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(54) THERMOSENSITIVE RECORDING MATERIAL

(57) The present invention relates to a thermosensitive recording medium comprising at least:
- a transparent support layer;
- a thermosensitive colouring layer over the transparent support layer, the thermosensitive colouring layer containing a leuco dye, a developer and a hydrophobic resin;
- a protective layer over the thermosensitive colouring layer;

characterized in that the weight amount of hydrophobic resin, expressed with respect to 100% total weight of the thermosensitive colouring layer, is more than 30%.

The present invention further relates to a consumer product package which is at least partially transparent and to which such a thermosensitive recording medium is attached, notably wherein the package is for one or more perishable food items.

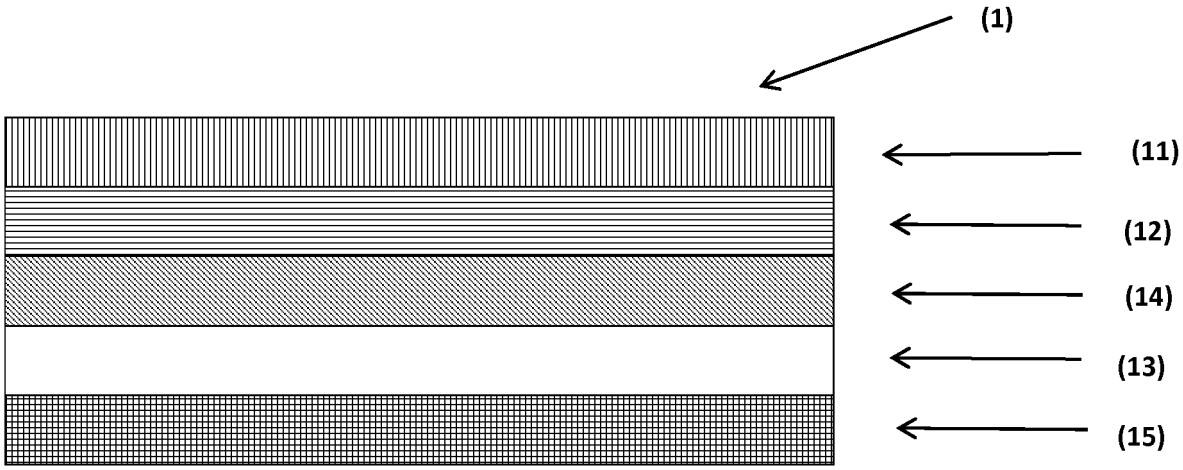


Figure 4

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Description

Field of the Invention

[0001] The present invention relates to a thermosensitive recording medium and a consumer product package which is at least partially transparent and to which a thermosensitive recording medium has been attached.

Technical Background to the Invention

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

[0003] Recently, there has been a request from the market to develop transparent thermosensitive recording media for labelling perishable foods. Indeed, with European food labelling regulation (EU1169/2011), many additional items of information are required on such labels and as a consequence the size of the label has increased drastically. In parallel, due to a change in lifestyle, the market of "prepacked" ready-made food and cut fruits and vegetables and fruit has increased. However, consumers want to choose the food after confirming its freshness. In order to allow consumers to see the freshness of the food, there is a requirement in the market to replace standard white labels by transparent ones.

[0004] In the past, several transparent thermal recording media based on a leuco dye and developer were developed for recording medical images. Among such improvements, a product has been proposed in EP 1 538 005 wherein a backside layer is applied, on the other side of the transparent film support to the heat-sensitive recording layer, in order to prevent the adhesion of the front side and the backside when exposed to highly humid conditions e.g. 40°C and 90%RH. A binder is proposed for the heat-sensitive recording layer containing ionomeric urethane-based resin and styrene-butadiene based resin.

[0005] Specific transparent thermal recording media which enable direct recording with a thermal head have also been proposed for multicolor development and use of an overhead projector. Among such improvements, transparency is achieved by coating a mix of either microencapsulated dye or microencapsulated developer. The transparency is adjusted by selecting the ratio of the two refractive indexes, one refractive index being that of the microencapsulated component and the other of the oily component contained in the other component emulsion or microcapsules. Such a system is described in EP 0 273 752. Such methods do not allow good pre-printability anchorage to be achieved.

Summary of the Invention

[0006] However, the above-mentioned products were not developed for prepacked fresh food applications for which good water resistance is required due to condensation in fridges as well as plasticizer resistance as packages are stacked in displays and labels in contact with plasticizer. It has been observed that all grades currently available in the market become white when dipped in water and lose optical image density if brought into contact with plasticizer. Also, such commercial products show poor preprint properties, especially for anchorage.

[0007] An object of the present invention is to provide a thermosensitive recording medium showing a high transparency level which remains even if the product is dipped in water and which shows at the same time enhanced plasticizer resistance and preprint anchorage. It is also an object to provide acceptable background reflectance. Higher background reflectance value is relevant in reducing greyish appearance. In essence, the thermosensitive recording medium looks more white if applied to a white support.

[0008] Concerning preprint anchorage, in typical practical applications, a commercial sample of thermal recording medium, with the ability to display detailed information such as food content information after recording e.g. by thermal printing or laser irradiation, will be subjected on the protective layer surface to (pre-)printing, by another technique such as offset printing, to provide more general commercial information (distributor, general food type etc.). The ability of the product to provide preprint anchorage, measured for example by resistance to pre-print removal in a tape tearing test, is a property of value in the present invention.

[0009] It is also of importance to provide a thermosensitive recording medium layer assembly which has high overall transparency, typically measured by haze value i.e. the ratio of transmitted light to the incident light subjected to wide angle scattering. For food packaging, the consumer wishes to see clearly material just on the other side of the transparent package, and the ability to clearly distinguish patterns on the other side of the barrier is reflected in a quantitative automatic measurement through haze value. ASTM D 1003 defines haze as that percentage of light which in passing through deviates from the incident beam greater than 2.5 degrees on the average.

[0010] With a view to solving problems among those indicated above, the present invention, in one aspect, relates to a thermosensitive recording medium comprising at least:

- a transparent support layer;
- a thermosensitive colouring layer over the transparent support layer, the thermosensitive colouring layer containing a leuco dye, a developer and a hydrophobic resin;
- a protective layer over the thermosensitive colouring layer;

characterized in that the weight amount of hydrophobic resin, expressed with respect to 100% total weight of the thermosensitive colouring layer, is more than 30%.

[0011] In preferred embodiments, the quantity of hydrophobic resin, expressed with respect to 100% weight of all components of the thermosensitive colouring layer taken together, is at least 40% and at most 65%.

[0012] In another aspect, the present invention relates to a consumer product package which is at least partially transparent and to which a thermosensitive recording medium of the invention is attached. The consumer product package may be partially or fully transparent, flexible or rigid, and may contain one or more perishable food items, such as delicatessen products or box lunches. In certain embodiments, the consumer product package may be based on a flexible polymer film such as, for example, a PVC film, with information printed thereupon. The consumer product package may be fully transparent, or alternatively almost fully transparent, for example if the only non-transparent parts of the package are those containing printed information, or alternatively the consumer product package may comprise a transparent portion. Where the consumer product package comprises a transparent portion, a non-transparent portion may exist which is either not based on the same basic material (such as a transparent plastic film or rigid material) as the transparent portion, or alternatively has undergone substantial surface or in-depth pigmentation beyond printing of information. The attachment of the thermosensitive recording medium of the invention to a fully or almost transparent consumer product package, or to the transparent portion of a consumer product package, provides the advantage of allowing further information to be incorporated for the benefit of the consumer without obscuring the inner content of the consumer product package, such as a food content, which is thereby visible both before and after the attachment of the thermosensitive recording medium of the invention.

Brief Summary of the Figures

[0013]

Figure 1 is a schematic representation of an illustrative, non-limiting example of a thermosensitive recording medium according to one embodiment of the present invention. In this type of embodiment, in the thermosensitive recording medium (1), the thermosensitive colouring layer (12), placed over the transparent support layer (13), is in contact with the transparent support layer (13), and the thermosensitive colouring layer (12) is also in contact with the protective layer (11).

Figure 2 is a schematic representation of an illustrative, non-limiting example of a thermosensitive recording medium according to another embodiment of the present invention. In this type of embodiment, in the thermosensitive recording medium (1), the thermosensitive colouring layer (12) is not in contact with the transparent support layer (13), because there is an undercoat layer (14) between the thermosensitive colouring layer (12) and the transparent support layer (13). However, the thermosensitive colouring layer (12) is in contact with the protective layer (11).

Figure 3 is a schematic representation of an illustrative, non-limiting example of a thermosensitive recording medium according to a further embodiment of the present invention. Here, the arrangement is analogous to the embodiment shown in Figure 1, except that a back layer (15), placed under the transparent support layer (13), is in contact with the transparent support layer (13).

