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

(11) **EP 4 420 887 A1**

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.08.2024 Bulletin 2024/35

(21) Application number: **23305230.7**

(22) Date of filing: **22.02.2023**

(51) International Patent Classification (IPC):
B41M 5/333 *(2006.01)* ***B41M 5/42*** *(2006.01)*
B41M 5/44 *(2006.01)* *B41M 5/323* *(2006.01)*
B41M 5/327 *(2006.01)* *B41M 5/337* *(2006.01)*

(52) Cooperative Patent Classification (CPC):
B41M 5/3333; B41M 5/42; B41M 5/44;
B41M 5/323; B41M 5/3275; B41M 5/3377;
B41M 2205/04; B41M 2205/38; B41M 2205/40

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

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(54) THERMOSENSITIVE RECORDING MEDIUM

(57) The present invention relates to a thermosensitive recording medium comprising at least:
- a support layer,
- an undercoat layer over the support layer,
- a thermosensitive colouring layer over the undercoat layer,
- a protective layer over the thermosensitive colouring layer,
wherein
- the undercoat layer comprises at least one type of plastic hollow particles as organic fillers, the plastic hollow particles comprising at least 20% of hollow particles, by mass with respect to the mass of all the hollow particles, which have a hollow ratio at 60% or more, the hollow ratio being a percentage ratio of the inner diameter of the hollow particles to the outer diameter of the hollow particles;
- the thermosensitive colouring layer comprises at least two types of colour developers from groups with (1) an N-phenylureido-phenyl-benzenesulfonamide structure, (2) an N-phenylureido-phenyl-oxysulfonyl-aryl structure, and/or or (3) an N,N'-di-([arylsulfonyloxyl]-phenyl)urea structure.

The present invention relates to the use of such a thermosensitive recording medium in food packaging.

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Description

Field of the Invention

[0001] The present invention relates in one of its aspects to a thermosensitive recording medium. In further aspects, the present invention relates to a label for attachment to a product comprising the thermosensitive recording medium of the invention, and to a consumer product package to which a thermosensitive recording medium or a label of the invention has been attached.

Technical Background to the Invention

[0002] Thermosensitive recording mediums 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. Concerning the leuco dye - developer couple, phenols can successfully be used as developers in thermal paper. However, notably for environmental and human health reasons, it is preferred to try to avoid using phenols, especially Bisphenol-A, Bisphenol-S and its derivertives in this context. N-phenylureido-phenyl-benzenesulfonamides have been proposed, for example in EP 2 923 851, JP-2015-150764 and EP3670205, as non-phenol developers in this context. Moreover, several structures of non-phenol developers have been proposed, for example in EP3395583 and EP3677569.

[0003] However, when using an N-phenylureido-phenyl-benzenesulfonamide as a colour developer in the thermosensitive colouring layer of a thermosensitive recording medium, a dynamic sensitivity is still not achieved at the same level as bis-phenol type developers. Several countermeasures such as combination with a sensitizer or other developers have been proposed to improve this problem, but it is difficult to keep higher heat resistance while improving the dynamic sensitivity. There is a market where thermosensitive recording mediums are converted into labels through a digital printing process. In this field, due to its printing process through heating rolls, extremely high heat resistance such as resistance above 110°C is desirable. When a thermosensitive recording medium with not enough heat resistance is processed in digital printing machines, undesirable colour developing may occur. It is difficult to simultaneously resolve this compatibility problem of dynamic sensitivity and at the same provide very high heat resistance.

Purpose of Invention

[0004] The purpose of this invention is to provide a thermosensitive recording medium achieving a good dynamic sensitivity and a good plasticizer resistance, oil resistance and alcohol resistance of the printed image. In preferred embodiments of the present invention, high heat resistance of background up to 110°C is also achieved.

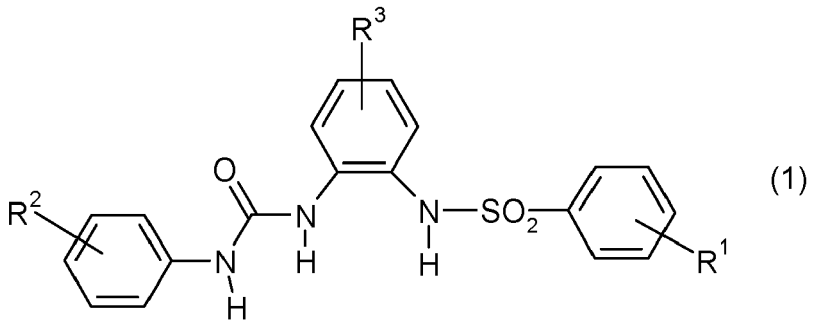
Summary of the Invention

[0005] 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:

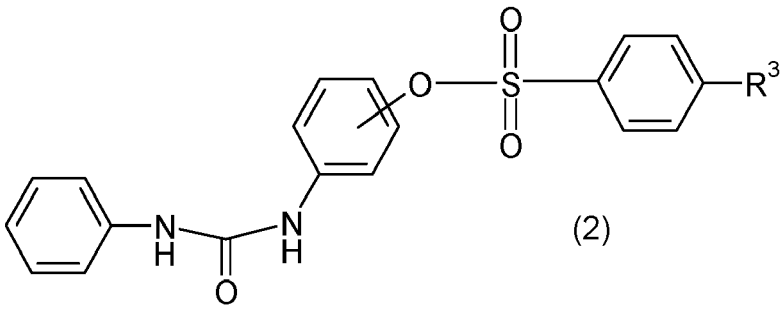
- a support layer,
- an undercoat layer over the support layer,
- a thermosensitive colouring layer over the undercoat layer,
- a protective layer over the thermosensitive colouring layer,

wherein

- the undercoat layer comprises at least one type of plastic hollow particles as organic fillers, the plastic hollow particles comprising at least 20% of hollow particles, by mass with respect to the mass of all the hollow particles, which have a hollow ratio at 60% or more, the hollow ratio being a percentage ratio of the inner diameter of the hollow particles to the outer diameter of the hollow particles; and
- the thermosensitive colouring layer comprises at least two types of colour developers selected from general formulae (1), (2) and (3):



(1)



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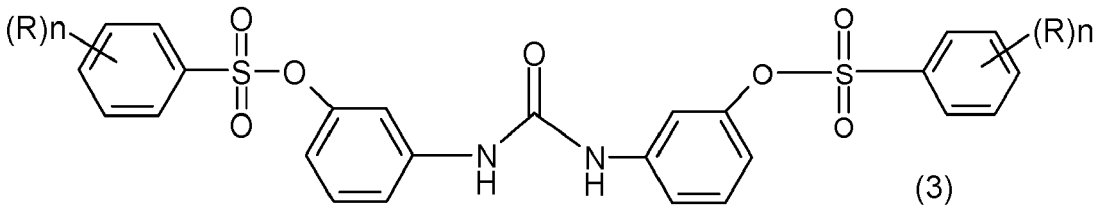


(3)

wherein,

- in formula (1), R_1 to R_3 each independently represent a hydrogen atom, a halogen atom, a C1-C6 alkyl group, a C1-C6 alkoxyl group, a C1-C6 fluoroalkyl group;
- in formula (2), R^3 is a hydrogen atom, a halogen atom, a nitro group, an amino group, an alkyl group, an alkoxy group, an aryloxy group, an alkylcarbonyloxy group, an arylcarbonyloxy group, an alkylcarbonylamino group, an arylcarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a monoalkylamino group, a dialkylamino group, or an arylamino group;
- in formula (3), R represents an alkyl group and n represents an integer ranging from 0 to 3.

[0006] In the thermosensitive recording medium of the present invention, the at least 20% of hollow particles the undercoat layer preferably has a hollow ratio at 80% or more. In preferred embodiments, the hollow ratio of hollow particles of the undercoat layer may be at least 85%, or at least 90%.

[0007] In the thermosensitive recording medium of the present invention, the thermosensitive colouring layer preferably further comprises 1,3-diphenylurea. This has been found to be a useful stabilizer (preservability-improving agent) in the context of the present invention.

[0008] In another aspect, the present invention relates to a consumer product package to which a thermosensitive recording medium of the invention has been attached or incorporated. In particular, food packaging incorporating the thermosensitive recording medium of the invention is envisaged. The thermosensitive recording medium of the invention may be converted into a label, for example by lamination, die-cutting and pre-printing, and then put onto the food packaging. 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.

Brief Summary of the Figures

[0009]

Figure 1 is a schematic representation of an illustrative, non-limiting example of a thermosensitive recording medium according to an embodiment of the present invention. In this particular and non-limiting embodiment, in the thermosensitive recording medium (1), the thermosensitive colouring layer (12) is placed over the support layer (13), with an undercoat layer (14) being incorporated between the support layer (13) and the thermosensitive colouring layer (12). The thermosensitive colouring layer (12) is also in contact with a protective layer (11), on the opposite side of the thermosensitive colouring layer (12) with respect to the undercoat layer (14) and support layer (13).

Figure 2 is a schematic representation of another 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 two successive protective layers, here numbered (11a) and (11b), (11a) being the lower protective layer and (11b) being the upper protective layer, are applied to the thermosensitive colouring layer (12).

List of Reference Signs

[0010]

1: Thermosensitive recording medium
11, 11a, 11b: Protective layer(s)
12: Thermosensitive colouring layer
13: Support layer
14: Undercoat layer

Detailed Description of the Invention

<Support layer>

[0011] The support layer (which may also be called "substrate") in the thermosensitive recording medium of the present invention is suitably selected depending on the intended purpose without any particular restriction. It is possible for this support layer to be transparent or non-transparent.

[0012] Possible supports may include supports made of wood-free paper, recycled pulp (containing 50% or more of recycled pulp), synthetic paper, polyethylene films, and laminated paper. The thickness of a paper layer varies depending on the composition of the layer and intended use of the thermosensitive recording materials and cannot be specified flatly, but it is preferably 30 μm to 250 μm, more preferably 50 μm to 200 μm.

[0013] A transparent support may also be used in the form of 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.

[0014] Film materials to be used in the transparent support 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).

<Undercoat layer(s)>

[0015] In the technical field of thermosensitive recording mediums 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.

[0016] If present in the thermosensitive recording medium of the present invention, the undercoat layer will normally contain a binder resin.

[0017] 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.

[0018] 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. A particularly preferred binder material for an undercoat layer of the present invention is polyvinyl alcohol.

[0019] 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. In the present invention, particularly preferred embodiment consists in the combination of polyvinyl alcohol as binder material and styrene-butadiene copolymer added as an aqueous polymer emulsion.

[0020] 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.

