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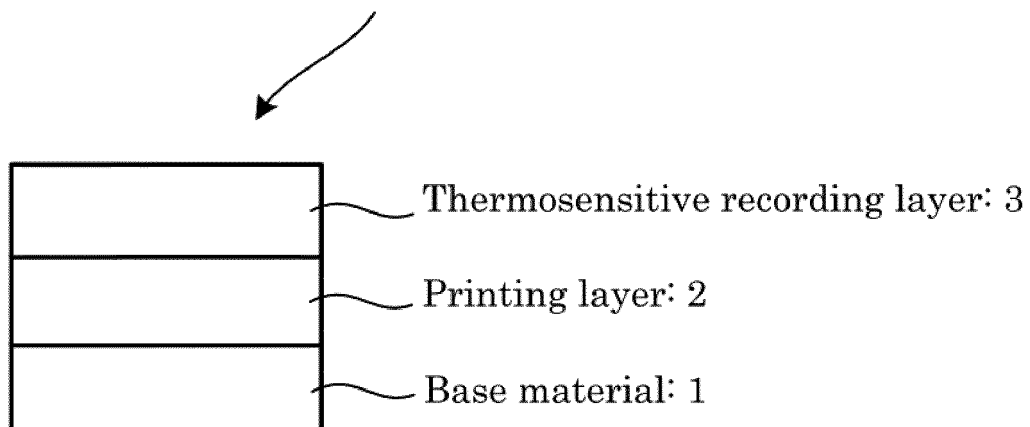
(54) **THERMOSENSITIVE RECORDING MEDIUM, LASER PRINTING METHOD, AND LASER PRINTING APPARATUS**

(57) Provided is a thermosensitive recording medium including a base material, a thermosensitive recording layer, and a printing layer. An average absorbance A1 (%) of the printing layer with respect to visible light having a wavelength of 400 nm or longer but 700 nm or shorter, an average absorbance A2 (%) of the thermosensitive

recording layer with respect to the visible light, and an average absorbance B1 (%) of the printing layer with respect to an irradiation wavelength of laser light during printing by a laser satisfy the following formula: $A1 > A2$ and the following formula: $A1 > B1$.

FIG. 2

Thermosensitive recording medium: 100



Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present disclosure relates to a thermosensitive recording medium, a laser printing method, and a laser printing apparatus.

10 Description of the Related Art

[0002] In general, various designs have been printed on labels. As well, traceability information such as a date of manufacture or a manufacture code, and security information have also been printed on labels.

15 **[0003]** It is possible to print the various designs in a unified manner in the label production stage. On the other hand, the traceability information and the security information are typically printed by an inkjet method. According to the inkjet printing, inks may not attach on printing surfaces well or attached inks may bleed if, for example, water is adhering to the printing surfaces.

[0004] Hence, for example a proposed label includes a front layer, an intermediate layer, and a back layer. The front layer and the back layer contain a laser coloring agent. When irradiated with laser light, a part of the front layer or a part of the back layer carbonizes and the laser coloring agent develops a color (for example, see Japanese Unexamined Patent Application Publication No. 2015-232610).

SUMMARY OF THE INVENTION

25 **[0005]** The present disclosure has an object to provide a thermosensitive recording medium that can satisfy both of a hiding power and color developability and of which printing layer and base material are less likely to be damaged by laser printing.

[0006] According to one aspect of the present disclosure, a thermosensitive recording medium includes a base material, and a thermosensitive recording layer, and a printing layer. An average absorbance A1 (%) of the printing layer with respect to visible light having a wavelength of 400 nm or longer but 700 nm or shorter, an average absorbance A2 (%) of the thermosensitive recording layer with respect to the visible light, and an average absorbance B1 (%) of the printing layer with respect to an irradiation wavelength of laser light during printing by a laser satisfy the following formula: $A1 > A2$ and the following formula: $A1 > B1$.

35 **[0007]** The present disclosure can provide a thermosensitive recording medium that can satisfy both of a hiding power and color developability and of which printing layer and base material are less likely to be damaged by laser printing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

40 FIG. 1 is a graph plotting absorbance of carbon black and infrared (IR)-transmissive black per wavelength;
FIG. 2 is a schematic view illustrating an example of a thermosensitive recording medium of the present disclosure;
FIG. 3 is a schematic view illustrating another example of a thermosensitive recording medium of the present disclosure;
45 FIG. 4 is a schematic view illustrating a laser light irradiated state of a thermosensitive recording medium;
FIG. 5 is a schematic view illustrating an example of a laser printing apparatus of the present disclosure; and
FIG. 6 is a schematic view illustrating another example of a laser printing apparatus of the present disclosure.

DESCRIPTION OF THE EMBODIMENTS

50 (Thermosensitive recording medium)

[0009] A thermosensitive recording medium of the present disclosure includes a base material, a thermosensitive recording layer, and a printing layer. An average absorbance A1 (%) of the printing layer with respect to visible light having a wavelength of 400 nm or longer but 700 nm or shorter, an average absorbance A2 (%) of the thermosensitive recording layer with respect to the visible light, and an average absorbance B1 (%) of the printing layer with respect to an irradiation wavelength of laser light during printing by a laser satisfy the following formula: $A1 > A2$ and the following formula: $A1 > B1$. The thermosensitive recording medium further includes other layers as needed.

[0010] Existing techniques print, for example, traceability information and security information by irradiating labels with laser light. However, existing techniques have difficulty satisfying both of a hiding power and color develop ability. Particularly, for security applications, a hiding power that protects the printed content so as not to be seeable from the back surface is strongly needed. Here, when the pigment in the printing layer used as a background color for ensuring a hiding power excessively absorbs laser light, the printing layer has a large sensitivity gap from the thermosensitive recording layer, leading to a problem that the printing density cannot be adjusted appropriately. Another problem is that even if an appropriate pigment is used in the printing layer so as not to excessively absorb laser light, unless the laser parameter is adjusted, the pigment in the printing layer absorbs laser light, and the printing layer and the base material are damaged by laser printing.

[0011] The present disclosure can realize a thermosensitive recording medium that can satisfy both of a hiding power and color developability and of which printing layer and base material are less likely to be damaged by laser printing, by providing the thermosensitive recording medium with a base material, and a thermosensitive recording layer and a printing layer on the base material, and making an average absorbance A1 (%) of the printing layer with respect to visible light having a wavelength of 400 nm or longer but 700 nm or shorter, an average absorbance A2 (%) of the thermosensitive recording layer with respect to the visible light, and an average absorbance B1 (%) of the printing layer with respect to an irradiation wavelength of laser light during printing by a laser satisfy the following formula: $A1 > A2$ and the following formula: $A1 > B1$.

[0012] When the following formula: $A1 > A2$ is satisfied, i.e., when the average absorbance of the printing layer with respect to visible light is higher than the average absorbance of the thermosensitive recording layer with respect to visible light, the hiding power can be improved because the printing layer can absorb visible light appropriately. Particularly, when a hiding power for, for example, security applications is needed, it is preferable to solidly blacken the printing layer.

[0013] When the following formula: $A1 > B1$ is satisfied, it is possible to optimize the average absorbance of the printing layer with respect to the irradiation wavelength of the laser light during laser printing. This makes it possible to prevent damages on the printing layer and the base material due to laser printing.

[0014] The average absorbances of the printing layer and the thermosensitive recording layer per wavelength can be measured with, for example, a spectrophotometer.

[0015] The irradiation wavelength of the laser light is the wavelength when laser printing is performed on the thermosensitive recording medium, and is typically from 900 nm through 1,000 nm.

[0016] The thermosensitive recording medium of the present disclosure includes a base material, and a thermosensitive recording layer and a printing layer on the base material, preferably includes a protective layer, and further includes other layers as needed.

[0017] As the thermosensitive recording medium, it is preferable to use a thermosensitive recording medium on which an image is recorded once. It is also possible to use a thermally reversible recording medium on which images can be recorded and erased repeatedly.

[0018] It is preferable that the thermosensitive recording medium include a thermosensitive recording layer, a printing layer, and a base material in this order in a laser light irradiating direction. When the thermosensitive recording layer, the printing layer, and the base material are in this order in the laser light irradiating direction, laser light that comes incident into the thermosensitive recording layer is absorbed and attenuated in the thermosensitive recording layer, and the energy to come incident into the printing layer can be reduced. This makes it possible to prevent damages on the printing layer and the base material.

<Base material>

[0019] For example, the shape, structure, size, and constituent material of the base material are not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the shape include a flat plate shape, a sheet shape, and a film shape. The structure may be a single-layer structure or a laminate structure. The size may be appropriately selected depending on, for example, the size of the thermosensitive recording medium.

[0020] The constituent material of the base material is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the constituent material of the base material include inorganic materials and organic materials.

[0021] Examples of the inorganic materials include glass, quartz, silicon, silicon oxide, aluminum oxide, SiO_2 , and metals.

[0022] Examples of the organic materials include: paper such as high-quality paper, art paper, coat paper, and synthetic paper; cellulose derivatives such as cellulose triacetate; polyester resins such as polyethylene terephthalate (PET) and polybutylene terephthalate; and plastic films of polycarbonate, polystyrene, polymethyl methacrylate, polyethylene, and polypropylene. One of these materials may be used alone or two or more of these materials may be used in combination.

[0023] In order to improve adhesiveness of an undercoat layer, it is preferable to reform the surface of the base material

by, for example, corona discharge treatment, oxidation reaction treatment (with, for example, chromic acid), etching treatment, treatment for imparting easy adhesiveness, and antistatic treatment.

[0024] It is preferable that the base material be a transparent film in order not to give influence on the degree of color development of the thermosensitive recording layer. Here, a transparent base material means a base material that does not absorb light of any wavelength ranges at all but transmits all wavelength ranges through itself. So long as the base material has a value of about 10% or lower as haze (turbidity), which is an indicator of film transparency, there is no particular problem. However, in order to achieve the object of the present disclosure, the haze of the base material is more preferably 5% or lower.

[0025] The average thickness of the base material is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 20 micrometers or greater but 2,000 micrometers or less and more preferably 50 micrometers or greater but 1,000 micrometers or less.

<Thermosensitive recording layer>

[0026] The thermosensitive recording layer contains a leuco dye, a developer, and a photo-thermal conversion material, preferably contains a binder resin, and further contains other components as needed.

[0027] The leuco dye is not particularly limited and may be appropriately selected depending on the intended purpose from leuco dyes used in thermosensitive recording media. Preferable examples of the leuco dye include triphenylmethane-based, fluoran-based, phenothiazine-based, auramine-based, spiropyran-based, and indolinophthalide-based leuco compounds.

