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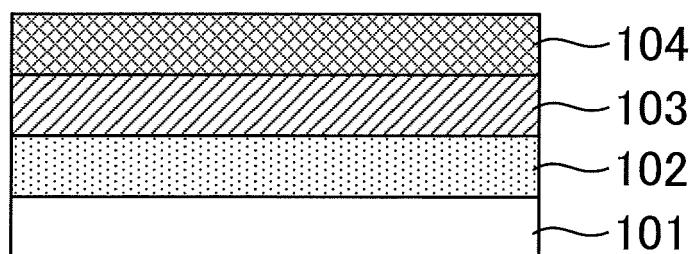
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(54) **Thermosensitive recording medium and image processing method**

(57) A thermosensitive recording medium, including:  
a support (101); an image recording layer (102), which  
is provided on the support, and contains a leuco dye, a  
color developer, and a metal oxide having absorbance  
in the near infrared region; an oxygen barrier layer (104);  
and a light-blocking layer (103), wherein the oxygen bar-  
rier layer (104) and the light-blocking layer (103) are pro-  
vided on the surface of the image recording layer, which

is on the opposite side to the surface thereof where the  
support is provided, and wherein an average transmit-  
tance of the light-blocking layer (103) to light in a wave-  
length range of 300 nm to 400 nm is 5% or less, and an  
average transmittance of the light-blocking layer (103) to  
light in a wavelength range of 380 nm to 495 nm is 20%  
or less.

**FIG. 1A**



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**Description**

## BACKGROUND OF THE INVENTION

## 5 Field of the Invention

**[0001]** The present invention relates to a thermosensitive recording medium and an image processing method, which can be suitably used for write-only image recording, as well as repetitive image recording and image erasing.

## 10 Description of the Related Art

**[0002]** As for a thermosensitive recording medium, there are a thermosensitive recording medium, to which write-only image recording is performed, and a thermosensitive recording medium, to which image recording and image erasing can be repeatedly performed.

15 **[0003]** The thermoreversible recording medium has been recently used at a delivery and physical distribution center (see, for example, Japanese Patent Application Laid-Open (JP-A) No. 2000-136022 and Japanese Patent (JP-B) No. 3998193).

**[0004]** Proposed is a thermoreversible recording medium, in which laser light is used for recording the thermoreversible recording medium, and particles of metal boride or metal oxide or both are used as a photothermal converting material (see JP-A No. 2011-194883). Among these photothermal converting materials, a tungsten oxide compound has relatively low absorbance in the visible range, and a larger amount thereof can be added compared to other metal boride or metal oxide. Therefore, use of the tungsten oxide compound can improve image recording sensitivity and image erasing sensitivity.

25 **[0005]** However, the tungsten oxide compound has a problem that a color thereof is turned into blue, as the tungsten oxide compound is irradiated with light, such as sun light, for a long period (see JP-A No. 2008-208274). It is considered that, as the tungsten oxide compound is irradiated with light, such as sun light, for a long period, radicals generated by irradiation of ultraviolet rays reduces tungsten atoms in the tungsten oxide compound to generate pentavalent tungsten that has a color. However, the color of the tungsten oxide compound tends to be returned back to the original as it is left to stand in the dark for a certain period, and the absorbance in the near infrared region is also returned back to the original (see JP-A No. 2013-173642). The reason for this is considered that the pentavalent tungsten is oxidized with oxygen to return to hexavalent tungsten.

30 **[0006]** As a result of the study conducted by the present inventors to confirm the aforementioned matter, it has been found that the tungsten oxide compound increases not only the absorbance in the visible region, but also the absorbance in the near infrared region, as it is irradiated with light, such as sun light for a long period. If the absorbance in the infrared region increases, the absorbance of laser light increases when laser light is used for recording an image on a thermosensitive recording medium. Therefore, the thermosensitive recording medium is excessively heated, to thereby cause a problem that a width of writing line is widened to lower readability of a resulting bar code. In the case where laser light is used for recording a thermoreversible recording medium, moreover, the thermoreversible recording medium is excessively heated as image recording is repeated, which may cause a problem that unerased portions are remained due to the deterioration to thereby lower resistance to repetitive use.

35 **[0007]** To solve the aforementioned problems, various proposals are disclosed, for example, in JP-A No. 2006-282736, International Patent Publication No. WO/2010/101211, and JP-A Nos. 2010-99979 and 2010-274585. Any of these proposals have some effect of suppressing coloring of the tungsten oxide compound, but the effect thereof is not sufficient.

40 **[0008]** Moreover, an image recording layer of a thermosensitive recording medium contains a leuco dye. The leuco dye however does not have sufficient resistance to light, and it is necessary to block not only ultraviolet rays but also oxygen to prevent deterioration of the leuco dye due to light (see JP-A No. 2010-195035). If oxygen is blocked, however, oxygen is not supplied into a thermosensitive recording medium using a tungsten oxide compound as a photothermal converting material so that pentavalent tungsten tends not to be oxidized, and therefore a color of the tungsten oxide compound, and the increased absorbance in the near infrared region tend not to be returned to the original states. For example, in the state where oxygen is sufficiently blocked by sandwiching a layer containing the tungsten oxide compound with two oxygen barrier layers, there is a problem that the color of the tungsten oxide compound and the increased absorbance in the near infrared region are hardly returned to the original states even after a few weeks. This problem occurs not only with the tungsten oxide compound, but also with other metal oxides having absorbance in the near infrared region, such as indium-doped tin oxide.

55 **[0009]** Accordingly, there is a need for a thermosensitive recording medium, which uses metal oxide particles as a photothermal converting material, has excellent image recording sensitivity and image erasing sensitivity, does not change its image recording sensitivity and image erasing sensitivity over time even when it is left outside, and irradiated with light, such as sun light, for a long period, and does not leave unerased portions after repetitive use.

## SUMMARY OF THE INVENTION

**[0010]** The present invention aims to provide a thermosensitive recording medium, which has excellent image recording sensitivity, and image erasing sensitivity, does not change the image recording sensitivity and image erasing sensitivity with time even when left to stand outdoor, and irradiated with light, such as sun light, for a long period, and does not cause an erasion failure due to repetitive use.

**[0011]** The thermosensitive recording medium of the present invention, as the means for solving the aforementioned problems, contains:

a support;  
 an image recording layer, which is provided on the support, and contains a leuco dye, a color developer, and a metal oxide having absorbance in the near infrared region;  
 an oxygen barrier layer; and  
 a light-blocking layer,  
 wherein the oxygen barrier layer and the light-blocking layer are provided a surface of the image recording layer, which is an opposite side to a surface thereof where the support is provide, and  
 wherein an average transmittance of the light-blocking layer to light in a wavelength range of 300 nm to 400 nm is 5% or less, and an average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 20% or less.

**[0012]** The present invention can solve the aforementioned various problems in the art, achieve the aforementioned object, and provide a thermosensitive recording medium, which has excellent image recording sensitivity, and image erasing sensitivity, does not change the image recording sensitivity and image erasing sensitivity with time even when left to stand outdoor, and irradiated with light, such as sun light, for a long period, and does not cause an erasion failure due to repetitive use.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0013]**

FIG. 1A is a schematic diagram illustrating one example of a layer structure of the thermosensitive recording medium.  
 FIG. 1B is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 2A is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 2B is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 2C is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 2D is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 2E is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 3A is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 3B is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 3C is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 3D is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 3E is a schematic diagram illustrating another example of a layer structure of the thermosensitive recording medium.  
 FIG. 4A is a graph depicting coloring-erasing properties of the thermoreversible recording medium.  
 FIG. 4B is a schematic diagram explaining a mechanism of coloring-erasing changes of the thermoreversible recording medium.  
 FIG. 5 is a diagram explaining one example of an image processing device for use in the image processing method of the present invention.

FIG. 6 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Examples 1, 2, 3, and 9, and Comparative Example 9.

FIG. 7 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Example 4.

FIG. 8 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Examples 5, 6, 7, and 8.

FIG. 9 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Examples 10, 11, 12, 13, and 14.

FIG. 10 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Example 15.

FIG. 11 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Comparative Examples 1, 2, 3, 4, and 5.

FIG. 12 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Comparative Example 6.

FIG. 13 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Comparative Example 7.

FIG. 14 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Comparative Example 8.

FIG. 15 is a graph depicting relationship between a wavelength and a transmittance of the light-blocking layer of Comparative Example 10.

## DETAILED DESCRIPTION OF THE INVENTION

### (Thermosensitive Recording Medium)

**[0014]** In the first embodiment, the thermosensitive recording medium of the present invention contains: a support; an image recording layer, which is provided on the support, and contains a leuco dye, a color developer, and a metal oxide having absorbance in the near infrared region; an oxygen barrier layer; and a light-blocking layer, where the oxygen barrier layer and the light-blocking layer are provided a surface of the image recording layer, which is an opposite side to a surface thereof where the support is provide, and where an average transmittance of the light-blocking layer to light in a wavelength range of 300 nm to 400 nm is 5% or less, and an average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 20% or less. The thermosensitive recording medium may further contain other layers, as necessary. Each of these layers may have a single-layer structure, or a laminate structure. Moreover, these layers may be provided on the other surface of the support.

**[0015]** In the second embodiment, the thermosensitive recording medium of the present invention contains: a support; an image recording layer containing a leuco dye and a color developer; a photothermal conversion layer containing a metal oxide having absorbance in the near infrared region; an oxygen barrier layer; and a light-blocking layer, where the image recording layer and the photothermal conversion layer are provided on the support, and the oxygen barrier layer and the light-blocking layer are provided on a surface of the image recording layer or the photothermal conversion layer, which is an opposite side to a surface thereof where the support is provided, and

**[0016]** wherein an average transmittance of the light-blocking layer to light in a wavelength range of 300 nm to 400 nm is 5% or less, and an average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 20% or less. The thermosensitive recording medium may further contain other layers, as necessary. Each of these layers may have a single-layer structure, or a laminate structure. Moreover, these layers may be provided on the other surface of the support.

**[0017]** The thermosensitive recording media of the first embodiment and the second embodiment of the present invention can be used for both an embodiment where a thermosensitive recording layer, to which write-only image recording is performed once, is provided as an image recording layer, and an embodiment where a thermoreversible recording layer, to which image recording and image erasing are repeatedly performed, is provided as an image recording layer. It is however particularly preferred that the thermosensitive recording medium is a thermoreversible recording medium, which can be used by repeatedly performing image recording and image erasing, as it can be used repeatedly.

### <Image Recording Layer>

**[0018]** In the first embodiment the image recording layer contains a leuco dye, a color developer, and a metal oxide having absorbance in the near infrared region, and may further contain other components, if necessary.

**[0019]** In the second embodiment, the image recording layer contains a leuco dye, and a color developer, and may further contain other components, as necessary.

**[0020]** In the case where recording is performed only once, the image recording layer is a thermosensitive recording layer. In the case where image recording and image erasing are repeatedly performed, the image recording layer is a thermoreversible recording layer. The thermosensitive recording layer and the thermoreversible recording layer are separately explained, hereinafter.

#### «Thermosensitive Recording Layer»

**[0021]** The thermosensitive recording layer contains at least a leuco dye, a color developer, and a binder resin, and may further contain other components, as necessary.

**[0022]** In the case where the thermosensitive recording layer contains the metal oxide having absorbance in the near infrared region as in the first embodiment, an amount of the metal oxide is preferably 0.005 g/m<sup>2</sup> to 20 g/m<sup>2</sup>, more preferably 0.01 g/m<sup>2</sup> to 10 g/m<sup>2</sup>.

#### -Metal Oxide Having Absorbance in Near Infrared Region-

**[0023]** Examples of the metal oxide having absorbance in the near infrared region include a metal oxide having absorbance in the near infrared region, which is a wavelength region of 700 nm to 2,000 nm.

**[0024]** For example, the metal oxide is preferably at least one selected from the group consisting of a tungsten oxide compound, indium-doped tin oxide, and antimony-doped tin oxide. The aforementioned metal oxide having absorbance in the near infrared region has high resistance to heat, unlike an organic dye, such as phthalocyanine. Moreover, the metal oxide does not have an interaction with a leuco dye, when the metal oxide is mixed with the leuco dye, and the absorbance thereof in the near infrared region does not decrease when the metal oxide is irradiated with laser light repeatedly. Therefore, use of the metal oxide gives an advantage that a highly durable thermosensitive recording medium can be attained.

**[0025]** Among the tungsten oxide compound, the indium-doped tin oxide, and the antimony-doped tin oxide, the tungsten oxide compound and the indium-doped tin oxide are preferable, as they have low absorbance in the visible range, and the tungsten oxide compound is more preferable.

**[0026]** Examples of the tungsten oxide compound include composite tungsten oxide particles represented by the general formula: WyOz (where W is tungsten, O is oxygen, and  $2.2 \leq z/y \leq 2.999$ ), and tungsten oxide particles represented by the general formula: MxWyOz (where M is at least one element selected from the group consisting of H, He, an alkali metal, an alkaline earth metal, a rare earth element, 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 is tungsten, O is oxygen,  $0.001 \leq x/y \leq 1$ , and  $2.2 \leq z/y \leq 3.0$ ), as disclosed in International Patent Publication No. WO/2005/037932, and JP-A No. 2005-187323.

**[0027]** Among them, cesium-containing tungsten oxide is particularly preferable, as it has large absorbance in the near infrared region, and small absorbance in the visible region.

**[0028]** Since the metal oxide having absorbance in the near infrared has absorbance in the near infrared region, which is a wavelength range of 700 nm to 2,000 nm, excellent recording sensitivity can be attained by setting a wavelength of laser light sued for recording and erasing of an image to the aforementioned wavelength range.

**[0029]** The average particle diameter of the metal oxide having absorbance in the near infrared region is preferably 800 nm or smaller to reduce absorbance in the visible region, and is preferably 200 nm or smaller to reduce scattering due to the particles. The lower limit of the average particle diameter is preferably 1 nm or greater.

**[0030]** The average particle diameter can be measured, for example, by a laser diffraction/scattering particle size distribution analyzer.

**[0031]** An amount of the metal oxide having absorbance in the near infrared region varies depending on a type of the metal oxide for use, and cannot be collectively determined. However, the amount thereof is preferably 0.005 g/m<sup>2</sup> to 20 g/m<sup>2</sup>, more preferably 0.01 g/m<sup>2</sup> to 10 g/m<sup>2</sup>, relative to a layer containing the metal oxide. When the amount thereof is less than 0.005 g/m<sup>2</sup>, sufficient recording sensitivity may not be attained. When the amount thereof is greater than 20 g/m<sup>2</sup>, a degree of tint on the background increases as the metal oxide has slight absorbance in the visible region, which reducing contrast of an image.

**[0032]** Note that, whether or not the metal oxide having absorbance in the near infrared region is present can be judged by measuring absorbance properties in the near infrared region by means of a spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation), as all of the metal oxides having the absorbance in the near infrared region have unique absorbance properties.

#### -Leuco Dye-

**[0033]** The leuco dye is appropriately selected from leuco dyes typically used for thermosensitive recording materials,

without any limitation. As for the leuco dye, for example, a leuco compound, such as a triphenylmethane-based dye, a fluoran-based dye, a phenothiazine-based dye, an auramine-based dye, a spiropyran-based dye, an indolinophthalide-based dye, is preferably used.

**[0034]** Examples of the leuco dye include 2-anilino-3-methyl-6-dibutylaminofluoran, 3,3-bis(p-dimethylaminophenyl)-phthalide, 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide (another name: Crystal Violet Lactone), 3,3-bis(p-dimethylaminophenyl)-6-diethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)-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-diethylaminofluoran, 2-{3,6-bis(diethylamino)-9-(o-chloroanilino)xanthylbenzoic acid lactam}, 3-diethylamino-6-methyl-7-(m-trichloromethylanilino)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-( $\alpha$ -phenylethylamino)fluoran, 3-(N-ethyl-p-toluidino)-7-( $\alpha$ -phenylethylamino)fluoran, 3-diethylamino-7-(o-methoxycarbonylphenylamino)fluoran, 3-diethylamino-5-methyl-7-( $\alpha$ -phenylethylamino)fluoran, 3-diethylamino-7-piperidinofluoran, 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- $\alpha$ -naphthylamino-4'-bromofluoran, 3-diethylamino-6-chloro-7-anilino-fluoran, 3-diethylamino-6-methyl-7-cimetidino-4',5'-benzfluoran, 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-( $\alpha$ -phenylethylamino)fluoran, 3-(N-ethyl-p-toluidino)-7-( $\alpha$ -phenylethylamino)fluoran, 3-diethylamino-7-(o-methoxycarbonylphenylamino)fluoran, 3-diethylamino-5-methyl-7-( $\alpha$ -phenylethylamino)fluoran, 3-diethylamino-7-piperidinofluoran, 2-chloro-3-(N-methyltoluidino)-7-(p-N-butylanilino)fluoran, 3,6-bis(dimethylamino)fluorenespiro(9,3')-6'-dimethylaminophthalide, 3-(N-benzyl-N-cyclohexylamino)-5,6-benzo-7- $\alpha$ -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-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-dibromophthalide, bis(p-dimethylaminostyryl)-1-naphthalenesulfonylmethane, and bis(p-dimethylaminostyryl)-1-p-trisulfonylmethane. These may be used alone, or in combination.

-Color Developer-

**[0035]** As for the color developer, various electron-accepting compounds or oxidizing agents, which colors the leuco dye when they are in contact with the leuco dye, are suitably used.

