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## (54) Thermal recording material containing stilbene disulphonic acid fluorescent whitening agent

(57) The present invention describes a coating composition comprising:
- polyvinyl alcohol; and
- a bis[triazinyl-amino]-stilbene disulphonic fluorescent whitening agent,

wherein the amount of dry mass of fluorescent whitening agent is 1.5 to 150 parts by mass relative to 100 parts by mass of dry polyvinyl alcohol.

The coating composition can be used to prepare protective layers (overlayers) of thermal recording materials.

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## Description

Field of the Invention

**[0001]** The present invention relates to a coating composition, which can be used to prepare a layer of a thermal (thermosensitive) recording material and an image forming method using the same.

Technical background to the invention

**[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:

- 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.

**[0004]** Such a thermosensitive recording material layer assembly is described in EP 2 345 541.

**[0005]** 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.

**[0006]** Rod-blade / vari-bar coating and curtain coating technologies are known as typical layer coating methods to manufacture thermal recording materials. The vari-bar technology is a coating method where the applied liquid thickness is adjusted by pressing, to a greater or lesser degree, a rod-blade on the coated surface. Curtain coating technology is a process where a single layer or a multilayer coating (simultaneously) is carried out. Both of these coating technologies used in thermal recording media manufacturing processes, generate strong kinematic stress on coating liquids.

**[0007]** On the other hand, when a thermal recording media needs higher whiteness properties, it is known that addition of fluorescent whitening agents (FWAs), also known as optical brightener agents (OBAs), into the thermosensitive layer or/and in the protective layer, improves whiteness properties.

**[0008]** However, simultaneously satisfying the requirements for whiteness and coatability according to preferred coating technologies is difficult. In effect, the use of significant quantities of FWAs (OBAs) into a liquid composition for producing a layer such as a thermosensitive layer or protective layer in a thermal recording material assembly, can give rise to very viscous compositions. A direct consequence is, if a conventional application liquid containing fluorescent whitening agent is used, it will need more power to press the vari-bar in order to coat an uniform layer with vari-bar coating technology, and also with the curtain coating method it will be necessary to boost circulation pump flowrate in order to have required flow volume during the application stage. Those negative impacts could be balanced by decreasing the applied formulation solid content, but this directly decreases liquid preparation productivity (more water-less dry material), given that it is desired to keep the same dry coating weight. Also, during the coating stage, more energy will be consumed in order to dry the coated layer in question, more water will need to be eliminated, and so it will be necessary to increase dryer temperatures, and moreover, $CO_2$ emissions will be higher (more gas consumed = more $CO_2$). Another negative issue of solid content adjustment to decrease dynamic viscosity, is that production flexibility is lower. Thermal recording media manufacturers produce several whiteness range products, so, if the solid content has to be adjusted when the FWA (OBA) is adjusted, this will cause less flexibility and more wasted liquids.

**[0009]** An object of the present invention was thus to provide a coating system using a coating composition containing an FWA (OBA), satisfying the potentially contradictory requirements of acceptable viscosity in liquid solution/dispersion, as well as whiteness level and water resistance.

Summary of the Invention

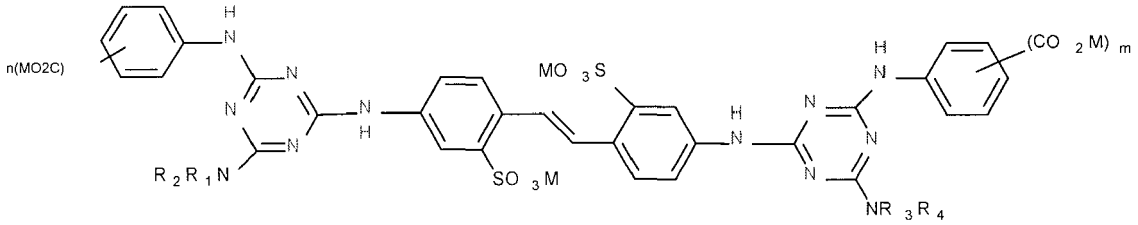
**[0010]** As a result of investigations, the present inventors have identified coating compositions comprising fluorescent whitening agents (FWAs) that satisfy the requirements of acceptable viscosity in liquid solution/dispersion, as well as whiteness level and water resistance. These coating compositions can be used to provide suitable protective layers (overlayers) of thermal recording materials.