[0028] The leuco dye is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the leuco dye include 3,3-bis(p-dimethylaminophenyl)-phthalide, 3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide (also known as crystal violet lactone), 3,3-bis(p-dimethylaminophenyl)-6-diethylamino phthalide, 3,3-bis(p-dimethylamino phenyl)-6-chlorophthalide, 3,3-bis(p-dibutylaminophenyl)phthalide, 3-cyclohexylamino-6-chlorofluoran, 3-dimethylamino-5,7-dimethylfluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-7-methylfluoran, 3-diethylamino-7,8-benzfluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-(N-p-tolyl-N-ethylamino)-6-methyl-7-anilino fluoran, 2-{N-(3'-trifluoromethylphenyl)amino}-6-diethylamino fluoran, 2-{3,6-bis(diethylamino)-9-(o-chloroanilino)xanthyl lactam benzoate}, 3-diethylamino-6-methyl-7-(m-trichloromethyl-anilino)fluoran, 3-diethylamino-7-(o-chloroanilino)fluoran, 3-pyrrolidino-6-methyl-7-anilino fluoran, 3-di-n-butylamino-7-o-chloroanilino)fluoran, 3-N-methyl-N,n-amylamino-6-methyl-7-anilino fluoran, 3-N-methyl-N-cyclohexylamino-6-methyl-7-anilino fluoran, 3-diethylamino-6-methyl-7-anilino fluoran, 3-(N,N-diethylamino)-5-methyl-7-(N,N-dibenzylamino)fluoran, benzoyl leuco methylene blue, 6'-chloro-8'-methoxy-benzoindolino-spiropyran, 6'-bromo-3'-methoxy-benzoindolino-spiropyran, 3-(2'-hydroxy-4'-dimethylaminophenyl)-3-(2'-methoxy-5' chlorophenyl)phthalide, 3-(2'-hydroxy-4'-dimethylaminophenyl)-3-(2'-methoxy-5'-nitrophenyl)phthalide, 3-(2'-hydroxy-4'-diethylaminophenyl)-3-(2'-methoxy-5'-methylphenyl)phthalide, 3-(2'-methoxy-4'-dimethylaminophenyl)-3-(2'-hydroxy-4'-chloro-5'-methylphenyl)phthalide, 3-(N-ethyl-N-tetrahydrofurfuryl)amino-6-methyl-7-anilino fluoran, 3-N-ethyl-N-(2-ethoxypropyl)amino-6-methyl-7-anilino fluoran, 3-N-methyl-N-isobutyl-6-methyl-7-anilino fluoran, 3-morpholino-7-(N-propyl-trifluoromethyl-anilino)fluoran, 3-pyrrolidino-7-trifluoromethyl-anilino fluoran, 3-diethylamino-5-chloro-7-(N-benzyl-trifluoromethyl-anilino)fluoran, 3-pyrrolidino-7-(di-p-chlorophenyl)methylaminofluoran, 3-diethylamino-5-chloro-7-(a-phenylethylamino)fluoran, 3-(N-ethyl-p-toluidino)-7-(a-phenylethylamino)fluoran, 3-diethylamino-7-(o-methoxycarbonylphenylamino)fluoran, 3-diethylamino-5-methyl-7-(a-phenylethylamino)fluoran, 3-diethylamino-7-piperidino fluoran, 2-chloro-3-(N-methyltoluidino)-7-(p-n-butylanilino)fluoran, 3-di-n-butylamino-6-methyl-7-anilino fluoran, 3,6-bis(dimethylamino)fluorenespiro(9,3')-6'-dimethylaminophthalide, 3-(N-benzyl-N-cyclohexylamino)-5,6-benzo-7-a-naphthylamino-4'-promofluoran, 3-diethylamino-6-chloro-7-anilino fluoran, 3-diethylamino-6-methyl-7-mesitidino-4',5'-benzofluoran, 3-N-methyl-N-isopropyl-6-methyl-7-anilino fluoran, 3-N-ethyl-N-isoamyl-6-methyl-7-anilino fluoran, 3-diethylamino-6-methyl-7-(2',4'-dimethylanilino)fluoran, 3-morpholino-7-(N-propyl-trifluoromethyl-anilino)fluoran, 3-pyrrolidino-7-trifluoromethyl-anilino fluoran, 3-diethylamino-5-chloro-7-(N-benzyl-trifluoromethyl-anilino)fluoran, 3-pyrrolidino-7-(di-p-chlorophenyl)methylaminofluoran, 3-diethylamino-5-chloro-(a-phenylethylamino)fluoran, 3-(N-ethyl-p-toluidino)-7-(a-phenylethylamino)fluoran, 3-diethylamino-7-(o-methoxycarbonylphenylamino)fluoran, 3-diethylamino-5-methyl-7-(a-phenylethylamino)fluoran, 3-diethylamino-7-piperidino fluoran, 2-chloro-3-(N-methyltoluidino)-7-(p-N-butylanilino)fluoran, 3,6-bis(dimethylamino)fluorenespiro(9,3')-6'-dimethylamino phthalide, 3-(N-benzyl-N-cyclohexylamino)-5,6-benzo-7-a-naphthylamino-4'-bromofluoran, 3-diethylamino-6-chloro-7-anilino fluoran, 3-N-ethyl-N-(2-ethoxypropyl)amino-6-methyl-7-anilino fluoran, 3-N-ethyl-N-tetrahydrofurfurylamino-6-methyl-7-anilino fluoran, 3-diethylamino-6-methyl-7-mesitidino-4',5'-benzofluoran, 3-p-dimethylaminophenyl)-3-{1,1-bis(p-dimethylaminophenyl)ethylen-2-yl}phthalide, 3-(p-dimethylaminophenyl)-3-{1,1-bis(p-dimethylaminophenyl)ethylen-2-yl}-6-dimethylaminophthalide, 3-(p-dimethylaminophenyl)-3-(1-p-dimethylaminophenyl-1-phenylethylen-2-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(1-p-dimethylaminophenyl-1-p-chlorophenylethylen-2-yl)-6-dimethylaminophthalide, 3-(4'-dimethylamino-2'-methoxy)-3-(1"-p-dimethylaminophenyl-1"-p-chlorophenyl-1",3"-butadien-4"-yl)benzophthalide, 3-(4'-dimethylamino-2'-benzyloxy)-3-(1"-p-dimethylaminophenyl-1"-phenyl-1",3"-butadien-4"-

yl)benzophthalide, 3-dimethylamino-6-dimethylamino-fluorene-9-spiro-3'-(6'-dimethylamino)phthalide, 3,3-bis(2-(p-dimethylaminophenyl)-2-p-methoxyphenyl)ethenyl-4,5,6,7-tetrachlorophthalide, 3-bis{1,1-bis(4-pyrrolidinophenyl)ethylen-2-yl}-5,6-dichloro-4,7-dipromophthalide, bis(p-dimethylaminostyryl)-1-naphthalene sulfonylmethane, and bis(p-dimethylaminostyryl)-1-p-trisulfonylmethane. One of these leuco dyes may be used alone or two or more of these leuco

dyes may be used in combination.

[0029] The content of the leuco dye is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 5% by mass or greater but 40% by mass or less and more preferably 10% by mass or greater but 30% by mass or less.

- Developer-

[0030] As the developer, various electron-accepting substances that react with the leuco dye during heating to make the leuco dye develop a color may be used. Examples of the developer include phenolic substances, organic or inorganic acidic substances, esters or salts of these substances, such as gallic acid, salicylic acid, 3-isopropyl salicylic acid, 3-cyclohexyl salicylic acid, 3,5-di-tert-butylsalicylic acid, 3,5-di- α -methylbenzyl salicylic acid, 4,4'-isopropylidene diphenol, 1,1'-isopropylidene bis(2-chlorophenol), 4,4'-isopropylidene bis(2,6-dibromophenol), 4,4'-isopropylidene bis(2,6-dichlorophenol), 4,4'-isopropylidene bis(2-methyl phenol), 4,4'-isopropylidene bis(2,6-dimethylphenol), 4,4-isopropylidene bis(2-tert-butylphenol), 4,4'-sec-butylidene diphenol, 4,4'-cyclohexylidene bisphenol, 4,4'-cyclohexylidene bis(2-methylphenol), 4-tert-butylphenol, 4-phenylphenol, 4-hydroxydiphenoxide, α -naphthol, β -naphthol, 3,5-xyleneol, thymol, methyl-4-hydroxybenzoate, 4-hydroxyacetophenone, novolac-type phenol resin, 2,2'-thiobis(4,6-dichlorophenol), catechol, resorcin, hydroquinone, pyrogallol, fluoroglycine, fluoroglycine carboxylic acid, 4-tert-octyl catechol, 2,2'-methylene bis(4-chlorophenol), 2,2'-methylene bis(4-methyl-6-tert-butylphenol), 2,2'-dihydroxydiphenyl, ethyl p-hydroxybenzoate, propyl p-hydroxybenzoate, butyl p-hydroxybenzoate, benzyl p-hydroxybenzoate, p-hydroxybenzoic acid-p-chlorobenzyl, p-hydroxybenzoic acid-o-chlorobenzyl, p-hydroxybenzoic acid-p-methylbenzyl, p-hydroxybenzoic acid-n-octyl, benzoic acid, zinc salicylate, 1-hydroxy-2-naphthoic acid, 2-hydroxy-6-naphthoic acid, zinc 2-hydroxy-6-naphthoate, 4-hydroxydiphenyl sulfone, 4-hydroxy-4'-chlorodiphenyl sulfone, bis(4-hydroxyphenyl)sulfide, 2-hydroxy-p-toluic acid, zinc 3,5-di-tert-butyl salicylate, tin 3,5-di-tert-butyl salicylate, tartaric acid, oxalic acid, maleic acid, citric acid, succinic acid, stearic acid, 4-hydroxyphthalic acid, boric acid, thiourea derivatives, 4-hydroxy thiophenol derivatives, bis(4-hydroxyphenyl)acetic acid, ethyl bis(4-hydroxyphenyl)acetate, n-propyl bis(4-hydroxyphenyl)acetate, m-butyl bis(4-hydroxyphenyl)acetate, phenyl bis(4-hydroxyphenyl)acetate, benzyl bis(4-hydroxyphenyl)acetate, phenethyl bis(4-hydroxyphenyl)acetate, bis(3-methyl-4-hydroxyphenyl)acetic acid, methyl bis(3-methyl-4-hydroxyphenyl)acetate, n-propyl bis(3-methyl-4-hydroxyphenyl)acetate, 1,7-bis(4-hydroxyphenylthio)3,5-dioxaheptane, 1,5-bis(4-hydroxyphenylthio)3-oxaheptane, dimethyl 4-hydroxyphthalate, 4-hydroxy-4'-methoxydiphenyl sulfone, 4-hydroxy-4'-ethoxydiphenyl sulfone, 4-hydroxy-4'-isopropoxydiphenyl sulfone, 4-hydroxy-4'-propoxydiphenyl sulfone, 4-hydroxy-4'-butoxydiphenyl sulfone, 4-hydroxy-4'-isobutoxydiphenyl sulfone, 4-hydroxy-4-butoxydiphenyl sulfone, 4-hydroxy-4'-tert-butoxydiphenyl sulfone, 4-hydroxy-4'-benzyloxydiphenyl sulfone, 4-hydroxy-4'-phenoxydiphenyl sulfone, 4-hydroxy-4'-(m-methylbenzyloxy)diphenyl sulfone, 4-hydroxy-4'-(p-methylbenzyloxy)diphenyl sulfone, 4-hydroxy-4'-(O-methyl benzyloxy)diphenyl sulfone, 4-hydroxy-4'-(p-chlorobenzyloxy)diphenyl sulfone, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane, and 1,1,1-tris(4-hydroxyphenyl)ethane.