Figure 4 is a schematic representation of an illustrative, non-limiting example of a thermosensitive recording medium according to a further embodiment of the present invention. Here, the arrangement is analogous to the embodiment shown in Figure 2, except that a back layer (15), placed under the transparent support layer (13), is in contact with the transparent support layer (13).

Figure 5 is a schematic diagram showing glass transition temperature (Tg) measurement by using a differential scanning calorimetry (DSC) method.

List of Reference Signs

[0014]

1: Thermosensitive recording medium
11: Protective layer
12: Thermosensitive colouring layer
13: Transparent support layer

14: Undercoat layer
15: Back layer

Detailed Description of the Invention

<Transparent support laver>

[0015] The base layer in the thermosensitive recording medium of the present invention is a transparent support layer suitably selected depending on the intended purpose without any particular restriction.

[0016] The transparent support used in the present invention is a polymeric material present in the form of a thin film. The total light transmittance of the transparent film is preferably at least 60%, more preferably at least 70% and most preferably at least 90%. Preferred films show a haze value less than 3. The transparent film may also be coloured. The thickness of the transparent film is preferably from 20 μm to 100 μm, more preferably 40 μm to 70 μm.

[0017] Film materials to be used in the transparent support of the thermosensitive recording medium of the present invention may be selected from the group consisting of: ionomer film (IO), polyethylene film (PE), poly(vinyl chloride) film (PVC), poly(vinylidene chloride) film (PVDC), poly(vinyl alcohol) film (PVA), polypropylene film (PP) including biaxially oriented (bi-oriented) polypropylene (BOPP), polyester film, poly(ethylene terephthalate) film (PET), polyethylene naphthalate) film (PEN), polycarbonate film (PC), polystyrene film (PS), polyacrylonitrile film (PAN), ethylene-vinyl acetate copolymer film (EVA), ethylene-vinyl alcohol copolymer film (EMAA), nylon film (NY), polyamide film (PA), triacetyl cellulose film (TAC), norbornane film (NB), and Arton film. Other possibilities include polyethylene (PE) and polymethyl methacrylate (PMMA).

[0018] Preferred transparent support materials in the present invention are: poly(ethylene terephthalate) film (PET) and biaxially oriented (bi-oriented) polypropylene (BOPP).

[0019] As the PET film, Toyobo Ester (R) film E5107, E5100, E5101, Cosmo Shine (R) A4100, A 4300, A8300 and the like from Toyo Boseki K.K may be cited. As BOPP film, Cosmo Films PCT-2 (S/S) LBS, Lichang Plastic PF-P, Jindal Films LL210, and Taghleef Industries LSA, generally produced by co-extrusion, may be cited.

[0020] The transparent film may also contain various additives such as UV absorption agents, oxidation inhibitors, flame retarding agents, thermal stabilizers, colour developing agents, mould releasing agents, softening materials, and electrostatic inhibitors.

[0021] To improve the adhesion of the coated layers on the film substrate, the surface of the film is preferably treated in order to achieve a surface tension of 38 dyn/cm at least. This surface treatment is generally carried out by corona or plasma treatment.

<Undercoat layer(s)>

[0022] In the technical field of thermosensitive recording media in general, the expression "undercoat" is understood by the skilled person to refer to the layer between the support and thermosensitive colouring layer. The expression "under layer" may also be used synonymously with "undercoat layer" by skilled persons in the field.

[0023] In the present invention, an undercoat layer may be provided or not i.e. the undercoat layer is merely an option in the present invention, and the thermosensitive recording medium of the present invention may or may not contain such an undercoat layer.

[0024] In the thermosensitive recording medium of the present invention, if an undercoat layer is used, the technical effect sought after through its used may notably be to improve weakness of adhesion between the substrate and the thermal layer, or to improve printing quality. Such an undercoat layer, if used, should not prevent the thermosensitive recording medium from keeping its transparency, and may appropriately be characterized by a haze value of at most 15.

[0025] As mentioned above, the thermosensitive recording medium of the present invention may optionally contain an undercoat layer disposed between the transparent support and the thermosensitive colouring layer.

[0026] If present in the thermosensitive recording medium of the present invention, the undercoat layer contains a binder resin, and the undercoat layer may further contain other components such as a filler, and other additives.

[0027] As for the binder resin to be used in an undercoat layer, either of a water-dispersible resin or a water-soluble resin may be used. Specific examples thereof include conventionally known water-soluble polymers, and aqueous polymer emulsions.

[0028] The water-soluble polymer that may be used in the binder resin in an undercoat layer may be 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, polyvinyl pyrrolidone, alkali salts of styrene-maleic anhydride copolymers, alkali salts of isobutylene-maleic anhydride copolymers, alginate soda, gelatin and casein. These may be used alone or in combination.

[0029] The aqueous polymer emulsion that may be used in the binder resin in an undercoat layer may be suitably selected depending on the intended purpose without any restriction. Examples thereof include latexes of, for example, styrene-butadiene copolymers; and emulsions of, for example, vinyl acetate resins, acryl-based resins and polyurethane resins. These may be used alone or in combination.

[0030] An inorganic filler may be used or may be omitted from an undercoat layer if an undercoat layer is used in the thermosensitive recording medium of the present invention. If an inorganic filler is used, 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] As components contained in undercoat layers of thermosensitive recording media, it is known, in order to improve printing quality, to use hollow particles having a hollow ratio of 50% or more or indeed 80% or more, or 90% or more, wherein the hollow ratio (in %) is the (inner diameter of a hollow particle / outer diameter of the hollow particle) x 100. Each of such hollow particles may have a shell made of a thermoplastic resin and contain therein air or other gas, typically with a volume average particle diameter of 1 μm to 10 μm, most commonly having a thermoplastic resin as a shell, made from polystyrene, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyacrylic ester, polyacrylonitrile, and polybutadiene, and copolymer resins thereof. In the thermosensitive recording medium of the present invention, even if an undercoat layer is present, on account of the negative effect on transparency if hollow fillers are added, these tending to be white after drying, it is preferred not to include any hollow particles in the undercoat layer.

[0032] If an undercoat layer is used in the thermosensitive recording medium of the present invention, the deposition amount of a first undercoat layer in the thermosensitive recording medium is appropriately 0.4 g/m^2 to 10 g/m^2, more preferably 0.6 g/m^2 to 4 g/ m^2.

[0033] Generally speaking, a key function of an undercoat layer in a conventional thermosensitive recording medium is to fill up and compensate for the non-uniformity of supports such as paper supports in particular. Generally such an undercoat layer is chosen, through its constituents, to be a low-cost layer which ensures a smoother surface before coating with the thermal layer which is expensive - such a way of proceeding optimizes the use of and avoids loss of thermal layer materials. Undercoat layers have been modified to improve pre-print properties and sensitivity by adding hollow fillers which reflect the heat to thermosensitive colouring layer rather than the latter being lost to the paper support layer. In the present invention however, due to the high smoothness of the transparent film support in comparison to paper supports for other thermosensitive recording media, an undercoat layer is not normally necessary. Consequently, in one preferred embodiment of the present invention, one side of the transparent support layer is in contact with one side of the thermosensitive layer, without any undercoat layer between the transparent support layer and the thermosensitive colouring layer. In the present invention, where the base layer in the thermosensitive recording medium is a transparent support layer in the form of a polymeric thin film, an undercoat layer may however still be used to effectively utilize generated heat for higher sensitivity, improve adhesiveness between the transparent support and the thermosensitive layer, and prevent permeation of the recording layer materials into the transparent support.

<Thermosensitive Colouring Layer>

[0034] In the thermosensitive recording medium of the present invention, the thermosensitive colouring layer is situated over the transparent support layer, and the thermosensitive colouring layer contains a leuco dye, a developer and a hydrophobic resin. The thermosensitive colouring layer may be in contact with one face of the transparent support layer or alternatively, as discussed above, an undercoat layer may be present between the transparent support layer and the thermosensitive colouring layer.

<Thermosensitive Colouring Layer - leuco dve and developer>

[0035] The thermosensitive colouring layer contains a colorant system wherein a dye, such as a leuco dye, in one layer of the medium reacts, upon the application of heat, with another component, a so-called "developer", in order to give rise to a coloured product.

[0036] 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 colourless or light-coloured 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 colouring property, fogging of the background, and colour 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-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-(α-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-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.

[0037] The amount of the leuco dye contained in the thermosensitive coloring layer is preferably 3% by mass to 20% by mass.

[0038] 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 colours. 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-α-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, β-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, 4-hydroxy-4'-oxyaryl diphenyl sulfone, 4-hydroxy-4-allyloxy diphenyl sulfone, N-(2-[(phenylcarbamoyl)amino)phenyl)benzene sulfonamide, 4,4'-sulfonylbisphenol, polymer with 1,1'-oxybis[2-chloroethane], 2-(4-Hydroxyphenylsulfonyl)phenol, (Bis(3-allyl-4-hydroxyphenyl)sulfone), 2,2'-diallyl-4,4'-sulfonyldiphenol. These may be used alone or in combination.