**[0011]** The present invention thus relates to a coating composition comprising:

- polyvinyl alcohol; and
- a bis[triazinyl-amino]-stilbene disulphonic fluorescent whitening agent,

wherein the amount of dry mass of fluorescent whitening agent is 1.5 to 150 parts by mass relative to 100 parts by mass of dry polyvinyl alcohol.

**[0012]** In a preferred embodiment of the said coating composition, the fluorescent whitening agent has the following structure:




wherein:

n and m are each independently, 0, 1 or 2, but n and m cannot both be zero, and preferably m = n = 1;
M is H, ammonium or mono-, di-, tri- or tetra- C1-C4 alkyl- or C1-C4 hydroxyalkyl-ammonium, or M is a monocation metal equivalent, preferably an alkali metal such as Li, Na or K, or a half stoichiometric equivalent of an alkaline earth metal such as Mg or Ca;
$R_1$, $R_2$, $R_3$ and $R_4$ are C2-C4 hydroxyalkyl, preferably $-CH_2CH_2OH$.

**[0013]** Also in a preferred embodiment, the fluorescent whitening agent does not contain any urea.

**[0014]** Also in a preferred embodiment, when equal amounts, as dry mass, of fluorescent whitening agent and polyvinyl alcohol are dispersed and/or dissolved in water to a dry mass solid content of 7.0 %, the resulting liquid composition has a viscosity of 200 mPa·s or less when the applied shear velocity is $5.0 \times 10^4$ $s^{-1}$.

**[0015]** In a further aspect of the present invention, a liquid coating composition is provided that can be obtained by dissolving and/or dispersing in water a solid composition containing a polyvinyl alcohol and a bis[triazinyl-amino]-stilbene disulphonic fluorescent whitening agent as set out hereinabove.

**[0016]** A further aspect of the present invention is directed to the use of such a liquid coating composition in order to form a protective layer (overlayer) that is part of a thermal recording material.

**[0017]** A further aspect of the present invention is directed to a thermal recording material comprising:

- a base layer;
- one or more undercoat layers which is/are laid down on the base layer;
- a thermo-sensitive coloring layer containing a leuco dye and a developer 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 (overlayers) which is/are laid down on the thermo-sensitive coloring layer, on the opposite side with respect to the undercoat layer(s);

wherein the one or more protective layers (overlayers) is obtained by coating with a coating composition as set out hereinabove.

**[0018]** In a preferred embodiment of the thermal recording material of the invention, wherein the protective layers contain a first protective layer containing the 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.

**[0019]** In a further aspect, the present invention is directed to an image forming method including recording an image

on the thermal recording material as set out hereinabove using an image recording unit, which is any one of a thermal head and a laser. In a preferred image forming method of the invention, the laser is a $CO_2$ laser which emits light having a wavelength of 9.3 μm to 10.6 μm.

Detailed Description of the Invention

Base (support) layer

**[0020]** 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)

**[0021]** The undercoat layer(s) is/are suitably selected depending on the intended purpose without any restriction. There may be a single undercoat layer or the undercoat may be formed of two or more layers.

**[0022]** A water-soluble resin is used in the undercoat, such as polyvinyl alcohol, or 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.

**[0023]** The amount of the polyvinyl alcohol as water-soluble resin in the undercoat, consisting of the one or more undercoat layers present, is suitably selected depending on the intended purpose without any restriction. It is preferably 20% by mass to 80% by mass. More preferably, the percentage of dry polyvinyl alcohol in the dry mass of the undercoat is at least 30% by mass, more preferably at least 40% by mass, still more preferably at least 50% by mass, most preferably more preferably at least 60% by mass.

**[0024]** When the amount of the water-soluble resin in the undercoat is less than 20% by mass, 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 more than 80% by mass, in the case where an image is formed using a thermal head, sufficient coloring sensitivity may not be easily obtained.