[0031] The content ratio between the leuco dye and the developer is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 1 part by mass or greater but 4 parts by mass or less of the developer relative to 1 part by mass of the leuco dye.

-Photo-thermal conversion material-

[0032] The photo-thermal conversion material is a material that absorbs laser light and converts it to heat, and is roughly classified into inorganic materials and organic materials.

[0033] Examples of the inorganic materials include particles of at least one selected from carbon black, metal borides, and metal oxides of, for example, Ge, Bi, In, Te, Se, and Cr. Among these inorganic materials, a material that greatly absorbs light in the near infrared wavelength range and poorly absorbs light in the visible wavelength range is preferable, and metal borides and metal oxides are more preferable. As the metal borides and the metal oxides, for example, at least one selected from hexaborides, tungsten oxide compounds, antimony tin oxide (ATO), indium tin oxide (ITO), and zinc antimonate is preferable.

[0034] Examples of the hexaborides include LaB_6 , CeB_6 , PrB_6 , NdB_6 , GdB_6 , TbB_6 , DyB_6 , HoB_6 , YB_6 , SmB_6 , EuB_6 , ErB_6 , TmB_6 , YbB_6 , LuB_6 , SrB_6 , CaB_6 , and $(\text{La,Ce})\text{B}_6$.

[0035] Examples of the tungsten oxide compounds include particles of tungsten oxides represented by General formula: WyOz (where W represents tungsten, O represents oxygen, and $2.2 \leq z/y \leq 2.999$), or particles of composite tungsten oxides represented by General formula: MxWyOz (where M represents one or more elements selected from H, He, alkali

metals, alkali earth metals, rare earth elements, Mg, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Tl, Si, Ge, Sn, Pb, Sb, B, F, P, S, Se, Br, Te, Ti, Nb, V, Mo, Ta, Re, Be, Hf, Os, Bi, and I, W represents tungsten, O represents oxygen, $0.001 \leq x/y \leq 1$, and $2.2 \leq z/y \leq 3.0$), described in, for example, International Publication No. WO 2005/037932 and Japanese Unexamined Patent Application Publication No. 2005-187323). Among these tungsten oxide compounds, cesium-containing tungsten oxide that greatly absorbs the near infrared range and poorly absorbs the visible range is particularly preferable.

[0036] Among antimony tin oxide (ATO), indium tin oxide (ITO), and zinc antimonate, ITO is particularly preferable because ITO greatly absorbs the near infrared range and poorly absorbs the visible range.

[0037] These inorganic materials are formed in a layer form by a vacuum vapor deposition method or by bonding particles of these materials with each other using, for example, a resin.

[0038] As the organic materials, various dyes may be appropriately used depending on the wavelength of the light to be absorbed. When a semiconductor laser is used as the light source, a near infrared absorbing pigment that has an absorption peak at about from 600 nm through 1,200 nm is used. Specific examples of the near infrared absorbing pigment include cyanine pigments, quinone-based pigments, quinoline derivatives of indonaphthol, phenylenediamine-based nickel complexes, and phthalocyanine-based pigments.

[0039] One of these photo-thermal conversion materials may be used alone or two or more of these photo-thermal conversion materials may be used in combination.

[0040] The photo-thermal conversion material may be contained in the thermosensitive recording layer or may be contained in any other layer than the thermosensitive recording layer. When the photo-thermal conversion material is contained in any other layer than the thermosensitive recording layer, it is preferable to provide a photo-thermal conversion layer in a manner to adjoin the thermosensitive recording layer.

[0041] The content of the photo-thermal conversion material is preferably 0.1% by mass or greater but 10% by mass or less and more preferably 0.3% by mass or greater but 5% by mass or less.

-Binder resin-

[0042] The binder resin is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the binder resin include polyvinyl alcohol resins; starch or derivatives of starch; cellulose derivatives such as hydroxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, methyl cellulose, and ethyl cellulose; water-soluble polymers such as soda polyacrylate, polyvinyl pyrrolidone, acrylamide-acrylic acid ester copolymers, acrylamide-acrylic acid ester-methacrylic acid terpolymers, alkali salts of styrene-maleic anhydride copolymers, alkali salts of isobutylene-maleic anhydride copolymers, polyacrylamide, soda alginate, gelatin, and casein; emulsions of polyvinyl acetate, polyurethane, polyacrylic acid, polyacrylic acid esters, vinyl chloride-vinyl acetate copolymers, polybutyl methacrylate, and ethylene-vinyl acetate copolymers; and latexes of, for example, styrene-butadiene copolymers and styrene-butadiene-acrylic copolymers. One of these binder resins may be used alone or two or more of these binder resins may be used in combination.

-Other components-

[0043] Examples of the other components include an auxiliary additive, a lubricant, a filler, a thermally meltable substance, a sensitizer, an antioxidant, a light stabilizer, and a surfactant.

[0044] As the auxiliary additive, for example, various hindered phenol compounds or hindered amine compounds that have electron acceptability but have a relatively low color developability may be added. Specific examples of such auxiliary additives include 2,2'-methylenebis(4-ethyl-6-tertiary butylphenol), 4,4'-butylidene bis(6-tertiary butyl-2-methylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-tertiary butylphenyl)butane, 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl)butane, 4,4'-thiobis(6-tertiary butyl-2-methylphenol), tetrabromo bisphenol A, tetrabromo bisphenol 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.

[0045] Examples of the lubricant include higher fatty acids or metal salts of higher fatty acids, higher fatty acid amides, higher fatty acid esters, animal waxes, plant waxes, mineral waxes, and petroleum waxes.

[0046] Examples of the filler include: inorganic particles of, for example, calcium carbonate, silica, zinc oxide, titanium oxide, aluminum hydroxide, zinc hydroxide, barium sulfate, clay, kaolin, talc, surface-treated calcium, and surface-treated silica; and organic particles of, for example, urea-formalin resins, styrene-methacrylic acid copolymers, polystyrene resins, and vinylidene chloride resins.

-Method for forming thermosensitive recording layer-

[0047] The thermosensitive recording layer can be formed by any known method not particularly limited. For example,

it is possible to form the thermosensitive recording layer by grinding and dispersing the developer, the leuco dye, the photo-thermal conversion material, the binder resin, and the other components using a disperser such as a ball mill, an attritor, and a sand mill until the dispersion particle diameter becomes 0.1 micrometers or greater but 3 micrometers or less and subsequently mixing the resultant with, for example, the filler as needed, to prepare a thermosensitive recording layer coating liquid, coating a support with the thermosensitive recording layer coating liquid, and drying the thermosensitive recording layer coating liquid.

[0048] The coating method is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the coating method include a blade coating method, a gravure coating method, a gravure offset coating method, a bar coating method, a roll coating method, a knife coating method, an air knife coating method, a comma coating method, a U-comma coating method, an AKKU coating method, a smoothing coating method, a micro-gravure coating method, a reverse roll coating method, a four or five-roll coating method, a dip coating method, a curtain coating method, a slide coating method, and a die coating method.

[0049] The average thickness of the thermosensitive recording layer is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 1 micrometer or greater but 20 micrometers or less and more preferably 1.5 micrometers or greater but 10 micrometers or less.

<Printing layer>

[0050] Through printing of, for example, inks, the printing layer is formed with various colors, various materials, and various thicknesses, and constitutes the background of the image printed on the thermosensitive recording layer. Providing the printing layer enables previously describing, for example, a product name, the name of the manufacturer, and ingredient labeling before the product is packaged, and can impart an excellent design property to the product.

[0051] It is preferable to provide the printing layer at any of the followings: on the thermosensitive recording layer; between the base material and the thermosensitive recording layer; and on a surface of the base material opposite to the thermosensitive recording layer.

[0052] The average absorbance of the printing layer with respect to visible light having a wavelength of 400 nm or longer but 700 nm or shorter is preferably 50% or higher and more preferably 60% or higher.

[0053] The average absorbance of the printing layer with respect to the irradiation wavelength of laser light is preferably 10% or lower and more preferably 5% or lower.

[0054] When the printing layer has the above-described average absorbances with respect to the visible light and the irradiation wavelength of laser light, it is possible to prevent damages on the base material while maintaining a hiding power.

[0055] The method for measuring the average absorbances of the printing layer and the irradiation wavelength of the laser light are as described above.

[0056] The printing layer contains an infrared-transmissive coloring material and a binder resin, and further contains other components as needed.

[0057] The infrared-transmissive coloring material is not particularly limited and may be appropriately selected depending on the intended purpose so long as the infrared-transmissive coloring material can satisfy the above-described average absorbances with respect to the visible light and the irradiation wavelength of the laser light. Infrared-transmissive pigments or infrared-transmissive dyes may be used.

[0058] Examples of the infrared-transmissive coloring material include infrared (IR)-transmissive black pigments.

[0059] FIG. 1 is a graph plotting the absorbances of carbon black and infrared (IR)-transmissive black per wavelength.

[0060] It can be seen that carbon black and IR-transmissive black both look black because both have high absorbances with respect to the wavelength range of from 380 nm through 780 nm, which is the visible range. When a medium coated with these pigments is irradiated with laser light, the base material of the medium is damaged because the absorbance of carbon black with respect to the near infrared range is almost the same as the absorbance thereof with respect to the visible range. On the other hand, the IR-transmissive black, which has a significantly lower absorbance with respect to the near infrared range, can make the thermosensitive recording layer develop a color at the optimum density without damaging the base material, and can hide the color-developed region with black when the medium is seen from the printing layer side.

[0061] As the binder resin and the other components, the same materials as used in the thermosensitive recording layer may be used.

[0062] The printing layer can be formed by, for example, a bar coating method, gravure printing, flexographic printing, offset printing, UV printing, and inkjet printing.