**[0036]** The color developer is appropriately selected from those known in the art depending on the intended purpose without any limitation. Examples thereof include 4,4'-isopropylidenebisphenol, 4,4'-isopropylidenebis(o-methylphenol), 4,4'-sec-butylidenebisphenol, 4,4'-isopropylidenebis(2-tert-butylphenol), zinc p-nitrobenzoate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,2-(3,4'-dihydroxydiphenyl)propane, bis(4-hydroxy-3-methylphenyl)sulfide, 4-{ $\beta$ -(p-methoxyphenoxy)ethoxy}salicylic acid, 1,7-bis(4-hydroxyphenylthio)-3,5-dioxahexane, 1,5-bis(4-hydroxyphenylthio)-5-oxahexane, monocalcium salt of monobenzyl phthalate, 4,4'-cyclohexylidene diphenol, 4,4'-isopropylidenebis(2-chlorophenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(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), 4,4'-diphenolsulfone, 4-isopropoxy-4'-hydroxydiphenylsulfone(4-hydroxy-4'-iso-

propoxydiphenylsulfone), 4-benzyloxy-4'-hydroxydiphenylsulfone, 4,4'-diphenolsulfoxide, isopropyl p-hydroxybenzoate, benzyl p-hydroxybenzoate, benzyl protocatechuate, stearyl gallate, lauryl gallate, octyl gallate, 1,3-bis(4-hydroxyphenylthio)-propane, N,N'-diphenylthiourea, 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,  $\alpha,\alpha$ -bis(4-hydroxyphenyl)- $\alpha$ -methyltoluene, an antipyrine complex of zinc thiocyanate, tetrabromobisphenol A, tetrabromobisphenol S, 4,4'-thiobis(2-methylphenol), 4,4'-thiobis(2-chlorophenol), dodecylphosphonic acid, tetradecylphosphonic acid, hexadecylphosphonic acid, octadecylphosphonic acid, eicosylphosphonic acid, docosylphosphonic acid, tetracosylphosphonic acid, hexacosylphosphonic acid, octacosylphosphonic acid,  $\alpha$ -hydroxydodecylphosphonic acid,  $\alpha$ -hydroxytetradecylphosphonic acid,  $\alpha$ -hydroxyhexadecylphosphonic acid,  $\alpha$ -hydroxyoctadecylphosphonic acid,  $\alpha$ -hydroxyeicosylphosphonic acid,  $\alpha$ -hydroxydocosylphosphonic acid,  $\alpha$ -hydroxytetracosylphosphonic acid, dihexadecyl phosphate, dioctadecyl phosphate, dieicosyl phosphate, didocosyl phosphate, monohexadecyl phosphate, monooctadecyl phosphate, monoicosyl phosphate, monodocosyl phosphate, methylhexadecyl phosphate, methyloctadecyl phosphate, methyleicosyl phosphate, methyl docosyl phosphate, amylhexadecyl phosphate, octyl hexadecyl phosphate, and lauryl hexadecyl phosphate. These may be used alone, or in combination.

**[0037]** An amount of the color developer is preferably 1 part by mass to 20 parts by mass, more preferably 2 parts by mass to 10 parts by mass, relative to 1 part by mass of the leuco dye.

-Binder Resin-

**[0038]** The binder resin is appropriately selected from binder resins known in the art depending on the intended purpose without any limitation. Examples of the binder resin include: a water-soluble polymer, such as polyvinyl alcohol, starch or a derivative thereof, a cellulose derivative (e.g., methoxy cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, methyl cellulose, and ethyl cellulose), sodium polyacrylate, polyvinylpyrrolidone, an acrylamide/acrylate copolymer, an acrylamide/acrylate/methacrylic acid tercopolymer, an alkali salt of a styrene/maleic anhydride copolymer, an alkali salt of an isobutylene-maleic anhydride copolymer, polyacrylamide, sodium alginate, gelatin, and casein; an emulsion, such as polyvinyl acetate, polyurethane, polyacrylic acid, polyacrylate, polymethacrylate, polybutyl methacrylate, a vinyl chloride-vinyl acetate copolymer, and an ethylene-vinyl acetate copolymer; latex, such as a styrene-butadiene copolymer, and a styrene-butadiene/acryl-based copolymer; polyethylene; polyvinyl acetate; polyacrylic amide; a maleic acid copolymer; polyacrylate; polymethacrylate; a vinyl chloride/vinyl acetate copolymer; styrene copolymer; polyester; polyurethane; polyvinyl butyral; ethyl cellulose; polyvinyl acetal; polyvinyl acetoacetal; polycarbonate; an epoxy resin; and polyamide. These may be used alone, or in combination.

**[0039]** In the thermosensitive recording layer, various thermoplastic materials can be used as a sensitivity improving agent.

**[0040]** Examples of the thermoplastic material include fatty acid, fatty acid amide, fatty acid metal salt, p-benzylbiphenyl, terphenyl, triphenylmethane, benzyl p-benzyloxybenzoate, B-benzyloxynaphthalene, phenyl  $\beta$ -naphthoate, phenyl 1-hydroxy-2-naphthoate, methyl 1-hydroxy-2-naphthoate, diphenyl carbonate, dibenzyl terephthalate, dimethyl terephthalate, 1,4-dimethoxynaphthalene, 1,4-diethoxynaphthalene, 1,4-dibenzyloxynaphthalene, 1,2-bis(phenoxy)ethane, 1,2-bis(3-methylphenoxy)ethane, 1,2-bis(4-methylphenoxy)ethane, 1,4-bis(phenoxy)butane, 1,4-bis(phenoxy)-2-butene, 1,2-bis(4-methoxyphenylthio)ethane, dibenzoylmethane, 1,4-bis(phenylthio)butane, 1,4-bis(phenylthio)-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-aryloxybiphenyl, p-propargyloxybiphenyl, dibenzoyloxymethane, 1,3-dibenzoyloxypropane, dibenzyl disulfide, 1,1-diphenyl ethanol, 1,1-diphenyl propanol, p-(benzyloxy)benzyl alcohol, 1,3-diphenoxy-2-propanol, N-octadecylcarbamoyl-p-methoxycarbonylbenzene, N-octadecylcarbamoylbenzene, dibenzyl oxalate, and 1,5-bis(p-methoxyphenyloxy)-3-oxapentane. These may be used alone, or in combination.

**[0041]** An antioxidant or photostabilizer is preferably added to the thermosensitive recording layer for the purpose of suppressing absorbance increase of the metal oxide in the infrared region due to light irradiation.

**[0042]** The antioxidant or photostabilizer is appropriately selected depending on the intended purpose without any limitation. Examples thereof include a phenol-based compound, a hindered phenol-based compound, an amine-based compound, a hindered amine-based compound, an amide-based compound, a sulfur-based compound, a thioether-based compound, a phosphorus-based compound, and a lactone-based compound. Among them, a hindered phenol-based compound is preferable, as it has a large effect to the tungsten oxide compound.

**[0043]** Examples of the hindered phenol-based compound include pentaerythritol-tetrakis(3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate), thiodiethylene-bis(3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate), octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene, N,N'-hexan-1,6-diyl-bis(3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionamide), diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl) phosphate, 3,3',3'',5,5',5''-hexa-*t*-butyl-*a,a',a''*-(mesitylene-2,4,6-triyl)tri-*p*-cresol, ethylenebis(oxyethylene)bis(3-(5-*t*-butyl-4-

hydroxy-m-triyl)propionate), hexamethylene-bis(3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate), 1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tris((4-t-butyl-3-hydroxy-2,6-xylyl)methyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, 2,6-di-t-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino)phenol, and 3,9-bis(2-(3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane. These may be used

alone, or in combination.

**[0044]** An amount of the antioxidant or photostabilizer cannot be collectively determined, as it varies depending on a type of the metal oxide for use, but the amount thereof is preferably 0.1 parts by mass to 100 parts by mass, more preferably 1 part by mass to 50 parts by mass relative to 100 parts by mass of the metal oxide. When the amount thereof is less than 0.1 parts by mass, an effect of suppressing absorbance increase may not be attained. When the amount thereof is greater than 100 parts by mass, the thermal strength of the thermosensitive recording layer may be low, or the adhesion to another layer may be reduced.

**[0045]** To the thermosensitive recording medium, various additives, such as a surfactant, a lubricant, and filler, may be used in combination, as necessary. Examples of the lubricant include higher fatty acid or a metal salt thereof, higher fatty acid amide, higher fatty acid ester, animal wax, vegetable wax, mineral wax, and petroleum wax.

**[0046]** Examples of the filler include: inorganic powder, such as calcium carbonate, silica, zinc oxide, titanium oxide, aluminium hydroxide, zinc hydroxide, barium sulfate, clay, kaolin, talc, surface-treated calcium, and surface-treated silica; and organic powder, such as a urea-formaldehyde resin, a styrene/methacrylic acid copolymer, a polystyrene resin, and a vinylidene chloride resin.

**[0047]** The thermosensitive recording layer can be formed by a method generally known in the art without any limitation. For example, the thermosensitive recording layer can be formed by grinding and dispersing a leuco dye, and a color developer separately with a binder resin and other components by means of a disperser, such as a ball mill, Attritor, and a sand mill until the dispersed particle diameter thereof becomes 0.1  $\mu\text{m}$  to 3  $\mu\text{m}$ , blending the resultants with optional filler and/or a lubricant according to the predetermined formulation to thereby prepare a thermosensitive recording layer coating liquid, and applying the thermosensitive recording layer coating liquid onto a support.

**[0048]** The average thickness of the thermosensitive recording layer is appropriately selected depending on the intended purpose without any limitation, but the average thickness thereof is preferably 1  $\mu\text{m}$  to 20  $\mu\text{m}$ , more preferably 3  $\mu\text{m}$  to 15  $\mu\text{m}$ .

#### «Thermoreversible Recording Layer»

**[0049]** The thermoreversible recording layer contains at least a leuco dye, a reversible color developer, and a binder resin, and may further contain other components, as necessary.

#### -Metal Oxide Having Absorbance in Near Infrared Region-

**[0050]** In the case where the thermoreversible recording layer contains the metal oxide having absorbance in the near infrared region as in the first embodiment, an amount of the metal oxide is preferably 0.005 g/m<sup>2</sup> to 20 g/m<sup>2</sup>, more preferably 0.01 g/m<sup>2</sup> to 10 g/m<sup>2</sup>.

#### -Leuco Dye-

**[0051]** The leuco dye is appropriately selected from those known in the art without any limitation. For example, those usable for the thermosensitive recording layer can be used.

#### -Reversible Color Developer-

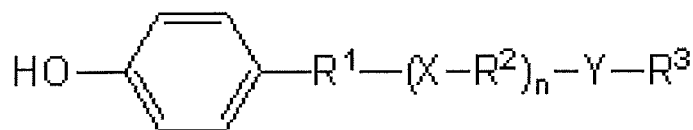
**[0052]** The reversible color developer is appropriately selected depending on the intended purpose without any limitation, provided that it is capable of reversibly coloring and erasing using heat as a factor. Preferred examples thereof include (1) a structure having an ability of coloring the leuco dye (e.g., a phenolic hydroxyl group, a carboxylic acid group, and a phosphoric acid group), or (2) a structure for controlling aggregation force between molecules (e.g., a structure linked with a long-chain hydrocarbon group), or both in a molecule thereof. Note that, the linking part may contain a bivalent or higher linking group containing a hetero atom, and the long-chain hydrocarbon group may contain the same linking group, or an aromatic group, or both.

**[0053]** As for the (1) structure having an ability of coloring the leuco dye, phenol is particularly preferable.

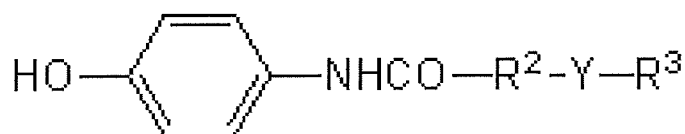
**[0054]** As for the (2) structure for controlling aggregation force between molecules, a C8 or higher long-chain hydrocarbon group is preferable, a C11 or higher long-chain hydrocarbon group is more preferable. Moreover, the upper limit of the number of carbon atoms is preferably 40 or less, more preferably 30 or less.

**[0055]** Among the aforementioned reversible color developers, a phenol compound represented by the following

general formula (1) is preferable, and a phenol compound represented by the following general formula (2) is more preferable.



General Formula (1)



General Formula (2)

**[0056]** In the general formulae (1) and (2) above,  $\text{R}^1$  is a single bond or C1-C24 aliphatic hydrocarbon group;  $\text{R}^2$  is a C2 or higher aliphatic hydrocarbon group that may have a substituent, in which a number of the carbon atoms is preferably 5 or greater, more preferably 10 or greater; and  $\text{R}^3$  is a C1 to C35 aliphatic hydrocarbon group, the number of carbon atoms of which is preferably 6 to 35, and more preferably 8 to 35. These aliphatic hydrocarbon groups may be used alone, or in combination.

**[0057]** A total number of carbon atoms in  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  is appropriately selected depending on the intended purpose without any limitation, but the lower limit thereof is preferably 8 or greater, more preferably 11 or greater, and the upper limit thereof is preferably 40 or less, more preferably 35 or less. When the total number of the carbon atoms is less than 8, the stability of coloring and erasing ability may be low. The aliphatic hydrocarbon group may be a straight-chain aliphatic hydrocarbon group, or a branched-chain aliphatic hydrocarbon group, and may contain an unsaturated bond. However, the aliphatic hydrocarbon group is preferably a straight-chain aliphatic hydrocarbon group. Moreover, examples of a substituent bonded to the hydrocarbon group include a hydroxyl group, a halogen atom, and an alkoxy group. X and Y may be identical or different, and each represents a bivalent group containing an N atom or an O atom. Specific examples thereof include an oxygen atom, an amide group, a urea group, a diacylhydrazine group, an oxalic acid diamide group, and an acyl urea group. Among them, an amide group, and a urea group are preferable. In the general formulae (1) and (2), n is an integer of 0 to 1.

**[0058]** The reversible color developer is preferably used in combination with a compound containing a -NHCO- group, or a -OCONH- group, or both in a molecule thereof as an erasing accelerator, as an intermolecular interaction is induced between the erasing accelerator and the color developer in the process of forming an erased state to thereby improve coloring and erasing properties. The erasing accelerator is appropriately selected depending on the intended purpose without any limitation.

**[0059]** To the thermoreversible recording layer, a binder resin, and optionally various additives for improving or controlling coating properties of the thermoreversible recording layer or coloring and erasing properties can be added. Examples of the additives include a surfactant, a conducting agent, filler, an antioxidant, a photostabilizer, a coloring stabilizer, and a photothermal conversion agent.

-Binder Resin-

**[0060]** The binder resin is appropriately selected depending on the intended purpose without any limitation, provided that it can bind the thermoreversible recording layer on the support. One, or two or more selected from resins known in the art can be used alone or in combination, as the binder resin. Among them, a resin curable by heat, UV rays, or electron beams is preferable in view of an improvement in durability for repetitive use, and a thermoset resin using an isocyanate-based compound as a crosslinking agent is particularly preferable. Examples of the binder resin include a resin containing a group reactable with a crosslinking agent, such as a hydroxyl group and a carboxyl group, and a resin obtained by copolymerizing a monomer containing a hydroxyl group or a carboxyl group with another monomer.

**[0061]** Examples of the resin include a phenoxy resin, a polyvinyl butyral resin, a cellulose acetate propionate resin, a cellulose acetate butylate resin, an acryl polyol resin, a polyester polyol resin, and a polyurethane polyol resin. Among them, particularly preferred are an acryl polyol resin, a polyester polyol resin, and a polyurethane polyol resin.

**[0062]** As for the blending ratio (mass ratio) of the binder resin to the leuco dye in the thermoreversible recording layer,

the ratio of the binder resin is preferably 0.1 to 10, relative to the leuco dye (1). When the ratio of the binder resin is too low, thermal strength of the thermoreversible recording layer may become insufficient. When the ratio of the binder resin is too high, coloring density of the thermoreversible recording layer may become low.

**[0063]** The crosslinking agent is appropriately selected depending on the intended purpose without any limitation, and examples thereof include isocyanate, an amino resin, a phenol resin, amine, and an epoxy compound. Among them, isocyanate is preferably, and a polyisocyanate compound having a plurality of isocyanate groups is particularly preferable. As for an amount of the crosslinking agent to the binder resin, preferred is an amount thereof with which a ratio of the number of functional groups of the crosslinking agent to the number of active groups contained in the binder resin is in the range of 0.01 to 2. When the ratio is less than 0.01, the thermal strength may be low. When the ratio is greater than 2, coloring and erasing properties may be adversely affected. Moreover, a catalyst typically used for the aforementioned use may be used as a crosslinking accelerator. In the case where the heat-activated crosslink reaction is carried out, the gel fraction of the heat-crosslinkable resin is preferably 30% or greater, more preferably 50% or greater, and even more preferably 70% or greater. When the gel fraction is less than 30%, the crosslinked state is not sufficient, which may lead to insufficient durability.

**[0064]** Examples of a method for determining whether or not the binder resin is in the crosslinked state or in the non-crosslinked state include a method where a coating film is immersed in a solvent having high solubility. Specifically, the binder resin in the non-crosslinked state is dissolved in the solvent, and does not remain in the solute.

**[0065]** Other components for use in the thermoreversible recording layer are appropriately selected depending on the intended purpose without any limitation. Examples thereof include a surfactant, and a plasticizer for the purpose of making image recording easier.