**[0025]** 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.

**[0026]** 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.

**[0027]** 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.

**[0028]** 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.

**[0029]** 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%.

**[0030]** 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.

**[0031]** 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.

**[0032]** 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/m$^2$ to 10 g/m$^2$, more preferably 0.6 g/m$^2$ to 7 g/ m$^2$. When the deposition amount of the first undercoat layer is less than 0.4 g/m$^2$, it is difficult to appropriate air permeance. When the deposition amount is more than 10 g/m$^2$, the binding properties of the first undercoat layer may decrease.

Thermosensitive Coloring Layer

**[0033]** 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.

**[0034]** 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-bromoanihno)-6-diethyl amino fluoran, 2-(o-chloranilino)-6-dibutyl amino fluoran, 2-(o-fluoroanilino)-6-dibutyl amino fluoran, 2-(m-trifluoro methyl anilino)-6-diethylamino 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) phtahlide, 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-chlorphthalide, 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'-methoxy-benzoindolino spiropyran, and 6'-bromo-2'-methoxy benzoindolino spiropyran. These may be used alone or in combination.

**[0035]** 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.

**[0036]** 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, a-naphthol, p-naphthol, 3,5-xylenol, 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-dioxaheptane, 1,5-bis (4-hydroxyphenylthio) 3-oxaheptane, 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 sulfone, 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.

**[0037]** 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.

**[0038]** 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-meltable material, a crosslinking agent, a pigment, a surfactant, a fluorescent whitening agent and a lubricant.

**[0039]** 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.

**[0040]** 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.

**[0041]** The hot-meltable 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 amid; 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.

**[0042]** 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.

**[0043]** 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 Atriter and a sand mill. The resultant dispersion is mixed, if necessary, together with a filler and a hot-meltable 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.

**[0044]** 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

**[0045]** 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.

**[0046]** It may be noted that the preferred fluorescent whitening agents to be used in the present invention can also be used in the thermosensitive layer.

**[0047]** 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.

**[0048]** A first protective layer may contain the fluorescent whitening agent and the water-soluble resin, and further contain a crosslinking agent.

Fluorescent whitening agents

**[0049]** Among fluorescent whitening agents known in thermal recording media, stilbene disulfonic acid compounds are known, such as:

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-anilino-4-di(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-sulfophenylamino)-4-(2-hydroxypropyl)amino-1,3,5-triazinyl-6-amino}stilben e-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-acetylamino-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-acetylamino-4-(4,8-disulfo-2-naphthylazo)]anilino-6-chloro-1,3,5-triazin-2-yla mino]-2,2'-stilbene disulfonic acid hexasodium salt,
4,4'-bis[4-[3-[3-carboxy-5-hydroxy-1-(p-sulfophenyl)-4-pyrazolylazo]-4-sulfoanilino]-6-chl oro-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid octasodium salt,
4,4'-bis[4-chloro-6-[3-[1-(2-chloro-5-sulfophenyl)-5-hydroxy-3-methyl-4-pyrazolylazo]-4-s ulfoanilino]-1,3,5-triazin-