[0063] The average thickness of the printing layer is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 1 micrometer or greater but 20 micrometers or less and more preferably 1.5 micrometers or greater but 10 micrometers or less.

<Protective layer>

[0064] The protective layer contains a binder resin and a crosslinking agent, and further contains other components as needed. It is preferable to provide the protective layer on the thermosensitive recording layer.

[0065] The binder resin is not particularly limited and may be appropriately selected depending on the intended purpose. Water-soluble resins are particularly preferable.

[0066] Examples of the water-soluble resins include polyvinyl alcohols, modified polyvinyl alcohols, starch or derivatives of starch, cellulose derivatives such as methoxy cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, methyl cellulose, and ethyl cellulose, soda polyacrylate, polyvinyl pyrrolidone, acrylamide-acrylic acid ester copolymers, acrylamide-acrylic acid ester-methacrylic acid terpolymers, alkali salts of styrene-maleic anhydride copolymers, alkali salts of isobutylene-maleic anhydride copolymers, polyacrylamide, modified polyacrylamide, methyl vinyl ether-maleic anhydride copolymers, carboxy-modified polyethylene, polyvinyl alcohol-acrylamide block copolymers, melamine-formaldehyde resins, urea-formaldehyde resins, soda alginate, gelatin, and casein. One of these water-soluble resins may be used alone or two or more of these water-soluble resins may be used in combination. Among these water-soluble resins, modified polyvinyl alcohols are preferable.

[0067] Examples of the modified polyvinyl alcohols include diacetone-modified polyvinyl alcohols; acetoacetyl-modified polyvinyl alcohols; and carboxylic acid-modified polyvinyl alcohols such as itaconic acid-modified polyvinyl alcohols and maleic acid-modified polyvinyl alcohols.

[0068] The crosslinking agent is not particularly limited and may be appropriately selected depending on the intended purpose so long as the crosslinking agent can reduce water solubility of the water-soluble resin by reacting with the water-soluble resin. Examples of the crosslinking agent include glyoxal derivatives, methylol derivatives, epichlorohydrin, polyamide epichlorohydrin, epoxy compounds, azilidine compounds, hydrazine, hydrazide derivatives, oxazoline derivatives, and carbodiimide derivatives. One of these crosslinking agents may be used alone or two or more of these crosslinking agents may be used in combination. Among these crosslinking agents, polyamide epichlorohydrin is particularly preferable because polyamide epichlorohydrin has a high handling safety and needs only a short time for curing needed for water resistance treatment.

[0069] The content of the polyamide epichlorohydrin is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 10 parts by mass or greater but 60 parts by mass or less and more preferably 20 parts by mass or greater but 50 parts by mass or less relative to 100 parts by mass of the binder resin.

[0070] As needed, it is preferable to add a pigment (filler) in the protective layer. Examples of the pigment used in the protective layer include: inorganic pigments such as zinc oxide, calcium carbonate, barium sulfate, titanium oxide, lithopone, talc, pyrophyllite, kaolin, aluminum hydroxide, and calcined kaolin; and organic pigments such as crosslinked polystyrene resins, urea resins, silicone resins, crosslinked polymethyl methacrylate resins, and melamine-formaldehyde resins.

[0071] In addition to the resin, the water resistance treatment agent, and the pigment described above, auxiliary additives hitherto used, such as a surfactant, a thermally meltable substance, a lubricant, and a pressure anti-coloring agent may be used in combination in the protective layer.

[0072] The protective layer can be formed by any known method not particularly limited.

[0073] The average thickness of the protective layer is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 0.5 micrometers or greater but 5 micrometers or less and more preferably 1 micrometer or greater but 3 micrometers or less.

<Other layers>

[0074] The other layers are not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the other layers include a back layer and an undercoat layer.

-Back layer-

[0075] As needed, the back layer may be provided on a surface of the base material at a side at which the thermosensitive recording layer is not provided.

[0076] The back layer contains a filler and a binder resin, and further contains other components such as a lubricant and a coloring pigment as needed.

[0077] As the filler, for example, an inorganic filler or an organic filler may be used.

[0078] Examples of the inorganic filler include carbonates, silicates, metal oxides, and sulfuric acid compounds.

[0079] Examples of the organic filler include silicone resins, cellulose, epoxy resins, nylon resins, phenol resins, polyurethane resins, urea resins, melamine resins, polyester resins, polycarbonate resins, styrene resins, acrylic resins, polyethylene resins, formaldehyde resins, and polymethyl methacrylate resins.

[0080] The binder resin is not particularly limited and may be appropriately selected depending on the intended purpose. For example, the same binder resin as used in the thermosensitive recording layer may be used.

[0081] The average thickness of the back layer is not particularly limited, may be appropriately selected depending on the intended purpose and is preferably 0.1 micrometers or greater but 20 micrometers or less and more preferably 0.3 micrometers or greater but 10 micrometers or less.

-Undercoat layer-

[0082] The undercoat layer is not particularly limited and may be appropriately selected depending on the intended purpose. The undercoat layer contains, for example, an adhesive resin and thermoplastic hollow resin particles, and preferably further contains other components as needed.

[0083] The thermoplastic hollow resin particles contain air or any other gas inside the shell of the particles formed of a thermoplastic resin, and are hollow particles already foamed.

[0084] The average particle diameter (particle outer diameter) of the thermoplastic hollow resin particles is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 0.2 micrometers or greater but 20 micrometers or less and more preferably 2 micrometers or greater but 5 micrometers or less.

[0085] When the average particle diameter of the thermoplastic hollow resin particles is less than 0.2 micrometers, it is technically difficult to make the particles hollow, and the undercoat layer cannot serve the function sufficiently. On the other hand, when the average particle diameter of the thermoplastic hollow resin particles is greater than 20 micrometers, the surface coated with the thermoplastic hollow resin particles and then dried has a poor smoothness, and coating of the thermosensitive recording layer on the poorly smooth surface becomes nonuniform. In order to make the coating uniform, there is a need for applying the thermosensitive recording layer coating liquid in an amount more than necessary.

[0086] Hence, it is preferable that the thermoplastic hollow resin particles have an average particle diameter in the range described above and have a small variation and a uniform distribution peak.

[0087] The ratio of hollowness of the thermoplastic hollow resin particles is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 50% or higher but 95% or lower and more preferably 80% or higher but 95% or lower.

[0088] When the ratio of hollowness of the thermoplastic hollow resin particles is lower than 30%, the thermoplastic hollow resin particles have an insufficient heat insulating property, and make thermal energy from the thermal head dissipate to outside the thermosensitive recording medium through the base material. Hence, a sensitivity improving effect is insufficient.

[0089] Here, the ratio of hollowness is a ratio between the outer diameter and the inner diameter (i.e., the diameter of the hollow portion) of the hollow particles, and is represented by the following formula.

[0090] Ratio of hollowness (%) = (inner diameter of hollow particles/outer diameter of hollow particles) × 100

[0091] As described above, the shell of the thermoplastic hollow resin particles is formed of a thermoplastic resin. The thermoplastic resin is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the thermoplastic resin include styrene-acrylic resins, polystyrene resins, acrylic resins, polyethylene resins, polypropylene resins, polyacetal resins, chlorinated polyether resins, polyvinyl chloride resins, and copolymer resins containing vinylidene chloride and acrylonitrile as the main components.

[0092] Among these thermoplastic resins, styrene-acrylic resins, and copolymer resins containing vinylidene chloride and acrylonitrile as the main components are preferable because these resins have a high ratio of hollowness and a small particle diameter variation, and are suitable for blade coating.

[0093] The coating amount of the plastic hollow particles is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably from 1 g through 3 g per 1 m² of the base material in terms of maintaining sensitivity and coating uniformity. When the coating amount is less than 1 g/m², a sufficient sensitivity may not be obtained. When the coating amount is greater but 3 g/m², the layer has a low bindability.

[0094] The embodiment of the thermosensitive recording medium of the present disclosure is not particularly limited and may be appropriately selected depending on the intended purpose. For example, the thermosensitive recording medium may be used as a label as it is, or may be embodied as a form including an adhesive layer on a side of the base material opposite to the side at which the thermosensitive recording layer is provided.

[0095] The shape of the thermosensitive recording medium of the present disclosure is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the shape of the thermosensitive recording medium include a label shape, a film shape, a sheet shape, and a roll shape.

[0096] Because the thermosensitive recording medium of the present disclosure can satisfy both of color developability and a hiding power, the thermosensitive recording medium is suitable for security applications in which a hiding power that protects the printed content so as not to be seeable from the back surface is strongly needed.

[0097] FIG. 2 is a schematic cross-sectional view illustrating an example of the thermosensitive recording medium of the present disclosure. The thermosensitive recording medium 100 of FIG. 2 includes a base material 1, a printing layer

2, and a thermosensitive recording layer 3.

[0098] The base material 1 is formed of a transparent film of, for example, polyethylene terephthalate (PET), and supports the printing layer 2. The thermosensitive recording layer 3 contains, for example, a coloring agent such as a leuco dye, a developer, and a photo-thermal conversion material. The photo-thermal conversion material absorbs incident laser light and converts the laser light to heat. Along with this temperature elevation, the developer contacts and reacts with the coloring agent, which develops a color and forms an image on the thermosensitive recording medium 100. The thermosensitive recording layer 3 forms an image through a chemical reaction. However, the method for forming an image is not limited to this method.

[0099] The image is not particularly limited and may be appropriately selected depending on the intended purpose so long as the image is visible information. Examples of the image include letters, symbols, lines, figures, solid images, or combinations thereof, QR codes (registered trademark), barcodes, and two-dimensional codes.

[0100] Through coating of, for example, inks, the printing layer 2 is formed with various colors, various materials, and various thicknesses, and constitutes the background of the image printed on the thermosensitive recording layer 3. The printing layer 2 is a layer optionally provided when the user uses a laser printing apparatus. The disposition of the base material 1, the printing layer 2, and the thermosensitive recording layer 3 is an example and not limited to the configuration illustrated in FIG. 2.

[0101] FIG. 3 is a schematic cross-sectional view illustrating another example of the thermosensitive recording medium of the present disclosure. The thermosensitive recording medium 100 of FIG. 3 includes a base material 1, a printing layer 2, a thermosensitive recording layer 3 and a protective layer 4. The protective layer 4 prevents permeation of, for example, water and chemicals, and scratch or scrape of the image, and maintains the image. Moreover, the thermosensitive recording medium 100 may include a layer that absorbs ultraviolet rays in order to prevent property changes of the coloring agent due to absorption of ultraviolet rays. The disposition of the base material 1, the printing layer 2, the thermosensitive recording layer 3, and the protective layer 4 is an example and not limited to the configuration illustrated in FIG. 3.