**[0066]** A method for forming the thermoreversible recording layer is appropriately selected from methods known in the art depending on the intended purpose without any limitation. Preferable examples thereof include: (1) a method containing applying a thermoreversible recording layer coating liquid, which is prepared by dissolving or dispersing the resin, the leuco dye, and the reversible color developer in a solvent, onto a support, and crosslinking at the same time as, or after evaporating the solvent and forming into a sheet, (2) a method containing applying a thermoreversible recording layer coating liquid, which is prepared by dispersing the leuco dye and the reversible color developer in a solvent to which only the resin has been dissolved, onto a support, and crosslinking at the same time as, or after evaporating the solvent and forming into a sheet. Note that, in these methods, a sheet-shaped thermoreversible recording medium can be also shaped without using the support. The solvent for use in the aforementioned methods cannot be collectively determined, as it varies depending on the resin, leuco dye, and reversible color developer for use. Examples of the solvent include tetrahydrofuran, methyl ethyl ketone, methyl isobutyl ketone, chloroform, carbon tetrachloride, ethanol, toluene, and benzene. Note that, the reversible color developer is present as dispersed particles in the thermoreversible recording layer.

**[0067]** To the thermoreversible recording layer coating liquid, various pigments, defoaming agents, coloring agents, dispersing agents, slipping agents, preservatives, crosslinking agents, and plasticizers may be added for the purpose of realizing high performance as a coating material.

**[0068]** Examples of the coating method include blade coating, wire-bar coating, spray coating, air-knife coating, bead coating, curtain coating, gravure coating, kiss coating, reverse roll coating, dip coating, and die coating.

**[0069]** The average thickness of the thermoreversible recording layer is appropriately selected depending on the intended purpose without any limitation. For example, the average thickness thereof is preferably 1  $\mu\text{m}$  to 20  $\mu\text{m}$ , more preferably 3  $\mu\text{m}$  to 18  $\mu\text{m}$ . When the average thickness of the thermoreversible recording layer is less than 1  $\mu\text{m}$ , a contrast of a resulting image may be low, as the coloring density is low. When the average thickness thereof is greater than 20  $\mu\text{m}$ , a heat distribution within the layer becomes wide so that there is an area which does not reach the coloring temperature and does not color, and therefore desired color density cannot be attained.

**[0070]** In the case where a photothermal conversion layer is provided as in the second embodiment, a first thermoreversible recording layer and a second thermoreversible recording layer can be provided in the manner that the photothermal conversion layer is sandwiched with the first and second thermoreversible recording layers. As a result of this structure, heat generated in the photothermal conversion layer is efficiently used to thereby attain excellent recording sensitivity.

**[0071]** In the case where a first thermoreversible recording layer and a second thermoreversible recording layer are provided, the average thickness of the first thermoreversible recording layer is preferably 0.1  $\mu\text{m}$  to 15  $\mu\text{m}$ , and the average thickness of the second thermoreversible recording layer is preferably 0.1  $\mu\text{m}$  to 15  $\mu\text{m}$ .

#### <Photothermal Conversion Layer>

**[0072]** In the case where laser light having a wavelength in the near infrared region, such as semiconductor laser, YAG laser, and fiber laser, is used, a photothermal conversion layer is preferably provided.

**[0073]** The photothermal conversion layer contains at least metal oxide having absorbance in the near infrared region,

which is configured to absorb the aforementioned laser light at high efficiency to generate heat. The metal oxide having absorbance in the near infrared region may be contained in one of layers in contact with the thermoreversible recording layer. In the case where the metal oxide having absorbance in the near infrared region is contained in the thermoreversible recording layer, the thermoreversible recording layer also functions as the photothermal conversion layer. Moreover,

there is a case where a barrier layer is formed between the thermoreversible recording layer and the photothermal conversion layer for the purpose of preventing an interaction between constitutional materials of the thermoreversible recording layer and the photothermal conversion layer. In this case, a resin curable by heat, ultraviolet rays, or electron beams is preferably contained as a material. The layer provided between the thermoreversible recording layer and the photothermal conversion layer is appropriately selected depending on the intended purpose without any limitation.

**[0074]** In the case where the photothermal conversion layer is provided, the photothermal converting material is typically used in combination with a binder resin.

**[0075]** The binder resin is appropriately selected from binder resins known in the art without any limitation, provided that it can hold the metal oxide having absorbance in the near infrared region. As for the binder resin, a thermoplastic resin, and a thermoset resin are preferable, and resins identical to those listed as the binder resin for the thermoreversible recording layer can be suitably used. Among them, a resin curable by heat, ultraviolet rays, or electron beam is preferable for improving resistance to repetitive use, and a heat-crosslinkable resin using an isocyanate-based compound as a crosslinking agent is particularly preferable.

**[0076]** The average thickness of the photothermal conversion layer is appropriately selected depending on the intended purpose without any limitation, but the average thickness thereof is preferably 0.1  $\mu\text{m}$  to 20  $\mu\text{m}$ .

**[0077]** An amount of the metal oxide having absorbance in the near infrared region is preferably 0.005  $\text{g}/\text{m}^2$  to 20  $\text{g}/\text{m}^2$ , more preferably 0.01  $\text{g}/\text{m}^2$  to 10  $\text{g}/\text{m}^2$ .

**[0078]** To the photothermal conversion layer, an antioxidant or a photostabilizer is preferable added to prevent an increase in absorbance of the metal oxide in the near infrared region.

**[0079]** The antioxidant or photostabilizer is appropriately selected depending on the intended purpose without any limitation, and examples thereof include a phenol-based compound, a hindered phenol-based compound, an amine-based compound, a hindered amine-based compound, an amide-based compound, a sulfur-based compound, a thioether-based compound, a phosphorus-based compound, and a lactone-based compound. Among them, a hindered phenol-based compound is preferable, as an effect to the tungsten oxide compound is large.

**[0080]** Examples of the hindered phenol-based compound include pentaerythritol-tetrakis(3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate), thiodiethylene-bis(3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate), octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene, *N,N'*-hexan-1,6-diyl-bis(3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionamide), diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl) phosphate, 3,3',3",5,5',5"-hexa-*t*-butyl-*a,a'*-(*a*)-(mesitylene-2,4,6-triyl)tri-*p*-cresol, ethylenebis(oxyethylene)bis(3-(5-*t*-butyl-4-hydroxy-*m*-tryl)propionate), hexamethylene-bis(3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate), 1,3,5-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione, 1,3,5-tris((4-*t*-butyl-3-hydroxy-2,6-xylyl)methyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione, 2,6-di-*t*-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino)phenol, and 3,9-bis(2-(3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane. These may be used alone, or in combination.

**[0081]** An amount of the antioxidant or the photostabilizer is not collectively defined, as it varies depending on a type of the metal oxide for use. The amount thereof is preferably 0.1 parts by mass to 100 parts by mass, more preferably 1 part by mass to 50 parts by mass, relative to 100 parts by mass of the metal oxide. When the amount thereof is less than 0.1 parts by mass, an effect of preventing an increase in absorbance cannot be attained. When the amount thereof is greater than 100 parts by mass, the photothermal conversion layer may have low thermal resistance, or low adhesion to other layers.

#### <Light-Blocking Layer>

**[0082]** The light-blocking layer is appropriately selected depending on the intended purpose without any limitation, provided that the average transmittance thereof to light in a wavelength range of 300 nm to 400 nm is 5% or less, and the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm is 20% or less. The light-blocking layer may have a single-layer structure, or a laminate structure composed of an ultraviolet ray-blocking layer and the below-mentioned blue light-blocking layer.

**[0083]** In case of the laminate structure, an order of laminating the ultraviolet ray-blocking layer and the blue light-blocking layer is appropriately selected depending on the intended purpose without any limitation. In the case where it is desired to protect a material in the blue light-blocking layer from ultraviolet rays, for example, the ultraviolet ray-blocking layer is preferably provided at a surface side of the thermosensitive recording medium. In the case where the blue light-blocking layer functioning also as a protective layer, which is described later, is provided at the surface side of the thermosensitive recording layer, a number of the layers provided can be reduced, to thereby improve productivity.

**[0084]** Moreover, the ultraviolet ray-blocking layer and the blue light-blocking layer may be provided next to each other, or another layer, such as the oxygen barrier layer, may be provided between the ultraviolet ray-blocking layer and the blue light-blocking layer.

**[0085]** The transmittance of the light-blocking layer can be measured by the following method.

**[0086]** In the case where a thermosensitive recording medium is a thermosensitive recording medium, in which layers, such as an image recording layer, are provided on an opaque substrate, and the light-blocking layer is laminated thereon, and moreover, other layers, such as a protective layer, are provided on the light-blocking layer, first, the opaque substrate is peeled by gradually scraping the substrate with a blade edge of a cutter. Thereafter, other opaque layers, such as the image recording layer, are gradually scraped from the back surface side of the thermosensitive recording medium using the blade edge of the cutter and sand paper, to thereby remove the opaque layers, such as the substrate and the image recording layer. Thereafter, the transmittance of the remaining layers is measured by means of a spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) per 1 nm in a wavelength range of 300 nm to 700 nm. Then, the average value of the measured transmittance at each wavelength is calculated to thereby determine the average transmittance to light in the wavelength range of 380 nm to 495 nm, or the average transmittance to light in the wavelength range of 300 nm to 400 nm. Note that, the average transmittance of the light-blocking layer to light in the wavelength range of 300 nm to 400 nm is 5% or less in order to prevent photodeterioration of the leuco dye contained in the image recording layer, preferably 3% or less, and more preferably 1% or less.

**[0087]** The light-blocking layer contains a binder resin, and a compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter, and may further contain other components, such as filler, and a lubricant. The light-blocking layer may also function as a protective layer.

#### -Binder Resin-

**[0088]** The binder resin is appropriately selected depending on the intended purpose without any limitation, and examples thereof include any of the binder resins described in the image recording layer, a thermoplastic resin, a thermoset resin, and an ultraviolet ray-curable resin.

**[0089]** Examples of the binder resin include polyethylene, polypropylene, polystyrene, polyvinyl alcohol, polyvinyl butyral, polyurethane, saturated polyester, unsaturated polyester, an epoxy resin, a phenol resin, polycarbonate, polyamide, acryl polyol, polyester polyol, and polyurethane polyol. These may be used alone, or in combination.

**[0090]** The binder resin may be crosslinked with a crosslinking agent.

**[0091]** The crosslinking agent is appropriately selected depending on the intended purpose without any limitation, and examples thereof include isocyanate, an amino resin, a phenol resin, amine, and an epoxy compound. Among them, isocyanate is preferable, and a polyisocyanate compound containing a plurality of isocyanate groups is particularly preferable.

**[0092]** As for an amount of the crosslinking agent in the binder resin, preferred is the amount with which a ratio of the number of the functional groups of the crosslinking agent to the number of active groups contained in the binder resin is to be 0.01 to 2.

#### -Compound That Absorbs, Reflects, or Scatters Light Having Wavelength of 500 nm or Shorter-

**[0093]** As for the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter, any of an organic compound or an inorganic compound can be used. Moreover, a polymer having a structure that absorbs light in a wavelength range of 500 nm or shorter at a principle chain or side chain may be used. In this case, such the polymer can also function as a binder resin.

**[0094]** The compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter can be selected from any of an organic compound or an inorganic compound, provided that it is a yellowish compound. In the case where a thermosensitive recording medium is used over a long period, the compound is preferably a yellowish pigment, which has excellent resistance to light or heat. However, any of a pigment or a dye can be used. Examples thereof include a quinophthalone-based compound, an isoindoline-based compound, an isoindolinone-based compound, an anthraquinone-based compound, an azo-based compound, a disazo-based compound, a benzimidazolone-based compound, and a complex oxide pigment. Among them, a quinophthalone-based compound, an isoindoline-based compound, an isoindolinone-based compound, an anthraquinone-based compound, an azo-based compound, a disazo-based compound, and a benzimidazolone-based compound are preferable.

**[0095]** Examples of the quinophthalone-based compound include Pigment Yellow 138.

**[0096]** Examples of the isoindoline-based compound include Pigment Yellow 139.

**[0097]** Examples of the isoindolinone-based compound include Solvent Yellow 163, and Solvent Yellow 167.

**[0098]** Examples of the anthraquinone-based compound include Pigment Yellow 109, Pigment Yellow 110, Pigment Yellow 137, and Pigment Yellow 173.

**[0099]** Examples of the azo-based compound and the disazo-based compound include Pigment Yellow 17, Pigment Yellow 55, Pigment Yellow 83, Pigment Yellow 169, Pigment Yellow 180, and Solvent Orange 54.

**[0100]** Examples of the benzimidazolone-based compound include Pigment Yellow 120, Pigment Yellow 151, Pigment Yellow 154, and Pigment Yellow 175.

**[0101]** Examples of the complex oxide pigment include Pigment Yellow 53, Pigment Yellow 157, Pigment Yellow 158, Pigment Yellow 160, and Pigment Yellow 184.

**[0102]** In the case where absorbance, reflection, or scattering of light having a wavelength range of 300 nm to 400 nm is insufficient only with the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter, a conventional ultraviolet ray-blocking material known in the art can be used in combination.

**[0103]** The ultraviolet ray-blocking material can be any material selected from an organic ultraviolet ray-blocking material, an organic UV-ray absorber, and an inorganic ultraviolet ray-blocking material.

**[0104]** Examples of the organic ultraviolet ray-blocking material include a benzotriazole-based UV-ray absorber, a benzophenone-based UV-ray absorber, a salicylic acid ester-based UV-ray absorber, a cyanoacrylate-based UV-ray absorber, a cinnamic acid-based UV-ray absorber, and a triazine-based UV-ray absorber. Among them, a benzotriazole-based UV-ray absorber, and a triazine-based UV-ray absorber are preferable, and a UV-ray absorber a hydroxyl group of which is protected with an adjacent bulky functional group is particularly preferable.

**[0105]** Examples of the organic UV-ray absorber include 2-(2'-hydroxy-3',5'-di-*t*-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-*t*-butyl-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-*t*-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-*t*-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-5'-*t*-octylphenyl)benzotriazole, 2,2'-methylenebis[6-2H-benzotriazol-2-yl]-4-(1,1,3,3-tetramethylbutyl)phenol], 6,6',6''-(1,3,5-triazin-2,4,6-triyl)tris(3-hexyloxy-2-methylphenol), and 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[2-(2-ethylhexyloxy)ethoxy]phenol. In the case where a thermosensitive recording medium is used over a long period, moreover, used as the organic UV-ray absorber may be the one where a skeleton having the UV-ray absorbing ability is added in the form of a pendant to a polymer prepared by copolymerizing an acrylic resin or a styrene-based resin, or the one where a surface of an inorganic material (e.g. talc) is coated with the organic UV-ray absorber, followed by surface treated with dimeticone, in order to prevent aggregation or bleeding of the UV-ray absorber.

**[0106]** As for the inorganic ultraviolet ray-blocking material, a metal-based compound having the average particle diameter of 100 nm or less is preferable. Examples thereof include: metal oxide, such as zinc oxide, indium oxide, alumina, silica, zirconium oxide, tin oxide, cerium oxide, iron oxide, antimony oxide, barium oxide, calcium oxide, barium oxide, bismuth oxide, nickel oxide, magnesium oxide, chromium oxide, manganese oxide, tantalum oxide, niobium oxide, thorium oxide, hafnium oxide, molybdenum oxide, iron ferrite, nickel ferrite, cobalt ferrite, barium titanate, and calcium titanate, or composite oxide thereof; metal sulfide or a sulfuric acid, such as zinc sulfide, and barium sulfide; metal carbide, such as titanium carbide, silicon carbide, molybdenum carbide, tungsten carbide, and tantalum carbide; and metal nitride, such as aluminium nitride, silicon nitride, boron nitride, zirconium nitride, vanadium nitride, titanium nitride, niobium nitride, and gallium nitride. Among them, metal oxide-based particles are preferable, and silica, alumina, zinc oxide, titanium oxide, cerium oxide, and bismuth oxide are more preferable. These may be surface treated with silicone, wax, organic silane, or silica.

**[0107]** An amount of the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter is preferably 1% by mass to 95% by mass relative to the light-blocking layer.

**[0108]** A solvent used for a coating liquid of the light-blocking layer, a dispersing device used for the coating liquid, a coating method, and a curing method are appropriately selected from those known in the art depending on the intended purpose without any limitation.

**[0109]** The average thickness of the light-blocking layer is preferably 0.1  $\mu\text{m}$  to 30  $\mu\text{m}$ , more preferably 0.5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

**[0110]** It is preferred that the average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm be made 20% or less, preferably 10% or less, more preferably 5% or less by adjusting the amount of the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter contained in the light-blocking layer, or the average thickness of the light-blocking layer. As a result of this, an increase in the absorbance in the near infrared region of the metal oxide having the absorbance in the near infrared region, which is caused by irradiation of light, can be prevented.

**[0111]** In the case where the metal oxide having the absorbance in the absorbance in the near infrared region, and the leuco dye are contained in the same layer, moreover, the metal oxide may be tinted as it is irradiated with light, such as sun light, for a long period, if the transmittance of the light-blocking layer to light having a wavelength of 470 nm is greater than 10%, even when the average transmittance of the light-blocking layer to light in the wavelength range of 380 nm to 495 nm is 10% or less. This is a phenomenon occurred only when the metal oxide having the absorbance in the near infrared region and the leuco dye are mixed. Moreover, this phenomenon cannot expected because the leuco dye before reacting with a color developer does not typically have absorbance in a wavelength range of 420 nm to 430 nm or greater. To avoid this phenomenon, it is necessary to sufficiently block light of longer wavelengths, and it is more preferred that the transmittance of the light-blocking layer to light having a wavelength of 470 nm be 10% or less, and

even more preferably 5% or less.

