraffin wax, ester wax and metal salts thereof; higher fatty acid amides, higher fatty acid esters, animal wax, vegetable wax, mineral wax, and petroleum wax.

[0063] In the thermosensitive recording material, the amount of the fluorescent whitening agent is preferably 55% by mass or less relative to the total amount of the fluorescent whitening agent contained in the first protective layer and the water-soluble resin contained in the first protective layer and the second protective layer. When the amount is more than 55% by mass, the water resistance of the thermosensitive recording material becomes poor, and peeling may occur. The minimum amount of the fluorescent whitening agent is preferably 20% by mass or more in terms of the decrease in the coloring properties caused by the increase of the total amount of the protective layers.

[0064] The amount of the fluorescent whitening agent in the total amount of the fluorescent whitening agent contained in the first protective layer and the water-soluble resin contained in the first protective layer and the second protective layer is measured as follows. The first protective layer and the second protective layer are both separated from the thermosensitive recording material, followed by dissolving each layer in a solvent, and then component analysis is performed on each resulting solution by HPLC analysis, IR analysis, or mass spectrometry, etc.

[0065] A method for forming the first protective layer and the second protective layer is suitably selected depending on the intended purpose without any restriction. Examples thereof include blade coating, roll coating, wire bar coating, die coating, and curtain coating.

Other layers

[0066] The thermosensitive recording material may appropriately contain a back layer containing a pigment, a water-soluble resin (binder resin) and a crosslinking agent, disposed on the surface of the support opposite to the surface thereof where the undercoat layer is disposed.

[0067] The back layer may further contain other components such as a filler, a lubricant, an antistatic agent, and the like.

[0068] As for the binder resin, either of a water-dispersible resin or a water-soluble resin is used. Specific examples thereof include conventionally known water-soluble polymers, and aqueous polymer emulsions.

[0069] The water-soluble polymer is suitably selected depending on the intended purpose without any restriction. Examples thereof include polyvinyl alcohol, starch and derivatives thereof, cellulose derivatives such as methoxy cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, methyl cellulose and ethyl cellulose, polyacrylate soda, polyvinyl pyrrolidone, acryl amide-acrylate copolymers, acryl amide-acrylate-methacrylic acid terpolymers, alkali salts of styrene-maleic anhydride copolymers, alkali salts of isobutylene-maleic anhydride copolymers, polyacrylamide, alginate soda, gelatin and casein. These may be used alone or in combination.

[0070] The aqueous polymer emulsion is suitably selected depending on the intended purpose without any restriction. Examples thereof include latexes of, for example, acrylate copolymers, styrene-butadiene copolymers and styrene-

butadiene-acryl copolymers; and emulsions of, for example, vinyl acetate resins, vinyl acetate-acrylate copolymers, styrene-acrylate copolymers, acrylate resins and polyurethane resins. These may be used alone or in combination.

[0071] As the crosslinking agent, the same crosslinking agent as those in the second protective layer may be used.

[0072] As the filler, either an inorganic filler or an organic filler may be used. Examples of the inorganic filler include carbonates, silicates, metal oxides and sulfate compounds. Examples of the organic filler include silicone resins, cellulose resins, epoxy resins, nylon resins, phenol resins, polyurethane resins, urea resins, melamine resins, polyester resins, polycarbonate resins, styrene resins, acrylic resins, polyethylene resins, formaldehyde resins and polymethyl methacrylate resins.

[0073] A method for forming the back layer is suitably selected depending on the intended purpose without any restriction. The back layer is preferably formed by applying a coating liquid of the back layer to a support.

[0074] The coating method is suitably selected depending on the intended purpose without any restriction. Examples thereof include blade coating, roll coating, wire bar coating, die coating, and curtain coating.

[0075] The thickness of the back layer is suitably selected depending on the intended purpose without any restriction. It is preferably 0.1 μm to 10 μm , more preferably 0.5 μm to 5 μm .

Image recording method

[0076] An image recording method of the present invention includes recording an image on the thermosensitive recording material of any of the embodiments of the present invention using an image recording unit, which is any one of a thermal head and a laser.

[0077] The thermal head is suitably selected depending on the intended purpose without any restriction regarding the shape, structure and size thereof.