[0021] In a preferred thermosensitive recording medium according to the present invention, the undercoat layer comprises inorganic filler which has an oil absorption property of 60 g/100 g or less. Such a low oil absorption property is preferable in terms of liquid properties as mentioned above. A particularly preferred inorganic filler for the undercoat layer in this respect is non-calcined kaolin, preferable in this context to calcined kaolin.

[0022] In undercoat layers of a thermosensitive recording medium according to present invention, hollow particles are used.

[0023] For all hollow particles, the hollow ratio given as a percentage (%) is the (inner diameter of a hollow particle / outer diameter of the hollow particle) x 100.

[0024] 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 esters and polymethacrylic esters (polymethacrylates), polyacrylonitrile, and polybutadiene, and copolymer resins thereof.

[0025] In the thermosensitive recording medium of the present invention, the at least 20% of hollow particles the undercoat layer preferably has a hollow ratio at 80% or more. In preferred embodiments, the hollow ratio of hollow particles of the undercoat layer may be at least 85%, or at least 90%.

[0026] In preferred embodiments of the thermosensitive recording medium according to the present invention, a total pigment ratio (the inorganic filler and the organic filler) in the undercoat layer is from at least 20% by weight to at most 80% by weight with respect to the total dry weight of the undercoat layer.

[0027] If an undercoat layer is used in the thermosensitive recording medium of the present invention, the deposition amount thereof is appropriately 0.4 g/m^2 to 10 g/m^2, more preferably 0.6 g/m^2 to 4 g/ m^2.

[0028] The thickness of an undercoat layer in the present invention, if used, varies depending on the composition of the layer and intended use of the thermosensitive recording materials and cannot be specified flatly, but it is preferably 0.5 μm to 15 μm, more preferably 0.8 μm to 6 μm.

<Thermosensitive Colouring Layer>

[0029] 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 and a developer. In the present invention, an undercoat layer (or undercoat layers) is/are present between the transparent support layer and the thermosensitive colouring layer.

[0030] 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.

[0031] 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 lactuam 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-

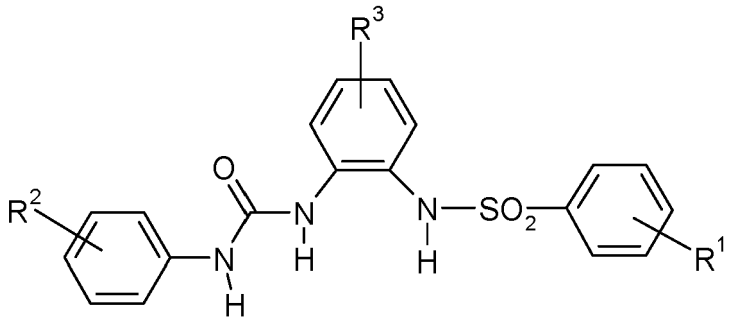
isopropyl-N-methyl amino) fluoran, 2-anilino-3-methyl-6-(N-isobutyl-N-methyl amino) fluoran, 2-anilino-3-methyl-6-(N-n-amyl-N-methyl amino) fluoran, 2-anilino-3-methyl-6-(N-sec-butyl-N-ethyl amino) fluoran, 2-anilino-3-methyl-6-(N-n-amyl-N-ethyl amino) fluoran, 2-anilino-3-methyl-6-(N-iso-amyl-N-ethyl 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.

[0032] The amount of the leuco dye contained in the thermosensitive colouring layer is preferably 3% by mass to 30% by mass, with respect to the total mass of the thermosensitive colouring layer taken as 100%.

[0033] As the developer, various electron accepting materials are known to be able to react with the aforementioned leuco dye at the time of heating so as to develop colours, such as phenolic compounds, organic or inorganic acidic compounds and esters or salts thereof.

[0034] In the present invention, the thermosensitive colouring layer comprises at least two types of colour developer. The three types of colour developer among which at least two, or indeed all three, are present in the thermosensitive colouring layer of a thermosensitive recording medium of the present invention, correspond most preferably to compounds having an N-phenylureido-phenyl-benzenesulfonamide structure, an N-phenylureido-phenyl-oxy-sulfonyl-aryl structure, or an N,N'-di-([arylsulfonyloxyl]-phenyl)urea structure.

[0035] Concerning colour developers of type (1), with an N-phenylureido-phenyl-benzenesulfonamide structure, the general preferred compounds have the following structure:



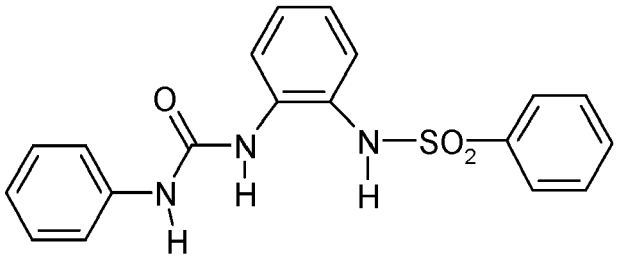
(1)

wherein R_1 to R_3 each independently represent a hydrogen atom, a halogen atom, a C1-C6 alkyl group, a C1-C6 alkoxyl group, or a C1-C6 fluoroalkyl group.

[0036] Such developers can be prepared according to methods of synthesis disclosed for example in EP 2 923 851. Most preferably, the aromatic ring attached to the SO_2 group in formula (1) above has either no (R^1) substituents, or

one Me group or one Cl group, or -NHAc or -OMe. Most preferably, the middle ring above has Me groups as possible (R^3) substituents. The aromatic ring attached via the urea group (on the left in the figure above) may show a -OMe, -F, $-CF_3$, Cl, as well as CH_3 (Me) substituent.

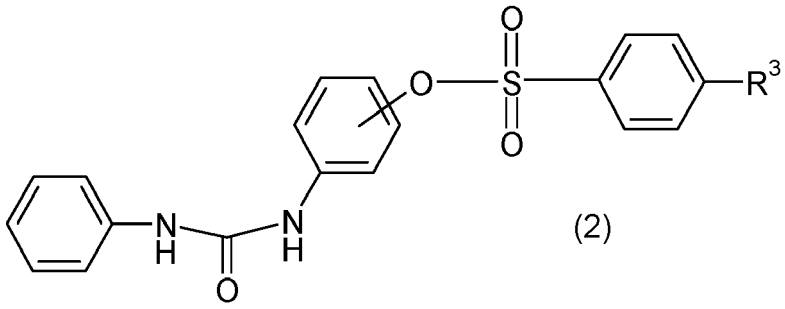
[0037] In a particularly preferred embodiment, the thermosensitive colouring layer of the thermosensitive recording medium of the invention comprises a developer having the following formula (4):



(4)

[0038] The above compound, N-[2-(3-phenylureido)phenyl]benzenesulfonamide, is thus a preferred colour developer of general formula (1). This corresponds to the general formula (1) above in which R^1, R^2 and R^3 are all hydrogen atoms.

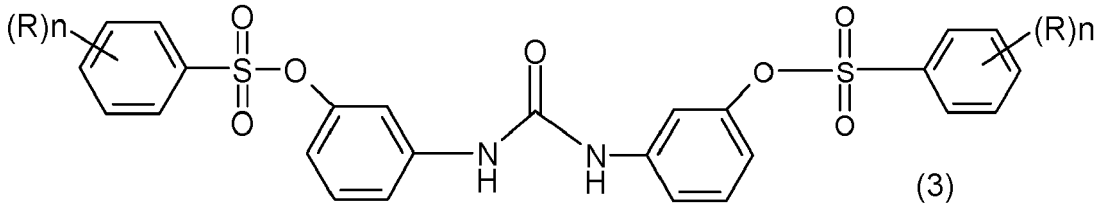
[0039] Colour developers of type (2) have an N-phenylureido-phenyl-oxysulfonyl-aryl structure:



(2)

wherein, in formula (2), R^3 is a hydrogen atom, a halogen atom, a nitro group, an amino group, an alkyl group, an alkoxy group, an aryloxy group, an alkylcarbonyloxy group, an arylcarbonyloxy group, an alkylcarbonylamino group, an arylcarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a monoalkylamino group, a dialkylamino group, or an arylamino group. Such developers can be prepared according to methods of synthesis disclosed for example in EP 3 395 583. Most preferably, R^3 is a methyl group. Most preferably in the present invention, the colour developer (2) has a structure wherein the -O-SO_2-(phenyl)-para-R^3 group is in the meta position with respect to the -NH-CO-NH-phenyl substituent, and R^3 = methyl.

[0040] Colour developers of type (3) have an N,N'-di-([arylsulfonyloxyl]-phenyl)urea structure:



(3)

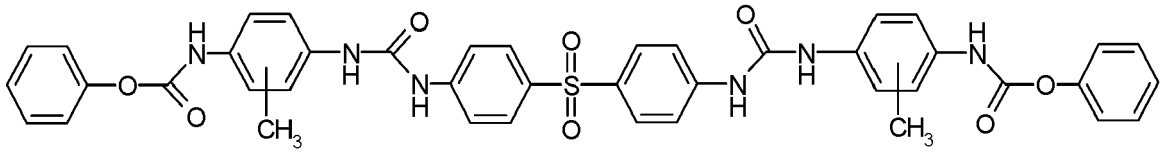
wherein, in formula (3), R represents an alkyl group and n represents an integer ranging from 0 to 3. Such developers can be prepared according to methods of synthesis disclosed for example in EP 3 677 569. Most preferably in the present invention, the colour developer of formula (3) has a structure wherein each (R)n system is constituted by a single methyl group in the para position with respect to the -SO_2-O- group.

[0041] In the thermosensitive colouring layer, the mixing ratio of the developer(s) to the leuco dye(s) is such that the developer(s) is (are) 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(s).