**[0112]** The average transmittance of the light-blocking layer to light in a wavelength range of 600 nm to 700 nm is preferably 80% or greater. When a bar code recorded on the thermosensitive recording medium is read, a bar code reader typically uses red light having the wavelength of around 650 nm. Therefore, it is preferred that the light-blocking layer transmit light having a wavelength around 650 nm. As a result of this, a contrast of an image recorded on the thermosensitive recording medium is sufficiently attained, and excellent bar code readability can be attained.

«Blue Light-Blocking Layer»

**[0113]** In the present specification, the term "blue light" means blue-colored light in a wavelength range of 380 nm to 495 nm within visible light.

**[0114]** The blue light-blocking layer contains a binder resin, and a compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter, and may further contain other components, such as fillers, and a lubricant, as necessary.

-Binder Resin-

**[0115]** The binder resin is appropriately selected depending on the intended purpose without any limitation, and examples thereof include any of the binder resins described in the descriptions of the image recording layer, a thermoplastic resin, and a thermoset resin. Preferable examples thereof include polyethylene, polypropylene, polystyrene, polyvinyl alcohol, polyvinyl butyral, polyurethane, saturated polyester, unsaturated polyester, an epoxy resin, a phenol resin, polycarbonate, polyamide, acryl polyol, polyester polyol, and polyurethane polyol.

**[0116]** The binder resin may be crosslinked with a crosslinking agent. As for these materials, those used for the thermoreversible recording layer are suitably used. Moreover, the blue light-blocking layer may contain other components, such as filler, as necessary.

-Compound That Absorbs, Reflects, or Scatters Light in Wavelength Range of 500 nm or Shorter-

**[0117]** As for the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter, the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter, which is described in the descriptions of the light-blocking layer, can be used.

**[0118]** An amount of the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter is preferably 1% by mass to 95% by mass relative to the blue light-blocking layer.

**[0119]** A solvent used in a coating liquid of the blue light-blocking layer, a dispersing device of the coating liquid, a coating method, and a curing method are appropriately selected from those known in the art depending on the intended purpose without any limitation.

**[0120]** The average thickness of the blue light-blocking layer is preferably 0.1  $\mu\text{m}$  to 30  $\mu\text{m}$ , more preferably 0.5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

**[0121]** As for the measuring method of the transmittance of the blue light-blocking layer, a method similar to the measuring method of the transmittance of the light-blocking layer can be used.

«Ultraviolet Ray-Blocking Layer»

**[0122]** The ultraviolet ray-blocking layer is preferably provided on a surface of the image recording layer, which is opposite to the surface thereof where the support is provided, for the purpose of preventing deterioration of the resin component contained in the image recording layer due to ultraviolet rays, or preventing an erosion failure caused by tinting of the leuco dye due to ultraviolet rays, or caused by photodeterioration of the leuco dye.

**[0123]** Moreover, the ultraviolet ray-blocking layer may be additionally provided at a surface side of the light-blocking layer in order to prevent discoloring or photodeterioration of constitutional materials of the light-blocking layer.

**[0124]** The ultraviolet ray-blocking layer contains at least an ultraviolet ray-blocking material, and may further contain other components, such as a binder resin, filler, a lubricant, and a color pigment.

-Ultraviolet Ray-Blocking Material-

**[0125]** As for the ultraviolet ray-blocking material, the ultraviolet ray-blocking material described in the descriptions of the light-blocking layer can be used.

**[0126]** In the case where an organic UV-ray absorber is used as the ultraviolet ray-blocking material, an amount of the ultraviolet ray-blocking material is preferably 1% by mass to 95% by mass relative to a total mass of the ultraviolet

ray-blocking layer. In the case where an inorganic UV-ray absorber is used as the ultraviolet ray-blocking material, an amount of the ultraviolet ray-blocking material based on the volume fraction is preferably 1% by volume to 95% by volume.  
**[0127]** Note that, any of these organic or inorganic ultraviolet ray-blocking materials may be contained in the image recording layer.

#### -Binder Resin-

**[0128]** The binder resin is not particularly limited, and the binder resin of the thermosensitive recording layer, or a resin component such as a thermoplastic resin, and a thermoset resin, can be used as the binder resin. Examples thereof include polyethylene, polypropylene, polystyrene, polyvinyl alcohol, polyvinyl butyral, polyurethane, saturated polyester, unsaturated polyester, an epoxy resin, a phenol resin, polycarbonate, polyamide, acryl polyol, polyester polyol, and polyurethane polyol.

**[0129]** As for the binder resin, an UV-ray absorbing polymer may be used, and the binder resin may be crosslinked with a crosslinking agent. As for these materials, the materials described in the descriptions of the recording layer or the protective layer are suitably used. The ultraviolet ray-blocking layer may further contain other components, such as filler, as necessary.

**[0130]** The average thickness of the ultraviolet ray-blocking layer is preferably 0.1  $\mu\text{m}$  to 30  $\mu\text{m}$ , more preferably 0.5  $\mu\text{m}$  to 20  $\mu\text{m}$ . As for a solvent used in a coating liquid of the ultraviolet ray-blocking layer, a dispersing device of the coating liquid, a coating method of the ultraviolet ray-blocking layer, and a curing method of the ultraviolet ray-blocking layer, those used for the thermosensitive recording layer can be used.

**[0131]** As for the measuring method of the transmittance of the ultraviolet ray-blocking layer, a method similar to the measuring method of the transmittance of the light-blocking layer can be used. In the case where the blue light-blocking layer and the ultraviolet ray-blocking layer are laminated to compose the light-blocking layer, the transmittance can be measured with the blue light-blocking layer and the ultraviolet ray-blocking layer being laminated by a method similar to the measuring method of the transmittance of the light-blocking layer.

#### <Support>

**[0132]** A shape, structure, and size of the support are appropriately selected depending on the intended purpose without any limitation. Examples of the shape thereof include a plate shape. The structure of the support may be a single-layer structure, or a laminate structure. The size of the support is appropriately selected depending on a size of the thermosensitive recording medium.

**[0133]** Examples of a material of the support include an inorganic material, and an organic material. These may be used alone, or in combination.

**[0134]** Examples of the inorganic material include glass, quartz, silicon, silicon oxide, aluminium oxide,  $\text{SiO}_2$ , and metal.

**[0135]** Examples of the organic material include paper, a cellulose derivative (e.g. cellulose triacetate), synthetic paper, and a film of polyethylene terephthalate, polycarbonate, polystyrene, or polymethyl methacrylate.

**[0136]** Among them, the organic material is preferable, a film of polyethylene terephthalate (PET), polycarbonate, or polymethyl methacrylate is more preferable, and polyethylene terephthalate (PET) is particularly preferable.

**[0137]** The support is preferably subjected to a surface treatment through corona discharging, an oxidation reaction treatment (chromic acid), etching, an easy adhesion treatment, or an anti-charging treatment, for the purpose of improving the adhesion with a coating layer. The support is preferably turned into white by adding a white pigment, such as titanium oxide.

**[0138]** The average thickness of the support is appropriately selected depending on the intended purpose without any limitation, but the average thickness thereof is preferably 10  $\mu\text{m}$  to 2,000  $\mu\text{m}$ , more preferably 20  $\mu\text{m}$  to 1,000  $\mu\text{m}$ .

#### -Oxygen Barrier Layer-

**[0139]** The permeation of oxygen into the image recording layer can be provided by providing an oxygen barrier layer on the image recording layer in the thermosensitive recording medium. Therefore, use of the oxygen barrier layer can prevent an unerased portion to be left, or coloring of the back ground due to photodeterioration of the leuco dye contained in the image recording layer.

**[0140]** The oxygen permeation rate of the oxygen barrier layer at 25°C, 80%RH is preferably 20  $\text{mL/m}^2/\text{day/MPa}$  or less, more preferably 5  $\text{mL/m}^2/\text{day/MPa}$  or less, and even more preferably 1  $\text{mL/m}^2/\text{day/MPa}$  or less.

**[0141]** When the oxygen permeation rate is greater than 20  $\text{mL/m}^2/\text{day/MPa}$ , oxygen cannot be sufficiently blocked, and therefore light deteriorates the leuco dye. As a result, an image cannot be completely erased. Note that, the oxygen permeation rate is influenced by temperature and humidity of the atmosphere. Therefore, the oxygen permeation rate is preferably low also under the high temperature and high humidity conditions of 30°C, 80%RH, or 35°C, 80%RH, not

only the conditions of 25°C, 80%RH.

**[0142]** As for the measurement of the oxygen permeation rate, for example, there is a measuring method according to JIS K7126B (isopiestic method), or ATSM D3985. Examples of the measuring device include: an oxygen permeation rate measuring device OX-TRAN2/21, and OX-TRAN2/61 (both manufactured by MOCON, Inc); and an oxygen permeation analyzer Model 8001 (manufactured by Systech Instruments Ltd.).

**[0143]** In the case where a water-soluble resin (e.g. polyvinyl alcohol, and an ethylene/polyvinyl alcohol copolymer) is used as a material of the oxygen barrier layer, the resulting oxygen barrier layer exhibits excellent oxygen barrier properties in the low humidity environment, but the oxygen barrier layer absorbs moisture and significantly reduces its oxygen barrier properties, as the surrounding humidity increases, because the water-soluble resin is hydrophilic. In the case where the thermosensitive recording medium is used outside in summer when the humidity is typically high, therefore, sufficient oxygen barrier properties may not be attained. Accordingly, preferably used are an inorganic oxide (e.g., silica, and alumina) vapor deposition layer having the oxygen permeation rate of 20 mL/m<sup>2</sup>/day/MPa or less at 25°C, 80%RH, or an inorganic vapor deposition film having the oxygen permeation rate of 20 mL/m<sup>2</sup>/day/MPa or less at 25°C, 80%RH, in which inorganic oxide is deposited on a polymer film (e.g., polyethylene terephthalate (PET) and nylon) by vapor deposition. Examples of the organic vapor deposition film include a silica vapor deposition film, an alumina vapor deposition film, and a silica/alumina vapor deposition film. Among them, a silica vapor deposition film is particularly preferable, as it is low in cost, has high oxygen barrier properties, and receives less influence from temperature or humidity. Moreover, the base material of the inorganic vapor deposition film is preferably polyethylene terephthalate (PET) in view of vapor deposition compatibility, its stable oxygen barrier properties, and heat resistance.

#### <Other Layers>

**[0144]** Other layers, such as an intermediate layer, protective layer, an adhesive layer, and a bonding layer, may be provided between the oxygen barrier layer and the image recording layer.

**[0145]** The oxygen barrier layer is provided on a surface of the image recording layer, which is opposite to the surface thereof where the support is provided. Moreover, it is preferred that a second oxygen barrier layer be provided between the support and the image recording layer, or on a surface of the support, which is opposite to the surface whereof where the image recording layer is provided, or both therebetween and thereon. Oxygen can be more efficiently blocked by providing a first oxygen barrier layer on a surface of the image recording layer, which is opposite to the surface thereof where the support is provided, and a second oxygen barrier layer at the support side of the image recording layer to sandwich the image recording layer with the first and second oxygen barrier layers. Moreover, the first oxygen barrier layer and the second oxygen barrier layer may be identical or different.

**[0146]** A formation method of the oxygen barrier layer is selected from conventional methods known in the art without any limitation, and examples thereof include a typical coating method, and a typical laminating method. In the case where only an inorganic vapor deposition layer is formed as the oxygen barrier layer, moreover, examples of the formation method include PVD, and CVD as a vapor deposition method.

**[0147]** The average thickness of the oxygen barrier layer is not particularly limited, and varies depending on the oxygen permeation degree thereof. However, the average thickness thereof is preferably 0.005 μm to 1,000 μm, more preferably 0.007 μm to 500 μm. When the average thickness thereof is greater than 1,000 μm, a transparency thereof or recording sensitivity of a resulting thermosensitive recording medium may be reduced. In the case where a first oxygen barrier layer and a second oxygen barrier layer are provided as the oxygen barrier layer, the average thickness of each of the first oxygen barrier layer and the second oxygen barrier layer is preferably 0.005 μm to 1,000 μm.

**[0148]** In the case here an inorganic vapor deposition layer or inorganic vapor deposition film is used as the oxygen barrier layer, the average thickness of the inorganic vapor deposition layer is preferably 5 nm to 100 nm, more preferably 7 nm to 80 nm. When the average thickness thereof is less than 5 nm, the oxygen barrier properties may be insufficient. When the average thickness thereof is greater than 100 nm, a transparency thereof may be reduced, or the barrier layer may be tinted.

#### -Adhesive Layer or Bonding Layer-

**[0149]** The adhesive layer or bonding layer may be provided between the oxygen barrier layer and the layer below the oxygen barrier layer. A formation method of the adhesive layer or bonding layer is not particularly limited, and a typical coating method or laminating method is used as the formation method. The average thickness of the adhesive layer or bonding layer is appropriately selected depending on the intended purpose without any limitation, but the average thickness thereof is preferably 0.1 μm to 20 μm.

**[0150]** A material of the adhesive layer or bonding layer is appropriately selected depending on the intended purpose without any limitation, and examples thereof include a urea resin, a melamine resin, a phenol resin, an epoxy resin, a vinyl acetate-based resin, a vinyl acetate/acryl-based copolymer, an ethylene/vinyl acetate copolymer, an acryl-based

resin, a polyvinyl ether-based resin, a vinyl chloride/vinyl acetate-based copolymer, a polystyrene-based resin, a polyester-based resin, a polyurethane-based resin, a polyamide-based resin, a polyolefin chloride-based resin, a polyvinyl butyral-based resin, an acrylic acid ester-based copolymer, a methacrylic acid ester-based copolymer, natural rubber, a cyanoacrylate-based resin, and a silicone-based resin. These materials may be crosslinked with a crosslinking agent.

Moreover, the material of the adhesive layer or bonding layer may be of hot-melt type.

**[0151]** In the present invention, oxygen barrier properties are further improved by laminating two or more inorganic vapor deposition films. In the case where inorganic vapor deposition films are laminated, the films can be laminated using the adhesive layer or bonding layer. The adhesive layer or bonding layer may contain a compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter.

**[0152]** As for a method for determining whether or not the oxygen barrier layer is present in the thermosensitive recording medium, for example, it can be determined by measuring the oxygen permeation rate of the thermosensitive recording medium by an oxygen permeation rate measuring device. Specifically, in the case where the oxygen permeation rate of the thermosensitive recording medium is 20 mL/m<sup>2</sup>/day/MPa or less, the thermosensitive recording medium is determined to contain an oxygen barrier layer.

#### -Protective Layer-

**[0153]** In the thermoreversible recording medium, a protective layer is preferably provided on the thermoreversible recording layer for the purpose of protecting the thermoreversible recording layer. The protective layer is appropriately selected depending on the intended purpose without any limitation. For example, the protective layer may be formed on one or more layers, and the protective layer is preferably provided on the exposed outermost layer.

**[0154]** The protective layer contains a binder resin, and may further contain other components, such as a release agent, and fillers, as necessary. The binder resin of the protective layer is appropriately selected depending on the intended purpose without any limitation, and examples thereof include a heat-crosslinkable resin, a thermoset resin, an ultraviolet ray (UV) curable resin, and an electron beam curable resin. Among them, a UV-ray curable resin, and a heat-crosslinkable resin are particularly preferable.

**[0155]** The UV-ray curable resin can form an extremely hard film after being cured, and the hard film can prevent a damage caused by physical contact on a surface, and a deformation of a medium by laser heat. Therefore, use of the UV-ray curable resin can provide a thermoreversible recording medium having excellent durability against repetitive use. Moreover, the heat-crosslinkable resin can also harden the surface, although it is slightly inferior to the UV-ray curable resin, and can give excellent resistance to repetitive use.

**[0156]** The UV-ray curable resin is appropriately selected depending on the intended purpose without any limitation, and examples thereof include: an oligomer, such as a urethaneacrylate-based oligomer, an epoxyacrylate-based oligomer, a polyester acrylate-based oligomer, a polyether acrylate-based oligomer, a vinyl-based oligomer, and an unsaturated polyester-based oligomer; and a monomer, such as monofunctional or polyfunctional acrylate, monofunctional or polyfunctional methacrylate, vinyl ester, an ethylene derivative, and acrylic compound. Among them, tetrafunctional or higher polyfunctional monomer or oligomer is particularly preferable. A hardness, contraction rate, flexibility, and coating film strength of a resin film can be appropriately adjusted by blending two or more monomers or oligomers listed above. Moreover, it is necessary to use a photopolymerization initiator, or a photopolymerization accelerator to cure the monomer or oligomer using ultraviolet rays.

**[0157]** An amount of the photopolymerization initiator or photopolymerization accelerator is preferably 0.1% by mass to 20% by mass, more preferably 1% by mass to 10% by mass relative to a total mass of the resin components in the protective layer.

**[0158]** The irradiation of ultraviolet rays to cure the ultraviolet ray-curable resin is appropriately selected depending on the intended purpose without any limitation, and examples thereof include irradiation performed by an ultraviolet ray irradiation device. Examples of the ultraviolet ray irradiation device include a device equipped with a light source, a lamp, a power source, a cooling device, or a transporting device.

**[0159]** Examples of the light source include a mercury lamp, a metal halide lamp, a potassium lamp, a mercury xenon lamp, and a flash lamp. A wavelength of light emitted from the light source is appropriately selected depending on a wavelength of UV absorbance of a photopolymerization initiator or photopolymerization accelerator contained in the thermoreversible recording medium. The conditions of the ultraviolet ray irradiation are appropriately selected depending on the intended purpose without any limitation. For example, the output of the lamp, or transporting speed can be determined depending on the irradiation energy required for curing the resin.