[0078] The laser is suitably selected depending on the intended purpose without any restriction. A CO_2 laser which emits light having a wavelength of 9.3 μm to 10.6 μm is preferably used. By using the CO_2 laser which emits light having a wavelength of 9.3 μm to 10.6 μm , a satisfiable laser print image can be obtained without using a photothermal conversion agent such as a phthalocyanine pigment.

EXAMPLES

[0079] Hereinafter, the present invention will be specifically described based on Examples and Comparative Examples. However, it should be noted that the present invention is not confined to these Examples in any way. It should be noted that in the following examples, the unit "part(s)" means "part(s) by mass" and the unit "%" means "% by mass" unless otherwise specified.

Examples 1 to 2 and Comparative Examples 1 to 3

[0080] In these experiments, the effect of poly(vinyl alcohol) (PVA) molecular weight (n number, the number of repeating units in the polymer chain) on layer uniformity, image resolution and head permeability were measured.

[0081] A base paper support (wood-free paper having a basis weight of about 60 g/m^2) was provided.

[0082] Then, to prepare the undercoat, the following composition was prepared:

[Liquid A - for Example-1]

[0083]

-10% aqueous polyvinyl alcohol solution: (PVA with PVA PW n number of 600)	100 parts
-33% R-500 Hollow particles:	30.3 parts
-50% Styrene-butadiene copolymer latex	4 parts
-water	12.36 parts

[0084] For the PVA, an itaconic-modified PVA available from Kurare was used with PVA PW n number of 600. The PW is the chain length $I+m+n$, comprising the (average) sum of monomer residues in the polymer chain, where I is the number of $(-\text{CH}_2-\text{CHOH}-)$ groups, m is the number of $(-\text{CH}_2-\text{CHO}-\text{CO}-\text{Me})$ groups, and number of $(-\text{CH}_2-\text{C}(\text{CO}_2\text{Na})(\text{CH}_2\text{CO}_2\text{Na})-)$ groups.

[0085] The commercial supplier of R-500 plastic spherical hollow particles was Matsumoto Yushi-Seiyaku Co., Ltd.

[0086] These materials were mixed and stirred to prepare a coating liquid of an undercoat layer [Liquid A]. The coating liquid of the undercoat layer [Liquid A] was uniformly applied to a surface of a base paper support so as to have a

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deposition amount of 0.75 g/m² of hollow particle coating weight on a dry basis, and then dried, to thereby form an undercoat layer.

[0087] The above composition was used for Example 1. Example 2 and the Comparative Examples 1 and 2 use different grades of PVA with different n numbers.

[0088] With regard to the preparation of a coating liquid of a thermosensitive coloring layer, the following compositions were prepared:

[Liquid B]

[0089]

2-anilino-3-methyl-6-(di-n-butylamino)fluoran:	20 parts
10% itaconic-modified polyvinyl alcohol aqueous solution:	20 parts
Water :	60 parts

[Liquid C]

[0090]

4-hydroxy-4'-allyloxydiphenylsulfone:	20 parts
10% itaconic-modified polyvinyl alcohol aqueous solution:	20 parts
Silica (MIZUKASIL P-527 manufactured by MIZUSAWA INDUSTRIAL CHEMICALS,LTD.) :	10 parts
Water :	50 parts

[0091] [Liquid B] and [Liquid C] having the aforementioned compositions respectively, were each dispersed using a sand mill, so that particles contained in each liquid had an average particle diameter of 1.0 μm or less, to thereby prepare a dye dispersion liquid [Liquid B] and a developer dispersion liquid [Liquid C]. Then, [Liquid B] and [Liquid C] were mixed in the ratio of 1/3, so as to adjust the solid content to 25%, followed by stirring, to thereby prepare a coating liquid of a thermosensitive coloring layer [Liquid D]. [Liquid D] was uniformly applied to the undercoat layer to thereby form a thermosensitive coloring layer. The coating amount of the thermal layer was such as to produce a dye coating weight of about 0.5 g/m² on a dry basis, where [Liquid D]'s amount is 3.0g/m² on a dry basis.