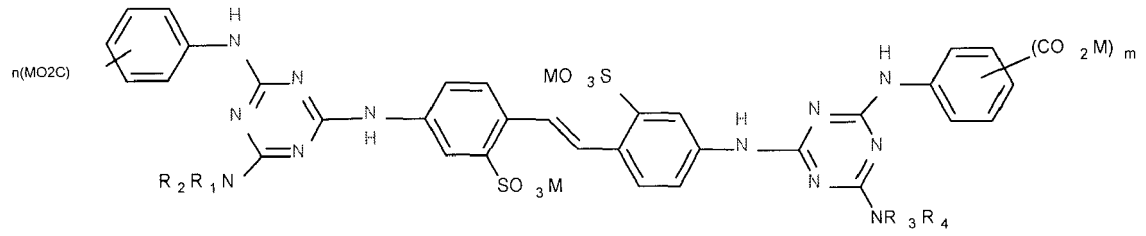
2-ylamino]-2,2'-stilbene disulfonic acid=hexasodium salt,
4,4'-bis[6-[N-(2-cyanoethyl)-N-[2-(2-hydroxyethoxy)ethyl]amino]-4-(2,5-disulfoanilino)-1, 3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid hexasodium salt,
4,4'-bis[4-bis(2-hydroxypropyl)amino-6-(4-sulfoanilino)-1,3,5-triazin-2-ylamino]-2,2'-stilbe ne 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'-stilb ene disulfonic acid,
4,4'-bis[6-(m-sulfoanilino)-4-(2-hydroxydiethylamino)-1,3,5-triazin-2-ylamino]-2,2'-stilben e 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-mehylamino-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-ylamino]-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, potassium hydrogen
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'-stilb ene disulfonic acid, potassium hydrogen
4,4'-bis[4-anilino-6-[N-(2-hydroxyethyl)-N-methylamino]-1,3,5-triazin-2-ylamino]-2,2'-stilb ene 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'-sti lbene 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 acid,
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-sulfophenoxy-1,3,5-triazin-2-ylamino)-2,2'-stilbe ne 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,
4-[4-bis(2-hydroxyethyl)amino-6-(p-sulfoanilino)-1,3,5-triazin-2-ylamino]-4'-[4-bis(2-hydro xyethyl)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-morph olino-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-hydroxysulfonylethylamino)-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-yla mino)-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, potassium 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-ylamino)-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-sulfophenyloxy)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid,
4,4'-bis[4-chloro-6-(p-sulfophenoxy)-1,3,5-triazin-2-ylamino]-2,2'-stilbene disulfonic acid disodium salt, 4,4'-bis[4-chloro-6-(p-sulfophenoxy)-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-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 disulfonic 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-ylamino)-2,2'-stilbene disulfonic acid, potassium hydrogen
4,4'-bis(4-anilino-6-chloro-1,3,5-triazin-2-ylamino)-2,2'-stilbene disulfonic 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-ylaminol-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, secondary 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, tertiary salt, or quaternary salt),
4,4'-bis[4-chloro-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-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 (primary 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'ylamino]-2,2'-stilbene disulfonic acid, potassium 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-(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,
4,4'-bis[4-chloro-6-(7-phenylazo-8-disulfo-1-naphtylamino)-1,3,5-triazin-2-ylaminol-2,2'-sti lbene 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-yl amino]-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)stilbene-2,2'-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.

**[0050]** In the present invention, in order to achieve appropriate properties, it is preferred to use a bis[triazinyl-amino]-stilbene disulphonic fluorescent whitening agent.

**[0051]** In particular, it is preferred to use a fluorescent whitening agent having the following structure:




wherein:

n and m are each independently, 0, 1 or 2, but n and m cannot both be zero, and preferably m = n = 1;
M is H, ammonium or mono-, di-, tri- or tetra- C1-C4 alkyl- or C1-C4 hydroxyalkyl-ammonium, or M is a monocation metal equivalent, preferably an alkali metal such as Li, Na or K, or a half stoichiometric equivalent of an alkaline earth metal such as Mg or Ca; $R_1$, $R_2$, $R_3$ and $R_4$ are C2-C4 hydroxyalkyl, preferably $-CH_2CH_2OH$.

**[0052]** Such molecules can be obtained by the syntheses given in patent applications EP 2 431 519 and WO 2011/033064. Such molecules are sold by the company Blankophor, and in the present invention a particularly preferred FWA is the one sold under the product number TP-0306 by the Blankophor company, wherein it is believed that m = n = 1 and $R_1$, $R_2$, $R_3$ and $R_4$ are all $-CH_2CH_2OH$.

**[0053]** In the present invention, it is furthermore preferred that the fluorescent whitening agent does not contain any urea. In effect, since a number of stilbene disulphonic fluorescent whitening agents do not show a very high water solubility, urea is added as solubilizing agent and it is preferred to use a fluorescent whitening agents which does not require this. This will reduce pollution risks associated with the use of large quantities of such FWAs.