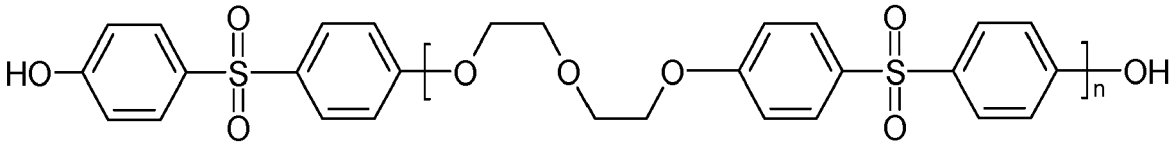
[0042] In the present invention, various other known developers can optionally be used as long as the effects of the

present invention are not impaired. These other developers are color developers including various electron-accepting compounds and oxidants capable of coloring the leuco dye. Examples thereof include 4,4'-isopropylidene bisphenol, 4,4'-isopropylidene bis(o-methylphenol), 4,4'-secondary butylidene bisphenol, 4,4'-isopropylidene bis(2-tert-butylphenol), zinc p-nitrobenzoate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)isocyanurate, 2,2-(3,4'-dihydroxydiphenyl)propane, bis(4-hydroxy-3-methylphenyl) sulfide, 4'{ 6-(p-methoxyphenoxy)ethoxy }sal icylate, 1,7-bis(4-hydroxyphenylthio)-3,5-dioxaheptane, 1,5-bis(4-hydroxyphenylthio)-5-oxapentane, monocalcium monobenzyl phthalate, 4,4'-cyclohexylidene diphenol, 4,4'-isopropylidene bis(2-chlorophenol), 4,4'-diphenolsulfone, 4-isopropoxy-4'-hydroxydiphenylsulfone, 4-benzyloxy-4'-hydroxydiphenylsulfone, 4,4'-diphenolsulfoxide, isopropyl-p-hydroxy benzoate, benzyl p-hydroxy benzoate, benzyl protocatechuic acid, stearyl gallate, lauryl gallate, octyl gallate, 1,3-bis(4-hydroxyphenylthio)-propane, N,N'-diphenyl thiourea, N,N'-di(m-chlorophenyl)thiourea, salicylanilide, methyl bis-(4'hydroxyphenyl) acetate, benzyl bis-(4-hydroxyphenyl) acetate, 1,3-bis(4-hydroxycumyl)benzene, 1,4-bis(4-hydroxycumyl)benzene, 2,4'-diphenolsulfone, 2,2'-diallyl-4,4'-diphenolsulfone, 3,4-dihydroxyphenyl-4'-methyldiphenylsulfone, zinc 1-acetyloxy-2-naphthoate, zinc 2-acetyloxy-1-naphthoate, zinc 2-acetyloxy-3-naphthoate, α,α-bis(4-hydroxyphenyl)-α-methyltoluene, an antipyrine complex of zinc thiocyanate. These may be used alone, or in combination.

[0043] Among other further developers that may be added to the thermosensitive colouring layer of the thermosensitive recording medium, the following urea urethane and D90 commercial products may also be considered:



Urea Urethane Compound



D90

[0044] An amount of the additional colour developer is appropriately selected depending on the intended purpose as long as the effects of the present invention are not impaired. In preferred embodiments, the combined mass of other developer(s), not being those of formula (1), (2) or (3), is less than 2 parts by mass, relative to 1 part by mass of the leuco dye(s) in the thermosensitive colouring layer, more preferably less than 0.5 parts by mass relative to 1 part by mass of the leuco dye(s) in the thermosensitive colouring layer. In certain embodiments of the present invention, there may be substantially no other developer(s) present in the thermosensitive colouring layer other than those of formula (1), (2) or (3).

[0045] Various known stabilizers (preservability-improving agents) can optionally be used as long as the effects of the present invention are not impaired. Most commonly, these stabilizers are hindered phenol compounds or hindered amine compounds. The latter type of electron-accepting compounds have relatively low colouring ability, and may be optionally added to the thermosensitive recording layer as an auxiliary additive. Specific examples thereof include:

2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 4,4'-butylidene bis(6-tert-butyl-2-methylphenol), 1,1,3-tris (2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl)butane, 4,4'-thiobis(6-tert-butyl-2-methylphenol), tetrabromobisphenol A, tetrabromobisphenol S, 4,4-thiobis(2-methylphenol), 4,4'-thiobis(2-chlorophenol),
tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)-1,2,3,4-butane tetracarboxylate, and
tetrakis(1,2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane tetracarboxylate.

[0046] Besides the above-described leuco dyes, developers and stabilizers, 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 sensitizer, a crosslinking agent, a pigment, a surfactant, a fluorescent whitening agent and a lubricant.

[0047] 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.

[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. Calcined kaolin is preferable in the framework of the present invention. In the thermosensitive colouring layer of a thermosensitive recording medium according to the present invention, it is preferred to use inorganic fillers which have a high oil absorption such as 80 g/100g or more. Example of appropriate fillers in this context for the thermosensitive colouring layer are calcined kaolin, or amorphous silica.

[0049] To a thermosensitive colouring layer, various thermoplastic materials are commonly added as a sensitivity improving agent (sensitizers). In the present invention, in preferred embodiments, no sensitizer is added to the thermosensitive colouring layer. It has been observed in the present invention that the absence of any sensitizer may in particular allow an increase in heat resistance, for example as measured at 110°C. A sensitizer may improve the colouring effect in some instances by melting under the effect of heat and thereby providing a temporary solvent facilitating reaction between the leuco dye and developer. It is to be noted that, in the case heat resistance is required, such as in use for labeling of ready cooked food or digital printing process, it is preferred that the thermoplastic material not be added, or a compound having a melting point of 90°C or higher be selected.

[0050] Examples of sensitizers include: (1) fatty acids such as stearic acid, and behenic acid; (2) fatty acid amides, such as stearic acid amide, and palmitic acid amide; (3) metal salts of fatty acids, such as zinc stearate, aluminum stearate, calcium stearate, zinc palmitate, and zinc behenate; (4) sensitizers with N-octadecyl chains such as N-octadecylcarbamoyl-p-methoxycarbonylbenzene, N-octadecylcarbamoylbenzene; (5) polyphenyl hydrocarbons such as p-benzylbiphenyl, terphenyl, triphenylmethane; (6) benzyloxy derivatives, benzoates and napthates such as benzyl p-benzyloxy benzoate, β-benzyloxynaphthalene, phenyl β-naphthoate, phenyl 1-hydroxy-2-naphthoate, methyl 1-hydroxy-2-naphthoate, dibenzoyl methane, dibenzoyloxy methane, dibenzoyloxy propane; (7) carbonates such as diphenyl carbonate, glycol carbonate; (8) terephthalates such as dibenzyl terephthalate, dimethyl terephthalate; (9) oxalate sensitizers such as dibenzyl oxalate, bis(4-methylbenzyl) oxalate, and bis(4-chlorobenzyl) oxalate; (10) alkoxy and aryloxy sensitizers such as 1,4-dimethoxy naphthalene, 1,4-diethoxy naphthalene, 1,4-dibenzyloxynaphthalene, 1,2-diphenoxyethane, 1,2-bis(3-methylphenoxy)ethane, 1,2-bis(4-methylphenoxy)ethane, 1,4-diphenoxy-2-butene, 1,2-bis(4-methoxyphenylthio)ethane, 1,3-bis(2-vinyloxyethoxy)benzene, 1,4-bis(2-vinyloxyethoxy)benzene, p-(2-vinyloxyethoxy)biphenyl, p-aryloxy biphenyl, p-propargyloxy biphenyl, 1,2-bis(4-methoxyphenoxy)propane, 1,5-bis(4-methoxyphenoxy)-3-oxapentane; (11) alcohol sensitizers such as 1,1-diphenyl ethanol, 1,1-diphenyl propanol, p-benzyloxy benzyl alcohol, 1,3-phenoxy-2-propanol; (12) sulphur-based sensitizers such as 1,4-diphenyl thiobutane, 1,4-diphenylthio-2-butene, dibenzyl disulphide;

[0051] In preferred embodiments of the present invention, the thermosensitive colouring layer may in particular not comprise a compound known in the field of thermosensitive recording media as a sensitizer, such as compounds containing aryloxy groups (such as phenoxy, tolyloxy groups) and alkoxy groups, oxaate groups and benzyloxy groups. It is of particular interest for the thermosensitive colouring layer thus not to contain sensitizers of the types indicated in groups 6, 9, 10 and 11 indicated above. The absence of such sensitizers may in particular allow an increase in heat resistance, for example as measured at 110°C.

[0052] The colouring layer can be formed by commonly known methods. To avoid reaction between components of the thermosensitive colouring 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 0.2 μm to 1 μm by using a disperser such as a ball mill, an Atriter or 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 colouring layer, followed by applying the thus-prepared coating liquid onto a support.

[0053] The thickness of the thermosensitive colouring layer varies depending on the composition of the thermosensitive colouring 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 2 μm to 20 μm.

<Protective Layer(s)>

[0054] At least one protective layer is provided over the thermosensitive layer in the present invention. Several different

protective layers can be overlaid on each other to focus respectively more on matching or barrier properties.

[0055] At least one protective layer in the thermosensitive recording medium of the present invention may appropriately comprise particles of wax, preferably with an average particle size of at least 0.05 and at most 2.0 μm. Where there is more than one protective layer, it is solely the uppermost protective layer, the one furthest removed from the thermosensitive colouring layer and on the surface exposed to the outside, which may appropriately contain wax particles. In preferred embodiments, where the uppermost protective layer contains wax particles, the underlying protective layers may contain do not contain wax particles.

[0056] Concerning the average particle size of the wax particles, the value is as obtained in a method to measure average particle size, in the form of the median size (D_{50}), as measured by laser diffraction using a Laser Diffraction Particle Size Distribution Analyzer. This measurement can be carried out for example by the LA-950 machine produced by the company HORIBA LA-950.

[0057] Preferably, the melting point of the wax if wax particles are used in the protective layer / uppermost protective layer is at least 80°C and at most 200°C. More preferably, the wax melting point is at least 90°C and at most 130°C, most preferably at least 100°C and at most 120°C.

[0058] More preferably, the wax particle size is at least 0.1 μm and at most 0.5 μm.

[0059] In advantageous embodiments, the particles of wax constitute at least 2.0 wt.% and at most 20 wt.% with respect to 100 wt.% constituted by all the components of the protective layer taken as a whole, more preferably at least 5.0 wt.% and at most 10 wt.% with respect to 100 wt.% constituted by all the components of the protective layer taken as a whole.

[0060] The wax material of the wax particles in the present invention may be polyethylene wax, salts of higher fatty acids such as zinc stearate and calcium stearate, montanate 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.

[0061] A particularly preferred wax material for the wax particles of a protective layer of the thermosensitive recording medium of the present invention is polyethylene wax. Low density or high density polyethylene wax particles may be used.

[0062] The protective layer(s) typically contain(s) at least a binder, and each of the protective layer(s) may contain an inorganic filler and a surfactant.

[0063] 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. A particularly preferred binder material for the protective layer of the present invention is polyvinyl alcohol.

[0064] The thickness of the protective layer(s) varies preferably from 0.2 μm to 10 μm, more preferably from 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. 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.

[0065] 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 protective layer(s) 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.

[0066] In one advantageous embodiment of the present invention, a first protective layer is laid down on the thermosensitive colouring layer, and whilst it contains a binder such as polyvinyl alcohol (PVA), it does not contain wax particles. However, a second protective layer may be laid down on the first protective layer, the second protective layer thus not being in direct contact with the thermosensitive colouring layer, the second protective layer containing wax particles and possibly filler such as inorganic filler.