[0092] On the top of the thermal layer, a protective layer was laid down. For the preparation of a coating liquid of a protective layer, following [Liquid E] was prepared:

10% itaconic acid-modified polyvinyl alcohol aqueous solution:	100 parts
25% Aminopolyamide-epichlorohydrin resin :	40 parts
Dispersion liquid of aluminum hydroxide (solid content: 30%):	50 parts
Montanate wax (solid content: 30%):	3.3 parts
Fluorescent whitening agent (stilbene compound, Tinopal UP, solid content: 45%, manufactured by BASF) 14.4 parts (solid content: 6.5 parts)	
Water	90 parts

[0093] The coating liquid of a protective layer [Liquid E] was uniformly applied so as to have a deposition amount of 3.0 g/m² on a dry basis, and then dried, to thereby form a protective layer. The multilayered product was then kept at 40°C for 3 days. Then, surface treatment by calendaring was performed to produce a surface smoothness of 3000 s.

[0094] The underlayer compositions for Examples 1 and 2 and for Comparative Examples 1 to 3 were as follows:

	PVA PW n number	PVA dry ratio	Hollow particle dry ratio	Hollow particle dry CW (g/m ²)	Total dry CW g/m ²
Example 1	600	1.00	1.00	0.75	2.4
Example 2	1000	1.00	1.00	0.75	2.4
Comp. Ex. 1	300	1.00	1.00	0.75	2.4

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(continued)

	PVA PW n number	PVA dry ratio	Hollow particle dry ratio	Hollow particle dry CW (g/m ²)	Total dry CW g/m ²
Comp. Ex. 2	1400	1.00	1.00	0.75	2.4
Comp. Ex. 3	1700	1.00	1.00	0.75	2.4

[0095] Here, on a single undercoat layer was used and the total dry CW (coating weight) is for this single under layer only.

Evaluation

[0096] Prepared thermal recording materials were evaluated in terms of (1) color uniformity, (2) image resolution, and (3) air permeance.

[0097] For evaluating colour uniformity (1), visual inspection was carried out, and the following ranking system (Ranking A) was applied:

Undercoat layer uniformity (Ranking A)	
5	Flat and uniform
4	Slightly higher roughness
3	Uneven surface
2	Wavy surface
1	Very wavy surface

[0098] This ranking is in descending order of preference, 5 being the best performance, and a ranking of at least 4, i.e. 4 or 5, is preferred in order to meet a normal user's expectations under normal conditions. It is further to be noted that for this evaluation (1), a colour pigment 0.01 ratio was added. In effect, the under coat colour is white. Thus, using only the undercoat liquid, it is difficult to analyse layer uniformity. For facilitating detection, a colour pigment was thus added, malachite green solution.

[0099] Similarly, for evaluating thermal image resolution (2), visual inspection was carried out, based on the following ranking system (Ranking B):

Undercoat layer uniformity (Ranking B)	
5	Uniform black pattern
4	Few white spots
3	Many white spots
2	White spots and waves
1	Very high unevenness

[0100] Here also, a ranking of at least 4, i.e. 4 or 5, is preferred in order to meet a normal user's expectations under normal conditions.

[0101] For evaluating image resolution of different samples, testing was carried out using Printer 110 Xi4 of Zebra Technologies Corporation, run at a speed of 200 m/sec with energy temperature 25.

[0102] Air permeance (3) was measured using a Bendtsen tester (manufactured by Messmer Instruments Ltd.) in accordance with ISO563

[0103] The results of these three evaluations are presented in the table below:

	Undercoat layer layer uniformity (Ranking A)	All layer coated image resolution (Ranking B)	Undercoat layer air permeability ml/min
Example 1	5	5	120
Example 2	4	4	90
Comp. Ex. 1	5	5	170
Comp. Ex. 2	3	3	65
Comp. Ex. 3	1	1	40

[0104] From a study of the experimental data, the inventors determined that in order to achieve high performance both as regards layer uniformity and image resolution, a PVA PW n number of more than 1000 was not appropriate. However, too low a PVA PW n number gave a relatively high air permeability, which is believed in this field to be correlated in general with reduced light resistance. A range of PVA PW n number from 400 to 1000 thus appears to be suitable to achieve good performance under all three evaluations (1) to (3) as detailed above.

Examples 3 to 6 and Comparative Examples 4 and 5

[0105] A new series of experiments was performed in order to study the effect of the relative amount of polyvinyl alcohol (PVA) in the undercoat and its influence on thermal image sensitivity and air permeability.