[0102] FIG. 4 is a schematic view illustrating a laser light irradiated state of the thermosensitive recording medium illustrated in FIG. 2.

[0103] The arrow in FIG. 4 indicates a laser light incident path, and the patched portion indicates heat absorption in each layer. Laser light incident into the thermosensitive recording layer 3 is partially absorbed by the photo-thermal conversion material contained in the thermosensitive recording layer 3 and converted to heat, to elevate the temperature. Next, any laser light that is transmitted through the thermosensitive recording layer 3 is partially reflected on the interface between the printing layer 2 and the thermosensitive recording layer 3 and partially absorbed by the printing layer 2. Any laser light that is transmitted through the printing layer 2 is transmitted through the base material 1.

[0104] The user can variously change the pigment of the color used in the printing layer 2. Hence, laser printing settings are determined by the pigment of the printing layer 2. When the pigment of the printing layer does not absorb laser light in the laser wavelength range, it is possible to adjust the settings in a manner to make the thermosensitive recording layer 3 develop a color at the optimum density without considering the influence of the printing layer 2. On the other hand, when the pigment of the printing layer absorbs laser light in the laser wavelength range, the printing layer 2 is damaged before the thermosensitive recording layer 3 develops a color at the optimum density. Hence, in order to make the thermosensitive recording layer develop a color without damaging the printing layer, it is desirable not to use a pigment that absorbs laser light in the laser wavelength range in the printing layer 2.

(Laser printing method and laser printing apparatus)

[0105] A laser printing method of the present disclosure includes performing printing on the thermosensitive recording medium of the present disclosure by irradiation with laser light.

[0106] A laser printing apparatus of the present disclosure includes the thermosensitive recording medium of the present disclosure and an irradiating unit configured to irradiate the thermosensitive recording medium with laser light, preferably includes an optical fiber array, and further includes other units as needed.

[0107] In an embodiment of the present disclosure, it is preferable that the laser printing method and the laser printing apparatus perform printing by irradiation with laser light in a manner that the following formula: $T1 > T2 + T4$ is satisfied and the following formula: $T2 + T5 > T3$ is satisfied.

[0108] In the formulae, $T1$ represents the melting point (degree C) of the base material, $T2$ represents the temperature (degree C) of the thermosensitive recording medium before printing, $T3$ represents the color developing temperature (degree C) of the thermosensitive recording layer, $T4$ represents the amount (degree C) of temperature elevation of the printing layer during printing by irradiation with laser light, and $T5$ represents the amount (degree C) of temperature elevation of the thermosensitive recording layer during printing by laser light.

[0109] By setting the fluence and the irradiation time of the laser light to suit to the layer configuration of the thermosensitive recording medium within the range in which the following formula: $T1 > T2 + T4$ is satisfied and the following

formula: $T_2 + T_5 > T_3$ is satisfied, it is possible to prevent the heat generated by laser printing from exceeding the melting point of the base material and hence prevent damage on the base material. By suppressing the amount of heat generation in the printing layer below the amount of heat generation in the thermosensitive recording layer due to laser light, it is possible to make the thermosensitive recording layer develop a color without damaging the printing layer.

[0110] In order to control the amount of temperature elevation of the thermosensitive recording layer or the amount of temperature elevation of the printing layer in this way, the parameters of the laser light (fluence and irradiation time, i.e., energy to be applied) are controlled to suit to the parameters of the thermosensitive recording layer or the printing layer. Specifically, the amount of temperature elevation of the thermosensitive recording layer or the amount of temperature elevation of the printing layer (T_4 or T_5) can be calculated according to the mathematical formula below.

$$\text{Amount of temperature elevation} = \frac{(\text{Laser output} \times \text{Pulse width} \times \text{Laser light absorbance})}{(\text{Beam area} \times \text{Layer thickness} \times \text{Density} \times \text{Specific heat})}$$

[0111] The laser output represents the peak power (W) of the laser light.

[0112] The pulse width represents the light emission time (s) per laser dot.

[0113] The laser light absorbance represents the average absorbance (%) of the thermosensitive recording layer or the printing layer with respect to the laser light irradiation wavelength. Absorbance per wavelength can be measured with a spectrophotometer.

[0114] The beam area represents the area of a laser beam spot on the base material, and can be measured with a beam profiler.

[0115] The layer thickness represents the average thickness of the thermosensitive recording layer or the printing layer, and can be measured with a film thickness meter.

[0116] The density and the specific heat of the base material can be determined based on the values stipulated based on the constituent material of the base material. The present inventor has experimentally found that the density and the specific heat of the base material substantially conform to the density and the specific heat of the base material because the thickness of the thermosensitive recording layer and the printing layer is by far smaller than the thickness of the base material in the thermosensitive recording medium and the base material is also dominant in terms of heat capacity.

[0117] In an embodiment of the present disclosure, it is preferable that the beam profile at the focal point of the laser light be a top hat shape. When a laser beam of a common semiconductor laser or fiber laser is condensed, the beam profile of the laser beam is that of a Gaussian beam. A Gaussian beam has a higher peak power at the center region thereof than at the peripheral region thereof, and may damage the printing layer and the base material at the center region thereof. Because a top hat beam has a substantially uniform peak power within a beam spot, the top hat beam can prevent damages on the printing layer and the base material.

[0118] In an embodiment of the present disclosure, it is preferable to irradiate the thermosensitive recording medium with laser light while setting the thermosensitive recording medium at a position different from a maximum condensing position at which the laser light is condensed the most. The peak power is the highest at the position at which the beam is condensed the most. In order to prevent damages on the base material and the printing layer, it is preferable to set the thermosensitive recording medium at a position shifted frontward or rearward from the position at which the beam is condensed the most.

-Optical fiber array-

[0119] The optical fiber array includes a plurality of optical fibers that are arranged side by side in a main scanning direction orthogonal to a sub-scanning direction, which is the travelling direction of the thermosensitive recording medium. A light outputting unit irradiates the thermosensitive recording medium with output laser light through the optical fiber array, and records an image.

[0120] The arrangement of the optical fibers is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the arrangement of the optical fibers include a line shape and a planar shape. Of these arrangements, the line shape is preferable.

[0121] The shortest distance (pitch) between the centers of the optical fibers is preferably 1.0 mm or less, more preferably 0.5 mm or less, and yet more preferably 0.03 mm or greater but 0.15 mm or less.

[0122] When the shortest distance (pitch) between the centers of the optical fibers is 1.0 mm or less, high-resolution recording is available and a higher-definition image than hitherto obtained can be realized.

[0123] The number of the optical fibers arranged in the optical fiber array is preferably 10 or greater, more preferably 50 or greater, and yet more preferably 100 or greater but 400 or less.

[0124] When the number of the optical fibers arranged is 10 or greater, high-speed recording is available and a higher-

definition image than hitherto obtained can be realized.

[0125] An optical system including, for example, lenses may be provided at the succeeding stage of the optical fiber array in order to control the spot diameter of the laser light.

[0126] Depending on the dimension of the thermosensitive recording medium in the main scanning direction, a plurality of optical fiber arrays may be arranged in a line shape extending in the main scanning direction.

[0127] The optical fiber is an optical waveguide for the laser light output by the light outputting unit.

[0128] Examples of the optical fiber include an optical fiber.

[0129] For example, the shape, size (diameter), material, and structure of the optical fiber are not particularly limited and may be appropriately selected depending on the intended purpose.

[0130] The size (diameter) of the optical fiber is preferably 15 micrometers or greater but 1,000 micrometers or less and more preferably 20 micrometers or greater but 800 micrometers or less. When the diameter of the optical fiber is 15 micrometers or greater but 1,000 micrometers or less, there is an advantage in terms of image definition.

[0131] The material of the optical fiber is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the material of the optical fiber include quartz, glass, and resins.

[0132] The transmission wavelength range of the material of the optical fiber is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 700 nm or longer but 2,000 nm or shorter and more preferably 780 nm or longer but 1,600 nm or shorter.

[0133] A preferable structure of the optical fiber is formed of a core at the center through which laser light is passed, and a clad layer provided on the circumference of the core.

[0134] The diameter of the core is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 10 micrometers or greater but 500 micrometers or less and more preferably 15 micrometers or greater but 400 micrometers or less.

[0135] The material of the core is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the material of the core include glass doped with germanium or phosphorus.

[0136] The average thickness of the clad layer is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 10 micrometers or greater but 250 micrometers or less and more preferably 15 micrometers or greater but 200 micrometers or less.

[0137] The material of the clad layer is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the material of the clad layer include glass doped with boron or fluorine.

-Irradiating unit-

[0138] The irradiating unit is a unit configured to irradiate the thermosensitive recording medium with output laser light through the optical fiber array.

[0139] The irradiating unit is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the irradiating unit include a semiconductor laser and a solid-state optical fiber laser. Of these lasers, a semiconductor laser is preferable because a semiconductor laser has a wide wavelength selectivity, is a small-sized laser light source for a printing apparatus, and can reduce the size and the price of the apparatus.

[0140] The wavelength of the laser light is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 700 nm or longer but 2,000 nm or shorter and more preferably 780 nm or longer but 1,600 nm or shorter.

[0141] The output power of the laser light is not particularly limited, may be appropriately selected depending on the intended purpose, and is preferably 1 W or higher and more preferably 3 W or higher. When the output power of the laser light is 1 W or higher, there is an advantage in terms of high-density printing of an image.

[0142] The shape of the spot image-forming unit of the laser light is not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the shape of the spot image-forming unit include a circular shape, an elliptical shape, and various polygonal shapes such as a triangular shape, a quadrangular shape, a pentagonal shape, and a hexagonal shape. Among these shapes, a circular shape or an elliptical shape is preferable.

-Other units-

[0143] The other units are not particularly limited and may be appropriately selected depending on the intended purpose. Examples of the other unit include a driving unit, a control unit, a main control unit, a cooling unit, a power supply unit, and a conveying unit.

[0144] An example of the laser printing apparatus of the present disclosure used in the laser printing method of the present disclosure will be described with reference to the drawings.

[0145] FIG. 5 is a schematic view illustrating an example of the laser printing apparatus of the present disclosure. The laser printing apparatus 10 of FIG. 5 irradiates a thermosensitive recording medium 100, which is a print target, with

laser light to perform surface processing treatment or image recording operations. The laser printing apparatus 10 includes, for example, a conveying unit configured to convey the thermosensitive recording medium 100, an optical head 20 configured to perform laser light irradiation, a main unit 30 configured to control the optical head 20, an optical fiber 42 coupling the optical head 20 with the main unit 30, an encoder unit 60 configured to obtain the conveying speed of the thermosensitive recording medium 100, and a system control device. The laser printing apparatus 10 irradiates the print target with laser light from the optical head 20, to apply processing treatment to the surface of the print target or record a visible image.