[0039] In the thermosensitive colouring 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.

<Thermosensitive Colouring Layer - hydrophobic resin>

[0040] In the thermosensitive recording medium of the present invention, a hydrophobic resin is used in the thermosensitive colouring layer along with a leuco dye and a developer. It has been found by the present inventors that a certain amount of hydrophobic resin in the thermosensitive colouring layer is useful to improve transparency both for the product as prepared and after exposure to water of the final product.

[0041] Concerning the hydrophobic resin to be used in the in the thermosensitive colouring layer, the hydrophobic resin is preferably a homopolymer or copolymer of one or more monomers selected from the group consisting of: styrene, dienes, alkylenes, vinyl acetate, acrylonitrile, and (meth)acrylic esters. Here, "(meth)acrylic esters" is understood as including both methacrylic esters, acrylic esters and combinations thereof. Diene monomers that can be used include: butadiene, isoprene, butenylene, and substituted, e.g. halogenated, versions of these dienes. Alkene monomers that can be used include ethylene, propylene, butene, pentene, hexene, heptene, and substituted, e.g. halogenated, versions of these alkenes. Specifically, the hydrophobic resin to be used in the thermosensitive colouring layer of the present invention may appropriately be one or more selected from the group consisting of: styrene-butadiene resin; styrene-acrylic resin; acrylonitrile-butadiene; acrylate ester resin; ethylene-vinyl acetate resin; methylacrylate-butadiene resin. The hydrophobic resin may also be a urethane resin. Among the possible materials mentioned, styrene-butadiene resin is a particularly preferred hydrophobic resin material for the thermosensitive colouring layer of the thermosensitive recording medium of the present invention. In effect, styrene-butadiene resin has been found to provide particularly improved background reflectance.

[0042] In a common situation, hydrophobic resins are distributed commercially as latex materials, dispersed in an aqueous phase. In a preferred method of preparing the thermosensitive colouring layer of the present invention, the hydrophobic resin is provided in water-borne form as a latex and mixed with a leuco dye and a developer in aqueous dispersion and dried in order to form the thermosensitive colouring layer.

[0043] In preferred embodiments, the hydrophobic resin used in the thermosensitive colouring layer, whatever its specific chemical nature, shows a glass transition temperature (Tg) below 25°C, more preferably a Tg below 20°C, yet further preferably of at most 15°C, still more preferably of at most 5°C, and most preferably of at most 0°C. In preferred embodiments, the Tg is at least -10°C. Particularly preferred Tg values are thus at least -10°C and below 20°C, most preferably at most 15°. A particularly preferred Tg range for the hydrophobic resin used in the thermosensitive colouring layer is at least -10°C and at most 5°C, very preferably at least -10°C and at most 0°C. The glass transition temperature is a well-known feature of such hydrophobic resins and is commonly designated in commercial samples. Polymers to be used as the hydrophobic resin in the thermosensitive colouring layer of the present invention, may show some degree of solubility in water, whilst showing an appropriate range of glass transition temperature (Tg) for the present invention, i.e. below 25°C, preferably below 20°C, more preferably at most 15°C, still more preferably at least -10°C and below 20°C, most preferably at most 15°C, the most preferred range being of at least -10°C and at most 0°C.

[0044] Without wishing to be limited by any particular theoretical interpretation, it is considered by the inventors that during coating, notably when the hydrophobic resin is provided in the form of a latex for coating the transparent support layer, or possibly for coating an undercoat which overlays the said transparent support layer, in the aqueous state, the latex particles are stabilized and exist individually. When the water is removed during drying, the latex particles come in contact. At this point, the particles either keep their shape, or they deform ("melt") and form a polymer film. A fully cured polymer film, where the particles have lost their shape, is usually transparent. On the other hand, a film that still contains the original particles will scatter light at the particle surfaces and will thus be opaque. Thus, to achieve a complete film formation, it is preferable that drying should be performed at temperatures clearly above the Tg. As the time of drying is limited by the coating speed and the drying temperature is limited by the fact that the materials used is thermosensitive and will start to react at 50°C, it has been found preferable that the Tg not exceed 25°C to achieve a good transparency with drying temperatures below 60°C.

[0045] In the present invention, the glass transition temperature (Tg) is as measured by differential scanning calorimetry (DSC) with a previously cooling at a rate of 10 K/mn followed by on heating at a rate of 10 K/mn until transformation from glass to metastable melt is achieved. The exact value of Tg is as determined on the inflection point placed at the middle point between the two tangents. The inflection point corresponds to point B in Figure 5. The glass transition temperature (Tg) can in particular be measured according to standard DIN 51007.

[0046] In the present invention, concerning the weight amount of hydrophobic resin, expressed with respect to 100% total weight of the thermosensitive colouring layer, this is more than 30%, whatever the chemical nature of the hydrophobic resin. In preferred embodiments, the minimum quantity of hydrophobic resin, expressed with respect to 100% weight of all components of the thermosensitive colouring layer taken together, is at least 40%, more preferably at least 45%. The maximum quantity of hydrophobic resin, expressed with respect to 100% total weight of the thermosensitive colouring layer, is preferably at most 65%, more preferably at most 61%, and most preferably at most 58%.

[0047] 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 media, such as a filler, a hot-meltable material, a crosslinking agent, a pigment, a surfactant and a lubricant.

[0048] 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.

[0049] 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 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, β-benzyloxy naphthalene, phenyl β-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.

[0050] In the present invention, the weight amount of hydrophobic resin, expressed with respect to the total weight of the thermosensitive coloring layer taken as 100%, is more than 30%. The total weight of the thermosensitive coloring layer is the sum of the weight of leuco dye(s), developer(s), hydrophobic resin(s), and any other additive used in the thermosensitive coloring layer, such as filler(s), hot-meltable materia(s), crosslinking agent(s), pigment(s), surfactant(s), and lubricant(s). Although the components of thermosensitive coloring layer are applied by coating with a liquid solution / suspension, the total weight amount of the thermosensitive coloring layer, and the weight amount of hydrophobic resin, are here expressed as dry weights after removal of solvents and any other volatile materials.

[0051] The thermosensitive coloring layer can be formed by commonly known methods. To avoid reaction between components of the thermosensitive coloring layer, in preferred embodiments, dispersion is carried out separately and then liquids are mixed. Grinding with a binder and other components is performed typically so as to have a particle diameter of 0.2 μm to 3 μm, preferably 0.4 μm to 1 μm by using a disperser such as a ball mill, an Atriter or a sand mill. The particle size target of each dispersion will be preferably set to get an optimum balance between transparency and background reflectance. Indeed, the lower the particle size is, the higher is the transparency but at the same time, the background reflectance will decrease as thermal layer will become more and more greyish. 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.

[0052] The thickness of the thermosensitive coloring layer varies depending on the composition of the thermosensitive coloring layer and intended use of the thermosensitive recording medium and cannot be specified flatly, but it is preferably 1 μm to 50 μm, more preferably 2 μm to 20 μm.

<Protective Layer(s)>

[0053] In order to achieve good matching properties to thermal head like no sticking, no scratches as well as various qualities such as water or plasticizer resistance, it is preferable to provide at least one protective layer on the thermosensitive layer. Several different protective layers can be overlaid on each other to focus respectively more on matching

or barrier properties. The protective layer(s) in the thermosensitive recording medium of the present invention may be suitably selected depending on the intended purpose without any particular restriction.

[0054] The protective layer(s) typically contain(s) at least a binder, and each of the protective layer(s) may contain an inorganic filler, a lubricant and a surfactant.

[0055] The binder of (each of) the protective layer(s) is suitably selected depending on the intended purpose without any restriction, it being possible to use the same binder in each protective layer or a different binder in separate protective layers. Examples of binders that may be used in the protective layer(s) include polyvinyl alcohol, modified polyvinyl alcohol, starch and derivatives thereof, cellulose derivatives, polyvinylpyrrolidone, polyethyleneimine, alginate soda, gelatin and casein. Acrylic binders may also be used. Hydrophobic resins that may be used as binders in the protective layer(s) include ones typically provided as aqueous emulsions during preparation of the protective layer(s), such as urethane resins, epoxy resins, vinyl acetate (co)polymers, vinylidene chloride (co)polymers, vinyl chloride (co)polymers, and styrene-butadiene copolymers.

[0056] The thickness of the protective layer(s) varies preferably 0.2 μm to 10 μm, more preferably 0.5 μm to 5 μm. In non-limiting exemplary embodiments for this invention, a protective layer of thickness 2.5 μm when dry can be used - when added during the manufacturing process the initial wet thickness of this layer is approximately 6 μm. In the event that several protective layers are applied, lower individual thicknesses for each one will be required. A preferred maximum cumulative thickness for the sum of all protective layers is 10 μm for the dried final product.