[0067] 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. Such methods can be used to apply other layers of the thermosensitive recording medium of the present invention, such as the undercoat layer(s). Curtain coating is a preferred method for applying protective layer(s) in the present invention and can also be used to apply the thermosensitive colouring layer.

<Back layer>

[0068] A back layer (which may also be called a "backing layer") may be provided under the support layer in the thermosensitive colouring layer of the present invention. Such a back 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 support layer opposite to the surface thereof where the thermosensitive layer is disposed, or where the undercoat layer between the 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 layer>

[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 support layer, or backing layer (back 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 thermosensitive recording medium of the invention can thus be provided with an adhesive surface attached to the support or backing layer, which is useful in order to provide a label which has an adhesive layer. A releasable liner may then be attached to the adhesive layer, to be removed before final attachment to a product to be labelled. 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 μm or greater but 20 μm 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. In one aspect of the invention, a label including the thermosensitive recording medium of the invention is in the form of a silicone linerless (SLL) label.

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 embodiment, 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).

EXAMPLES

[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

[0086] A thermosensitive recording medium was created in accordance with the following steps.

1) A coating liquid for an undercoat layer was applied over a substrate, and thereby the undercoat layer (having 2 g/m^2 as dry mass) was created. In this example, a wood free paper, having a basic weight of about 60 g/m^2, was used. The prescription of the coating liquid for the undercoat layer is below.

Prescription of the coating liquid for the undercoat layer

Preparation of coating liquid for under layer:

[Liquid A1] Undercoat liquid 1

[0087]

Fine spherical hollow plastic particles[1)]	24 parts
Spherical hollow plastic particles[2)]	16 parts
Latex of styrene/butadiene copolymer[3)]	10 parts
10% aqueous polyvinyl alcohol solution[4)]	6 parts

(continued)

Water	44 parts
1) AF-1055 from Dow, copolymer resin based on styrene/acryl, solid content: 26.5%, average particle diameter: 1 μm, hollow rate : 55% 2) AF-1570 from Dow, copolymer resin based on styrene/acryl, solid content: 17.5%, average particle diameter: 1.6 μm, hollow rate : 65% 3) Solid content: 50.0% 4) Fully hydrolysed PVA	

[0088] 2) A coating liquid for a thermal recording layer was applied over the undercoat layer, and thereby the thermal recording layer was created.

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

[Liquid B] Dye dispersion liquid

[0090]

2-anilino-3-methyl-6-(di-n-butylamino)fluoran (Dye)	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[1)]	32 parts
Water	36 parts
1) From Kuraray, Itaconic-modified polyvinyl alcohol	

[Liquid C1] Developer dispersion liquid 1

[0091]

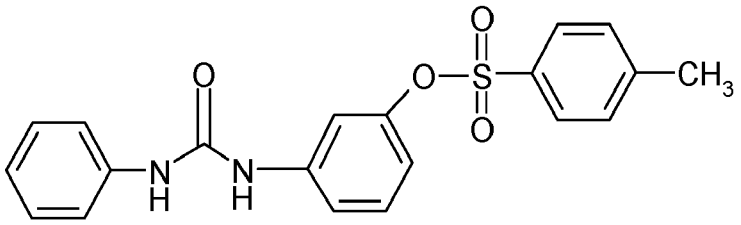
N-[2-(3-phenylureido)phenyl]benzenesulfonamide[1)] (of General Formula (1) = "Form. (1)")	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[2)]	32 parts
Water	36 parts
1) NKK-1304 from Nippon Soda Co., Ltd. 2) From Kuraray, Itaconic-modified polyvinyl alcohol	

[Liquid C2] Developer dispersion liquid 2

[0092]

General formula (2) ("Form. (2)")	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[1)]	32 parts
Water	36 parts
1) From Kuraray, Itaconic-modified polyvinyl alcohol	

[0093] The compound of general formula (2) mentioned above has the specific structure:



[Liquid D1] Filler dispersion liquid 1

[0094]

Calcined Kaolin[1)]	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[2)]	32 parts
Water	36 parts

1) Ansilex 93 from BASF, Oil absorption: 105~120 g/100g
2) From Kuraray, Itaconic-modified polyvinyl alcohol

[0095] [Liquid B], [Liquid C1], [Liquid C2] and [Liquid D1] having the aforementioned compositions respectively, were each dispersed using sand mill, so that particles contained in each liquid had an average particle size diameter of 1 μm or less, to thereby prepare a dye dispersion liquid [Liquid B] and a developer dispersion liquid [Liquid C1], [Liquid C2] and a filler dispersion liquid [Liquid D1]. Then [Liquid B], [Liquid C1], [Liquid C2] and [Liquid D1] were mixed in the ratio below:

[Liquid E1] Thermosensitive colouring layer liquid 1

[0096]

[Liquid B]	Dye dispersion	10 parts
[Liquid C1]	Developer disperision 1	15 parts
[Liquid C2]	Developer dispersion 2	15 parts
[Liquid D1]	Filler dispersion 1	31 parts
Water	Dye dispersion	29 parts

[0097] This mixture is put under stirring, to thereby prepare a coating liquid of a thermosensitive colouring layer [Liquid E1].

[0098] [Liquid E1] was uniformly applied to undercoat layer to thereby form a thermosensitive colouring layer.

[0099] The coating amount of the thermal layer was such as to produce a dye coating weight of 0.4 g/m^2 on a dry basis, then dried, to thereby form a thermosensitive colouring layer.

[0100] 3) Coating liquids (a first coating liquid and a second coating liquid) for a double-layered protective layer were applied over the thermosensitive colouring layer so that a lower protective layer formed of the first coating liquid is present below an upper protective layer formed of the second coating liquid, and thereby the double-layered protective layer was created over the thermal recording layer. The upper and lower protective layers had thickness of 1 g/m^2 and 1 g/m^2 respectively on a dry basis. The prescription of the coating liquids for the double-layered protective layer are below; they were then dried.

[Liquid F] First protective layer liquid

[0101]

10% itaconic-modified polyvinyl alcohol aqueous solution[1)]	70 parts
20% Polyamide epichlorohydrin[2)]	15 parts

(continued)

Water	15 parts

1) From Kuraray, Itaconic-modified polyvinyl alcohol
2) KYMENE-920 from SOLENIS

[Liquid G] Second protective layer liquid

[0102]

[Liquid H][1)]	18 parts
High density polyethylene wax[2)]	2 parts
20% Polyamide epichlorohydrin[3)]	4 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[4)]	20 parts
Water	56 parts

1) See below prescription of the dispersion liquid
2) Ultralube E-842N from Keim Additec GmbH
3) KYMENE-920 from SOLENIS
4) From Kuraray, Itaconic-modified polyvinyl alcohol

[Liquid H] Filler dispersion liquid for protective layer

[0103]

Apy-100[1)]	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[2)]	32 parts
Water	36 parts

1) Apy-100 from Nabaltec GmbH
2) From Kuraray, Itaconic-modified polyvinyl alcohol

[0104] After coating, samples were aged at 50°C during 48 h. Further to this process, samples were calendered at 20 kgF, before proceeding with quality evaluation.

EXAMPLES 2 TO 13

[0105] In Examples 2 to 12, in each case, a thermosensitive recording medium was prepared according to Example 1, except where changes are indicated in following Table 1.

[0106] [Liquid C3], [Liquid D2] and [Liquid E2] were prepared respectively as follows:

For Examples 2 to 4 and Examples 9 to 12

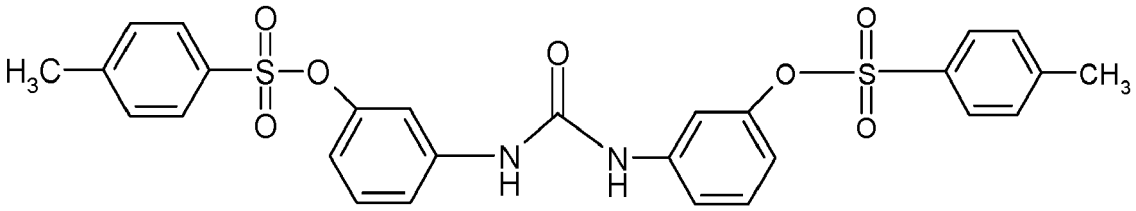
[Liquid C3] Developer dispersion liquid 3

[0107]

General formula (3) ("Form. (3)")	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[1)]	32 parts
Water	36 parts

1) From Kuraray, Itaconic-modified polyvinyl alcohol

[0108] The compound of general formula (3) mentioned above has the specific structure:



For Example 13

[Liquid D2] Filler dispersion liquid 2

[0109]

Amorphous silica[1)]	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[2)]	32 parts
Water	36 parts

1) Mizukasil P-527 from Mizusawa Industrial Chemicals, Ltd, Oil absorption: 140~180 g/100g
2) From Kuraray, Itaconic-modified polyvinyl alcohol

For Example 4

[Liquid E2] Thermosensitive colouring layer liquid 2

[0110]

[Liquid B]	Dye dispersion	10 parts
[Liquid C1]	Developer dispersion 1	10 parts
[Liquid C2]	Developer dispersion 2	10 parts
[Liquid C3]	Developer dispersion 3	10 parts
[Liquid D1]	Filler dispersion 1	31 parts
Water	Dye dispersion	29 parts

[0111] Thus, different combination of colour developers were compared in Examples 1 to 3. A combination of three different types of colour developer is tested in Example 4. Examples 5 to 12 test the effects of ratios between two different types of colour developers. Example 13 tests the effect of another type of inorganic filler in the thermosensitive colouring layer.

EXAMPLE 14

[0112] In Example 14, a thermosensitive recording medium was prepared according to Example 1, except where a [Liquid I] below was added to prepare a coating liquid of a thermosensitive colouring layer [Liquid E3].

[Liquid I] Preservative improver dispersion liquid

[0113]

1, 3-Diphenylurea	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[1)]	32 parts
Water	36 parts

1) From Kuraray, Itaconic-modified polyvinyl alcohol

[Liquid E3] Thermosensitive colouring layer liquid 3

[0114]

[Liquid B]	Dye dispersion	10 parts
[Liquid C1]	Developer dispersion 1	15 parts
[Liquid C2]	Developer dispersion 2	15 parts
[Liquid I]	Preservative improver dispersion	3 parts
[Liquid D1]	Filler dispersion 1	29 parts
Water		28 parts

EXAMPLES 15 TO 22

[0115] In Examples 15 to 22, in each case, a thermosensitive recording medium was prepared according to Example 1, except where changes are indicated in following Table 1.