[0146] In the description with reference to FIG. 5, the conveying direction of the thermosensitive recording medium 100 is the X axis direction, the vertical direction is the Z axis direction, and the direction orthogonal to both of the conveying direction and the vertical direction is the Y axis direction.

<Internal configuration of laser printing apparatus>

[0147] FIG. 6 is a schematic view illustrating the configuration of the laser printing apparatus.

[0148] As illustrated in FIG. 6, the laser printing apparatus 10 of the present embodiment is configured to perform surface processing treatment and image recording, using an optical fiber array in which the laser outputting portions of a plurality of optical fibers are arranged in an array formation side by side in the main scanning direction (Z axis direction) orthogonal to the sub-scanning direction (X axis direction), which is the travelling direction of the thermosensitive recording medium 100. By controlling laser light output from laser light emitting elements 41, the laser printing apparatus 10 records a visible image formed of image forming units on the thermosensitive recording medium 100 by laser printing with which the thermosensitive recording medium 100 is irradiated.

[0149] Specifically, the laser printing apparatus 10 includes a laser irradiating unit 14 formed of a laser array section 14a and an optical fiber array section 14b, and an optical unit 43. The laser array section 14a includes a plurality of laser light emitting elements 41 arranged in an array formation, a cooling unit 50 configured to cool the laser light emitting elements 41, a plurality of drivers 45 provided in correspondence with the laser light emitting elements 41 and configured to drive the corresponding laser light emitting elements 41, and a controller 46 configured to control the plurality of drivers 45. A power supply 48 configured to supply electricity to the laser light emitting elements 41 and an image information output unit 47 such as a personal computer configured to output image information are coupled to the controller 46.

Examples

[0150] The present disclosure will be described below by way of Examples. The present disclosure should not be construed as being limited to these Examples.

(Example 1)

<Production of thermosensitive recording medium>

-Preparation of printing layer forming liquid-

[0151] The components described below were added together and mixed, to prepare a printing layer forming liquid.

- Styrene-acrylic resin (obtained from Sainen Chemical Industry Co., Ltd., EK-61): 50 parts by mass
- Near infrared-transmissive black dispersion liquid (obtained from Tokushiki Co., Ltd., IRBK-0004): 50 parts by mass

-Formation of printing layer-

[0152] Using a bar coater, a printing layer having an average thickness of 4 micrometers was formed on one surface of a base material, which was a polyethylene terephthalate (PET) film (product name: E5100, with an average thickness of 50 micrometers, obtained from Toyobo Co., Ltd., with a haze of 4.5).

-Preparation of photosensitive recording layer coating liquid-

(1) Preparation of dye dispersion liquid (liquid A)

[0153] The components described below were subjected to dispersion treatment using a sand mill, to prepare a dye dispersion liquid (liquid A).

- 2-Amino-3-methyl-6-dibutyl aminofluoran: 20 parts by mass
- Ten percent by mass polyvinyl alcohol aqueous solution: 20 parts by mass
- Water: 60 parts by mass

5 (2) Preparation of developer dispersion liquid (liquid B)

[0154] The components described below were subjected to dispersion treatment using a ball mill, to prepare a liquid B.

- 4-Hydroxy-4'-isopropoxydiphenyl sulfone: 20 parts by mass
- 10 - Ten percent by mass polyvinyl alcohol aqueous solution: 20 parts by mass
- Water: 60 parts by mass

(3) Preparation of photo-thermal conversion material liquid (liquid C)

15 **[0155]** The components described below were subjected to dispersion treatment using a ball mill, to prepare a liquid C.

- Photo-thermal conversion material (indium tin oxide (ITO)): 20 parts by mass
- Polyvinyl alcohol aqueous solution (with a solid content of 10% by mass): 20 parts by mass
- Water: 60 parts by mass

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(4) Preparation of thermosensitive recording layer coating liquid

[0156] The components described below were mixed, to prepare a thermosensitive recording layer coating liquid.

- 25 - Liquid A described above: 20 parts by mass
- Liquid B described above: 40 parts by mass
- Liquid C described above: 2 parts by mass
- Polyvinyl alcohol aqueous solution (with a solid content of 10% by mass): 30 parts by mass
- Dioctyl sulfosuccinic acid aqueous solution (with a solid content of 5% by mass): 1 part by mass

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-Formation of thermosensitive recording layer-

[0157] Next, using a bar coater, the thermosensitive recording layer coating liquid was applied on the printing layer in a manner that the amount of the thermosensitive recording layer coating liquid remaining attached through drying would be 4.0 g/m², and dried, to form a thermosensitive recording layer. In the way described above, a thermosensitive recording medium of Example 1 was produced.

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(Example 2)

[0158] A thermosensitive recording medium of Example 2 was produced in the same manner as in Example 1, except that unlike in Example 1, an OPP film (obtained from Toyobo Co., Ltd., P2002) was used as the base material instead of the PET film.

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(Comparative Example 1)

[0159] A thermosensitive recording medium of Comparative Example 1 was produced in the same manner as in Example 1, except that the infrared (IR)-transmissive black in the printing layer forming liquid used in Example 1 was changed to carbon black (obtained from Mitsubishi Chemical Corporation, MITSUBISHI CARBON BLACK #52).

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[0160] Next, using a spectrophotometer, the average absorbance of the film in which only the thermosensitive recording layer was printed with respect to visible light having a wavelength of 400 nm or longer but 700 nm or shorter, the average absorbance of the film in which only the printing layer was printed with respect to the visible light having the wavelength of 400 nm or longer but 700 nm or shorter, and the average absorbance of the film alone with respect to the visible light having the wavelength of 400 nm or longer but 700 nm or shorter were measured from the obtained thermosensitive recording media of Examples 1 and 2 and Comparative Example 1. The average absorbance of the film alone with respect to the visible light was subtracted from the average absorbance of the film in which only the thermosensitive recording layer was printed with respect to the visible light, to obtain the average absorbance A2 (%) of the thermosensitive recording layer with respect to the visible light.

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[0161] The average absorbance of the film alone with respect to the visible light was subtracted from the average

absorbance of the film in which only the printing layer was printed with respect to the visible light, to obtain the average absorbance A1 (%) of the printing layer with respect to the visible light. The average absorbance B2 (%) of the thermosensitive recording layer and the average absorbance B1 (%) of the printing layer with respect to the irradiation wavelength (975 nm) of laser light during laser printing were obtained in the same manner. The results are presented in Table 1.

[0162] Next, laser printing was performed on the obtained thermosensitive recording media of Examples 1 and 2 and Comparative Example 1 in the manner described below.

<Laser printing>

[0163] Using the laser printing apparatus illustrated in FIG. 1 and FIG. 2, a solid image was printed by laser light irradiation under the printing conditions presented in Table 1.

(Example 3)

[0164] Using the thermosensitive recording medium of Example 1, laser printing was performed in the same manner as in Example 1, except that the beam diameter was changed from 125 micrometers to 60 micrometers and the pulse width was changed from 15 microseconds to 5 microseconds.

[0165] It was revealed that all of Examples 1 to 3 satisfied the following formula: $A1 > A2$ and the following formula: $A1 > B1$, and satisfied the following formula: $T1 > T2 + T4$ and the following formula $T2 + T5 > T3$ as presented in Table 1. As compared, it was revealed that Comparative Example 1 did not satisfy the following formula: $A1 > B1$ and the following formula: $T1 > T2 + T4$.

[0166] In the formulae, T1 represents the melting point (degree C) of the base material, T2 represents the temperature (degree C) of the thermosensitive recording medium before printing, T3 represents the color developing temperature (degree C) of the thermosensitive recording layer, T4 represents the amount (degree C) of temperature elevation of the printing layer during printing by irradiation with laser light, and T5 represents the amount (degree C) of temperature elevation of the thermosensitive recording layer during printing by laser light.

[0167] The melting point T1 of the base material can be determined based on the value stipulated based on the constituent material of the base material.

[0168] The temperature T2 of the thermosensitive recording medium before printing can be measured at room temperature of the room in which the printing apparatus is installed.

[0169] The color developing temperature T3 of the thermosensitive recording layer can be determined based on the material of the developer contained in the thermosensitive recording layer.

[0170] The amount of temperature elevation of the thermosensitive recording layer or the printing layer can be calculated according to the mathematical formula below.

$$\text{Amount of temperature elevation} = \frac{(\text{Laser output} \times \text{Pulse width} \times \text{Laser light absorbance})}{(\text{Beam area} \times \text{Layer thickness} \times \text{Density} \times \text{Specific heat})}$$

[0171] The laser output represents the peak power (W) of the laser light.

[0172] The pulse width represents the light emission time (s) per laser dot.

[0173] The laser light absorbance represents the average absorbance (%) of the thermosensitive recording layer or the printing layer with respect to the laser light irradiation wavelength. Absorbance per wavelength can be measured with a spectrophotometer.

[0174] The beam area represents the area of a laser beam spot on the base material, and can be measured with a beam profiler

[0175] The layer thickness represents the average thickness of the thermosensitive recording layer or the printing layer, and can be measured with a film thickness meter.

[0176] The density and the specific heat of the base material can be determined based on the values stipulated based on the constituent material of the base material. The present inventor has experimentally found that the density and the specific heat of the base material substantially conform to the density and the specific heat of the base material because the thickness of the thermosensitive recording layer and the printing layer is by far smaller than the thickness of the base material in the thermosensitive recording medium and the base material is also dominant in terms of heat capacity.

[0177] Next, "hiding power", "color developability", and "damage on printing layer and base material" were evaluated in the manners described below. The results are presented in Table 1.

<Hiding power>

[0178] The hiding power of each solid image was evaluated according to the criteria described below.

5 [Evaluation criteria]

[0179]

10 A: Good
B: Bad

<Color developability>

[0180] Color developability of each solid image was evaluated according to the criteria described below.

15 [Evaluation criteria]

[0181]

20 A: Good
B: Bad

<Damage on printing layer and base material>

25 **[0182]** Presence or absence of damage on the printing layer and the base material after laser printing was evaluated according to the criteria described below.

[Evaluation criteria]

30 **[0183]**

A: Damage was absent.
B: Damage was present.