[0057] The inorganic filler in the protective layer(s), if used, 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.

[0058] The lubricant, if used, 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.

[0059] A method for forming the first, second or subsequent 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.

<Intermediate laver>

[0060] An intermediate layer is a layer that may be provided between the thermosensitive colouring layer and the protective layer. Such an intermediate layer is however not required in the present invention, but instead is only optional. An intermediate layer containing a water-soluble resin can prevent the thermosensitive recording layer from being colored due to ultraviolet irradiation performed for forming the protective layer, or a reaction between the protective layer and pigments from the thermosensitive colouring layer. An intermediate layer, similar to a first protective layer may also improve background resistance.

[0061] An intermediate layer, if used, contains a water-soluble resin. The water-soluble resin is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the water-soluble resin include: polyvinyl alcohol resins, starch or derivatives of starch; cellulose derivatives such as hydroxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, methyl cellulose, and ethyl cellulose; water-soluble polymers such as sodium polyacrylate, polyvinyl pyrrolidone, acrylamide-acrylic acid ester copolymers, acrylamide-acrylic acid ester-methacrylic acid terpolymers, styrene-maleic anhydride copolymer alkali salts, isobutylene-maleic anhydride copolymer alkali salts, polyacrylamide, sodium alginate, gelatin, and casein; emulsions of, for example, polyvinyl acetate, polyurethane, polyacrylic acid, polyacrylic acid ester, vinyl chloride-vinyl acetate copolymers, polybutyl methacrylate, and ethylene-vinyl acetate copolymers; and latexes of, for example, styrene-butadiene copolymers and styrene-butadiene-acrylic copolymers. One of these water-soluble resins may be used alone or two or more of these water-soluble resins may be used in combination. Among these water-soluble resins, polyvinyl alcohol resins are preferable, and polyvinyl alcohol resins having a molecular weight of 15,000 or less are more preferable.

[0062] Other components of an intermediate layer are not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the other components include a cross-linking agent and a surfactant. One of these other components may be used alone or two or more of these other components may be used in combination.

[0063] The cross-linking agent is not particularly limited so long as the cross-linking agent can reduce water-solubility of the water-soluble resin by reacting with the water-soluble resin. Examples of the cross-linking agent include glyoxal

derivatives, methylol derivatives, epichlorohydrin, polyamide epichlorohydrin, epoxy compounds, aziridine compounds, hydrazine, hydrazide derivatives, oxazoline derivatives, and carbodiimide derivatives. One of these cross-linking agents may be used alone or two or more of these cross-linking agents may be used in combination. Among these cross-linking agents, polyamide epichlorohydrin is preferable because polyamide epichlorohydrin is highly safe in handling and takes a short curing time needed for water-resistance treatment. The content of polyamide epichlorohydrin is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 10 parts by mass or greater but 80 parts by mass or less and more preferably 20 parts by mass or greater but 60 parts by mass or less relative to 100 parts by mass of the water-soluble resin.

[0064] The surfactant is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the surfactant include anionic surfactants, nonionic surfactants, amphoteric surfactants, and fluorosurfactants. One of these surfactants may be used alone or two or more of these surfactants may be used in combination. Examples of the anionic surfactant include polyoxyethylene alkyl ether acetate, dodecylbenzene sulfonate, laurate, and polyoxyethylene alkyl ether sulfate salt. One of these anionic surfactants may be used alone or two or more of these anionic surfactants may be used in combination. Examples of the nonionic surfactant include acetylene glycol-based surfactants, polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene alkyl ester, and polyoxyethylene sorbitan fatty acid ester. One of these nonionic surfactants may be used alone or two or more of these nonionic surfactants may be used in combination. Examples of the acetylene glycol-based surfactant include 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 3,6-dimethyl-4-octyne-3,6-diol, 3,5-dimethyl-1-hexyne-3-diol, and 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol. One of these acetylene glycol-based surfactants may be used alone or two or more of these acetylene glycol-based surfactants may be used in combination.

[0065] The method for forming the intermediate layer is not particularly limited and may be appropriately selected depending on the intended purpose. For example, the intermediate layer can be formed through the step (1) and the step (2) described below.

Step (1): The water-soluble resin, and as needed, the cross-linking agent and the surfactant are mixed, to prepare an intermediate layer coating liquid.
Step (2): The intermediate layer coating liquid is coated over the thermosensitive recording layer and dried.

[0066] The coating method is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the coating method include a blade coating method, a gravure coating method, a gravure offset coating method, a bar coating method, a roll coating method, a knife coating method, an air knife coating method, a comma coating method, a U-comma coating method, an AKKU coating method, a smoothing coating method, a micro-gravure coating method, a reverse roll coating method, a 4-roll or 5-roll coating method, a dip coating method, a curtain coating method, a slide coating method, and a die coating method.

[0067] The amount of the intermediate layer remaining attached after drying is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably, for example, 0.4 g/m^2 or greater but 3.0 g/m^2 or less, more preferably 0.5 g/m^2 or greater but 1.5 g/m^2 or less, and particularly preferably 0.5 g/m^2 or greater but 1.0 g/m^2 or less.

<Back laver>

[0068] A back layer (which may also be called a "backing layer") may be provided under the transparent support layer in the thermosensitive colouring layer of the present invention. Such an intermediate layer is however not required in the present invention, but instead is only optional. In one embodiment, the thermosensitive recording medium may contain a back layer containing a pigment, a binder resin, and preferably a crosslinking agent. The back layer, if present, is to be disposed on the surface of the transparent support opposite to the surface thereof where the thermosensitive layer is disposed, or where the undercoat layer between the transparent support and the thermosensitive layer is situated, if such an undercoat layer is present.

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

[0070] As for the binder resin, either of a water-dispersible resin or a water-soluble resin can be 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, polyvinyl pyrrolidone, alkali salts of styrene-maleic anhydride copolymers, alkali salts of isobutylene-maleic anhydride copolymers, 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, styrene-butadiene copolymers; and emulsions of, for example, vinyl

acetate resins, acryl-based resins (e.g. acrylic acid-acrylic acid ester copolymer latexes), (meth)acrylamide-based resins, and polyurethane resins. These may be used alone or in combination.

[0073] 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, glutalaldehyde 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. 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 100 parts by mass, relative to 100 parts by mass of the binder resin.

[0074] 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, polyethylene resins, and formaldehyde resins.

[0075] The antistatic agent may, for example, be selected from commonly used ion-conducting antistatic agents and electron-conducting antistatic agents. Specific examples of the ion-conducting antistatic agents include inorganic salts such as sodium chloride; anionic polymers such as sodium polystyrenesulfonate; and resins containing quaternary ammonium salts that are electrolyte cations. Specific examples of the electron-conducting antistatic agents include conductive metal compounds such as conductive tin and antimony oxide; and conductive polymers such as polyaniline. Among these antistatic agents, polystyrene sulfonic acid salts, in particular, react with aziridine, thereby improving water resistance obtained by means of cross-linkage. Additionally, salts which have copolymerized with maleic acid are effective in that they have antistatic properties and also improve water resistance.

[0076] 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.

[0077] 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.

[0078] 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.

<Viscous laver>

[0079] A viscous layer, also called an adhesive layer, may be provided in the thermosensitive recording medium of the present invention. Such a viscous layer is however not required in the present invention, but instead is only optional.

[0080] A viscous layer may be provided on a surface of the transparent support layer opposite to the surface over which the protective layer is formed. The viscous layer may, for example, help to attach the thermosensitive recording medium to a food package in a typical application of the present invention. The viscous layer may also provide antistatic properties. The method for forming the viscous layer is not particularly limited. Examples of the method include common coating methods and laminating methods. The average thickness of the viscous layer is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 0.1 micrometers or greater but 20 micrometers or less.

[0081] The material of the viscous layer is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the material of the viscous layer include urea resins, melamine resins, phenol resins, epoxy resins, vinyl acetate-based resins, vinyl acetate-acrylic-based copolymers, ethylene-vinyl acetate copolymers, acrylic-based resins, polyvinyl ether-based resins, vinyl chloride-vinyl acetate-based copolymers, polystyrene-based resins, polyester-based resins, polyurethane-based resins, polyamide-based resins, chlorinated polyolefin-based resins, polyvinyl butyral-based resins, acrylic acid ester-based copolymers, methacrylic acid ester-based copolymers, natural rubbers, cyano acrylate-based resins, and silicone-based resins. One of these materials may be used alone or two or more of these materials may be used in combination. These materials may be cross-linked by means of a cross-linking agent. The material of the viscous layer may be a hot-melt type.

Image recording method

[0082] An image recording method may be used for recording an image on the thermosensitive recording medium 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.

[0083] The thermal head is suitably selected depending on the intended purpose without any restriction regarding the shape, structure and size thereof.