**[0054]** In the present invention, it is furthermore preferred to use an FWA such that when equal amounts, as dry mass, of fluorescent whitening agent and polyvinyl alcohol are dispersed and/or dissolved in water to a dry mass solid content of 7.0 %, the resulting liquid composition has a viscosity of 200 mPa·s or less when the applied shear velocity is $5.0 \times 10^4\ s^{-1}$. For sample evaluation, a capillary Rheometer RH2200 from Malvern Instruments may here be used to measure viscosity. The capillary used in the equipment may be chosen to have a hole diameter of 0.25 mm and a length of 8.0 mm. With a fixed sample volume, 50 ml may be passed into the high shear stress machine with a controlled temperature of 20°C, and the dynamic viscosity measured at a shear rate of $5.0 \times 10^4\ s^{-1}$. Under these conditions, as set out above, it is preferred that a liquid composition containing equal amounts by mass of fluorescent whitening agent and polyvinyl alcohol at a total dry mass solid content of 7.0 % in water, show a viscosity of 200 mPa·s or less when the applied shear velocity is $5.0 \times 10^4\ s^{-1}$.

**[0055]** In the thermosensitive recording material, the dry mass of the fluorescent whitening agent in the first protective layer is preferably 0.5 g/m$^2$ to 1.5 g/m$^2$, 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/m$^2$, the light resistance cannot be sufficiently obtained. When the dry mass is more than 1.5 g/m$^2$, 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.

**[0056]** 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.

**[0057]** The maximum amount is preferably 80% by mass or less in terms of making the thermosensitive recording material water resistance.

**[0058]** 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.

**[0059]** In the protective layer (overlayer) of a thermal recording material according to the present invention, a polyvinyl alcohol is used as a water-soluble resin, in combination with a bis[triazinyl-amino]-stilbene disulphonic fluorescent whitening agent, wherein the amount of dry mass of fluorescent whitening agent is 1.5 to 150 parts by mass relative to 100 parts by mass of dry polyvinyl alcohol.

**[0060]** 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 ($-CH_2$-CHO-CO-Me) groups are present, in addition to the main monomer residue of ($-CH_2$-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 ($-CH_2$-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 ($-CH_2$-C($CO_2M$)($CH_2CO_2M$)-) 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, diacetonic modified PVAs, and acetoacetyl modified PVAs.

**[0061]** In preferred embodiments of the present invention, the protective layer(s) (overlayer(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, other water-soluble polymers can be used in conjunction with the PVAs used in protective layers (overlayers) of the present invention. Other water-soluble polymers

that can be used conjointly with PVAs include: 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.

**[0062]** In embodiments with two protective layers (overlayers), the water-soluble resins used in the two protective layer may be different.

**[0063]** An inorganic filler may be used in protective layers (overlayers), and suitably selected depending on the intended purpose without any restriction. Examples of 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.

**[0064]** 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.

**[0065]** In the coating composition and overlayer (protective layer) of the thermosensitive recording material of the invention, the amount of the fluorescent whitening agent is 1.5 to 150 parts by dry mass relative to 100 parts by mass of dry polyvinyl alcohol. If the key focus is to improve whiteness of the layer, an appropriate range is 1.5 to 10 parts of fluorescent whitening agent by dry mass relative to 100 parts by mass of dry polyvinyl alcohol. Above 10 parts by dry mass relative to 100 parts by mass of dry polyvinyl alcohol as water-soluble resin, some yellowing of the layer may be observed. However, this yellowing may be accepted if a maximum value of light resistance is sought after. In such situations, a minimum amount of 50 parts of fluorescent whitening agent by dry mass relative to 100 parts by mass of dry polyvinyl alcohol may be preferred, or more preferably 100 parts by mass with respect to 100 parts by mass of dry polyvinyl alcohol, so that for a layer with maximum light resistance, a preferable range is between 100 and 150 parts of fluorescent whitening agent by dry mass relative to 100 parts by mass of dry polyvinyl alcohol.

**[0066]** 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.

**[0067]** 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

**[0068]** 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.

**[0069]** The back layer may further contain other components such as a filler, a lubricant, an antistatic agent, and the like.

**[0070]** 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.

**[0071]** 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.

**[0072]** 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.

**[0073]** 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.

**[0074]** 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.

**[0075]** 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.

**[0076]** 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

**[0077]** 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.

**[0078]** The thermal head is suitably selected depending on the intended purpose without any restriction regarding the shape, structure and size thereof.