[0116] [Liquid A2], [Liquid A3], [Liquid A4], [Liquid A5], [Liquid A6], [Liquid A7], [Liquid A8] and [Liquid A9] were prepared respectively as follows:

For Example 15

[Liquid A2] Undercoat liquid 2

[0117]

Fine spherical hollow plastic particles[1)]	26 parts
Large spherical hollow plastic particles[2)]	7 parts
Latex of styrene/butadiene copolymer[3)]	10 parts
10% aqueous polyvinyl alcohol solution[4)]	7 parts
Water	50 parts

1) AF-1055 from Dow, copolymer resin based on styrene/acryl, solid content: 26.5%, average particle diameter: 1 μm, hollow rate : 55%
2) R-500 from Matsumoto Yushi-Seiyaku Co., Ltd., solid content: 33.0%, hollow rate : 90%
3) solid content: 50.0%
4) Fully hydrolysed PVA

For Example 16 and 17

[Liquid A3] Undercoat liquid 3

[0118]

Fine spherical hollow plastic particles[1)]	24 parts
Large spherical hollow plastic particles[2)]	10 parts
Latex of styrene/butadiene copolymer[3)]	10 parts
10% aqueous polyvinyl alcohol solution[4)]	6 parts
Water	50 parts

1) AF-1055 from Dow, copolymer resin based on styrene/acryl, solid content: 26.5%, average particle diameter: 1 μm, hollow rate : 55%
2) R-500 from Matsumoto Yushi-Seiyaku Co., Ltd., solid content: 33.0%, hollow rate : 90%
3) solid content: 50.0%
4) Fully hydrolysed PVA

For Example 18

[Liquid A4] Undercoat liquid 4

[0119]

Spherical hollow plastic particles[1)]	25 parts
Large spherical hollow plastic particles[2)]	11 parts
Latex of styrene/butadiene copolymer[3)]	11 parts
10% aqueous polyvinyl alcohol solution[4)]	7 parts
Water	46 parts

1) AF-1570 from Dow, copolymer resin based on styrene/acryl, solid content: 17.5%, average particle diameter: 1.6 μm, hollow rate : 65%
2) R-500 from Matsumoto Yushi-Seiyaku Co., Ltd., solid content: 33.0%, hollow rate : 90%
3) solid content: 50.0%
4) Fully hydrolysed PVA

For Example 19

[Liquid A5] Undercoat liquid 5

[0120]

Large spherical hollow plastic particles[1)]	17 parts
Latex of styrene/butadiene copolymer[2)]	17 parts
10% aqueous polyvinyl alcohol solution[3)]	11 parts
Water	55 parts

1) R-500 from Matsumoto Yushi-Seiyaku Co., Ltd., solid content: 33.0%, hollow rate : 90%
2) solid content: 50.0%
3) Fully hydrolysed PVA

For Example 20

[Liquid A6] Undercoat liquid 6

[0121]

Spherical hollow plastic particles[1)]	48 parts
Latex of styrene/butadiene copolymer[2)]	10 parts
10% aqueous polyvinyl alcohol solution[3)]	6 parts
Water	36 parts

1) AF-1570 from Dow, copolymer resin based on styrene/acryl, solid content: 17.5%, average particle diameter: 1.6 μm, hollow rate : 65%
2) solid content: 50.0%
3) Fully hydrolysed PVA

For Example 21

[Liquid A7] Undercoat liquid 7

[0122]

Fine spherical hollow plastic particles[1)]	12 parts
Large spherical hollow plastic particles[2)]	10 parts
Non calcined Kaolin[3)]	3 parts
Latex of styrene/butadiene copolymer[4)]	10 parts
10% aqueous polyvinyl alcohol solution[5)]	6 parts
Water	59 parts

1) AF-1055 from Dow, copolymer resin based on styrene/acryl, solid content: 26.5%, average particle diameter: 1 μm, hollow rate : 55%
2) R-500 from Matsumoto Yushi-Seiyaku Co., Ltd., solid content: 33.0%, hollow rate : 90%
3) UW-90
4) solid content: 50.0%
5) Fully hydrolysed PVA

For Example 22

[Liquid A8] Undercoat liquid 8

[0123]

Spherical hollow plastic particles[1)]	20 parts
Large spherical hollow plastic particles[2)]	9 parts
Non calcined Kaolin[3)]	3 parts
Latex of styrene/butadiene copolymer[4)]	9 parts
10% aqueous polyvinyl alcohol solution[5)]	6 parts
Water	53 parts

1) AF-1570 from Dow, copolymer resin based on styrene/acryl, solid content: 17.5%, average particle diameter: 1.6 μm, hollow rate : 65%
2) R-500 from Matsumoto Yushi-Seiyaku Co., Ltd., solid content: 33.0%, hollow rate : 90%
3) UW-90
4) solid content: 50.0%
5) Fully hydrolysed PVA

REFERENCE EXAMPLES 1 TO 5

[0124] In Reference Examples 1 to 5, in each case, a thermosensitive recording medium was prepared according to Example 1, except where changes are indicated in following Table 1. Thus, three types of sensitizer were added respectively in thermosensitive colouring layer liquid.

[Liquid J1] Sensitizer dispersion liquid 1

[0125]

1,2-bis(3-methylphenoxy)ethane[1)]	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[2)]	32 parts
Water	36 parts

1) KS-232 from SANKO Co., Ltd.
2) From Kuraray, Itaconic-modified polyvinyl alcohol

[Liquid J2] Sensitizer dispersion liquid 2

[0126]

Bis(4-methyl benzyl) oxalate[1)]	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[2)]	32 parts
Water	36 parts

1) HS-3520 from Dainippon Ink & Chemicals
2) From Kuraray, Itaconic-modified polyvinyl alcohol

[Liquid J3] Sensitizer dispersion liquid 3

[0127]

Stearamide	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[1)]	32 parts
Water	36 parts

1) From Kuraray, Itaconic-modified polyvinyl alcohol

[Liquid E4] Thermosensitive colouring layer liquid 4

[0128]

[Liquid B]	Dye dispersion	10 parts
[Liquid C]	Developer dispersion	15 parts
[Liquid C]	Developer dispersion	15 parts
[Liquid J]	Sensitizer dispersion	3 parts
[Liquid D1]	Filler dispersion 1	29 parts
Water		28 parts

[0129] Reference Example 1 here corresponds to Example 21 with KS-232 added, and Reference Example 2 corresponds to Example 17 with KS-232 added. Reference Example 3 corresponds to Example 2 with KS-232 added, Reference Example 4 corresponds to Example 21 with HS-3520 added, and Reference Example 5 corresponds to Example 1 with Stearamide added.

COMPARATIVE EXAMPLES 6 AND 7

[0130] In Comparative Examples 6 and 7, in each case, a thermosensitive recording medium was prepared according to Example 1, except where changes are indicated in following Table 1. Thus, another type of colour developer was combinined with [Liquid C1] and [Liquid C2] respectively in thermosensitive colouring layer liquid.

For Comparative Examples 6, 7 and 14

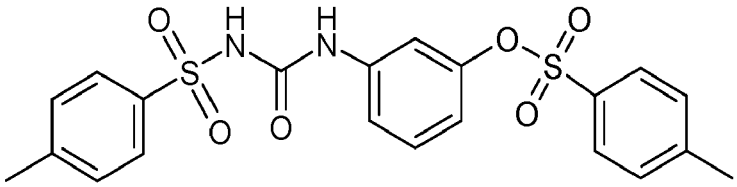
[Liquid C4] Developer dispersion liquid 4

[0131]

N-(p-toluenesulfonyl)-N'-(3-(p-toluenesulfonyloxy)phenyl)urea[1)]	32 parts
10% itaconic-modified polyvinyl alcohol aqueous solution[2)]	32 parts
Water	36 parts

1) Pergafast 201 from SOLENIS
2) From Kuraray, Itaconic-modified polyvinyl alcohol

[0132] Pergafast 201 has the following structure:



COMPARATIVE EXAMPLES 8 TO 10

[0133] In Comparative Examples 8 to 10, in each case, a thermosensitive recording medium was prepared according to Example 1, except where changes are indicated in following Table 1. Thus, three types of undercoat layer liquid [Liquid A12], [Liquid A13] and [Liquid A14] below were tested.

For Comparative Example 8

[Liquid A12] Undercoat liquid 12

[0134]

Fine spherical hollow plastic particles[1)]	36 parts
Latex of styrene/butadiene copolymer[2)]	10 parts
10% aqueous polyvinyl alcohol solution[3)]	6 parts
Water	48 parts

1) AF-1055 from Dow, copolymer resin based on styrene/acryl, solid content: 26.5%, average particle diameter: 1 μm, hollow rate : 55%
2) solid content: 50.0%
3) Fully hydrolysed PVA

For Comparative Example 9

[Liquid A13] Undercoat liquid 13

[0135]

Fine spherical hollow plastic particles[1)]	24 parts
Non calcined Kaolin[2)]	3 parts
Latex of styrene/butadiene copolymer[3)]	10 parts
10% aqueous polyvinyl alcohol solution[4)]	6 parts
Water	57 parts

1) AF-1055 from Dow, copolymer resin based on styrene/acryl, solid content: 26.5%, average particle diameter: 1 μm, hollow rate : 55%
2) UW-90
3) solid content: 50.0%
4) Fully hydrolysed PVA

For Comparative Example 10

[Liquid A14] Undercoat liquid 14

[0136]

Non calcined Kaolin[1)]	10 parts
Latex of styrene/butadiene copolymer[2)]	10 parts
10% aqueous polyvinyl alcohol solution[3)]	6 parts
Water	74 parts

1) UW-90
2) solid content: 50.0%
3) Fully hydrolysed PVA

COMPARATIVE EXAMPLES 11 TO 14

[0137] In Comparative Examples 11 to 14, in each case, a thermosensitive recording medium was prepared according to Example 1, except where changes are indicated in following Table 1. Thus, each developer dispersion liquid was used without combining with others.

[Liquid E5] Thermosensitive colouring layer liquid 5

[0138]

[Liquid B]	Dye dispersion	10 parts
[Liquid C]	Developer dispersion	31 parts
[Liquid D1]	Filler dispersion 1	31 parts
Water		28 parts

COMPARATIVE EXAMPLE 15

[0139] In Comparative Example 15, a thermosensitive recording medium was prepared according to Example 1, except where changes are indicated in following Table 1.
[0140] Thus, undercoat layer liquid [Liquid A15] was used instead of [Liquid A1].