**[0160]** As for the heat-crosslinkable resin, a binder resin usable for the thermoreversible recording layer is suitably used. The heat-crosslinkable resin is preferably crosslinked.

**[0161]** As for the heat-crosslinkable resin, for example, a resin containing a group reactable with a crosslinking agent, such as a hydroxyl group, an amino group, and a carboxyl group, is preferable, and a polymer containing a hydroxyl group is more preferable. As for the crosslinking agent, for example, a crosslinking agent usable for the thermoreversible

recording layer is suitably used.

**[0162]** As for the releasing agent, in order to improve transporting properties of a resulting media, silicone containing a polymerizable group, a polymer to which silicone has been grafted, zinc stearate, or silicone oil can be used. An amount of the release agent is preferably 0.01% by mass to 50% by mass, more preferably 0.1% by mass to 40% by mass, relative to a total mass of the resin component of the protective layer.

**[0163]** To the protective layer, a pigment, a surfactant, a leveling agent, or an anti-charging agent can be added, as necessary.

**[0164]** In the case where the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter, which insufficiently absorbs, reflects, or scatters light in a wavelength range of 300 nm to 400 nm, is contained, the compound does not interfere ultraviolet rays, which are used for UV curing. Therefore, the resulting protective layer can also function as the blue light-blocking layer. In this case, a number of layers provided can be reduced, to thereby improve productivity.

**[0165]** As a solvent used in a coating liquid of the protective layer, a dispersing device of the coating liquid, a coating method of the protective layer, and a drying method of the protective layer, those known in the art and used for the image recording layer can be used. In the case here an ultraviolet ray-curable resin is used in the protective layer, a curing step where a film prepared by coating and drying is irradiated with ultraviolet rays is required. The ultraviolet ray irradiation device, the light source, and the irradiation conditions are as described earlier.

**[0166]** The average thickness of the protective layer is preferably 0.1  $\mu\text{m}$  to 20  $\mu\text{m}$ , more preferably 0.5  $\mu\text{m}$  to 10  $\mu\text{m}$ , and even more preferably 1.5  $\mu\text{m}$  to 6  $\mu\text{m}$ . When the average thickness thereof is less than 0.1  $\mu\text{m}$ , the protective layer cannot sufficiently function as a protective layer of the thermosensitive recording medium. As a result, the materials used in the thermosensitive recording medium may be deteriorated by repetition hysteresis due to heat, and the thermosensitive recording medium may not be able to use repeatedly. When the average thickness thereof is greater than 20  $\mu\text{m}$ , head from the layer containing the photothermal converting material tends to escape to the side of the protective layer, and image recording and image erasing may not be sufficiently performed with heat.

-Intermediate Layer-

**[0167]** In the present invention, an intermediate layer is preferably provided on the image recording layer for the purpose of improving the adhesion between the image recording layer and the oxygen barrier layer, or leveling a surface of the image recording layer. By providing the intermediate layer, image quality can be improved.

**[0168]** The intermediate layer contains at least a binder resin, and may further contain filler, a lubricant, and a color pigment, as necessary. The binder resin is appropriately selected depending on the intended purpose without any limitation. As for the binder resin, the binder resin of the image recording layer, or a resin component, such as a thermoplastic resin, and a thermoset resin, can be used. Moreover, the intermediate layer may contain a UV-ray absorber. As for the UV-ray absorber, any of an organic compound or an inorganic compound can be used.

**[0169]** Moreover, the intermediate layer may contain a compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter.

**[0170]** The average thickness of the intermediate layer is preferably 0.1  $\mu\text{m}$  to 20  $\mu\text{m}$ , more preferably 0.5  $\mu\text{m}$  to 10  $\mu\text{m}$ . As for a solvent used in a coating liquid of the intermediate layer, a dispersing device of the coating liquid, a coating method of the intermediate layer, and a drying and curing method of the intermediate layer, those known in the art and used for the image recording layer can be used.

-Under Layer-

**[0171]** In the present invention, an under layer may be provided between the image recording layer and the support, for the purpose of effectively utilizing generated heat to increase sensitivity, or improving the adhesion between the support and the image recording layer, or preventing a material of the image recording layer from migrating into the support.

**[0172]** The under layer contains at least hollow particles, and may further contain other components, as necessary. Examples of the hollow particles include single-void particles, where only one hollow part is present in each particle, and multi-void particles, where a large number of hollow parts are present in each particle. These may be used alone, or in combination. A material of the hollow particles is appropriately selected depending on the intended purpose without any limitation. For example, a thermoplastic resin is suitably used as the material thereof. The hollow particles may be appropriately produced for use, or selected from commercial products. Examples of the commercial product thereof include: Microsphere R-300 (manufactured by Matsumoto Yushi-Seiyaku Co., Ltd.); Ropaque HP1055, Ropaque HP433J (both manufactured by Zeon Corporation); and SX866 (manufactured by JSR CORPORATION). An amount of the hollow particles in the under layer is appropriately selected depending on the intended purpose without any limitation. For example, the amount thereof is preferably 10% by mass to 80% by mass. As for the binder resin, a resin identical to the

binder resin used in the image recording layer, or the layer containing a polymer having a UV-ray absorbing structure, can be used.

**[0173]** To the under layer, filler, a lubricant, a surfactant, or a dispersing agent may be added, as necessary. Examples of the filler include inorganic filler and organic filler. As for the filler, the inorganic filler is preferable. Examples of the inorganic filler include calcium carbonate, magnesium carbonate, titanium oxide, silicon oxide, aluminium hydroxide, kaolin, and talc.

**[0174]** The average thickness of the under layer is appropriately selected depending on the intended purpose without any limitation, but the average thickness thereof is preferably 1  $\mu\text{m}$  to 80  $\mu\text{m}$ , more preferably 4  $\mu\text{m}$  to 70  $\mu\text{m}$ , and even more preferably 12  $\mu\text{m}$  to 60  $\mu\text{m}$ .

#### -Back Layer-

**[0175]** A back layer may be provided at the opposite side of the surface of the support to the side thereof where the image recording layer is provided, for the purpose of preventing curl or charging of the thermosensitive recording medium, and improving transporting properties thereof.

**[0176]** The back layer contains at least a binder resin, and may further contain other components, such as filler, a lubricant, and a color pigment, as necessary. The binder resin is appropriately selected depending on the intended purpose without any limitation, and examples thereof include a heat-crosslinkable resin, a thermoset resin, an ultraviolet ray (UV) curable resin, and an electron beam curable resin. Among them, an ultraviolet ray (UV) curable resin, and a heat-crosslinkable resin are particularly preferable. As for the ultraviolet ray curable resin, the heat-crosslinkable resin, the filler, the conductive filler, and the lubricant, those used in the image recording layer, or the protective layer are suitably used.

#### -Adhesive Layer or Bonding Layer-

**[0177]** In the present invention, an adhesive layer or bonding layer is provided on a surface of the support opposite to the surface thereof where the image recording layer is provided, to thereby use the thermosensitive recording medium as a thermosensitive recording label. As for a material of the adhesive layer or bonding layer, generally used materials can be used.

**[0178]** A material of the adhesive layer or bonding layer is appropriately selected depending on the intended purpose without any limitation, and examples thereof include a urea resin, a melamine resin, a phenol resin, an epoxy resin, a vinyl acetate-based resin, a vinyl acetate/acryl-based copolymer, an ethylene/vinyl acetate copolymer, an acryl-based resin, a polyvinyl ether-based resin, a vinyl chloride/vinyl acetate-based copolymer, a polystyrene-based resin, a polyester-based resin, a polyurethane-based resin, a polyamide-based resin, a chlorinated polyolefin-based resin, a polyvinyl butyral-based resin, an acrylic acid ester-based copolymer, a methacrylic acid ester-based copolymer, natural rubber, a cyanoacrylate-based resin, and a silicone-based resin. These materials may be crosslinked with a crosslinking agent.

**[0179]** The material of the adhesive layer or bonding layer may be of a hot-melt type. Release paper may be provided to the adhesive layer or bonding layer. Moreover, the adhesive layer or bonding layer may be of a type where no release paper is used. The resulting thermosensitive recording medium can be bonded to an entire or part of a thick substrate, to which it is difficult to apply a recording layer by coating, such as a vinyl chloride card with magnetic stripes by providing the adhesive layer or bonding layer. As a result of this, user friendliness of the thermosensitive recording medium is improved, such as in the manner that part of the information stored in the magnet can be displayed. The thermosensitive recording label containing the adhesive layer or bonding layer can be also used for a thick card, such as an IC card, and an optic card.

**[0180]** To the thermosensitive recording medium, a color layer may be provided between the support and the image recording layer for the purpose of improving visibility. The color layer may be formed by a method containing applying a solution or dispersion liquid containing a colorant, and a binder resin onto a surface of a target, and drying, or a method containing simply bonding a color sheet.

**[0181]** A color print layer may be provided to the thermosensitive recording medium.

**[0182]** In the thermosensitive recording medium, an irreversible recording layer may be used in combination. In this case, color tones of these recording layers may be different. Moreover, the color layer may be provided part or entire surface of the thermosensitive recording medium, which is the same or opposite side of the image recording layer, by providing the predetermined pattern by printing (e.g., offset printing, and gravure printing), or by means of an inkjet printer, a thermal transfer printer, or a dye-sublimation printer. Moreover, an OP varnish layer containing a curable resin as a main component may be provided on a part or entire surface of the color layer. Moreover, a dye or a pigment is simply added to any of the layers constituting the thermosensitive recording layer to color the layer.

**[0183]** A hologram may be provided to the thermosensitive recording medium to improve a security of the information recorded on the thermosensitive recording medium. Moreover, a design (e.g., a figure, an emblem, and a symbol mark)

may be provided to the thermosensitive recording medium by giving relief or intaglio surface textures.

**[0184]** The thermosensitive recording medium can be processed into a desired shape depending use thereof. Examples of the shape thereof include a card shape, a tag shape, a label shape, a sheet shape, and a roll shape.

**[0185]** Examples of the thermosensitive recording medium processed into the card shape include a prepaid card, a point card, and a credit card. The thermosensitive recording medium in the size of a tag, which is smaller than the card size, can be used for a price tag. Moreover, the thermosensitive recording medium in the size of a tag, which is larger than the card size, can be used for a process management, a shipping instruction, or a ticket. The thermosensitive recording medium in the form of a label can be attached to another object, and thus such the thermosensitive recording medium is processed into various sizes, and attached to a trolley, a container, a box, or a shipping container to be used for a process or product management. Moreover, the thermosensitive recording layer of a sheet size, which is larger than the card size, has a wider range to which an image can be recorded, and therefore such the thermosensitive recording layer can be used for general documents, or instructions for process management.

**[0186]** As for the layer structure of the thermosensitive recording medium of the present invention, there is an embodiment where a support 101, and on the support, an image recording layer 102, a light-blocking layer 103, and an oxygen barrier layer 104 are provided in this order, as illustrated in FIG. 1A. In this case, permeation of oxygen into the light-blocking layer is prevented, and therefore photodeterioration of the binder resin or the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter contained in the light-blocking layer 103 can be prevented.

**[0187]** Moreover, there is an embodiment where a support 101, and on the support, an image recording layer 102, an oxygen barrier layer 104, and a light-blocking layer 103 are provided in this order, as illustrated in FIG. 1B. In this case, light in a wavelength range of 500 nm or shorter does not reach the oxygen barrier layer, and therefore photodeterioration of the oxygen barrier layer is prevented.

**[0188]** There is an embodiment where a support 101, and on the support, an image recording layer 102, a photothermal conversion layer 105, a light-blocking layer 103, and an oxygen barrier layer 104 are provided in this order, as illustrated in FIG. 2A.

**[0189]** Moreover, there is an embodiment where a support 101, and on the support, an image recording layer 102, a photothermal conversion layer 105, an oxygen barrier layer 104, and a light-blocking layer 103 are provided in this order, as illustrated in FIG. 2B.

**[0190]** Moreover, there is an embodiment where a support 101, and on the support, a photothermal conversion layer 105, an image recording layer 102, a light-blocking layer 103 and an oxygen barrier layer 104 are provided in this order, as illustrated in FIG. 2C.

**[0191]** Moreover, there is an embodiment where a support 101, and on the support, a photothermal conversion layer 105, an image recording layer 102, an oxygen barrier layer 104, and a light-blocking layer 103 are provided in this order, as illustrated in FIG. 2D.

**[0192]** Moreover, there is an embodiment where a support 101, and on the support, a first image recording layer 102, a photothermal conversion layer 105, a second recording layer 102', a light-blocking layer 103, and an oxygen barrier layer 104 are provided in this order, as illustrated in FIG. 2E.

**[0193]** There is an embodiment where a support 101, and on the support, an image recording layer 102, a blue light-blocking layer 106, a ultraviolet ray-blocking layer 107, and an oxygen barrier layer 104 are provided in this order, as illustrated in FIG. 3A. In this case, permeation of oxygen and ultraviolet rays to the blue light-blocking layer 106 is prevented, and therefore photodeterioration of the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter contained in the blue light-blocking layer 106, via oxygen, can be prevented.

**[0194]** Moreover, there is an embodiment where a support 101, and on the support, an image recording layer 102, an ultraviolet ray-blocking layer 107, a blue light-blocking layer 106, and an oxygen barrier layer 104 are provided in this order, as illustrated in FIG. 3B. Even in the case where the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter contained in the blue light-blocking layer 106 is an acidic material, the acidic material does not come into contact with the leuco dye contained in the image recording layer 102 because of the aforementioned layer structure, and therefore background fogging can be prevented.

**[0195]** Moreover, there is an embodiment where a support 101, and on the support, an image recording layer 102, an oxygen barrier layer 104, a blue light-blocking layer 106, and an ultraviolet ray-blocking layer 107 are provided in this order, as illustrated in FIG. 3C. In this case, light in a wavelength range of 500 nm or shorter does not reach the oxygen barrier layer 106, and therefore photodeterioration of the oxygen barrier layer can be prevented. Moreover, ultraviolet rays do not reach the blue light-blocking layer 106, and therefore photodeterioration of the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter contained in the blue light-blocking layer 106 can be prevented.

**[0196]** Moreover, there is an embodiment where a support 101, and on the support, an image recording layer 102, an oxygen barrier layer 104, an ultraviolet ray-blocking layer 107, and a blue light-blocking layer 106 are provided in this order, as illustrated in FIG. 3D. In this case, light in a wavelength range of 500 nm or shorter does not reach the oxygen barrier layer, photodeterioration of the oxygen barrier layer can be prevented. In the case where absorbance, reflection,

or scattering of light in a wavelength range of 300 nm to 400 nm by the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter contained in the blue light-blocking layer 106 is insufficient, moreover, ultraviolet rays applied for ultraviolet ray curing are not disturbed, the blue light-blocking layer can also function as a protective layer, and therefore a number of the layers can be reduced, and productivity can be improved.

**[0197]** Moreover, there is an embodiment where a support 101, and on the support, an image recording layer 102, a blue light-blocking layer 106, an oxygen barrier layer 104, and an ultraviolet ray-blocking layer 107 are provided in this order, as illustrated in FIG. 3E. In this case, ultraviolet rays do not reach the oxygen barrier layer, and therefore photodeterioration of the oxygen barrier layer can be prevented. Moreover, ultraviolet rays and oxygen do not reach the blue light-blocking layer 106, and therefore photodeterioration of the compound that absorbs, reflects, or scatters light in a wavelength range of 500 nm or shorter contained in the blue light-blocking layer 106 can be prevented.

**[0198]** Although it is not illustrated, an under layer may be provided between the support and the image recording layer, and a back layer, or an oxygen barrier layer, or both may be provided on a surface of the support at which the image recording layer is not provided.

#### <Mechanism of Image Recording and Image Erasing>

**[0199]** The mechanism of image recording and image erasing is an embodiment where a color tone is reversibly changed with heat. This embodiment uses a leuco dye and a reversible color developer (may be referred to as a "color developer" hereinafter), and the color tone reversibly changes between a transparent state and a colored state upon application of heat.

**[0200]** FIG. 4A depicts one example of a temperature-coloring density change curve of the thermoreversible recording medium containing the thermoreversible recording layer, in which the leuco dye and the color developer are contained in the resin. FIG. 4B illustrates a coloring-erasing mechanism of the thermoreversible recording medium, which reversibly changes between the transparent state and the colored state with heat.

**[0201]** As the recording layer initially in the erased state (A) is heated, first, the leuco dye and the color developer are melted and mixed at the melting temperature  $T_1$ , to color and turn into a melt colored state (B). As the recording layer in the melt colored state (B) is quenched, the recording layer can be cooled to room temperature with maintaining the colored state, and is turned into the colored state (C) where the colored state is stabilized and fixed. Whether or not this colored state is obtained depends on the cooling speed from the melted state. When the temperature is slowly cooled, the color is erased in the process of cooling, the recording layer is turned into the erased state (A) that is identical to the initial state, or the state where the density is relatively lower than the colored state (C) obtained by quenching. As the recording layer in the colored state (C) is again heated, on the other hand, the color is erased (from D to E) at the temperature  $T_2$  lower than the coloring temperature. As the recording layer in this state is cooled, the recording layer is turned back to the erased state (A) that is identical to the initial state.