**[0079]** 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

**[0080]** 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.

Example 1 and Comparative Examples 1 to 3

**[0081]** In the first set of examples, the properties of different fluorescent whitening agents (FWAs, aka optical brightening agents OBAs) were compared. In each case, a mixture was prepared in water with a total solid content of 7.0 %, the mixtures containing simply polyvinyl alcohol (PVA), the FWA (OBA) and water. A total S.C. (solid content) of 7.0% S.C. in the solution is obtained when the coating liquid is prepared, based on a 10% aqueous PVA solution and an 18% S.C. preparation of the FWA (OBA) TP-0306. The PVA used was carboxylic PVA KL-318 made by KURARAY CO., LTD. The FWAs were obtained from the Blankophor company. The mixtures were stirred until perfectly homogeneous. The compositions were as indicated in the following table:

| | OBA name | OBA type | PVA resin dry mass | Active OBA dry mass | Mixture in water solid content (%) |
|---|---|---|---|---|---|
| Example 1 | Blankophor TP-0306 | Disulphonic stilbene | 100 | 100 | 7.0 |
| Comparative Example 1 | - (No OBA added) | - | 100 | 0 | 7.0 |
| Comparative Example 2 | Blankophor NC | Tetrasulphonic stilbene | 100 | 100 | 7.0 |
| Comparative Example 3 | Blankophor UWS | Hexasulphonic stilbene | 100 | 100 | 7.0 |

**[0082]** For sample evaluation, a capillary Rheometer RH2200 from Malvern Instruments was used to measure viscosity. The capillary used in the equipment had a hole diameter of 0.25 mm and a length of 8.0 mm. With a fixed sample volume, 50 ml is passed into the high shear stress machine with a controlled temperature of 20°C, and the dynamic viscosity is measured at a shear rate of $5.0 \times 10^4\ s^{-1}$.

| | Shear viscosity (mPa·s) measured at a shear rate of $5.0 \times 10^4\ s^{-1}$ |
|---|---|
| Example 1 | 25.5 |
| Comparative Example 1 | 0.5 |
| Comparative Example 2 | 19.7 |
| Comparative Example 3 | 17.1 |

Examples 2 to 5 and Comparative Examples 4 to 8

**[0083]** In these experiments, multilayer thermal recording material assemblies were provided, and with various protective layer (overlayer) compositions having different types and amounts of optical brightener agents (OBAs), water resistance and whiteness were measured, as well as the coating weight obtained when the same machine coating conditions were used.

**[0084]** A base paper support (wood-free paper having a basis weight of about 60 $g/m^2$) was provided.

**[0085]** Then, to prepare the undercoat, the following composition was prepared:

[Liquid A - for Example 2]

**[0086]**

| | |
|---|---|
| 33% Matsumoto Microsphere R-500 | 15.15 parts |
| 10% aqueous polyvinyl alcohol solution: | 100 parts |
| Water | 50 parts |

**[0087]** Matsumoto Microsphere R-500 are plastic spherical hollow particles obtained from the supplier Matsumoto Yushi-Seiyaku Co., Ltd.

**[0088]** 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 deposition amount of 3.0 $g/m^2$ on dry basis, and then dried, to thereby form an undercoat layer.

**[0089]** With regard to the preparation of a coating liquid of a thermosensitive coloring layer, the following compositions were prepared:

[Liquid B]

**[0090]**

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

**[0091]** Here the polyvinyl alcohol used was carboxylic PVA KL-318 made by KURARAY CO., LTD.

[Liquid C]

| | |
|---|---|
| 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 |

**[0092]** Here the polyvinyl alcohol used was carboxylic PVA KL-318 made by KURARAY CO., LTD.

**[0093]** [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 0.5 g/m$^2$ on a dry basis. An overall coating weight (CW) on a dry basis of [Liquid D] is 3.0g/m$^2$ can also be used.