[Liquid A15] Undercoat liquid 15

[0141]

Fine spherical hollow plastic particles[1)]	33 parts
Spherical hollow plastic particles[2)]	22 parts
Latex of styrene/butadiene copolymer[3)]	2 parts
10% aqueous polyvinyl alcohol solution[4)]	9 parts
Water	34 parts

1) AF-1055 from Dow, copolymer resin based on styrene/acryl, solid content: 26.5%, average particle diameter: 1 μm, hollow rate : 55%
2) AF-1570 from Dow, copolymer resin based on styrene/acryl, solid content: 17.5%, average particle diameter: 1.6 μm, hollow rate : 65%
3) Solid content: 50.0%
4) Fully hydrolysed PVA

COMPARATIVE EXAMPLE 16

[0142] In Comparative Examples 16, a thermosensitive recording medium was prepared according to Example 1, except where changes are indicated in following Table 1.
[0143] Thus, protective layers were not coated on the thermosensitive colouring layer.

METHODS OF EVALUATION

[0144] Static image density was assessed as follows:
A heat gradient tester (HG-100, available from Toyo Seiki Seisaku-sho, Ltd.) was used to apply heat energy from 140°C to 180°C for 1 sec with a pressure of 0.36 kgf. The black optical density was measured with a spectrophotometer (Instrument name = Exact, available from X-Rite, Inc.). The maximum value was recorded as a Static image density. The value is preferably 1.30 or greater.

Rank I: The optical density was more than 1.20
Rank II: The optical density was from 1.00 to 1.19
Rank III: The optical density was lower than 0.99

[0145] Dynamic image density was assessed as follows:
A ZEBRA 110Xi4 printer was used to print images using applied energies from +24 to +30 at a printing speed of 304 mm per sec (12 inches per sec). The black optical density at each energy was measured with a spectrophotometer (Instrument name = Exact, available from X-Rite, Inc.). The maximum value was recorded as a dynamic image density. The value is preferably 1.20 or greater.

Rank I: The optical density was more than 1.20
Rank II: The optical density was from 1.00 to 1.19
Rank III: The optical density was lower than 0.99

[0146] Barcode decodability was assessed as follows:
A ZEBRA 110Xi4 printer was used to print picket type barcodes (bars are printed parallelly to the printing direction) using applied energy of +15 at a printing speed of 304 mm per sec (12 inches per sec). The barcode was read with a barcode verifier (MICROSCAN LVS-9580, available from OMRON corporation) to evaluate its decodability. The results were recorded according to ANSI symbol grades. The value is preferably higher (Maximum 4.0).

[0147] Dynamic sensitivity was assessed as follows:
A MarkPoint MK2 printer was used to print images using an applied energy of 8.88 mJ per mm 2 at a printing speed of 102 mm per sec (4 inches per sec). The black optical density was measured with a spectrophotometer (Instrument name = Exact, available from X-Rite, Inc.). The value is preferably 1.20 or greater.

Rank I: The optical density was more than 1.20
Rank II: The optical density was from 1.00 to 1.19
Rank III: The optical density was lower than 0.99

[0148] 110°C heat resistance of the background was assessed as follows:
A heat gradient tester (HG-100, available from Toyo Seiki Seisaku-sho, Ltd.) was used to apply heat energy at 110°C for 1 sec with a pressure of 0.36 kgf. The black optical density was measured with a spectrophotometer (Instrument name = Exact, available from X-Rite, Inc.). The value is preferably 0.25 or lower.

Rank I: The optical density was 0.25 or less
Rank II: The optical density was from 0.26 to 0.35
Rank III: The optical density was higher than 0.36

[0149] Heat resistance of the background at 100°C and 90°C was assessed as follows:
The prepared samples were treated under 100°C or 90°C respectively for 1 hour. The black optical density was measured with a spectrophotometer (Instrument name = Exact, available from X-Rite, Inc.). The value is preferably 0.25 or lower.

Rank I: The optical density was 0.25 or less
Rank II: The optical density was from 0.26 to 0.35
Rank III: The optical density was higher than 0.36

[0150] Plasticizer resistance of the printed image was assessed as follows:
A thermal recording simulator (TH-PMD, available from Ohkura Denki) was used to produce an image on the prepared samples with a pulse width (applied energy) of 1.0 msec at 0.1 msec intervals under a head power of 0.45 w/dot. The printed samples were kept in contact with a sheet of polyvinyl chloride (PVC produced by Shin-Etsu Polymer Co., Ltd) at 40° C for 15 hours. The black optical density of the printed image was measured with a spectrophotometer (Instrument

name = Exact, available from X-Rite, Inc.). Then a preservation rate of the image was calculated as follows:

Preservation rate (%)= [degree of optical black density after test] / [degree of optical black density before test] *100

[0151] The value is preferably 90% or higher.

Rank I: The preservation rate was 90% or higher
Rank II: The preservation rate was from 70% to 89%
Rank III: The preservation rate was lower than 70%

[0152] Oil resistance of the printed image was assessed as follows:
A thermal recording simulator (TH-PMD, available from Ohkura Denki) was used to produce an image on the prepared samples with a pulse width (applied energy) of 1.0 msec at 0.1 msec intervals under a head power of 0.45 w/dot. One drop of cottonseed oil was applied on each sample and spread with a piece of cotton. The samples were kept at 40° C for 15 hours afterwards. The black optical density of the printed image was measured with a spectrophotometer (Instrument name = Exact, available from X-Rite, Inc.). Then a preservation rate of the image was calculated as follows:

Preservation rate (%)= [degree of optical black density after test] / [degree of optical black density before test] *100

[0153] The value is preferably 90% or higher.

Rank I: The preservation rate was 90% or higher
Rank II: The preservation rate was from 70% to 89%
Rank III: The preservation rate was lower than 70%

[0154] Ethanol (EtOH) resistance of the printed image was assessed as follows:
A thermal recording simulator (TH-PMD, available from Ohkura Denki) was used to produce an image on the prepared samples with a pulse width (applied energy) of 1.0 msec at 0.1 msec intervals under a head power of 0.45 w/dot. One drop of 99% by mass EtOH was applied on each sample. The samples were kept at 22° C for 3 hours to dry. The black optical density of the printed image was measured with a spectrophotometer (Instrument name = Exact, available from X-Rite, Inc.). Then a preservation rate of the image was calculated as follows:

Preservation rate (%)= [degree of optical black density after test] / [degree of optical black density before test] *100

[0155] The value is preferably 70% or higher.

Rank I: The preservation rate was 70% or higher
Rank II: The preservation rate was from 50% to 99%
Rank III: The preservation rate was lower than 50%

[0156] Anchorage level of the layer was assessed as follows:
A piece of scotch tape (NICHIBAN CT405AP-18) was applied on a surface of each sample. The tape was repeeled in three steps below.

step 1) Repeel slowly towards 180°
step 2) Repeel slowly towards 90°
step 3) Repeel rapidly towards 90°

[0157] The anchorage level was evaluated according to the rank below.

Rank III: The layer was peeled in 1st step
Rank II: The layer was peeled in 2nd step
Rank I: The layer was peeled in 3rd step or no peeling (substrate break)

[0158] Lastly, total scores were calculated with points of each item, following the rules below.

Rank I (or A for barcodes) = 3 points
Rank II (or B, C for barcodes) = 1 point
Rank III (or F for barcodes) = -3 points

[0159] In what follows, "SBR" stands for Styrene-Butadiene Resin, "Dev" for Developer, and "Pig" for Pigment. "Ratio" in Table 1a to 1d stands for dry ratio by mass. "Pig ratio in Undercoat" gives total pigment ratio (the inorganic filler and the organic filler) in the undercoat layer by weight with respect to the total dry weight of the undercoat layer. "Hollow in Pig" gives dry ratio of hollow particles in the underlayer by weight with respect to the total dry weight of the pigments in the undercoat layer. ">60% hollow" and ">80% hollow" give ratio of the hollow particles which has hollow ratio higher than 60% and 80% respectively, with respect to the total dry weight of the hollow particles in the undercoat layer.

[Table 1a]

			Examples										
			1	2	3	4	5	6	7	8	9	10	11
Protective layer			Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Thermal layer	Dev 1	Type	Form. (1)	Form. (1)	-	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)	-
		Ratio	1.5	1.5	-	1	2.5	2.2	1	0.5	2.5	0.5	-
	Dev 2	Type	Form. (2)	-	Form. (2)	Form. (2)	Form. (2)	Form. (2)	Form. (2)	Form. (2)	-	-	Form. (2)
		Ratio	1.5	-	1.5	1	0.5	0.8	2	2.5	-	-	2.5
	Dev 3	Type	-	Form. (3)	Form. (3)	Form. (3)	-	-	-	-	Form. (3)	Form. (3)	Form. (3)
		Ratio	-	1.5	1.5	1	-	-	-	-	0.5	2.5	0.5
	Dev 4	Type	-	-	-	-	-	-	-	-	-	-	-
		Ratio	-	-	-	-	-	-	-	-	-	-	-
	Filler	Type	- Ans 93	- Ans 93	Ans 93	- Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	- Ans 93	Ans 93	- Ans 93
		Ratio	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Preservative Improver	Type	-	-	-	-	-	-	-	-	-	-	-
		Ratio	-	-	-	-	-	-	-	-	-	-	-
	Sensitizer	Type	-	-	-	-	-	-	-	-	-	-	-
		Ratio	-	-	-	-	-	-	-	-	-	-	-

(continued)

			Examples										
			1	2	3	4	5	6	7	8	9	10	11
Protective layer			Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Undercoat layer	Pigment 1	50%	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0
	Pigment 2	90%	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
	Pigment 3	65%	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	AF-1670 1.0	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0
	Pigment 4	Kaolin	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
	SBR		SBR 1.5	SBR 1.5	- SBR 1.5	- SBR 1.5	- SBR 1.5	- SBR 1.5	- SBR 1.5	- SBR 1.5	- SBR 1.5	- SBR 1.5	- SBR 1.5
	Pig ratio in Undercoat		64%	64%	64%	64%	64%	64%	64%	64%	64%	64%	64%
	Hollow in Pig		100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
	>60% hollow		33%	33%	33%	33%	33%	33%	33%	33%	33%	33%	33%
	>80% hollow		0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

[Table 1b]

			Examples										
			12	13	14	15	16	17	18	19	20	21	22
Protective layer			Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Thermal layer	Dev 1	Type	-	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)	Form. (1)
		Ratio	-	1.5	15	1.5	1.5	15	1.5	1.5	1.5	1.5	1.5
	Dev 2	Type	Form. (2)	Form. (2)	Form. (2)	Form. (2)	Form. (2)	-	Form. (2)	Form. (2)	Form. (2)	Form. (2)	Form. (2)
		Ratio	0.5	1.5	1.5	1.5	1.5	-	1.5	1.5	1.5	1.5	1.5
	Dev 3	Type	Form. (3)	-	-	-	-	Form. (3)	-	-	-	-	-
		Ratio	2.5	-	-	-	-	1.5	-	-	-	-	-
	Dev 4	Type	-	-	-	-	-	-	-	-	-	-	-
		Ratio	-	-	-	-	-	-	-	-	-	-	-
	Filler	Type	Ans 93	P-527	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93
		Ratio	3.0	2.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Preservative Improver	Type	-	-	1.3-DPU	-	-	-	-	-	-	-	-
		Ratio	-	-	0.3	-	-	-	-	-	-	-	-
	Sensitizer	Type	-	-	-	-	-	-	-	-	-	-	-
		Ratio	-	-	-	-	-	-	-	-	-	-	-