**[0202]** The colored state (C) obtained by quenching from the melted state is a state where the leuco dye and the color developer are mixed in a manner that molecules thereof can cause a catalytic reaction to each other, and often forms a solid state. In this state, the melt mixture (the colored mixture) of the leuco dye and the color developer is crystallized to maintain the color, and it is considered that the color is stabilized by the formation of this structure. On the other hand, the erased state is a state where the phase separation of the leuco dye and the color developer phase is caused. In this case, at least molecules of one of the compounds are assembled together to form a domain, or crystallized, and a stable state is created by separating the leuco dye and the color developer due to the aggregation or crystallization. In most of cases, more perfect erasing is realized, as the leuco dye and the color developer causes phase separation and the color developer is crystallized.

**[0203]** Note that, the erasing realized by slowly cooling from the melted state, and the erasing realized by heating from the colored state illustrated in FIG. 4A both case phase separation or crystallization of the color developer, as the aggregated structure is changed at  $T_2$ .

**[0204]** In FIG. 4A, moreover, there is a case where an erasing failure where erasing cannot be carried out even after the recording layer is heated to the erasing temperature may occur, when the recording layer is repeatedly heated to the temperature  $T_3$  that is equal to or higher than the melting temperature  $T_1$ . It is assumed that this is because the color developer is thermally decomposed, and therefore it is difficult to aggregate or crystallize the color developer. As a result, it is difficult to separate the color developer from the leuco dye. In order to prevent the deterioration of the thermoreversible recording medium due to repetitive use, a difference between the melting temperature  $T_1$  and the temperature  $T_3$  of FIG. 4A is made small, when the thermoreversible recording medium is heated.

#### (Image Processing Method)

**[0205]** The image processing method of the present invention contains irradiating the thermosensitive recording medium of the present invention with light to perform image recording, or image erasing, or both.

**[0206]** As for the thermosensitive recording medium, any of an embodiment where a thermosensitive recording layer is provided as an image recording layer, and write-only image recording is performed thereon once, or an embodiment where a thermoreversible recording layer is provided as an image recording layer, and image recording and image erasing are repeatedly performed can be suitably used.

**[0207]** The image processing method of the present invention contains an image recording step, or an image erasing step, or both, and may further contain appropriately selected other steps, as necessary.

**[0208]** The image processing method of the present invention include an embodiment where both recording and erasing of an image is performed, an embodiment where only recording of an image is performed, and an embodiment where only erasing of an image is performed.

#### <Image Recording Step and Image Erasing Step>

**[0209]** The image recording step in the image processing method of the present invention is a step containing heating the thermosensitive recording medium to record an image on the thermosensitive recording medium. Examples of a method for heating the thermosensitive recording medium include heating methods known in the art. In case of the image processing method used in a physical distribution line, a method, in which the thermosensitive recording medium is irradiated with laser light to heat the thermosensitive recording medium, is particularly preferable, as an image can be formed in a non-contact manner.

**[0210]** The image erasing step in the image processing method of the present invention is a step containing heating the thermosensitive recording medium to erase the image recorded on the thermosensitive recording medium. As for the heat source, laser light may be used, or a heat source other than laser light may be used. If heating is performed by irradiation of laser light among the aforementioned heat sources, it takes a time to scan one beam of laser light to irradiate the predetermined entire area. In the case erasion is performed within a short period, it is preferred that the thermosensitive recording medium be heated by means of an IR ray lamp, a heat roller, a hot stamp, or a dryer to erase the image. In the case where the thermosensitive recording medium is provided on a styrene form box as a transporting container for use in a physical distribution line, the styrene form box is melted of the box itself is heated. Therefore, it is preferred that laser light be applied to the thermosensitive recording medium to heat only heat the thermosensitive recording medium, to thereby erase the image.

**[0211]** An image can be recorded on the thermosensitive recording medium in a non-contact manner by irradiating the thermosensitive recording medium with laser light to heat the thermosensitive recording medium.

**[0212]** In the image processing method of the present invention, typically, updating of an image (the image erasing step) is performed when the thermosensitive recording medium is reused, and then an image is recorded by the image recording step. However, the order for performing recording and erasing of an image is not limited to the aforementioned order. After recording an image by the image recording step, the image may be erased by the image erasing step.

**[0213]** The laser light is appropriately selected depending on the intended purpose without any limitation, and examples thereof include YAG laser, fiber laser, semiconductor laser (LD), and laser light emitted from a semiconductor laser array. In case of use of the thermosensitive recording medium in a physical distribution line, semiconductor laser light is particularly preferable among the aforementioned light, in view of advantages, such as a small size of the device, and low cost. In the image erasing step, light emitted from the semiconductor laser array is preferable, as it can irradiate a wide area at once to thereby reduce the time required for erasing.

**[0214]** The output of the laser light emitted in the image recording step is appropriately selected depending on the intended purpose without any limitation, but the output thereof is preferably 1 W or greater, more preferably 3 W or greater, and even more preferably 5 W or greater. When the output of the laser light is less than 1 W, it takes a long time to form an image, and the output is insufficient so that a high density image cannot be attained, as the duration for forming an image is shortened. Moreover, the upper limit of the output of the laser light is appropriately selected depending on the intended purpose without any limitation, but the upper limit thereof is preferably 200 W or lower, more preferably 150 W or lower, and even more preferably 100 W or lower. When the output of the laser light is greater than 200 W, a scale of the laser device may become large.

**[0215]** The scanning speed of the laser light emitted in the image recording step is appropriately selected depending on the intended purpose without any limitation, but the scanning speed thereof is preferably 300 mm/s or greater, more preferably 500 mm/s or greater, and even more preferably 700 mm/s or greater. When the scanning speed is less than 300 mm/s, it takes a long time to record an image. Moreover, the upper limit of the scanning speed of the laser light is appropriately selected depending on the intended purpose without any limitation, but the upper limit thereof is preferably 15,000 mm/s or less, more preferably 10,000 mm/s or less, and even more preferably 8,000 mm/s or less. When the scanning speed is greater than 15,000 mm/s, it is difficult to form an image uniformly.

**[0216]** The spot diameter of the laser light emitted in the image recording step is appropriately selected depending on the intended purpose without any limitation, but the spot diameter thereof is preferably 0.02 mm or greater, more preferably 0.1 mm or greater, and even more preferably 0.15 mm or greater. Moreover, the upper limit of the spot diameter of the

laser light is appropriately selected depending on the intended purpose without any limitation, but the upper limit thereof is preferably 3.0 mm or less, more preferably 2.5 mm or less, and even more preferably 2.0 mm or less. When the spot diameter is small, a line width of the image is thin, and thus the contrast is low to thereby reduce visibility of the image. When the spot diameter is large, a line width of the image is thick, so that adjacent lines are overlapped. As a result, it becomes impossible to record an image of a small character.

**[0217]** Moreover, the output of the laser light emitted in the image erasing step, where the thermosensitive recording medium is irradiated with the laser light to heat the thermosensitive recording medium to thereby erase the image, is appropriately selected depending on the intended purpose without any limitation. The output thereof is preferably 5 W or greater, more preferably 7 W or greater, and even more preferably 10 W or greater. When the output of the laser light is less than 5 W, it takes a long time to erase the image, and the output becomes insufficient to cause an erasion failure of an image, as the duration for erasing the image is shortened. Moreover, the upper limit of the output of the laser light is appropriately selected depending on the intended purpose without any limitation, but the upper limit thereof is preferably 200 W or less, more preferably 150 W or less, and even more preferably 100 W or less. When the output of the laser light is greater than 200 W, a scale of the laser device may become large.

**[0218]** The scanning speed of the laser light emitted in the image erasing step, where the thermosensitive recording medium is irradiated with the laser light to heat the thermosensitive recording medium to thereby erase the image, is appropriately selected depending on the intended purpose without any limitation. The scanning speed thereof is preferably 100 mm/s or greater, more preferably 200 mm/s or greater, and even more preferably 300 mm/s or greater. When the scanning speed is less than 100 mm/s, it takes a long time to erase the image. Moreover, the upper limit of the scanning speed is appropriately selected depending on the intended purpose without any limitation, but the upper limit thereof is preferably 20,000 mm/s or less, more preferably 15,000 mm/s or less, and even more preferably 10,000 mm/s or less. When the scanning speed is greater than 20,000 mm/s, it may be difficult to erase the image uniformly.

**[0219]** The spot diameter of the laser light emitted in the image erasing step, where the thermosensitive recording medium is irradiated with the laser light to heat the thermosensitive recording medium to thereby erase the image, is appropriately selected depending on the intended purpose without any limitation. The spot diameter thereof is preferably 0.5 mm or greater, more preferably 1.0 mm or greater, and even more preferably 2.0 mm or greater.

**[0220]** Moreover, the upper limit of the spot diameter of the laser light is appropriately selected depending on the intended purpose without any limitation, but the upper limit thereof is preferably 14.0 mm or less, more preferably 10.0 mm or less, and even more preferably 7.0 mm or less.

**[0221]** When the spot diameter is small, it takes a long time to erase the image. When the spot diameter is large, moreover, the output of the laser light is insufficient, hence causing an erasion failure of the image.

**[0222]** The semiconductor laser array for use in the image erasing step is a semiconductor laser light source, in which a plurality of semiconductor lasers are linearly aligned, and preferably contains 3 to 300 semiconductor lasers, more preferably 10 to 100 semiconductor lasers.

**[0223]** When the number of the semiconductor lasers is small, the irradiation power cannot be increased. When the number thereof is too large, it may be necessary to provide a large scale cooling device to cool the semiconductor laser array. Note that, in order to emit light from the semiconductor laser array, the semiconductor lasers are heated. Therefore, cooling is necessary, and hence a cost of the device may increase.

**[0224]** The length of the light source of the semiconductor laser array is appropriately selected depending on the intended purpose without any limitation, but the length thereof is preferably 1 mm to 50 mm, more preferably 3 mm to 15 mm. When the length of the light source of the semiconductor laser array is less than 1 mm, the irradiation power may not be increased. When the length thereof is greater than 50 mm, it may be necessary to provide a large scale cooling device to cool the semiconductor laser array, which may increase a cost of the device.

**[0225]** The laser light emitted from the semiconductor laser array can be made into a linear beam by collimating a width direction of the laser light with a width-direction collimating unit.

**[0226]** The width-direction collimating unit is appropriately selected depending on the intended purpose without any limitation, and examples thereof include a plane-convex cylindrical lens, and a combination of pluralities of convex cylindrical lens.

**[0227]** The laser light emitted from the semiconductor laser array has the larger beam divergence angle in the width direction than that in the length direction. As the width-direction collimating unit is provided adjacent to the output surface of the semiconductor laser array, the beam width is prevented from being wide, and the small size lens can be used. Therefore, such arrangement is preferable.

**[0228]** Moreover, the length of the linear beam can be made longer than the length of the light source of the semiconductor laser array, and the light distribution of the linear beam can be made uniform in the length direction thereof by a length-direction light distribution controlling unit.

**[0229]** The length-direction light distribution controlling unit is appropriately selected depending on the intended purpose without any limitation. For example, the length-direction light distribution controlling unit is composed of a combination of two spherical lenses, an aspherical cylindrical lens (length direction), and a cylindrical lens (width direction).

Examples of the aspherical cylindrical lens (length direction) include the Fresnel lens, a convex lens array, and a concave array.

The light distribution controlling unit is provided at the outlet side of the collimating unit.

**[0230]** Moreover, at least either length or width of the linear beam, which has a length longer than length of the light source of the semiconductor laser array, and a uniform light distribution in the length direction, can be adjusted on the thermosensitive recording medium, by a beam-size adjusting unit.

**[0231]** The beam-size adjusting unit is appropriately selected depending on the intended purpose without any limitation. Examples thereof include a unit configured to change a focal length of the cylindrical lens, or the spherical lens, a unit configured to change a position of the lens, and a unit configured to a work distance between the device and the thermoreversible recording medium.

**[0232]** The length of the linear beam after the adjustment is preferably 10 mm to 300 mm, more preferably 30 mm to 160 mm. As an erasable region is determined by the length of the beam, the erasable region is small when the length is short. When the length of the linear beam is long, on the other hand, energy is applied to a region that does not need to be erased, and thus energy loss may occur, or damage may be caused.

**[0233]** The length of the beam is preferably 2 times or greater the length of the light source of the semiconductor laser array, more preferably 3 times or greater. When the length of the beam is shorter than the length of the light source of the semiconductor laser array, it is necessary to make the light source of the semiconductor laser array long in order to secure a long erasion region, which may increase a cost or size of the device.

**[0234]** Moreover, the width of the linear beam after the adjustment is preferably 0.1 mm to 10 mm, more preferably 0.2 mm to 5 mm. The beam width can control the duration for heating the thermosensitive recording medium. When the beam width is narrow, the heating duration is short, which may reduce erasability. When the beam width is wide, the heating duration is long, which may apply excess energy to the thermosensitive recording medium, and require high energy to perform erasion at high speed. Therefore, the device desirably adjusts the beam width suitable for the erasion properties of the thermosensitive recording medium.

**[0235]** The output of the linear beam adjusted in the aforementioned manner is appropriately selected depending on the intended purpose without any limitation, but the output thereof is preferably 10 W or greater, more preferably 20 W or greater, and even more preferably 40 W or greater. When the output of laser light is less than 10 W, it takes a long time to erase an image, and the output becomes insufficient to cause an erasion failure of an image, as the duration for erasing the image is shortened. Moreover, the upper limit of the output of the laser light is appropriately selected depending on the intended purpose without any limitation, but the upper limit thereof is preferably 500 W or less, more preferably 200 W or less, and even more preferably 120 W or less. When the output of the laser light is greater than 500 W, a size of a cooling device used for the light source of semiconductor laser becomes large.

**[0236]** The scanning speed of the linear beam is appropriately selected depending on the intended purpose without any limitation, but the scanning speed thereof is preferably 2 mm/s or greater, more preferably 10 mm/s or greater, and even more preferably 20 mm/s or greater. When the scanning speed is less than 2 mm/s, it may take a long time to erase an image. Moreover, the upper limit of the scanning speed of the laser light is appropriately selected depending on the intended purpose without any limitation, but the upper limit thereof is preferably 1,000 mm/s or less, more preferably 300 mm/s or less, and even more preferably 100 mm/s or less. When the scanning speed is greater than 1,000 mm/s, it may be difficult to erase an image uniformly.

**[0237]** Moreover, it is preferred that an image recorded on the thermosensitive recording medium be erased by moving the thermosensitive recording medium using a moving unit relative to the linear beam, which is longer than the length of the light source of the semiconductor laser array, and has a uniform light distribution in the length direction, to thereby scan the linear beam on the thermosensitive recording medium. Examples of the moving unit include a conveyor, and a stage. In this case, it is preferred that the thermosensitive recording medium be attached to a surface of a boxy, and be moved by moving the box by the conveyor.

**[0238]** The image processing device for use in the present invention contains at least a laser light emitting unit, and may further contain other units, as necessary.

#### -Laser Light Emitting Unit-

**[0239]** The laser light emitting unit used in the image recording step and/or image erasing step is appropriately selected depending on the intended purpose, provided that it emits laser light having the maximum wavelength that is around the maximum absorbance peak of the photothermal converting material contained in the thermosensitive recording medium. Examples of the laser light emitting unit include a YAG laser, a fiber laser, a semiconductor laser (LD), and a semiconductor laser array.

**[0240]** The wavelength of the laser light is particularly preferably a single wavelength.

**[0241]** The wavelength of laser light emitted from the YAG laser, the fiber laser, the semiconductor laser, or the semiconductor laser array is in the visible to near infrared region (a several hundreds nanometers to about 2  $\mu\text{m}$ ), and use of such wavelength range has an advantage that a highly precise image can be formed because of short wavelengths. Moreover, the YAG laser, and the fiber laser have high outputs, and have an advantage that an image processing speed can be increased. The semiconductor laser itself is small in size, and thus has an advantage of a down-sizing of a device, and moreover low cost. In case of use in a physical distribution line, therefore, semiconductor laser light is particularly preferably used.

**[0242]** Moreover, the wavelength of the laser light emitted from the laser light emitting unit is appropriately selected depending on the intended purpose. The wavelength thereof is preferably 700 nm to 2,000 nm which various resins contained in the thermosensitive recording medium absorb less, and more preferably 780 nm to 1,600 nm. When the thermosensitive recording medium is irradiated with laser light in the wavelength range of shorter than 700 nm, there is a problem that the thermosensitive recording medium tends to be deteriorated. When the wavelength of the laser light is greater than 2,000 nm, the laser light is absorbed by the various resins contained in the thermosensitive recording medium, there is a problem that a semiconductor laser of high output is required, and a size of a device for use increases.

**[0243]** A basic structure of the image processing device is identical to that of so-called laser marker, provided that the image processing device contains at least the laser light emitting unit, and the image processing device is equipped with at least an oscillator unit, a power-source controlling unit, and a programming unit.

**[0244]** FIG. 5 illustrates one example of the image processing device focusing on the laser light emitting unit.

**[0245]** An oscillator unit contains a laser oscillator 1, a beam expander 2, and a scanning unit 5.

**[0246]** The laser oscillator 1 is used to attain laser light having high light intensity and directivity. For example, a couple of mirrors are respectively provided both sides of a laser medium. The laser medium is pumped (supplied with energy), and as a result, the number of atoms in the excited state is increased to form a reverse distribution, to thereby induce emission. Then, only light in the light axial direction is selectively amplified to increase the directivity of the light. In this manner, laser light is released from an output mirror.

**[0247]** The scanning unit 5 is composed of galvanometers 4, and mirrors 4A attached to the galvanometer 4. Then, the laser light output from the laser oscillator 1 is rotary scanned at high speed with the two mirrors 4A for the X-axis direction and the Y-axis direction, attached to the galvanometers 4, to thereby perform recording or erasing an image on a thermosensitive recording medium 7.