**[0094]** On top of the thermal layer, a protective layer (overlayer) was laid down. For the preparation of a coating liquid of a protective layer, a [Liquid E] was prepared. This contained PVA resin, as well as various relative amounts of different types of OBA as indicated in the table below:

For [Liquid E], the following formulation was used:

[Liquid E]

**[0095]**

| | |
|---|---|
| 10% diacetone-modified polyvinyl alcohol aqueous solution | 100 parts |
| 10% adipic acid dihydrazide aqueous solution | 20 parts |
| Dispersion liquid of aluminium hydroxide (S.C. : 30%) | 50 parts |
| Montanate wax (S.C. : 30%) | 3.3 parts |
| 18% TP-0306 | 2.8 parts |
| Water | 109 parts |

| | OBA name | OBA type | PVA resin dry mass | Active OBA dry mass |
|---|---|---|---|---|
| Example 2 | Blankophor TP-0306 | Disulphonic stilbene | 100 | 5.0 |
| Example 3 | Blankophor TP-0306 | Disulphonic stilbene | 100 | 1.5 |
| Example 4 | Blankophor TP-0306 | Disulphonic stilbene | 100 | 100 |
| Example 5 | Blankophor TP-0306 | Disulphonic stilbene | 100 | 150 |
| Comparative Example 4 | No OBA | No OBA | 100 | 0 |
| Comparative Example 5 | Blankophor-NC | Tetrasulphonic stilbene | 100 | 5.0 |
| Comparative Example 6 | Blankophor-UWS | Hexasulphonic stilbene | 100 | 5.0 |
| Comparative Example 7 | Blankophor TP-0306 | Disulphonic stilbene | 100 | 160 |
| Comparative Example 8 | Blankophor TP-0306 | Disulphonic stilbene | 100 | 1.0 |

**[0096]** The coating liquid of a protective layer [Liquid E] was uniformly applied and then dried, to thereby form a protective layer.

**[0097]** In order to evaluate the relative performance of these different examples, for testing water resistance and whiteness, a laboratory wire-bar coating method was used in order to reach 1.0 g/m$^2$ in dry coating weight of PVA. The samples were then kept at 40°C for 3 days. Then, surface treatment by calendaring was performed to achieve surface smoothness of 3000 s. In effect, after coating, surface smoothness is low. As a result, when an image is printed, the resolution may be poor and the gloss may also be poor after pre-printing with ink. Therefore, in order to improve these aspects, the surface smoothness is increased using a calendar machine.

**[0098]** In another test, the prepared liquids were used with the high speed machine by keeping for each liquid mixture tested exactly the same machine coating conditions, in order to respect exactly the same sheer coating stress for each evaluated liquid mixture.

**[0099]** For evaluating whiteness, the top coating surface whiteness was measured according to the CIE norm, using the machine Elrepho-3000 (from Datacolor International). A whiteness value of more than 100 is considered acceptable for a normal user's requirements.

**[0100]** For evaluating water resistance, samples were dipped for 1 hour in water at 23°C and then put on a glass

surface. While the surface is still wet, a finger is used to put sufficient and repeated pressure to make friction on the surface. Each movement back and forth is noted as 1 pass. The number of passes until the surface layer(s) start(s) to peel is recorded. It is possible to carry out 10 passes with no peeling, the evaluation test procedure is stopped. It is entirely acceptable for an ordinary user if there is no peeling after 10 passes.

**[0101]** For the coating weight test, each coated sample's dry coating weight was measured by an X-ray spectrometer, and by using calibration it was possible to determine the real dry coated amount for each sample. For reasonable productivity, it is desired to have a deviation of less than 20%. With a lower variation of this in terms of coating weight, the coating weight can be suitably adjusted using vari-bar pressure. It is considered that there is a correlation between viscosity at high shear (as measured in Example 1 and Comparative Examples 1 to 3 above) and coating weight. Samples with higher viscosity at high shear are expected to provide high, possibly an acceptable, coating weight.

**[0102]** The results were obtained were as follows:

| | CIE Whiteness | Water resistance | Coating weight (CW) |
|---|---|---|---|
| Example 2 | 130 | 10 | 2.0 |
| Example 3 | 114 | 10 | 2.0 |
| Example 4 | 137 | 10 | 2.1 |
| Example 5 | 125 | 10 | 2.1 |
| Comparative Example 4 | 94 | 10 | 2.0 |
| Comparative Example 5 | 128 | 6 | 2.0 |
| Comparative Example 6 | 136 | 4 | 2.0 |
| Comparative Example 7 | 124 | 8 | 2.2 |
| Comparative Example 8 | 98 | 10 | 2.0 |

**[0103]** Water resistance is not an acceptable for Comparative Examples 5 to 7, and it therefore appears that a disulphonic acid stilbene such as Blankophor TP-0306 is more suitable than a tetra- or hexa-sulphonic acid species. A suitable relative amount of the disulphonic acid stilbene such as Blankophor TP-0306, with respect to the water-soluble resin, is also necessary to simultaneously satisfy whiteness and water resistance requirements, as shown by Comparative Examples 7 and 8.