[0084] The laser may be selected depending on the intended purpose without any restriction. In one preferred em-

bodiment, a CO_2 laser which emits light having a wavelength of 9.3 μm to 10.6 μm may be used. By using the CO_2 laser which emits light having a wavelength of 9.3 μm to 10.6 μm, a satisfactory laser print image can be obtained without using a photothermal conversion agent such as a phthalocyanine pigment. Other laser types may be used, such as FLDA (Fiber Laser Diode Array).

EXAM PLES

[0085] 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

[Preparation of thermosensitive recording layer liquid C_1]

[0086] 2,2'-diallyl-4,4'-sulfonyldiphenol (50 parts by mass), a 35% by mass acrylic resin aqueous solution (10 parts by mass) and ion exchanged water (70 parts by mass) were dispersed using a sand mill in such a way that the 50% cumulative volume particle diameter (D50) measured by a laser diffraction/scattering particle diameter distribution measuring instrument (instrument name : LA-920, from HORIBA, Ltd.) is less than 0.7 μm to thereby prepare a developer dispersion liquid [Liquid A1].

[0087] Likewise, 2-Anilino-6-dibutylamino-3-methylfluoran (80 parts by mass), a 35% by mass acrylic resin aqueous solution (20 parts by mass) and ion exchanged water (90 parts by mass) were dispersed using a sand mill, in such a way that the 50% cumulative volume particle diameter (D50) than 0.7 μm to thereby prepare a dye dispersion liquid [Liquid B1].

[0088] Next, ion exchanged water (57 parts by mass) was mixed and stirred with respectively a 50% styrene-butadiene copolymer latex (27 parts by mass), the developer dispersion liquid [A1] (50 parts by mass) and the dye dispersion liquid [B1] (15 parts by mass) to obtain the thermosensitive recording layer liquid [C1] corresponding to an addition of 33% of styrene-butadiene with respect to 100% dry weight of all components.

[0089] The commercial grade of styrene-butadiene copolymer latex used for this preparation was HPD40 available from Trinseo Europe GmbH characterized by a glass transition temperature of 0°C.

[Preparation of protective layer liquid D1]

[0090] A 20% water-based acrylic resin (product name: Bariastar B-2000 available from Mitsui Chemicals, Inc.) (75 parts by mass), a 25% slurry of kaolin having a mean volume particle diameter of kaolin having a mean volume particle of 0.7 μm (Product name: UW90, available from Engelhard Corporation) (6 parts by mass), a 35% polyethylene wax (product name: Michem Emulsion 99235 available from Michelman, Inc.) (4 parts by mass), and 15 parts of water were mixed and stirred, to obtain the protective layer [D1].

[Preparation of thermosensitive recording medium]

[0091] The [C1] and [D1] liquids were coated and dried in this order over the surface of a bioriented polypropylene film (product name: 35LL410, with a thickness of 35 μm, available from Jindal Films) such that the amounts of the [C1] and [D1] remaining attached after drying would be 3.6 g/m^2 corresponding to a dye coating weight of 0.6 g/m^2 and 3.0 g/m^2 to obtain a thermosensitive recording medium precursor 1.

[0092] Then, the thermosensitive recording medium precursor 1 was put in a high density polyethylene bag, closely sealed, and cured in an environment of 40°C for 15 hours to produce the thermosensitive recording medium 1.

Example 2

[0093] A thermosensitive recording medium 2 was produced by preparing a thermosensitive recording layer liquid [C2] in the same manner as in Example 1, except that unlike Example 1, 41 parts by mass of 50% styrene butadiene copolymer latex and 44 parts by mass of water were used which corresponds to an addition of 43% of styrene-butadiene with respect to 100 dry weight of all components.

[0094] The [C2] and [D1] liquids were coated and dried in the same manner as in Example 1, except that unlike Example 1, the amounts of [C2] remaining attached after drying would be 4.2 g/m^2, corresponding to the same dye coating weight as in Example 1.

[0095] The [C2] and [D1] liquids were coated and dried in the same manner as in Example 1, except that unlike Example 1, the amounts of [C2] remaining attached after drying would be 4.2 g/m^2, corresponding to the same dye coating weight as in Example 1.

Example 3

[0096] A thermosensitive recording medium 3 was produced by preparing a thermosensitive recording layer liquid [C3] in the same manner as in Example 1, except that unlike Example 1, 55 parts by mass of 50% styrene butadiene copolymer latex and 30 parts by mass of water were used which corresponds to an addition of 50% of styrene-butadiene with respect to 100 dry weight of all components.

[0097] The [C3] and [D1] liquids were coated and dried in the same manner as in Example 1, except that unlike Example 1, the amounts of [C3] remaining attached after drying would be 4.8 g/m^2, corresponding to the same dye coating weight as in Example 1.

Example 4

[0098] A thermosensitive recording medium 4 was produced by preparing a thermosensitive recording layer liquid [C4] in the same manner as in Example 1, except that unlike Example 1, 68 parts by mass of 50% styrene butadiene copolymer latex and 16 parts by mass of water were used which corresponds to an addition of 56% of styrene-butadiene with respect to 100 dry weight of all components.

[0099] The [C4] and [D1] liquids were coated and dried in the same manner as in Example 1, except that unlike Example 1, the amounts of [C4] remaining attached after drying would be 5.4 g/m^2, corresponding to the same dye coating weight as in Example 1.

Example 5

[0100] A thermosensitive recording medium 5 was produced by preparing a thermosensitive recording layer liquid [C5] in the same manner as in Example 1, except that unlike Example 1, 82 parts by mass of 50% styrene butadiene copolymer latex and 3 parts by mass of water were used which corresponds to an addition of 60% of styrene-butadiene with respect to 100 dry weight of all components.

[0101] The [C5] and [D1] liquids were coated and dried in the same manner as in Example 1, except that unlike Example 1, the amounts of [C5] remaining attached after drying would be 6.0 g/m^2, corresponding to the same dye coating weight as in Example 1.

Example 6

[0102] A thermosensitive recording medium 6 was produced by preparing a thermosensitive recording layer liquid [C6] in the same manner as in Example 3, except that unlike Example 3, the 50% styrene butadiene copolymer latex commercial grade used for this preparation is characterized by a glass transition temperature of -25 °C (Product name : HPD42 available from Trinseo Europe GmbH).

[0103] The [C6] and [D1] liquids were coated and dried in the same manner as in Example 3.

Example 7

[0104] A thermosensitive recording medium 7 was produced by preparing a thermosensitive recording layer liquid [C7] in the same manner as in Example 3, except that unlike Example 3, the 50% styrene butadiene copolymer latex commercial grade used for this preparation is characterized by a glass transition temperature of -10 °C (Product name : HPD41 available from Trinseo Europe GmbH).

[0105] The [C7] and [D1] liquids were coated and dried in the same manner as in Example 3.

Example 8

[0106] A thermosensitive recording medium 8 was produced by preparing a thermosensitive recording layer liquid [C8] in the same manner as in Example 3, except that unlike Example 3, the 50% styrene butadiene copolymer latex commercial grade used for this preparation is characterized by a glass transition temperature of 15 °C (Product name : HPD39 available from Trinseo Europe GmbH).

[0107] The [C8] and [D1] liquids were coated and dried in the same manner as in Example 3.

Example 9

[0108] A thermosensitive recording medium 9 was produced by preparing a thermosensitive recording layer liquid [C9] in the same manner as in Example 1, except that unlike Example 1, the 50% styrene butadiene copolymer latex was replaced by a 41% self-crosslinking acrylic emulsion (Product name: FLX 5020 available from BTC Europe GmbH) (67 parts by mass) and 18 parts by mass of water were used which corresponds to an addition of 50 % of acrylic emulsion with respect to 100 dry weight of all components.

[0109] The [C9] and [D1] liquids were coated and dried in the same manner as in Example 3.

Example 10

[0110] A thermosensitive recording medium 10 was produced by preparing a thermosensitive recording layer liquid [C10] in the same manner as in Example 1, except that unlike Example 1, the 50% styrene butadiene copolymer latex was replaced by a 46% styrene acrylic emulsion (Product name : Joncryl Eco 2117 available from BTC Europe GmbH) (60 parts by mass) and 25 parts by mass of water were used which corresponds to an addition of 50 % of styrene acrylic emulsion with respect to 100 dry weight of all components.

[0111] The [C10] and [D1] liquids were coated and dried in the same manner as in Example 3.

Example 11

[0112] A thermosensitive recording medium 11 was produced in the same manner as in Example 3, except that unlike Example 3, an intermediate layer coating liquid composed of styrene butadiene (Product name: HPD40 available from Trinseo Europe GmbH) was coated and dried over the surface of the bioriented polypropylene film such that the amount of the liquid remaining attached after the drying would be 6.0 g/m^2, to form an undercoat layer.