**[0248]** The power-source controlling unit is composed of a driving power source of a light source to excite the laser medium, a driving power source of the galvanometers, a power source for cooling, such as Peltier element, and a control unit configured to control the entire image processing device.

**[0249]** The programming unit is configured to input conditions for image recording or image erasing, such as intensity of laser light, and scanning speed of laser light, and create and edit characters to be recorded through input from a touch panel, or key board.

**[0250]** Note that, the laser light emitting unit, specifically, a head for image recording, or image erasing, or both, is mounted in the image processing device. The image processing device contains other members, such as a transporting unit of the thermosensitive recording medium, a control unit thereof, and a monitor unit (touch panel).

**[0251]** The image processing method of the present invention can record and erase an image at high speed in a non-contact manner on a thermosensitive recording medium, such as a label attached to a transporting container (e.g., a cardboard box, and a plastic container), and uses the thermosensitive recording medium which does not reduce an image density or tints a background when exposed to light for a long period, and has sufficient erasability. Therefore, the image processing method of the present invention is particularly suitably used for a physical distribution or delivery system. In this case, an image can be recorded and erased on the thermosensitive recording medium (label), for example, while the cardboard box or plastic container placed on a belt conveyor is moved. Therefore, a time required for shipping can be reduced, as it is not necessary to stop the line. Moreover, the cardboard box or plastic container to which the label is attached can be reused as it is, without peeling the label off, and an image can be again recorded or erased on the label.

## Examples

**[0252]** Examples of the present invention are explained hereinafter, but Examples shall not be construed as to limit the scope of the present invention in any way.

**[0253]** In Examples and Comparative Examples, a thermoreversible recording medium was produced and evaluated as a preferable example of the thermosensitive recording medium. The case where image recording is performed on the thermoreversible recording medium only once without repeating image recording and image erasing is determined as Example which evaluates on a thermosensitive recording medium.

## &lt;Measurement of Transmittance of Light-Blocking Layer&gt;

**[0254]** In Examples and Comparative Examples, a transmittance of a light-blocking layer was measured by a spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation). The average transmittance to light in the wavelength range of 380 nm to 495 nm was calculated by measuring a transmittance per 1 nm in the wavelength region of 380 nm to 495 nm, and calculating the average value of the measured transmittance of each wavelength. The average transmittance to light in the wavelength range of 300 nm to 400 nm was also calculated by calculating the average value in the same manner.

(Example 1)

## &lt;Production of Thermoreversible Recording Medium&gt;

**[0255]** A thermoreversible recording medium, a color tone of which reversibly changed with heat, was produced in the following manner.

-Support-

**[0256]** As for the support, a 125  $\mu\text{m}$ -thick white polyester film (Tetron Film U2L98W, manufactured by Teijin DuPont Films Japan Limited) was used.

-Under Layer-

**[0257]** An under layer coating liquid was prepared by blending 30 parts by mass of a styrene-butadiene-based copolymer (PA-9159, manufactured by Nippon A & L Inc.), 12 parts by mass of a polyvinyl alcohol resin (POVAL PVA103, manufactured by Kuraray Co., Ltd.), 20 parts by mass of hollow particles (Microsphere R-300, manufactured by Matsumoto Yushi-Seiyaku Co., Ltd.), and 40 parts by mass of water, and stirring the mixture for about 1 hour until the mixture became homogeneous.

**[0258]** Subsequently, the obtained under layer coating liquid was applied on the support with a wire-bar, and the coated layer was heated for 2 minutes at 80°C to dry, to thereby form an under layer having a thickness of 20  $\mu\text{m}$ .

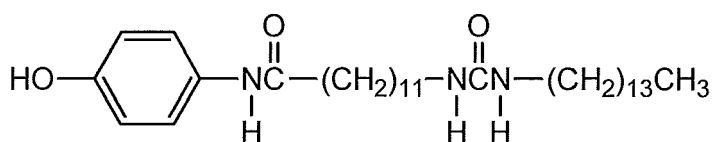
-Thermoreversible Recording Layer-

**[0259]** By means of a ball mill, 5 parts by mass of the reversible color developer represented by the following structural formula (1), 1 part by mass of the erasing accelerator represented by the following structural formula (2), 10 parts by mass of a 50% by mass acryl polyol solution (hydroxyl value: 200 mgKOH/g), and 80 parts by mass of methyl ethyl ketone were ground and dispersed until the average particle diameter thereof became 1  $\mu\text{m}$ .

[Reversible Color Developer]

**[0260]**

<Structural Formula (1)>



[Erasing Accelerator]

**[0261]**

<Structural Formula (2)>  $\text{C}_{17}\text{H}_{35}\text{CONHC}_{18}\text{H}_{37}$

**[0262]** To the dispersion liquid, in which the reversible color developer had ground and dispersed, 1 part by mass of 2-anilino-3-methyl-6-diethylaminofluoran serving as a leuco dye, 1.5 parts by mass of a 18.5% by mass cesium-containing

tungsten oxide compound (serving as metal oxide having absorbance in the near infrared region) dispersion liquid (YMF-01, manufactured by (Sumitomo Metal Mining Co., Ltd.), and 5 parts by mass of isocyanate (Coronate HL, manufactured by Tosoh Corporation) were added. The resulting mixture was sufficiently stirred, to thereby prepare a thermoreversible recording layer coating liquid.

[0263] Subsequently, the obtained thermoreversible recording layer coating liquid was applied on the support, to which the under layer had been formed, with a wire bar, and the coated layer was heated for 2 minutes at 100°C to dry. Thereafter, the dried layer was cured for 24 hours at 60°C, to thereby form a thermoreversible recording layer having a thickness of 10  $\mu\text{m}$ .

#### -Light-Blocking Layer-

[0264] A coating liquid was prepared by blending 5.0 parts by mass of a 40% by mass ultraviolet ray-absorbing polymer solution (UV-G302, manufactured by Nippon Shokubai Co., Ltd.), 1.3 parts by mass of an azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) serving as a compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter), 0.7 part by mass of hydrophobic silica (RX-200, manufactured by Nippon Aerosil Co., Ltd.), 1.0 part by mass of an isocyanate compound (Coronate HL, manufactured by Tosoh Corporation), and 9.2 parts by mass of methyl ethyl ketone, and sufficiently stirring the mixture.

[0265] Subsequently, the coating liquid was applied on the support, to which the under layer and the thermoreversible recording layer had been formed, and the coated layer was heated for 1 minute at 90°C to dry. Thereafter, the dried layer was heated for 24 hours at 60°C, to thereby form a light-blocking layer having a thickness of 4  $\mu\text{m}$ .

#### -First Oxygen Barrier Layer-

[0266] An adhesive layer coating liquid was prepared by blending 5 parts by mass of a urethane-based adhesive (TM-567, manufactured by Toyo-Morton, Ltd.), 0.5 parts by mass of isocyanate (CAT-RT-37, manufactured by Toyo-Morton, Ltd.), and 5 parts by mass of ethyl acetate, and sufficiently stirring the mixture.

[0267] Subsequently the adhesive layer coating layer was applied on a silica-vapor deposition PET film (IB-PET-C, manufactured by Dai Nippon Printing Co., Ltd., oxygen permeation rate: 15 mL/m<sup>2</sup>/day/MPa) with a wire bar, and the coated layer was heated for 1 minutes at 80°C to dry. Thereafter, the resultant was bonded on the support, to which the under layer, the thermoreversible recording layer, and the light-blocking layer had been formed, and heated for 24 hours at 50°C, to thereby form a first oxygen barrier layer having a thickness of 12  $\mu\text{m}$ .

#### -Protective Layer-

[0268] A protective layer coating liquid was prepared by blending 3 parts by mass of pentaerythritol hexaacrylate (KAYARAD DPHA, manufactured by Nippon Kayaku Co., Ltd.), 3 parts by mass of urethane acrylate oligomer (Art Resin UN-3320HA, manufactured by Negami Chemical Industrial Co., Ltd.), 3 parts by mass of acrylic acid ester of dipentaerythritol caprolactone (KAYARAD DPCA-120, manufactured by Nippon Kayaku Co., Ltd.), 0.5 parts by mass of a photopolymerization initiator (IRGACURE 184, manufactured by Nippon Chiba-Geigy K.K.), and 11 parts by mass of isopropyl alcohol, and sufficiently stirring the mixture.

[0269] Subsequently, the protective layer coating liquid was applied on the first oxygen barrier layer with a wire bar, and the coated layer was heated for 1 minute at 90°C to dry. Thereafter, the dried layer was cured with a 80 W/cm lamp, to thereby form a protective layer having a thickness of about 4  $\mu\text{m}$ .

#### -Bonding Agent Layer-

[0270] An acryl emulsion-based bonding agent (BPW6111, manufactured by TOYOICHEM CO., LTD., solid content: 60% by mass) was applied onto release paper (LSW, manufactured by LINTEC Corporation) with a wire bar to give a dry weight of 20 g/m<sup>2</sup>, followed by drying the bonding agent. The resultant was bonded on a surface of the support, which was opposite to the surface thereof where the thermoreversible recording layer was provided, followed by leaving to stand for 7 days at 23°C, to thereby form a bonding agent layer. In the manner as described above, a thermoreversible recording medium of Example 1 was produced.

[0271] The produced thermoreversible recording medium of Example 1 was cut into a piece in the size of 20 mm x 20 mm. The support was peeled from the cut piece by inserting a blade of a cutter into an interface between the support and the under layer from the cross section of the thermoreversible recording medium, and gradually scraping. Thereafter, the under layer and the thermoreversible recording layer were gradually scraped from the back surface of the thermoreversible recording medium using the cutter and sand paper to thereby remove the opaque layers, such as the support and the thermoreversible recording layer. Thereafter, the transmittance of the remaining layer was measured by a

spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) per 1 nm in the wavelength region of 300 nm to 700 nm. As a result, the average transmittance of the light-blocking layer to light in a wavelength range of 300 nm to 400 nm was 1.8%, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm was 15.0%, and the transmittance thereof to light having a wavelength of 470 nm was 17.3%. A graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer of Example 1 is presented in FIG. 6.

(Example 2)

<Production of Thermoreversible Recording Medium>

**[0272]** The following photothermal conversion layer coating liquid was applied on the under layer of Example 1 with a wire bar, and the coated layer was heated for 1 minute at 90°C to dry, followed by heating for 2 hours at 60°C, to thereby form a photoconversion layer having a thickness of 3 μm.

-Preparation of Photothermal Conversion Layer Coating Liquid-

**[0273]** A photothermal conversion layer coating liquid was prepared by blending 6 parts by mass of a 50% by mass acryl polyol resin solution (LR327, manufactured by Mitsubishi Rayon Co., Ltd.), 1.25 parts by mass of a 18.5% by mass cesium-containing tungsten oxide compound (serving as metal oxide having absorbance in the near infrared region) dispersion liquid (YMF-01, manufactured by Sumitomo Metal Mining Co., Ltd.), 2.4 parts by mass of isocyanate (Coronate HL, manufactured by Tosoh Corporation), and 14 parts by mass of methyl ethyl ketone, and sufficiently stirring the mixture.

**[0274]** Subsequently, a thermoreversible recording layer was formed on the photoconversion layer in the same manner as in Example 1, provided that metal oxide having absorbance in the near infrared region was excluded from the thermoreversible recording layer of Example 1.

**[0275]** Subsequently, the light-blocking layer identical to that of Example 1, the first oxygen barrier layer identical to that of Example 1, and the protective layer identical to that of Example 1 were formed on the thermoreversible recording layer in this order. Moreover, the bonding agent layer identical to Example 1 was formed in the same manner as in Example 1, to thereby produce a thermoreversible recording medium of Example 2.

**[0276]** The produced thermoreversible recording medium of Example 2 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 2 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 1. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 6.

(Example 3)

<Production of Thermoreversible Recording Medium>

**[0277]** A thermoreversible recording medium of Example 3 was produced in the same manner as in Example 1, provided that a second oxygen barrier layer was provided between the surface of the support of Example 1, which was opposite to the surface thereof where the thermoreversible recording layer was provided, and the bonding agent layer of Example 1, in the same manner as the formation of the first oxygen barrier layer of Example 1.

**[0278]** The produced thermoreversible recording medium of Example 3 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 3 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 1. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 6.

(Example 4)

<Production of Thermoreversible Recording Medium>

**[0279]** A thermoreversible recording medium of Example 4 was produced in the same manner as in Example 3, provided that the amount of the azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) serving as the compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter, which was contained in the light-blocking layer, was changed from 1.3 parts by mass to 2.4 parts by mass.

**[0280]** The produced thermoreversible recording medium of Example 4 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 4 to light in a wavelength range of 300 nm to 400 nm was 0.9%, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm was 8.9%, and the transmittance thereof to light having a wavelength of 470 nm was 10.2%. A graph depicting a relationship between wavelengths of the transmittance of the light-blocking layer of Example 4 is presented in FIG. 7.

(Example 5)

<Production of Thermoreversible Recording Medium>

**[0281]** A thermoreversible recording medium of Example 5 was produced in the same manner as in Example 3, provided that the amount of the azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) serving as the compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter, which was contained in the light-blocking layer, was changed from 1.3 parts by mass to 3.1 parts by mass.

**[0282]** The produced thermoreversible recording medium of Example 5 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 5 to light in a wavelength range of 300 nm to 400 nm was 0.5%, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm was 3.4%, and the transmittance thereof to light having a wavelength of 470 nm was 3.9%. A graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer of Example 5 is presented in FIG. 8.

(Example 6)

<Production of Thermoreversible Recording Medium>

**[0283]** A thermoreversible recording medium of Example 6 was produced in the same manner as in Example 5, provided that 0.03 parts by mass of a hindered phenol-based compound (SUMILIZER MDP-S, manufactured by Sumitomo Chemical Co., Ltd.) was added to the thermoreversible recording layer coating liquid.

**[0284]** The produced thermoreversible recording medium of Example 6 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 6 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 5. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 8.

(Example 7)

<Production of Thermoreversible Recording Medium>

**[0285]** A thermoreversible recording medium of Example 7 was produced in the same manner as in Example 5, provided that 1.5 parts by mass of the 18.5% by mass cesium-containing tungsten oxide compound (serving as the metal oxide having the absorbance in the near infrared region) dispersion liquid (YMF-01, manufactured by Sumitomo Metal Mining Co., Ltd.) was replaced with 15 parts by mass of a 20% by mass indium-doped tin oxide dispersion liquid (manufactured by Mitsubishi Materials Corporation).

**[0286]** The produced thermoreversible recording medium of Example 7 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 7 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 5. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 8.

(Example 8)

<Production of Thermoreversible Recording Medium>

**[0287]** A thermoreversible recording medium of Example 8 was produced in the same manner as in Example 5, provided that 1.5 parts by mass of the 18.5% by mass cesium-containing tungsten oxide compound (serving as the

metal oxide having the absorbance in the near infrared region) dispersion liquid (YMF-01, manufactured by Sumitomo Metal Mining Co., Ltd.) was replaced with 15 parts by mass of a 30% by mass antimony-doped tin oxide dispersion liquid (SN-14, manufactured by Ishihara Sangyo Kaisha, Ltd.).

**[0288]** The produced thermoreversible recording medium of Example 8 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 8 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 5. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 8.

(Example 9)

<Production of Thermoreversible Recording Medium>

**[0289]** After forming a thermoreversible recording layer in the same manner as in Example 3, the following intermediate layer coating liquid was applied to the support, to which the thermoreversible recording layer had been formed, with a wire bar, and the coated layer was heated for 1 minute at 90°C to dry. Thereafter, the dried layer was heated for 2 hours at 60°C, to thereby form an intermediate layer having a thickness of 2 μm.

-Preparation of Intermediate Layer Coating Liquid-

**[0290]** An intermediate layer coating liquid was prepared by blending 6 parts by mass of a 50% by mass acryl polyol resin solution (LR327, manufactured by Mitsubishi Rayon Co., Ltd.), 2.4 parts by mass of isocyanate (Coronate HL, manufactured by Tosoh Corporation), and 14 parts by mass of methyl ethyl ketone, and sufficiently stirring the mixture.

**[0291]** Subsequently, the first oxygen barrier layer identical to Example 3, the light-blocking layer identical to Example 3, and the protective layer identical to Example 3 were formed on the intermediate layer in this order. Moreover, the second oxygen barrier layer identical to Example 3, and the bonding agent layer identical to Example 3 were formed on the surface of the support, which was opposite to the surface thereof where the thermoreversible recording layer had been provided, to thereby produce a thermoreversible recording medium of Example 9.

**[0292]** The produced thermoreversible recording medium of Example 9 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 9 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 3. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 6.

(Example 10)

<Production of Thermoreversible Recording Medium>

**[0293]** After forming a thermoreversible recording layer in the same manner as in Example 3, the following blue light-blocking layer coating liquid was applied to the support, on which the thermoreversible recording layer had been formed, with a wire bar, and the coated layer was heated for 1 minute at 90°C to dry. Thereafter, the dried layer was heated for 2 hours at 60°C, to thereby form a blue light-blocking layer having a thickness of 4 μm.

-Preparation of Blue Light-Blocking Layer Coating Liquid-

**[0294]** A blue light-blocking layer coating liquid was prepared by blending 5.0 parts by mass of a 50% by mass acryl polyol resin solution (LR327, manufactured by Mitsubishi Rayon Co., Ltd.), 2.9 parts by mass of an isoindolinone-based compound (SD-TT1140, manufactured by RESINO COLOR INDUSTRY CO., LTD.) serving as a compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter, 1.2 parts by mass of isocyanate (Coronate HL, manufactured by Tosoh Corporation), and 14.0 parts by mass of methyl ethyl ketone, and sufficiently stirring the mixture.