(continued)

			Examples										
			12	13	14	15	16	17	18	19	20	21	22
Protective layer			Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Undercoat layer	Pigment 1	50%	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	- -	- -	- -	AF-1055 1.0	- -
	Pigment 2	90%	- -	- -	- -	R-500 0.7	R-500 1.0	R-500 1.0	R-500 1.0	R-500 1.0	- -	R-500 1.0	R-500 1.0
	Pigment 3	65%	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	- -	- -	- -	AF-1570 1.33	- -	AF-1570 300	- -	AF-1570 1.33
	Pigment 4	Kaolin	- -	- -	- -	- -	- -	- -	- -	- -	- -	UW-90 10	UW-90 1.0
	SBR	SBR	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5
	Pig ratio in Undercoat		64%	64%	64%	61%	64%	64%	58%	37%	64%	64%	66%
	Hollow in Pig		100%	100%	100%	100%	100%	100%	100%	100%	100%	67%	70%
	>60% hollow		33%	33%	33%	26%	33%	33%	100%	100%	100%	50%	100%
	>80% hollow		0%	0%	0%	26%	33%	33%	43%	100%	0%	50%	43%

[Table 1c]

			Reference Examples					Comparative Examples		
			1	2	3	4	5	6	7	8
Protective layer			Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Thermal layer	Dev 1	Type	Form. (1)	Form. (1)	-	Form. (1)	Form. (1)	Form. (1)	-	Form. (1)
		Ratio	1.5	1.5	-	1.5	1.5	1.5	-	1.5
	Dev 2	Type	Form. (2)	-	Form. (2)	Form. (2)	Form. (2)	-	Form. (2)	Form. (2)
		Ratio	1.5	-	1.5 -	1.5	1.5	-	1.5	1.5
	Dev 3	Type	-	Form. (3)	Form. (3)	-	-	-	-	-
		Ratio	-	1.5	1.5	-	-	-	-	-
	Dev 4	Type	-	-	-	-	-	P-201	P-201	-
		Ratio	-	-	-	-	-	1.5	1.5	-
	Filler	Type	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93
		Ratio	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Preservative Improver	Type	-	-	-	-	-	-	-	-
		Ratio	-	-	-	-	-	-	-	-
	Sensitizer	Type	KS-232	KS-232	KS-232	HS-3520	Stearamide	-	-	-
		Ratio	0.30	0.30	0.30	0.30	0.30	-	-	-

(continued)

			Reference Examples					Comparative Examples		
			1	2	3	4	5	6	7	8
Protective layer			Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Undercoat layer	Pigment 1	50%	AF-1055 1.0	AF-1055 2.0	AF-1055 2.0	AF-1055 1.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 3.0
	Pigment 2	90%	R-500 1.0	R-500 1.0	- -	R-500 1.0	- -	- -	- -	- -
	Pigment 3	65%	- -	- -	AF-1570 1.0	- -	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	- -
	Pigment 4	Kaolin	UW-90 1.0	- -	- -	UW-90 1.0	- -	- -	- -	- -
	SBR		SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5
	Pig ratio in Undercoat		64%	64%	64%	64%	64%	64%	64%	64%
	Hollow in Pig		67%	100%	100%	67%	100%	100%	100%	100%
	>60% hollow		50%	33%	33%	50%	33%	33%	33%	0%
	>80% hollow		50%	33%	0%	50%	0%	0%	0%	0%

[Table 1d]

			Comparalive Examples						
			9	10	11	12	13	14	15	16
Protective layer			Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Thermal layer	Dev 1	Type	Form. (1)	-	Form. (1)	-	-	-	-	-
		Ratio	1.5	-	3	-	-	-	-	-
	Dev 2	Type	-	Form. (2)	-	Form. (2)	-	-	Form. (2)	Form. (2)
		Ratio	-	1.5	-	3	-	-	1.5	1.5
	Dev 3	Type	Form. (3)	Form. (3)	-	-	Form. (3)	-	Form. (3)	Form. (3)
		Ratio	1.5	1.5	-	-	3	-	1.5	1.5
	Dev 4	Type	-	-	-	-	-	P-201	-	-
		Ratio	-	-	-	-	-	3	-	-
	Filler	Type	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93	Ans 93
		Ratio	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Preservative Improver	Type	-	-	-	-	-	-	-	-
		Ratio	-	-	-	-	-	-	-	-
	Sensitizer	Type	-	-	-	-	-	-	-	-
		Ratio	-	-	-	-	-	-	-	-

(continued)

			Comparalive Examples							
			9	10	11	12	13	14	15	16
Protective layer			Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Undercoat layer	Pigment 1	50%	AF-1055 2.0	- -	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0	AF-1055 2.0
	Pigment 2	90%	- -	- -	- -	- -	- -	- -	- -	- -
	Pigment 3	65%	- -	- -	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0	AF-1570 1.0
	Pigment 4	Kaolin	UW-90 1.0	UW-90 3.0	- -	- -	- -	- -	- -	- -
	SBR		SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 1.5	SBR 0.2	SBR 1.5
	Pig ratio in Undercoat		64%	64%	64%	64%	64%	64%	88%	64%
	Hollow in Pig		67%	0%	100%	100%	100%	100%	100%	100%
	>60% hollow		0%	0%	33%	33%	33%	33%	33%	33%
	>80% hollow		0%	0%	0%	0%	0%	0%	0%	0%

[Table 1e]

		Examples										
		1	2	3	4	5	6	7	8	9	10	11
Evaluation	Image density (Static)	1.40 I	1.40 I	1.39 I	1.40 I	1.39 I	1.41 I	1.43 I	1.42 I	1.40 I	1.42 I	1.45 I
	Image density (Dynamic)	1.25 I	1.27 I	1.26 I	1.25 I	1.24 I	1.26 I	1.27 I	1.28 I	1.25 I	1.24 I	1.31 I
	Barcode Readability	2.6 B	2.7 B	2.2 C	2.1 C	2.6 B	3.1 B	2.6 B	2.5 B	2.6 B	2 C	2.4 C
	Dynamic Sensitivity	II	II	II	II	II	II	II	II	II	II	II
	110°C Heat resistance	I	II	II	II	I	I	I	I	I		I II
	100 C Heat resistance	I	I	II	II	I	I	I	I	I	II	II
	90°C Heat resistance	I	I	I	I	I	I	I	I	I	I	I
	Plasticizer resistance	II	II	II	II	II	II	II	II	II	II	II
	Oil resistance	I	I	I	I	I	I	I	I	I	I	I
	EtOH resistance	II	II	II	II	II	II	II	II	II	II	II
	Anchorage	I	I	I	I	I	I	I	I	I	I	I
Scoring	Number of rank III	0	0	0	0	0	0	0	0	0	0	0
	Total Score	25	23	21	21	25	25	25	25	25	23	21

[Table 1f]

		Examples										
		12	13	14	15	16	17	18	19	20	21	22
Evaluation	Image density (Static)	1.41 I	1.40 I	1.40 I	1.42 I	1.40 I	1.40 I	1.43 I	1.40 I	1.40 I	1.40 I	1.39 I
	Image density (Dynamic)	1.30 I	1.26 I	1.25 I	1.25 I	1.25 I	1.24 I	1.24 I	1.29 I	1.29 I	1.24 I	1.28 I
	Barcode Readability	2.7 B	2.6 B	2.5 B	3.1 B	3.8 A	3.5 A	3.6 A	4 A	28 B	3.5 A	4 A
	Dynamic Sensitivity	II	II	II	I	I	I	I	I	I	I	I
	110°C Heat resistance	II	I	I	I	I	II	I	I	I	I	I
	100°C Heat resistance	II	I	I	I	I	I	I	I	I	I	I
	90°C Heat resistance	I	I	I	I	I	I	I	I	I	I	I
	Plasticizer resistance	II	II	I	II	II	II	II	II	II	II	II
	Oil resistance	I	I	I	I	I	I	I	I	I	I	I
	EtOH resistance	II	II	II	II	II	II	II	II	II	II	II
	Anchorage	I	I	I	I	I	I	I	I	I	I	I
Scoring	Number of rank III	0	0	0	0	0	0	0	0	0	0	0
	Total Score	21	25	27	27	29	27	29	29	27	29	29

[Table 1g]

		Reference Examples					Comparative Examples		
		1	2	3	4	5	6	7	8
Evaluation	Image density (Static)	1.39 I	1.40 I	1.41 I	1.43 I	1.42 I	1.39 I	1.40 I	1.39 I
	Image density (Dynamic)	1.25 I	1.24 I	1.26 I	1.24 I	1 26 I	1.29 I	1.25 I	1.11 II
	Barcode Readability	3.5 A	3.5 A	3.9 A	3.5 A	3.7 A	2.5 B	2.5 B	1.5 C
	Dynamic Sensitivity	I	I	I	I	I	II	II	III
	110°C Heat resistance	III	III	III	III	III	II	III	I
	100°C Heat resistance 90°C Heat resistance Plasticizer resistance Oil resistance EtOH resistance Anchorage	I I II I II I	I I II I II I	II I II I II I	II I II I II I	II I II I II I	II III II I II I	III III II I II I	I I II I II I
Scoring	Number of rank III Total Score	1 23	1 23	1 21	1 21	1 21	1 15	3 7	1 19

[Table 1h]

		Comparative Examples							
		9	10	11	12	13	14	15	16
Evaluation	Image density (Static)	1.42 I	1.33 I	1.41 I	1.43 I	1.43 I	1.43 I	1.40 I	1.40 I
	Image density (Dynamic)	0.96 III	0.53 III	1.21 I	1.25 I	1.29 I	1.30 I	1.24 I	1.24 I
	Barcode Readability	Undecodable F	Undecodable F	2.5 B	2.5 B	3 B	2.5 B	2.5 B	2.6 B
	Dynamic Sensitivity	III	III	III	II	II	II	II	II
	110°C Heat resistance	I	I	I	I	I	II	I	I
	100°C Heat resistance 90"C Heat resistance Plasticizer resistance Oil resistance EtOH resistance Anchorage	I I II I II I	II I II I II I	I I III II I I	I I III III II I	I I II I III I	I III II I II I	I I II I II III	I I III III II I
Scoring	Number of rank III Total Score	3 11	3 9	2 17	2 15	1 21	1 17	1 19	2 15