Comparative Example 1

[0113] A thermosensitive recording medium 12 was produced by preparing a thermosensitive recording layer liquid [C11] in the same manner as in Example 1, except that unlike Example 1, 7 parts by mass of 50% styrene butadiene copolymer latex and 78 parts by mass of water were used which corresponds to an addition of 11% of styrene-butadiene with respect to 100 dry weight of all components.

[0114] The [C11] and [D1] liquids were coated and dried in the same manner as in Example 1, except that unlike Example 1, the amounts of [C11] remaining attached after drying would be 2.7 g/m^2, corresponding to the same dye coating weight as in Example 1.

Comparative Example 2

[0115] A thermosensitive recording medium 13 was produced by preparing a thermosensitive recording layer liquid [C12] in the same manner as in Example 1, except that unlike Example 1, 14 parts by mass of 50% styrene butadiene copolymer latex and 71 parts by mass of water were used which corresponds to an addition of 20% of styrene-butadiene with respect to 100 dry weight of all components.

[0116] The [C12] and [D1] liquids were coated and dried in the same manner as in Example 1, except that unlike Example 1, the amounts of [C12] remaining attached after drying would be 3.0 g/m^2, corresponding to the same dye coating weight as in Example 1.

Comparative Example 3

[0117] A thermosensitive recording medium 14 was produced by preparing a thermosensitive recording layer liquid [C13] in the same manner as in Example 9, except that unlike Example 9, 17 parts by mass of the self-crosslinking acrylic emulsion and 68 parts by mass of water were used which corresponds to an addition of 20% of acrylic emulsion with respect to 100 dry weight of all components.

[0118] The [C13] and [D1] liquids were coated and dried in the same manner as in Comparative Example 2.

Comparative Example 4

[0119] Ion exchanged water (30 parts by mass) was mixed and stirred with respectively a 10% by mass itaconic acid modified polyvinyl alcohol aqueous solution (Product name : Poval 25-88 KL available from Kuraray Europe GmbH) (57 parts by mass), the developer dispersion liquid [A1] (10 parts by mass) and the dye dispersion liquid [B1] (3 parts by

mass) to obtain the thermosensitive recording layer liquid [C14] which corresponding to an addition of 50% of itaconic acid modified polyvinyl alcohol with respect to 100% dry weight of all components.

[0120] The [C14] and [D1] liquids were coated and dried in the same manner as in Example 1, except that unlike Example 1, the amounts of [C14] remaining attached after drying would be 4.8 g/m^2, corresponding to the same dye coating weight as in Example 1 to form the thermosensitive recording medium 15.

Comparative Example 5

[0121] A thermosensitive recording medium 16 was produced by preparing a thermosensitive recording layer liquid [C15] in the same manner as in Comparative Example 4, except that unlike Comparative Example 4, a 10% by mass partially hydrolyzed polyvinyl alcohol aqueous solution (Product name : Poval PVA 235 available from Kuraray Europe GmbH) was used in replacement of itaconic acid modified polyvinyl alcohol.

[0122] The [C15] and [D1] liquids were coated and dried in the same manner as in Comparative Example 4.

[0123] The type of resin, the quantity or resin expressed as dry weight with respect to 100% dry weight of all components and corresponding glass transition temperature of Examples 1 to 11 and Comparative Examples 1 to 5 are indicated in Table 1

Table 1

	Type	% Dry weight	Glass transition temperature °C
Ex. 1	Styrene-Butadiene	33.3	0
Ex. 2	Styrene-Butadiene	42.9	0
Ex. 3	Styrene-Butadiene	50.0	0
Ex. 4	Styrene-Butadiene	55.6	0
Ex. 5	Styrene-Butadiene	60	0
Ex. 6	Styrene-Butadiene	50	-25
Ex 7	Styrene-Butadiene	50	-10
Ex. 8	Styrene-Butadiene	50	15
Ex. 9	Acrylic	50	NA
Ex. 10	Styrene-acrylic	50	8
Ex. 11	Styrene-Butadiene	50	0
Comp. Ex. 1	Styrene-Butadiene	11.1	0
Comp. Ex. 2	Styrene-Butadiene	20.0	0
Comp. Ex. 3	Acrylic	20	NA
Comp. Ex. 4	Polyvinyl Alcohol	50	NA
Comp. Ex. 5	Polyvinyl alcohol	50	NA

[0124] Next, with each of the thermosensitive recording medium of Examples 1 to 11 and Comparative Examples 1 to 5 "transparency" (haze degree), "water resistance transparency" (haze degree), "color" (background reflectance), "preprint anchorage" and "plasticizer resistance" were evaluated.

< Transparency>

[0125] The transparency was evaluated by measuring a haze degree with a haze meter (instrument name: Haze-gard i, available from BYK-Gardner GmbH) and evaluated according to evaluation criteria below. For a value of "A" or "B", the thermosensitive recording medium is at an acceptable level.

A : Less than or equal to 23%
B : Between 23% and 25%
C : Between 25% and 35%
D : Greater than or equal to 35%

<Water resistance remaining transparency>

[0126] The water resistance remaining transparency was evaluated by firstly dipping a piece (5*6 cm) of the thermosensitive recording medium during 15 hours in a 150 ml glass beaker filled with tap water and drying it at 23°C 50% RH until no trace of water remains and then by measuring haze degree as described above. Evaluation was done according to criteria below. For a value of "A" or "B", the thermosensitive recording medium is at an acceptable level.

A : Less than or equal to 30%
B : Between 30% and 40%
C : Between 40% and 50%
D : Greater than or equal to 50% or removal of coated layer

<Color>

[0127] The color was evaluated by measuring background reflectance with a photoreflectometer (instrument name: PhotoVolt 577 PC, available from Photovolt Instruments, Inc) using a green filter and evaluated according to evaluation criteria below. For a value of "A" or "B", the thermosensitive recording medium is at an acceptable level.

A : Higher than or equal to 83
B : Between 82 and 83
C : Between 76 and 82
D : Less than or equal to 76

<Pre-print>

[0128] The preprint anchorage was evaluated by applying firstly a full printing of Sicuraflex 39-8 ink from Siegwerk Druckfarben AG & Co. KgaA with a flexo printer (Instrument name : Flexiproof 100, available from Erichsen GmbH & Co. KG) (Anilox = 4 cm^3 ; speed = 50 m/mn). Thereafter, ink deposited on thermal recording medium was cured under UV and left during 24 hours in normal room conditions (23°C 50% RH) for stabilisation.

[0129] Then a cellophane tape having a width of 18 mm and a length of 6 cm (Product name CT405 AP-18, available from Nichiban Co, Ltd.) was pasted over the printed samples along the direction of the flow of printing and rubbed 10 times with finger such that no bubbles would be included. Then tape was removed in three steps : i) Slowly stripping the tape with an angle of 180 degrees, ii) slowly stripping the tape to an angle of 90 degrees, iii) Quickly stripping the tape with an angle of 90 degrees. In case of ink removal, the thermosensitive recording medium was heated to confirm if peeling included thermosensitive coated layer or not. Evaluation was done according to evaluation criteria below. For a value of "A" or "B", the thermosensitive recording medium is at an acceptable level.

A : There was no stripping in all of the (i) to (iii) steps.
B : There was no ink stripping in the (i) and (ii) steps. There was stripping of the thermosensitive layer in the (iii) step.
C : There was no ink stripping in the (i) and (ii) steps. There was stripping of the ink but not of thermosensitive layer in the (iii) step.
D : There was stripping in the (i) or (ii) step.

<Plasticizer resistance>

[0130] The plasticizer resistance was evaluated by firstly printing a black pattern with a Tec B-SA4T equipment from Toshiba (300 dpi, temperature 5, 101.6 mm/s). Optical density of printed pattern was measured with a spectrophotometer (Instrument name= Exact available from X-Rite, Inc.). Subsequently, two sheets of polyvinyl chloride wrapping film (produced by Shin-Etsu Polymer Co., Ltd) were laid over the printed thermosensitive medium, and left to stand during 3 days at 40°C under a load of 5 kg. Then the remaining optical image density was measured on three points using the same spectrophotometer and the average recorded. Remaining ratio was calculated by dividing the remaining optical density measured after test by initial optical density measured before test.

[0131] Evaluation was done according to evaluation criteria below. For a value of "A" or "B", the thermosensitive recording medium is at an acceptable level.

A : Greater than or equal to 0.7
B : Less than 0.7

[0132] The results of above measurements of Examples 1 to 11 and Comparative Examples 1 to 5 are shown in Table 2.