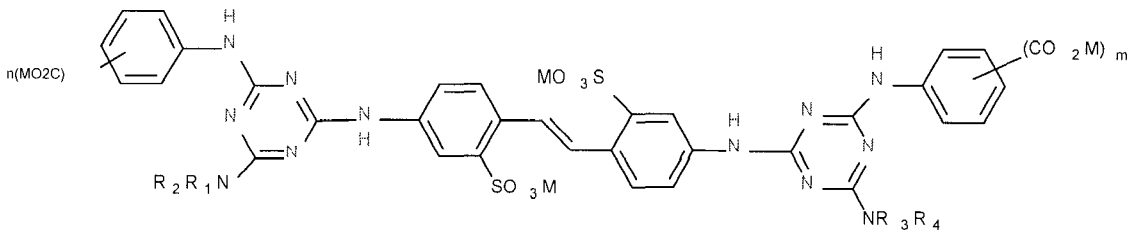
## Claims

**1.** A coating composition comprising:

- polyvinyl alcohol; and
- a bis[triazinyl-amino]-stilbene disulphonic fluorescent whitening agent,

wherein the amount of dry mass of fluorescent whitening agent is 1.5 to 150 parts by mass relative to 100 parts by mass of dry polyvinyl alcohol.

**2.** A coating composition according to claim 1, wherein the fluorescent whitening agent has the following structure:




wherein:

n and m are each independently, 0, 1 or 2, but n and m cannot both be zero, and preferably m = n = 1;

M is H, ammonium or mono-, di-, tri- or tetra- C1-C4 alkyl- or C1-C4 hydroxyalkyl-ammonium, or M is a monocation metal equivalent, preferably an alkali metal such as Li, Na or K, or a half stoichiometric equivalent of an alkaline earth metal such as Mg or Ca;
$R_1$, $R_2$, $R_3$ and $R_4$ are C2-C4 hydroxyalkyl, preferably $-CH_2CH_2OH$.

**3.** A coating composition according to claim 1 or 2, wherein the fluorescent whitening agent does not contain any urea.

**4.** A coating composition according to any of claims 1 to 3, wherein, when equal amounts, as dry mass, of fluorescent whitening agent and polyvinyl alcohol are dispersed and/or dissolved in water to a dry mass solid content of 7.0 %, the resulting liquid composition has a viscosity of 200 mPa·s or less when the applied shear velocity is $5.0 \times 10^4$ $s^{-1}$.

**5.** A liquid coating composition that can be obtained by dissolving and/or dispersing a solid composition according to any of claims 1 to 4 in water.

**6.** Use of a liquid coating composition according to claim 5 to form a protective layer (overlayer) that is part of a thermal recording material.

**7.** A thermal recording material comprising:

- a base layer;
- one or more undercoat layers which is/are laid down on the base layer;
- a thermo-sensitive coloring layer containing a leuco dye and a developer 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 (overlayers) which is/are laid down on the thermo-sensitive coloring layer, on the opposite side with respect to the undercoat layer(s);

wherein the one or more protective layers (overlayers) is obtained by coating with a coating composition according to any of claims 1 to 5.

**8.** The thermal recording material according to claim 7, wherein the protective layers contain a first protective layer containing the 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.

**9.** An image forming method including recording an image on the thermal recording material according to any of claims 1 to 8 using an image recording unit, which is any one of a thermal head and a laser.

**10.** The image forming method according to claim 9, wherein the laser is a $CO_2$ laser which emits light having a wavelength of 9.3 μm to 10.6 μm.

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# EUROPEAN SEARCH REPORT

Application Number
EP 12 30 6219

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| Munich | 5 March 2013 | Vogel, Thomas |

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X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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EPO FORM 1503 03.82 (P04C01)

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

## REFERENCES CITED IN THE DESCRIPTION

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