Claims

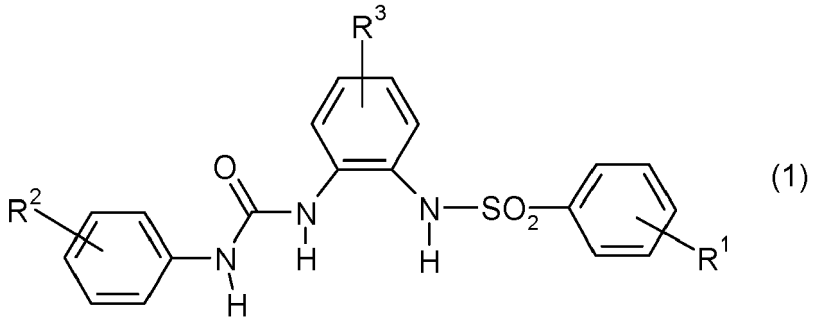
1. A thermosensitive recording medium comprising at least:

- a support layer,

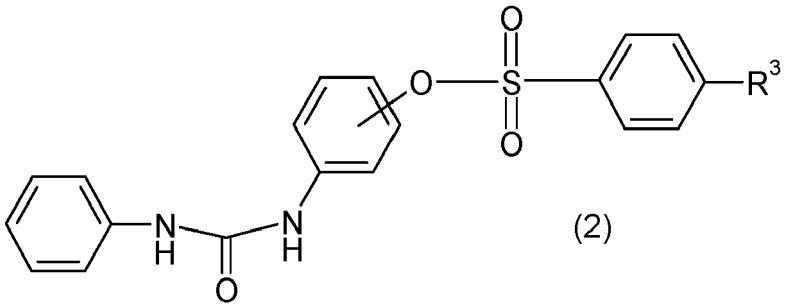
- an undercoat layer over the support layer,
- a thermosensitive colouring layer over the undercoat layer,
- a protective layer over the thermosensitive colouring layer,

wherein

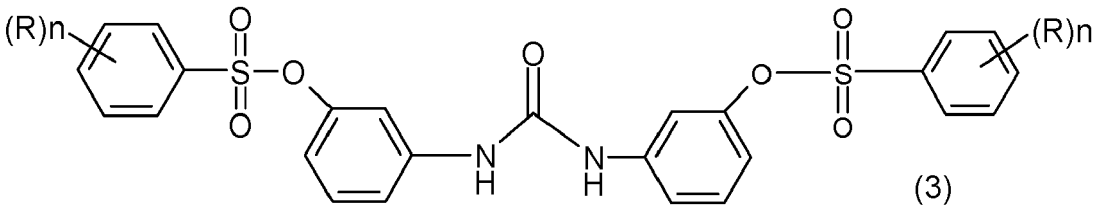
- the undercoat layer comprises at least one type of plastic hollow particles as organic fillers, the plastic hollow particles comprising at least 20% of hollow particles, by mass with respect to the mass of all the hollow particles, which have a hollow ratio at 60% or more, the hollow ratio being a percentage ratio of the inner diameter of the hollow particles to the outer diameter of the hollow particles; and
- the thermosensitive colouring layer comprises at least two types of colour developers selected from general formulae (1), (2) and (3):



(1)



(2)



(3)

wherein,

- in formula (1), R_1 to R_3 each independently represent a hydrogen atom, a halogen atom, a C1-C6 alkyl group, a C1-C6 alkoxyl group, a C1-C6 fluoroalkyl group;
- in formula (2), R^3 is a hydrogen atom, a halogen atom, a nitro group, an amino group, an alkyl group, an alkoxy group, an aryloxy group, an alkylcarbonyloxy group, an arylcarbonyloxy group, an alkylcarbonylamino group, an arylcarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a monoalkylamino group, a dialkylamino group, or an arylamino group;
- in formula (3), R represents an alkyl group and n represents an integer ranging from 0 to 3.

2. The thermosensitive recording medium according to claim 1, wherein the at least 20% of hollow particles has a hollow ratio at 80% or more.

3. The thermosensitive recording medium according to claim 1 or 2, wherein the thermosensitive colouring layer comprises N-[2-(3-phenylureido)phenyl]benzenesulfonamide as a colour developer.

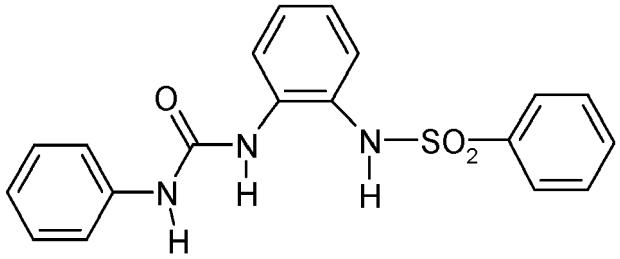
4. The thermosensitive recording medium according to claim 3, wherein the thermosensitive colouring layer comprises N-[2-(3-phenylureido)phenyl]benzenesulfonamide and a compound of general formula (2) as colour developers.

5. The thermosensitive recording medium according to any of claims 1 to 4, wherein the thermosensitive colouring layer further comprises 1,3-diphenylurea.

6. The thermosensitive recording medium according to any of claims 1 to 5, wherein the undercoat layer comprises inorganic filler which has an oil absorption property of 60 g/100 g or less.

7. The thermosensitive recording medium according to any of claims 1 to 6, wherein a total pigment ratio (the inorganic filler and the organic filler) in the undercoat layer is from at least 20% by weight to at most 80% by weight with respect to the total dry weight of the undercoat layer.

8. The thermosensitive recording medium according to any of claims 1 to 7, wherein the colour developer (1) has the following formula (4):



(4)

9. The thermosensitive recording medium according to any of claims 1 to 8, wherein the colour developer (2) has a structure wherein the -O-SO_2-(phenyl)-para-R^3 group is in the meta position with respect to the -NH-CO-NH-phenyl substituent, and R^3 = methyl.

10. The thermosensitive recording medium according to any of claims 1 to 9, wherein in the colour developer of formula (3), each (R)n system is constituted by a single methyl group in the para position with respect to the -SO_2-O- group.

11. The thermosensitive recording medium according to any of claims 1 to 10, wherein the thermosensitive colouring layer comprises at least one type of inorganic filler which has an oil absorption property of 80 g/100g or more.

12. The thermosensitive recording medium according to any of claims 1 to 11, wherein the thermosensitive colouring layer does not comprise a sensitizer.

13. The thermosensitive recording medium according to any of claims 1 to 12, wherein the thermosensitive colouring layer does not comprise a sensitizer in the form of a benzyloxy derivative, an oxalate sensitizer, an alkoxy or aryloxy sensitizer, and/or an alcohol sensitizer.

14. Food packaging comprising the thermosensitive recording medium according to any of claims 1 to 13.

15. Use of the thermosensitive recording medium according to any of claims 1 to 13 in food packaging.

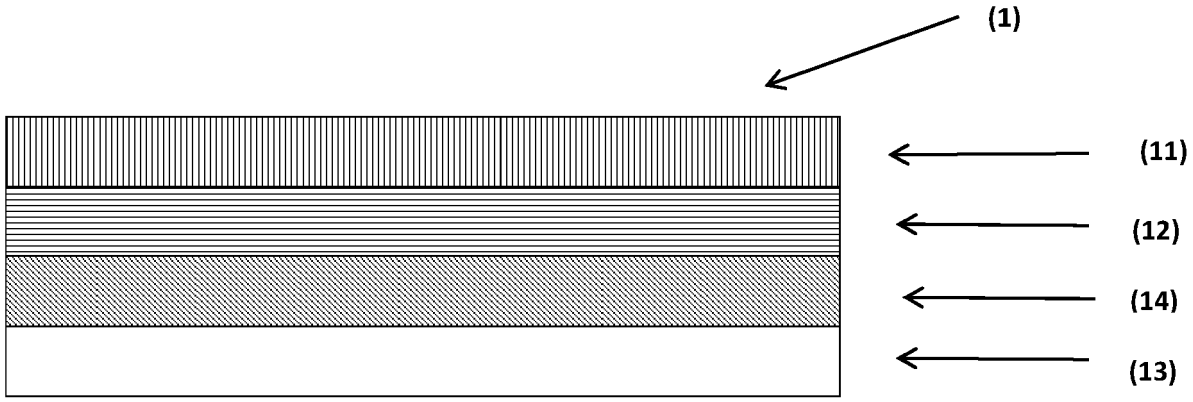


Figure 1

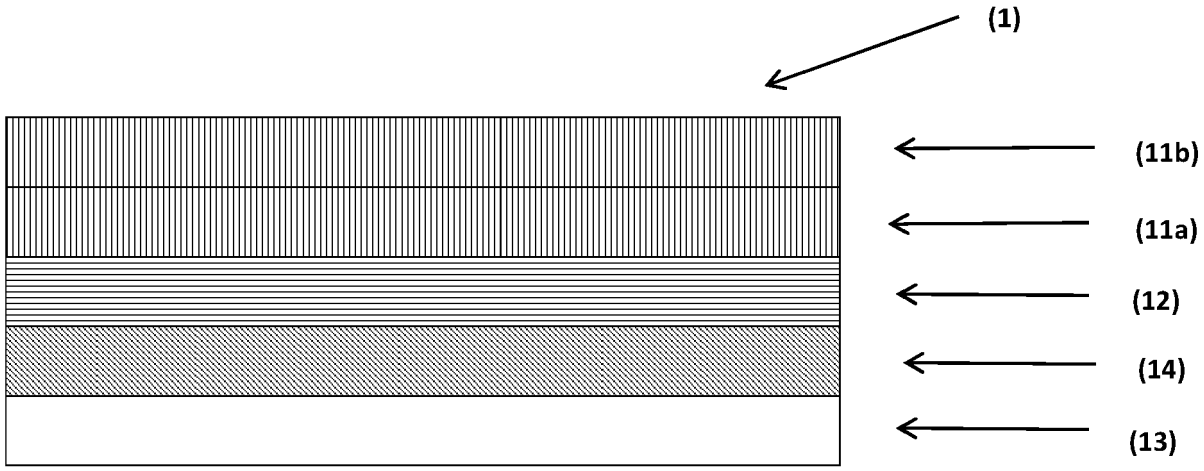


Figure 2

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EUROPEAN SEARCH REPORT

Application Number
EP 23 30 5230

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	11 July 2023	Vogel, Thomas

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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