[0106] A series of samples were prepared using the same base layer, underlayer, thermal layer and coating layer as described above for Examples 1 to 2, but in this case the PVA to hollow particle ratio was varied from 0.5 to 2.5, the hollow particle dry coating weight (CW) being maintained constant at 0.75 g/m². The following table sets out the composition of the underlayer in the tested samples:

	PVA PW n number	PVA dry ratio	Hollow particle dry ratio	Hollow particle dry CW (g/m ²)	Total dry CW g/m ²
Example 3	600	0.50	1.00	0.75	2.03
Example 4	600	1.00	1.00	0.75	2.40
Example 5	600	1.50	1.00	0.75	2.78
Example 6	600	2.00	1.00	0.75	3.15
Comp. Ex. 4	600	0.25	1.00	0.75	1.84
Comp. Ex. 5	600	2.50	1.00	0.75	3.53

[0107] In evaluation (4), a MarkPoint MK2 printer was used to print images using several different amounts of energy, measured in mJ of energy per mm² of printed area. The image density was measured using Densieye (DensiEye 700 from X-rite Inc.). The energy value is calculated that is needed for an image density of 1.0, and thus the sensitivity is determined. A value of 6.5 mJ/mm² corresponds to an ordinary user's requirement.

[0108] In these Examples 3 to 6 and Comparative Examples 4 and 5, evaluation (5) concerning air permeance was carried out as for evaluation (3) in Examples 1 and 2 and Comparative Examples 1 to 3 above.

[0109] The results obtained were shown in the following table:

	All layer coated image resolution (in mJ/mm ²)	Undercoat layer air permeability ml/min
Example 3	5.72	120
Example 4	5.86	80
Example 5	6.02	50
Example 6	6.44	10
Comparative Example 4	5.65	190

(continued)

	All layer coated image resolution (in mJ/mm ²)	Undercoat layer air permeability ml/min
Comparative Example 5	7.10	less than 5

[0110] The inventors determined from the above experiments that with a PVA/hollow particle dry ratio of more than 2.0, the sensitivity energy value exceeded the target maximum value of 6.5 mJ/mm². Consequently, a 2.0 ratio was determined as an appropriate upper limit. With respect to air permeance (permeability), in order to achieve a target value of less than 150 ml/minute, it appears that a PVA/hollow particle dry ratio of only 0.25 is not appropriate and a lower limit of 0.5 appears appropriate. To achieve both satisfactory results for image resolution and air permeability (correlated with light resistance), for a hollow particle dry weight of 1.0, a relative PVA weight of 0.5 to 2.0 was thus determined to be appropriate.

Claims

1. A thermal recording material comprising:

- a base layer;
 - one or more undercoat layers which is/are laid down on the base layer, wherein the undercoat layer(s) contain(s) a water-soluble resin and hollow particles;
 - a thermo-sensitive coloring layer which is laid down on the uppermost undercoat layer, on the opposite side with respect to the base layer; and
 - one or more protective layers which is/are laid down on the thermo-sensitive coloring layer, on the opposite side with respect to the undercoat layer(s);
- wherein the water soluble resin is a polyvinyl alcohol with a degree of the polymerisation which is at least 400 and at most 1000, and wherein the ratio by mass of the water-soluble resin in the dried state to the hollow particles in the dried state is at least 50% and at most 200%.

2. A thermal recording material according to claim 1, wherein the polyvinyl alcohol has a degree of the polymerisation which is at least 500 and at most 900, preferably at least 600 and at most 800.

3. A thermal recording material according to claim 1 or 2, wherein the thermo-sensitive layer contains a leuco dye and a developer.

4. The thermal recording material according to any of claims 1 to 3, wherein the protective layer(s) contain(s) a water-soluble resin and a fluorescent whitening agent.

5. The thermal recording material according to claim 4, wherein the protective layers contain a first protective layer containing a water-soluble resin and a fluorescent whitening agent and a second protective layer containing a water-soluble resin but no fluorescent whitening agent, and wherein the first protective layer and the second protective layer are formed in this order over the thermosensitive coloring layer.

6. An image forming method including recording an image on the thermal recording material according to any of claims 1 to 5 using an image recording unit, which is any one of a thermal head and a laser.

7. The image forming method according to claim 6, wherein the laser is a CO₂ laser which emits light having a wavelength of 9.3 μm to 10.6 μm.



EUROPEAN SEARCH REPORT

Application Number
EP 12 30 6220

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Place of search Munich		Date of completion of the search 6 February 2014	Examiner Patosuo, Susanna
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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