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Table 1

		Unit	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1
40	Laser wavelength	nm	975	975	975	975
	Laser output (peak power)	W	10	10	10	10
	Beam diameter	micrometer	125	125	60	125 ₅
45	Beam area	m ²	1.23E-08	1.23E-08	2.83E-09	1.23E-08
	Pulse width	microsecond	15	15	5	15
	Density of base material	kg/m ³	1,570	950	1,570	1,570
50	Specific heat of base material	J/kgK	1,260	2,300	1,260	1,260
	Average thickness of thermosensitive recording layer	mm	0.003	0.002	0.003	0.003
	Average thickness of printing layer	mm	0.01	0.01	0.01	0.01
55	Average absorbance (B2) of thermosensitive recording layer with respect to laser irradiation wavelength	%	5	5	5	10 5

(continued)

	Unit	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1
5	Average absorbance (A2) of thermosensitive recording layer with respect to visible light	%	5	5	5
	Average absorbance (B1) of printing layer with respect to laser irradiation wavelength	%	10	10	90
10	Average absorbance (A1) of printing layer with respect to visible light	%	90	90	90
	Melting point (T1) of base material	degree C	260	130	260
	Film temperature (T2) before printing	degree C	23	23	23
15	Color developing temperature (T3)	degree C	110	110	110
	Amount (T4) of temperature elevation of printing layer	degree C	62	56	89
20	Amount (T5) of temperature elevation of thermosensitive recording layer	degree C	103	140	149
	Following formula: $A1 > A2$	A	A	A	A
	Following formula: $A1 > B1$	A	A	A	B
25	Following formula: $T1 > T2 + T4$	A	A	A	B
	Following formula: $T2 + T5 > T3$	A	A	A	A
	Hiding power	A	A	A	A
	Color develop ability	A	A	A	B
30	Damage on printing layer and base material	A	A	A	B

[0184] Aspects of the present disclosure are, for example, as follows.

35 <1> A thermosensitive recording medium, including:

a base material;
a thermosensitive recording layer; and
a printing layer,

40 wherein an average absorbance A1 (%) of the printing layer with respect to visible light having a wavelength of 400 nm or longer but 700 nm or shorter, an average absorbance A2 (%) of the thermosensitive recording layer with respect to the visible light, and an average absorbance B1 (%) of the printing layer with respect to an irradiation wavelength of laser light during printing by a laser satisfy the following formula: $A1 > A2$ and the following formula: $A1 > B1$.

45 <2> The thermosensitive recording medium according to <1>,

wherein the average absorbance of the printing layer with respect to the visible light having the wavelength of 400 nm or longer but 700 nm or shorter is 50% or higher, and
50 the average absorbance of the printing layer with respect to the irradiation wavelength of the laser light is 10% or lower.

<3> The thermosensitive recording medium according to <1> or <2>,
wherein the thermosensitive recording medium includes the thermosensitive recording layer, the printing layer, and the base material in this order in a laser light irradiating direction.

55 <4> The thermosensitive recording medium according to any one of <1> to <3>,
wherein the thermosensitive recording layer contains a coloring agent, a developer, and a photo-thermal conversion material.

<5> The thermosensitive recording medium according to any one of <1> to <4>, wherein the base material is a transparent film.

<6> The thermosensitive recording medium according to any one of <1> to <5>, wherein the printing layer contains an infrared-transmissive coloring material.

<7> The thermosensitive recording medium according to any one of <1> to <6>, further including a protective layer on the thermosensitive recording layer.

<8> A laser printing method, including

performing printing on the thermosensitive recording medium according to any one of <1> to <7> by irradiation with laser light.

<9> The laser printing method according to <8>,

wherein the printing is performed by irradiation with the laser light in a manner that a following formula: $T1 > T2 + T4$ is satisfied and a following formula: $T2 + T5 > T3$ is satisfied, where in the formulae, T1 represents a melting point (degree C) of the base material, T2 represents a temperature (degree C) of the thermosensitive recording medium before printing, T3 represents a color developing temperature (degree C) of the thermosensitive recording layer, T4 represents an amount (degree C) of temperature elevation of the printing layer during printing by irradiation with the laser light, and T5 represents an amount (degree C) of temperature elevation of the thermosensitive recording layer during printing by the laser light.

<10> The laser printing method according to <8> or <9>,

wherein a beam profile at a focal point of the laser is a top hat shape.

<11> The laser printing method according to <9> or <10>,

wherein the thermosensitive recording medium is irradiated with the laser light while the thermosensitive recording medium is set at a position different from a maximum condensing position of the laser.

<12> A laser printing apparatus, including:

the thermosensitive recording medium according to any one of <1> to <7>; and

an irradiating unit configured to irradiate the thermosensitive recording medium with laser light.

<13> The laser printing apparatus according to <12>,

wherein the laser printing apparatus is configured to perform printing by irradiation with the laser light in a manner that the following formula: $T1 > T2 + T4$ is satisfied and the following formula: $T2 + T5 > T3$ is satisfied, where in the formulae, T1 represents a melting point (degree C) of the base material, T2 represents a temperature (degree C) of the thermosensitive recording medium before printing, T3 represents a color developing temperature (degree C) of the thermosensitive recording layer, T4 represents an amount (degree C) of temperature elevation of the printing layer during printing by irradiation with the laser light, and T5 represents an amount (degree C) of temperature elevation of the thermosensitive recording layer during printing by the laser light.

[0185] The thermosensitive recording medium according to any one of <1> to <7>, the laser printing method according to any one of <8> to <11>, and the laser printing apparatus according to <12> or <13> can solve the various problems in the related art and achieve the object of the present disclosure.

Claims

1. A thermosensitive recording medium, comprising:

a base material;

a thermosensitive recording layer; and

a printing layer,

wherein an average absorbance A1 (%) of the printing layer with respect to visible light having a wavelength of 400 nm or longer but 700 nm or shorter, an average absorbance A2 (%) of the thermosensitive recording layer with respect to the visible light, and an average absorbance B1 (%) of the printing layer with respect to an irradiation wavelength of laser light during printing by a laser satisfy a following formula: $A1 > A2$ and a following formula: $A1 > B1$.

2. The thermosensitive recording medium according to claim 1,

wherein the average absorbance of the printing layer with respect to the visible light having the wavelength of 400 nm or longer but 700 nm or shorter is 50% or higher, and

the average absorbance of the printing layer with respect to the irradiation wavelength of the laser light during printing by the laser is 10% or lower.

3. The thermosensitive recording medium according to claim 1 or 2,
wherein the thermosensitive recording medium comprises the thermosensitive recording layer, the printing layer, and the base material in this order in a laser light irradiating direction.
4. The thermosensitive recording medium according to any one of claims 1 to 3,
wherein the thermosensitive recording layer contains a coloring agent, a developer, and a photo-thermal conversion material.
5. The thermosensitive recording medium according to any one of claims 1 to 4,
wherein the base material is a transparent film.
6. The thermosensitive recording medium according to any one of claims 1 to 5,
wherein the printing layer contains an infrared-transmissive coloring material.
7. The thermosensitive recording medium according to any one of claims 1 to 6, further comprising
a protective layer on the thermosensitive recording layer.
8. A laser printing method, comprising
performing printing on the thermosensitive recording medium according to any one of claims 1 to 7 by irradiation with laser light.
9. The laser printing method according to claim 8,
wherein the printing is performed by irradiation with the laser light in a manner that a following formula: $T1 > T2 + T4$ is satisfied and a following formula: $T2 + T5 > T3$ is satisfied, where in the formulae, T1 represents a melting point (degree C) of the base material, T2 represents a temperature (degree C) of the thermosensitive recording medium before printing, T3 represents a color developing temperature (degree C) of the thermosensitive recording layer, T4 represents an amount (degree C) of temperature elevation of the printing layer during printing by irradiation with the laser light, and T5 represents an amount (degree C) of temperature elevation of the thermosensitive recording layer during printing by the laser light.
10. The laser printing method according to claim 8 or 9,
wherein a beam profile of the laser light at a focal point thereof is a top hat shape.
11. The laser printing method according to claim 9 or 10,
wherein the thermosensitive recording medium is irradiated with the laser light while the thermosensitive recording medium is set at a position different from a maximum condensing position of the laser light.
12. A laser printing apparatus, comprising:

the thermosensitive recording medium according to any one of claims 1 to 7; and
an irradiating unit configured to irradiate the thermosensitive recording medium with laser light.
13. The laser printing apparatus according to claim 12,
wherein the laser printing apparatus is configured to perform printing by irradiation with the laser light in a manner that a following formula: $T1 > T2 + T4$ is satisfied and a following formula: $T2 + T5 > T3$ is satisfied, where in the formulae, T1 represents a melting point (degree C) of the base material, T2 represents a temperature (degree C) of the thermosensitive recording medium before printing, T3 represents a color developing temperature (degree C) of the thermosensitive recording layer, T4 represents an amount (degree C) of temperature elevation of the printing layer during printing by irradiation with the laser light, and T5 represents an amount (degree C) of temperature elevation of the thermosensitive recording layer during printing by the laser light.