[0133] For a comprehensive understanding, a global notation of all results has been added according to following criteria :

AA : All items achieved A notation
A : Only one item achieved B, all others achieved A
B : at least two items achieved only B, but any items achieved only C or D
C : One item achieved at least C or D

Table 2

	Transparency		Water resistance remaining transparency		Color		Preprint	Plasticizer resistance		Global evaluation
	Haze degree %	Rank	Haze degree %	Rank	Background Reflectance	Rank	Rank	Ratio	Rank	
Ex. 1	24.1	B	34.0	B	83.7	A	B	0.94	A	B
Ex. 2	22.4	A	25.6	A	84,0	A	B	0.88	A	A
Ex. 3	22.2	A	26.5	A	83.5	A	A	0.86	A	AA
Ex. 4	22.8	A	26.2	A	84.0	A	A	0.74	A	AA
Ex. 5	21.2	A	24.5	A	85.1	A	A	0.69	B	A
Ex. 6	19.9	A	25.2	A	82.8	B	B	0.64	B	B
Ex. 7	22.2	A	27.5	A	83.9	A	A	0.71	A	AA
Ex. 8	22.7	A	30.4	B	83.6	A	A	0.90	A	A
Ex. 9	19.4	A	36.7	B	82.6	B	A	1.08	A	B
Ex. 10	25.0	B	38.5	B	82.9	B	B	0.95	A	B
Ex. 11	21.4	A	27.2	A	84.1	A	A	0.95	A	AA
Comp. Ex. 1	33.5	C	63.7	D	79.4	C	D	1.03	A	C
Comp. Ex. 2	24.8	B	53.4	D	83.7	A	C	0.97	A	C
Comp. Ex. 3	33.6	C	59.1	D	81.5	C	D	0.96	A	C
Comp. Ex. 4	39.6	C	Peeled	D	86.3	A	C	0.91	A	C
Comp. Ex. 5	46.2	D	Peeled	D	87.0	A	B	0.77	A	C

Claims

1. A thermosensitive recording medium comprising at least:

    - a transparent support layer;
    - a thermosensitive colouring layer over the transparent support layer, the thermosensitive colouring layer containing a leuco dye, a developer and a hydrophobic resin;
    - a protective layer over the thermosensitive colouring layer; and

    characterized in that the weight amount of hydrophobic resin, expressed with respect to 100% total weight of the thermosensitive colouring layer, is more than 30%.

2. A thermosensitive recording medium according to claim 1, wherein the quantity of hydrophobic resin, expressed with respect to 100% weight of all components of the thermosensitive colouring layer taken together, is at least 40% and at most 65%.

3. A thermosensitive recording medium according to claim 1 or 2, wherein the hydrophobic resin is a homopolymer or copolymer of one or more monomers selected from the group consisting of: styrene, dienes, alkylenes, vinyl acetate, acrylonitrile, (meth)acrylic esters.

4. A thermosensitive recording medium according to any of claims 1 to 3, wherein the hydrophobic resin is one or more selected from the group consisting of: styrene-butadiene resin; styrene-acrylic resin; acrylonitrile-butadiene; acrylate ester resin; ethylene-vinyl acetate resin; methylacrylate-butadiene resin; and urethane resin.

5. A thermosensitive recording medium according to any of claims 1 to 4, wherein the hydrophobic resin in the thermosensitive colouring layer shows a glass transition temperature below 25°C.

6. A thermosensitive recording medium according to claim 5, wherein the hydrophobic resin in the thermosensitive colouring layer shows a glass transition temperature of at least -10°C and at most 15°C.

7. A thermosensitive recording medium according to claim 5 or 6, wherein the hydrophobic resin in the thermosensitive colouring layer shows a glass transition temperature of at least -10°C and at most 0°C.

8. A thermosensitive recording medium according to any of claims 1 to 7, wherein the hydrophobic resin in the thermosensitive colouring layer is a styrene-butadiene resin.

9. A thermosensitive recording medium according to any of claims 1 to 7, wherein at least one undercoat layer is present between the transparent support layer and the thermosensitive colouring layer, and wherein the undercoat layer has a haze value of at most 15.

10. A thermosensitive recording medium according to claim 9, wherein the undercoat layer does not contain hollow particles.

11. Consumer product package which is at least partially transparent and to which a thermosensitive recording medium according to any of claims 1 to 10 is attached.

12. Consumer product package according to claim 11, wherein the consumer product package comprises a transparent portion and the thermosensitive recording medium according to any of claims 1 to 10 is attached to the transparent portion.

13. Consumer product package according to claim 11 or 12, wherein the package is for one or more perishable food items.

Amended claims in accordance with Rule 137(2) EPC.

1. A thermosensitive recording medium (1) comprising at least:

    - a transparent support layer (13);

- a thermosensitive colouring layer (12) over the transparent support layer, the thermosensitive colouring layer containing a leuco dye, a developer and a hydrophobic resin;
- a protective layer (11) over the thermosensitive colouring layer; and **characterized in that**
- the dry weight amount of hydrophobic resin, expressed with respect to 100% total dry weight of the thermosensitive colouring layer (12) is at least 40% and at most 65%; and
- the hydrophobic resin in the thermosensitive colouring layer (12) shows a glass transition temperature of at least -10°C and at most 0°C.

2. A thermosensitive recording medium (1) according to claim 1, wherein the hydrophobic resin is a homopolymer or copolymer of one or more monomers selected from the group consisting of: styrene, dienes, alkylenes, vinyl acetate, acrylonitrile, (meth)acrylic esters.

3. A thermosensitive recording medium (1) according to any of claim 1 or 2, wherein the hydrophobic resin is one or more selected from the group consisting of: styrene-butadiene resin; styrene-acrylic resin; acrylonitrile-butadiene; acrylate ester resin; ethylene-vinyl acetate resin; methylacrylate-butadiene resin; and urethane resin.

4. A thermosensitive recording medium (1) according to any of claims 1 to 3, wherein the hydrophobic resin in the thermosensitive colouring layer (12) is a styrene-butadiene resin.

5. A thermosensitive recording medium (1) according to any of claims 1 to 3, wherein at least one undercoat layer (14) is present between the transparent support layer (13) and the thermosensitive colouring layer (12), and wherein the undercoat layer has a haze value of at most 15.

6. A thermosensitive recording medium (1) according to claim 5, wherein the undercoat layer (14) does not contain hollow particles.

7. Consumer product package which is at least partially transparent and to which a thermosensitive recording medium (1) according to any of claims 1 to 6 is attached.

8. Consumer product package according to claim 7, wherein the consumer product package comprises a transparent portion and the thermosensitive recording medium (1) according to any of claims 1 to 6 is attached to the transparent portion.

9. Consumer product package according to claim 7 or 8, wherein the package is for one or more perishable food items.

Amended claims in accordance with Rule 137(2) EPC.

1. A thermosensitive recording medium (1) comprising at least:

- a transparent support layer (13);
- a thermosensitive colouring layer (12) over the transparent support layer, the thermosensitive colouring layer containing a leuco dye, a developer and a hydrophobic resin;
- a protective layer (11) over the thermosensitive colouring layer; and **characterized in that**
- the dry weight amount of hydrophobic resin, expressed with respect to 100% total dry weight of the thermosensitive colouring layer (12) is at least 45% and at most 58%; and
- the hydrophobic resin in the thermosensitive colouring layer (12) shows a glass transition temperature of at least -10°C and at most 0°C.

2. A thermosensitive recording medium (1) according to claim 1, wherein the hydrophobic resin is a homopolymer or copolymer of one or more monomers selected from the group consisting of: styrene, dienes, alkylenes, vinyl acetate, acrylonitrile, (meth)acrylic esters.

3. A thermosensitive recording medium (1) according to any of claim 1 or 2, wherein the hydrophobic resin is one or more selected from the group consisting of: styrene-butadiene resin; styrene-acrylic resin; acrylonitrile-butadiene; acrylate ester resin; ethylene-vinyl acetate resin; methylacrylate-butadiene resin; and urethane resin.

4. A thermosensitive recording medium (1) according to any of claims 1 to 3, wherein the hydrophobic resin in the

thermosensitive colouring layer (12) is a styrene-butadiene resin.

5. A thermosensitive recording medium (1) according to any of claims 1 to 3, wherein at least one undercoat layer (14) is present between the transparent support layer (13) and the thermosensitive colouring layer (12), and wherein the undercoat layer has a haze value of at most 15.

6. A thermosensitive recording medium (1) according to claim 5, wherein the undercoat layer (14) does not contain hollow particles.

7. Consumer product package which is at least partially transparent and to which a thermosensitive recording medium (1) according to any of claims 1 to 6 is attached.

8. Consumer product package according to claim 7, wherein the consumer product package comprises a transparent portion and the thermosensitive recording medium (1) according to any of claims 1 to 6 is attached to the transparent portion.