FIG. 1

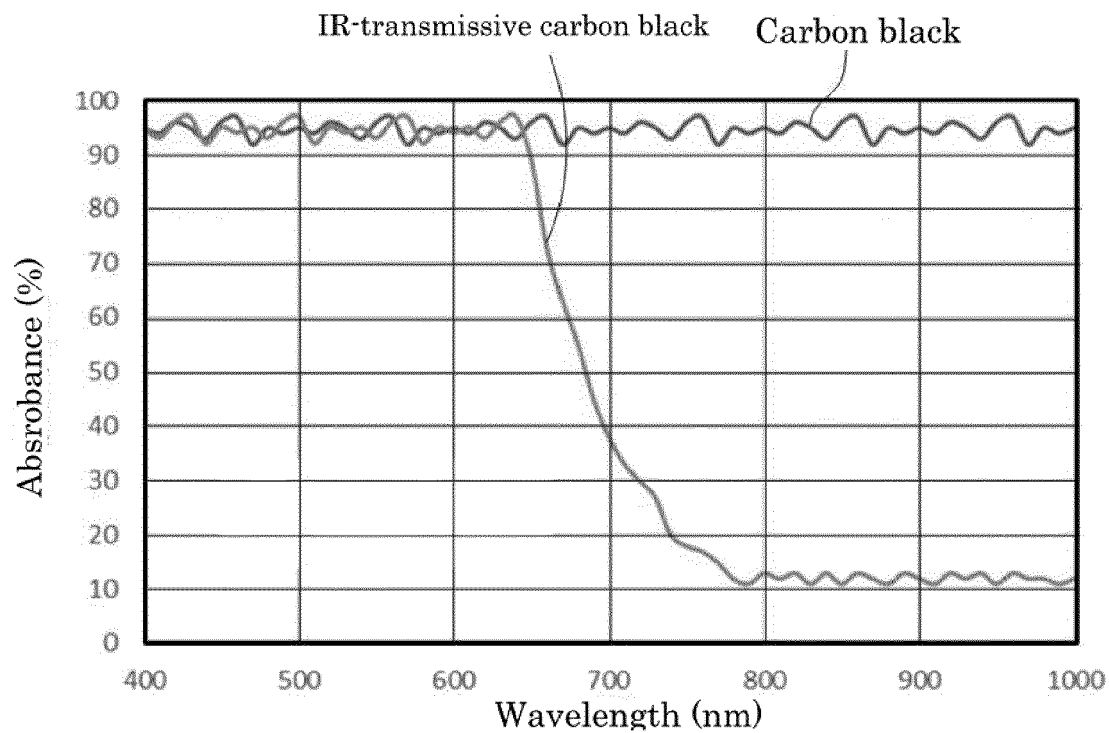


FIG. 2

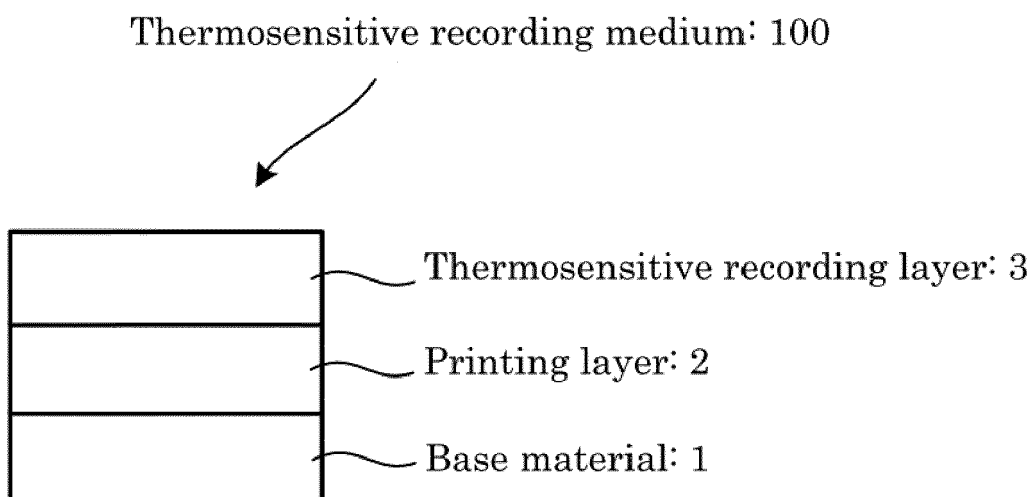


FIG. 3

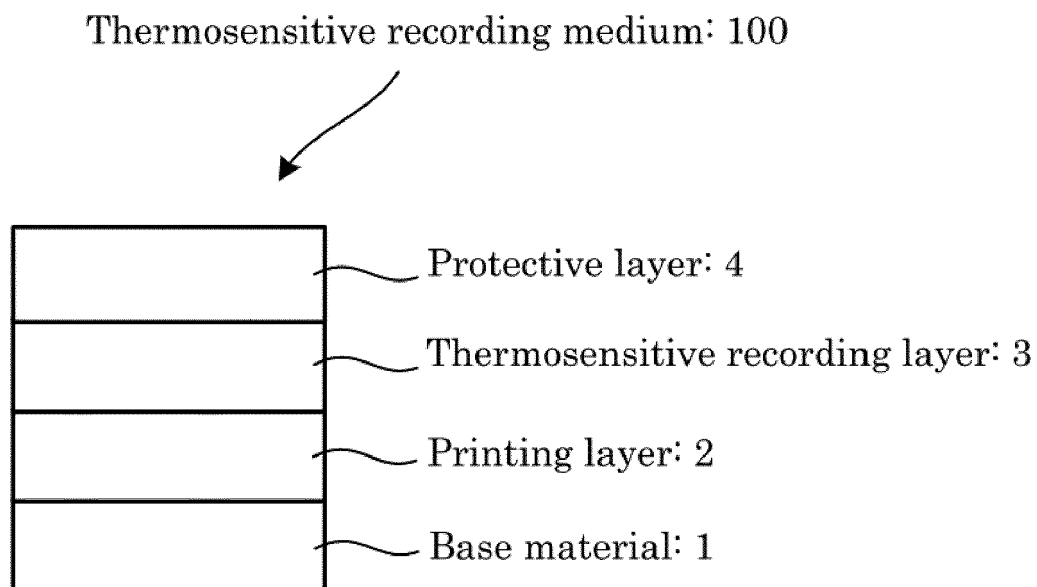


FIG. 4

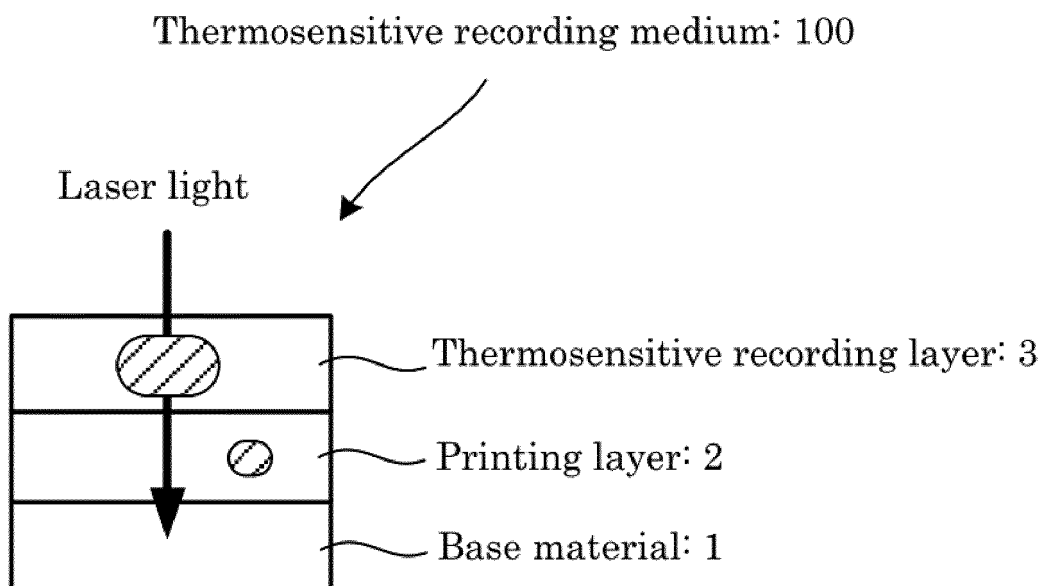


FIG. 5

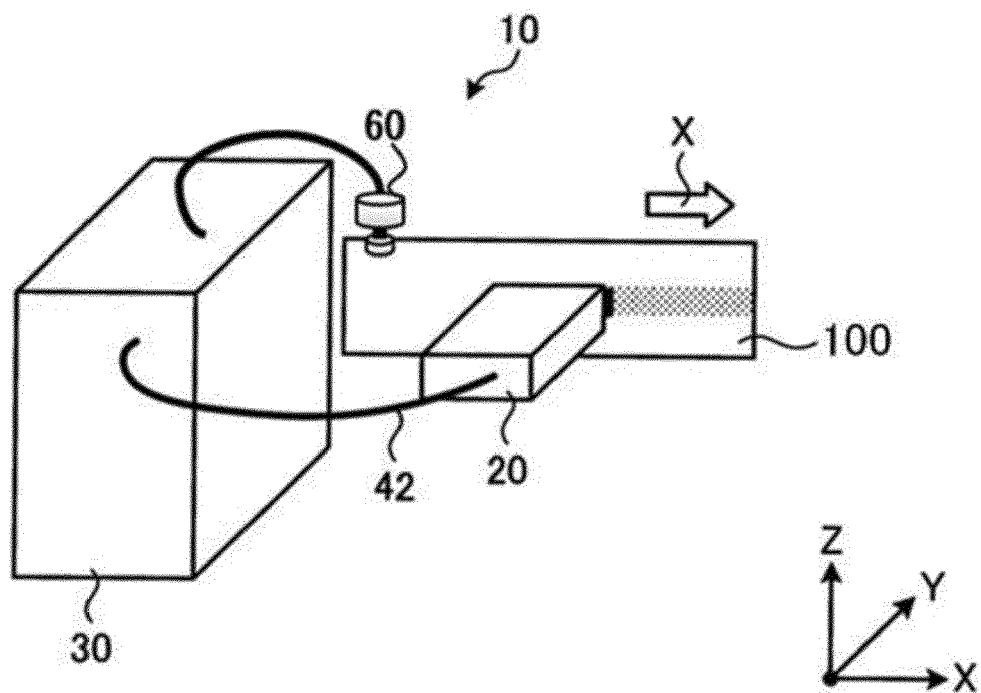
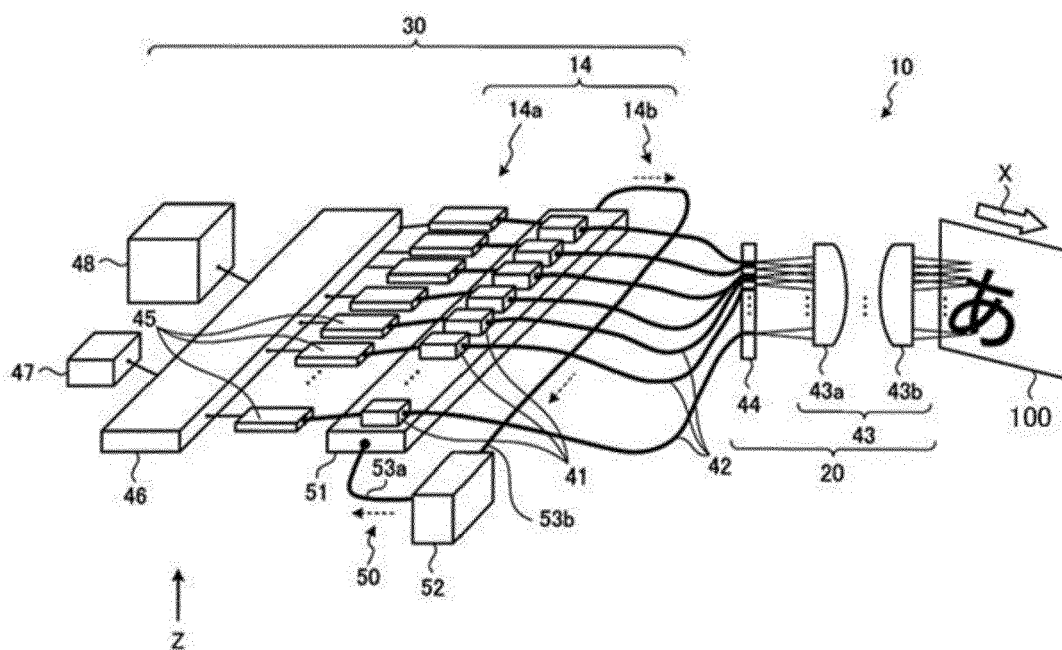


FIG. 6





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Application Number

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