9. Consumer product package according to claim 7 or 8, wherein the package is for one or more perishable food items.

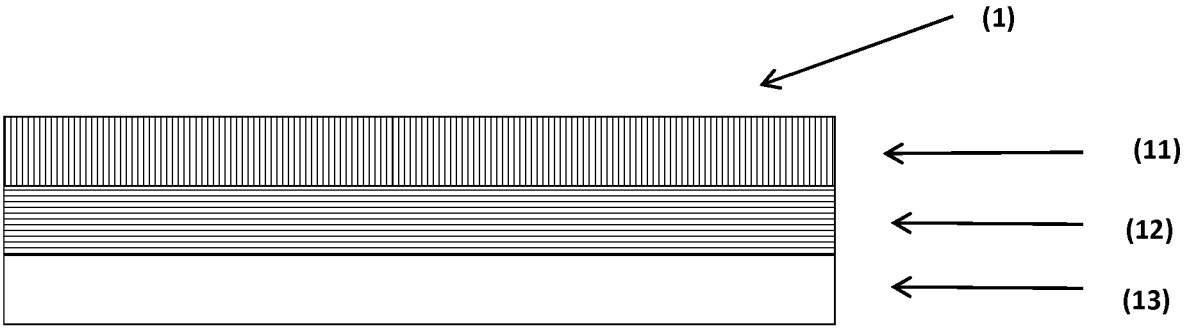


Figure 1

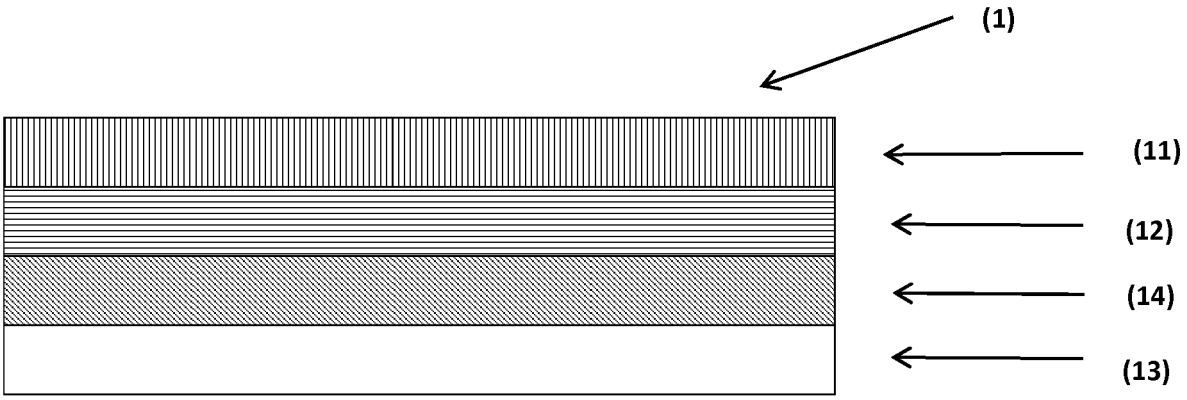


Figure 2

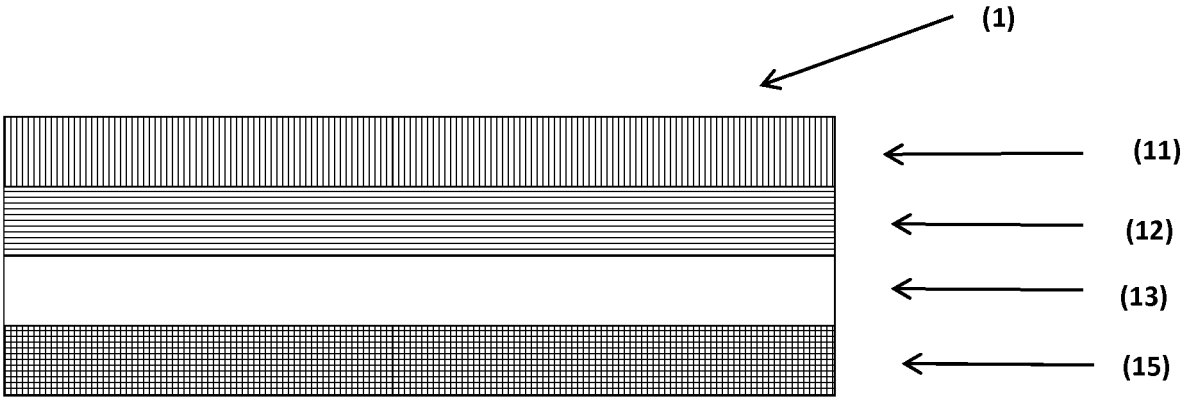


Figure 3

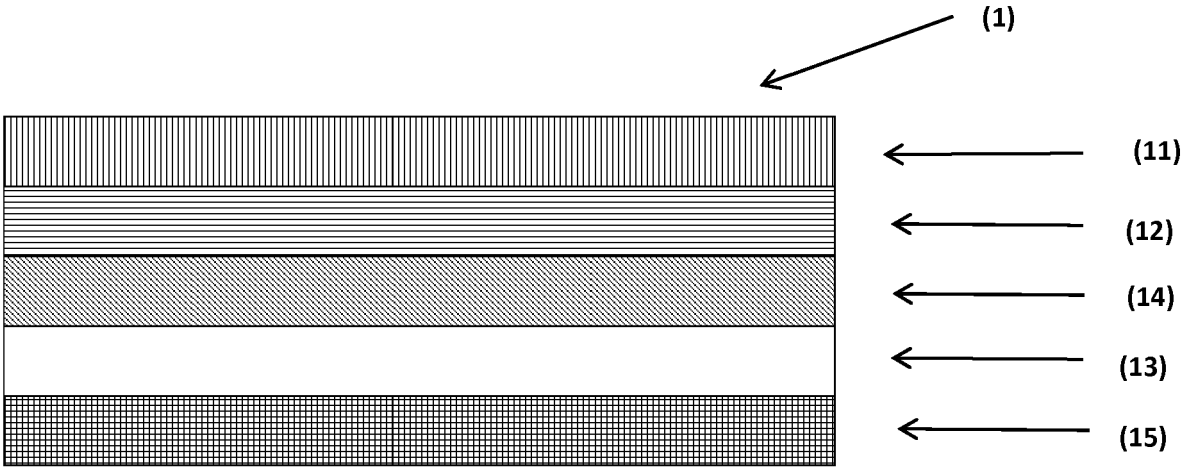


Figure 4

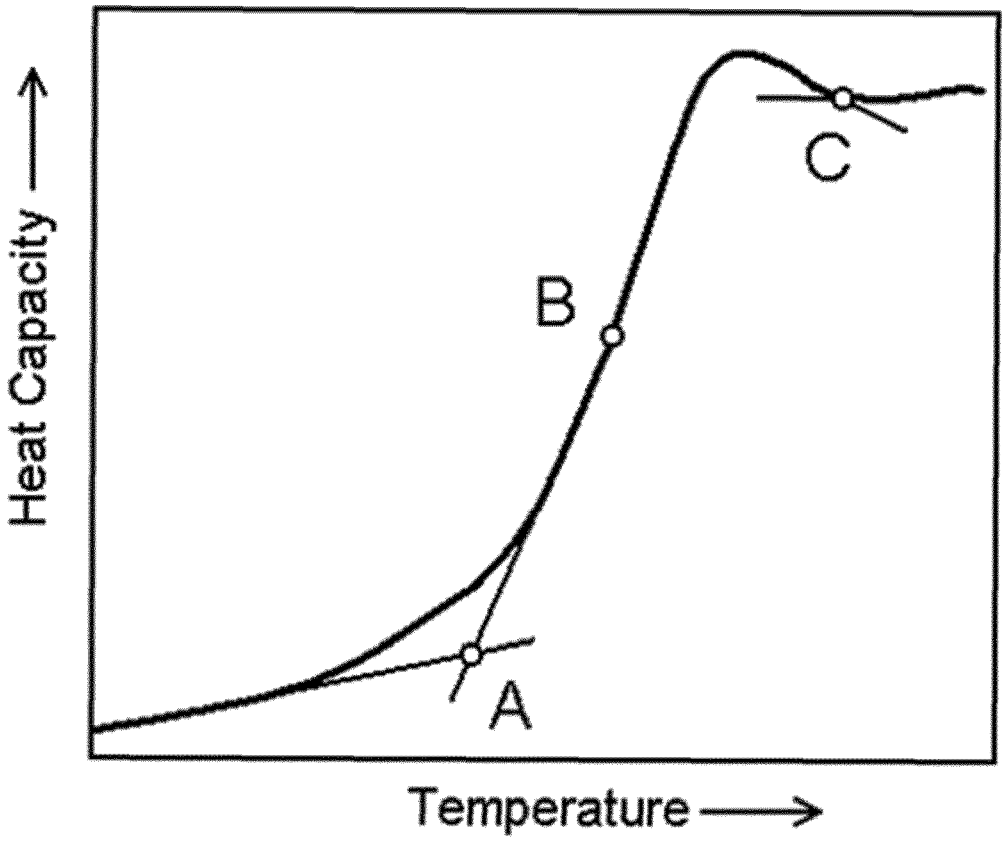


Figure 5

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EUROPEAN SEARCH REPORT

Application Number
EP 19 15 1664

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B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	2 August 2019	Pulver, Michael

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