**[0295]** Subsequently, the first oxygen barrier layer identical to Example 3 was formed on the blue light-blocking layer. Moreover, the following ultraviolet ray-blocking layer coating liquid was applied to the first oxygen barrier layer, and the coated layer was heated for 1 minute at 90°C to dry. Thereafter, the dried layer was heated for 2 hours at 60°C, to thereby form an ultraviolet ray-blocking layer having a thickness of 4 μm.

## -Preparation of Ultraviolet Ray-Blocking Layer Coating Layer-

**[0296]** A ultraviolet ray-blocking layer was prepared by blending 5.0 parts by mass of a 40% by mass ultraviolet ray-absorbing polymer solution (UV-G302, manufactured by Nippon Shokubai Co., Ltd.), 0.5 parts by mass of hydrophobic silica (RX-200, manufactured by Nippon Aerosil Co., Ltd.), 1.0 part by mass of an isocyanate compound (Coronate HL, manufactured by Tosoh Corporation), and 12 parts by mass of methyl ethyl ketone, and sufficiently stirring the mixture.

**[0297]** Subsequently, the protective layer identical to Example 3 was formed on the ultraviolet ray-blocking layer. Moreover, the second oxygen barrier layer identical to Example 3, and the bonding agent layer identical to Example 3 were formed on the surface of the support, which was opposite to the surface thereof where the thermoreversible recording layer had been provided, in the same manner as in Example 3, to thereby produce a thermoreversible recording medium of Example 10.

**[0298]** The produced thermoreversible recording medium of Example 10 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 10, in which the blue light-blocking layer and the ultraviolet ray-blocking layer were laminated, to light in a wavelength range of 300 nm to 400 nm was 0.6%, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm was 4.9%, and the transmittance thereof to light having a wavelength of 470 nm was 7.5%. A graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer of Example 10 is presented in FIG. 9.

(Example 11)

## &lt;Production of Thermoreversible Recording Medium&gt;

**[0299]** A thermoreversible recording medium of Example 11 was produced in the same manner as in Example 10, provided that the order for laminating the blue light-blocking layer and the ultraviolet ray-blocking layer was reversed.

**[0300]** The produced thermoreversible recording medium of Example 11 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 11, in which the blue light-blocking layer and the ultraviolet ray-blocking layer were laminated, to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 10. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 9.

(Example 12)

## &lt;Production of Thermoreversible Recording Medium&gt;

**[0301]** A thermoreversible recording medium of Example 12 was produced in the same manner as in Example 10, provided that the intermediate layer identical to Example 9 was formed on the thermoreversible recording layer identical to Example 10, and the first oxygen barrier layer identical to Example 10, the blue light-blocking layer identical to Example 10, the ultraviolet ray-blocking layer identical to Example 10, and the protective layer identical to Example 10 were formed on the intermediate layer in this order.

**[0302]** The produced thermoreversible recording medium of Example 12 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 12, in which the blue light-blocking layer and the ultraviolet ray-blocking layer were laminated, to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 10. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 9.

(Example 13)

## &lt;Production of Thermoreversible Recording Medium&gt;

**[0303]** A thermoreversible recording medium of Example 13 was produced in the same manner as in Example 12, provided that the order for laminating the blue light-blocking layer and the ultraviolet ray-blocking layer was reversed.

**[0304]** The produced thermoreversible recording medium of Example 13 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result,

the average transmittance of the light-blocking layer of Example 13, in which the blue light-blocking layer and the ultraviolet ray-blocking layer were laminated, to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 10. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 9.

(Example 14)

<Production of Thermoreversible Recording Medium>

**[0305]** A thermoreversible recording medium of Example 14 was produced in the same manner as in Example 10, provided that the order for laminating the ultraviolet ray-blocking layer and the oxygen barrier layer was reversed.

**[0306]** The produced thermoreversible recording medium of Example 14 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 14, in which the blue light-blocking layer and the ultraviolet ray-blocking layer were laminated, to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 10. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 9.

(Example 15)

<Production of Thermoreversible Recording Medium>

**[0307]** After forming a thermoreversible recording layer in the same manner as in Example 3, the following light-blocking layer coating liquid was applied to the support, to which the thermoreversible recording layer had been formed, with a wire bar, and the coated layer was heated for 1 minute at 90°C to dry, to thereby form a light-blocking layer having a thickness of 4 μm.

-Preparation of Light-Blocking Layer Coating Liquid-

**[0308]** A light-blocking layer coating liquid was prepared by blending 3.8 parts by mass of a 50% by mass acryl polyol resin solution (LR327, manufactured by Mitsubishi Rayon Co., Ltd.), 2.5 parts by mass of a screen ink containing a compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter (Vinyl Ink H-type Half-tone (blue-yellow), manufactured by Jujo Chemical Co., Ltd.), 0.5 parts by mass of hydrophobic silica (RX-200, manufactured by Nippon Aerosil Co., Ltd.), and 6.3 parts by mass of methyl isobutyl ketone, and sufficiently stirring the mixture.

**[0309]** Subsequently, the first oxygen barrier layer identical to that of Example 3, the protective layer identical to that of Example 3 were formed on the light-blocking layer, and the second oxygen barrier layer identical to that of Example 3, and the bonding agent layer identical to that of Example 3 were formed on the surface of the support opposite to the surface thereof where the thermoreversible recording layer had been provided in the same manner as in Example 3. In the manner as described, a thermoreversible recording medium of Example 15 was produced.

**[0310]** The produced thermoreversible recording medium of Example 15 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Example 15 to light having wavelength of 300 nm to 400 nm was 4.5%, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm was 14.8%, and the transmittance thereof to light having a wavelength of 470 nm was 25.6%. A graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer of Example 15 is presented in FIG. 10.

(Comparative Example 1)

<Production of Thermoreversible Recording Medium>

**[0311]** A thermoreversible recording medium of Comparative Example 1 was produced in the same manner as in Example 1, provided that the azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) was excluded from the light-blocking layer.

**[0312]** The produced thermoreversible recording medium of Comparative Example 1 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. Since the light-blocking layer of Comparative Example 1 did not contain the compound that absorbed, reflected, or

scattered light in a wavelength range of 500 nm or shorter, the light-blocking layer thereof was substantially an ultraviolet ray-blocking layer. The average transmittance of the light-blocking layer of Comparative Example 1 to light in a wavelength range of 300 nm to 400 nm was 6.0%, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm was 74.8%, and the transmittance thereof to light having a wavelength of 470 nm was 86.5%. The results are depicted in FIG. 11.

(Comparative Example 2)

<Production of Thermoreversible Recording Medium>

**[0313]** A thermoreversible recording medium of Comparative Example 2 was produced in the same manner as in Example 2, provided that the azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) was excluded from the light-blocking layer.

**[0314]** The produced thermoreversible recording medium of Comparative Example 2 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 2 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Comparative Example 1. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 11.

(Comparative Example 3)

<Production of Thermoreversible Recording Medium>

**[0315]** A thermoreversible recording medium of Comparative Example 3 was produced in the same manner as Example 5, provided that the azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) was excluded from the light-blocking layer.

**[0316]** The produced thermoreversible recording medium of Comparative Example 3 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 3 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Comparative Example 1. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 11.

(Comparative Example 4)

<Production of Thermoreversible Recording Medium>

**[0317]** A thermoreversible recording medium of Comparative Example 4 was produced in the same manner as in Example 7, provided that the azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) was excluded from the light-blocking layer.

**[0318]** The produced thermoreversible recording medium of Comparative Example 4 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 4 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Comparative Example 1. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 11.

(Comparative Example 5)

<Production of Thermoreversible Recording Medium>

**[0319]** A thermoreversible recording medium of Comparative Example 5 was produced in the same manner as in Example 8, provided that the azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) was excluded from the light-blocking layer.

**[0320]** The produced thermoreversible recording medium of Comparative Example 5 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 5 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Comparative Example 1. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 11.

(Comparative Example 6)

<Production of Thermoreversible Recording Medium>

**[0321]** A thermoreversible recording medium of Comparative Example 6 was produced in the same manner as in Example 15, provided that the light-blocking layer coating liquid was changed to the following light-blocking layer coating liquid.

-Preparation of Light-Blocking Layer Coating Liquid-

**[0322]** A light-blocking layer coating liquid was prepared by blending 6.0 parts by mass of a 50% by mass acryl polyol resin solution (LR327, manufactured by Mitsubishi Rayon Co., Ltd.), 2.0 parts by mass of a screen ink containing a compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter (Vinyl Ink H-type Half-tone (blue-yellow), manufactured by Jujo Chemical Co., Ltd.), 0.7 parts by mass of hydrophobic silica (RX-200, manufactured by Nippon Aerosil Co., Ltd.), and 9.5 parts by mass of methyl isobutyl ketone, and sufficiently stirring the mixture.

**[0323]** The produced thermoreversible recording medium of Comparative Example 6 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 6 to light in a wavelength range of 300 nm to 400 nm was 16.0%, the average transmittance to light in a wavelength range of 380 nm to 495 nm was 21.8%, and the transmittance thereof to light having a wavelength of 470 nm was 39.1%. A graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer of Comparative Example 6 is presented in FIG. 12.

(Comparative Example 7)

<Production of Thermoreversible Recording Medium>

**[0324]** A thermoreversible recording medium of Comparative Example 7 was produced in the same manner as in Example 3, provided that the amount of the azo-compound (LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) serving as the compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter was changed from 1.3 parts by mass to 0.6 parts by mass.

**[0325]** The produced thermoreversible recording medium of Comparative Example 7 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 7 to light in a wavelength range of 300 nm to 400 nm was 3.4%, the average transmittance to light in a wavelength range of 380 nm to 495 nm was 34.9%, and the transmittance thereof to light having a wavelength of 470 nm was 40.9%. A graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer of Comparative Example 7 is presented in FIG. 13.

(Comparative Example 8)

<Production of Thermoreversible Recording Medium>

**[0326]** A thermoreversible recording medium of Comparative Example 8 was produced in the same manner as in Example 3, provided that the light-blocking layer coating liquid was changed to the following light-blocking layer coating liquid.

-Preparation of Light-Blocking Layer Coating Liquid-

**[0327]** A light-blocking layer coating liquid was prepared by blending 2.0 parts by mass of a 50% by mass acryl polyol

resin solution (LR327, manufactured by Mitsubishi Rayon Co., Ltd.), 4.0 parts by mass of a screen ink containing a compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter (Vinyl Ink H-type Half-tone (blue-yellow), manufactured by Jujo Chemical Co., Ltd.), 0.4 parts by mass of hydrophobic silica (RX-200, manufactured by Nippon Aerosil Co., Ltd.), and 4.0 parts by mass of methyl isobutyl ketone, and sufficiently stirring the mixture.

**[0328]** The produced thermoreversible recording medium of Comparative Example 8 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 8 to light in a wavelength range of 300 nm to 400 nm was 22.3%, the average transmittance to light in a wavelength range of 380 nm to 495 nm was 11.1%, and the transmittance thereof to light having a wavelength of 470 nm was 10.4%. A graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer of Comparative Example 8 is presented in FIG. 14.

(Comparative Example 9)

<Production of Thermoreversible Recording Medium>

**[0329]** A thermoreversible recording medium of Comparative Example 9 was produced in the same manner as in Example 1, provided that the first oxygen barrier layer was excluded.

**[0330]** The produced thermoreversible recording medium of Comparative Example 9 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 9 to light in a wavelength range of 300 nm to 400 nm, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm, and a transmittance thereof to light having a wavelength of 470 nm were identical to those of Example 1. The graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer was identical to FIG. 6.

(Comparative Example 10)

<Production of Thermoreversible Recording Medium>

**[0331]** A thermoreversible recording medium of Comparative Example 10 was produced in the same manner as in Example 3, provided that the light-blocking layer coating liquid was replaced with the following light-blocking layer coating liquid.

-Preparation of Light-Blocking Layer Coating Liquid-

**[0332]** A light-blocking layer coating liquid was prepared by blending 2.5 parts by mass of a 50% by mass acrylic polyol resin solution (LR327, manufactured by Mitsubishi Rayon Co., Ltd.), 2.7 parts by mass of an azo-compound ((LIBERA COLOR TXL-200 YELLOW, manufactured by Cashew Co., Ltd.) serving as the compound that absorbed, reflected, or scattered light in a wavelength range of 500 nm or shorter, 0.6 parts by mass of hydrophobic silica (RX-200, manufactured by Nippon Aerosil Co., Ltd.), 1.2 parts by mass of an isocyanate compound (Coronate HL, manufactured by Tosoh Corporation), and 10.0 parts by mass of methyl ethyl ketone, and sufficiently stirring the mixture.

**[0333]** The produced thermoreversible recording medium of Comparative Example 10 was measured by the spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation) in the same manner as in Example 1. As a result, the average transmittance of the light-blocking layer of Comparative Example 10 to light in a wavelength range of 300 nm to 400 nm was 18.1%, the average transmittance thereof to light in a wavelength range of 380 nm to 495 nm was 7.2%, and the transmittance thereof to light having a wavelength of 470 nm was 6.6%. A graph depicting a relationship between the wavelength and the transmittance of the light-blocking layer of Comparative Example 10 is presented in FIG. 15.

**[0334]** A laser recording evaluation and evaluation of absorbance changes by light irradiation were performed on each of the thermoreversible recording media of Examples 1 to 15 and Comparative Examples 1 to 10 in the following manners. The results are presented in Table 1.

<Laser Recording Evaluation>

**[0335]** As for a laser device, Ricoh Rewritable Laser Marker (LDM200-110, manufactured by Ricoh Company Limited, center wavelength: 980 nm) was used. A solid image was recorded on each of the thermosensitive recording medium produced in Examples 1 to 5 and Comparative Examples 1 to 10 with adjusting the irradiation distance to 150 mm, and the scanning speed to 2,000 mm/s. During the recording, the output of the laser was 13.5 W in Example 2 and Comparative

Example 2, and was 11.0 W in other Examples and Comparative Examples.

**[0336]** As for erasure of the image, Ricoh Rewritable Laser Eraser (LDE800-A, manufactured by Ricoh Company Limited, center wavelength: 976 nm) was used. Laser light was applied to each of the recording media, to which the solid image had been recorded, with adjusting the irradiation distance to 110 mm, the beam short width to 1.1 mm, and the scanning speed to 45 mm/s, to thereby erase the image. During the erasing, the effective output of the laser on the thermosensitive recording medium was 36.0 W in Example 2 and Comparative Example 2, and was 30.0 W in other Examples and Comparative Examples.

#### <Evaluation of Absorbance Change by Light Irradiation>

**[0337]** At first, an initial state of each of thermosensitive recording media of Examples 1 to 15 and Comparative Examples 1 to 10 was subjected to the measurement of the absorbance of light having a wavelength of 980 nm by means of a spectrophotometer (U-4100, manufactured by Hitachi High-Technologies Corporation), followed by recording an image thereon under the aforementioned laser recording conditions.

**[0338]** Subsequently, the thermosensitive recording medium was irradiated with light by means of a solar simulator (manufactured by SERUC., Ltd.) for 14 days at 30°C, 80%RH, with 80 klx. Therefore, the absorbance of the thermosensitive recording medium to light having a wavelength of 980 nm was measured by the spectrophotometer in the same manner as described above. Moreover, the thermosensitive recording medium was left to stand for 24 hours at 22°C, 50%RH. Therefore, the absorbance of the thermosensitive recording medium to light having a wavelength of 980 nm was measured by the spectrophotometer in the same manner as described above. The results of the absorbance as measured were compared to the absorbance of the thermosensitive recording medium of the initial state to light having a wavelength of 980 nm. The results are presented in Table 1. Note that, the evaluation performed with simulated solar light here is a mandatory test, the properties required for a thermosensitive recording medium in the market are corresponded to exposure to light under the conditions of the present evaluation.

**[0339]** Next, after each of the thermosensitive recording media of Examples 1 to 15 and Comparative Examples 1 to 10 was irradiated with light by means of the solar simulator, followed by being left to stand for 24 hours, the image thereon was erased under the aforementioned laser erasing conditions. Then, the density of the erased area, and the density of the background were measured by means of a reflection densitometer (X-Rite938, manufactured by X-Rite Inc.), and a difference between the density of the erased area and the density of the background was determined as an unerased density. The unerased density being 0.040 or less was determined that the image could be erased. The unerased density being 0.030 or less was determined as that the image was sufficiently erased. The results are presented in Table 1.

Table 1-1

|        | Average transmittance at the wavelength of 300 nm to 400 nm(%) | Average transmittance at the wavelength of 380 nm to 495 nm(%) | Transmittance at the wavelength of 470 nm (%) |
|--------|----------------------------------------------------------------|----------------------------------------------------------------|-----------------------------------------------|
| Ex. 1  | 1.8                                                            | 15.0                                                           | 17.3                                          |
| Ex. 2  | 1.8                                                            | 15.0                                                           | 17.3                                          |
| Ex. 3  | 1.8                                                            | 15.0                                                           | 17.3                                          |
| Ex. 4  | 0.9                                                            | 8.9                                                            | 10.2                                          |
| Ex. 5  | 0.5                                                            | 3.4                                                            | 3.9                                           |
| Ex. 6  | 0.5                                                            | 3.4                                                            | 3.9                                           |
| Ex. 7  | 0.5                                                            | 3.4                                                            | 3.9                                           |
| Ex. 8  | 0.5                                                            | 3.4                                                            | 3.9                                           |
| Ex. 9  | 1.8                                                            | 15.0                                                           | 17.3                                          |
| Ex. 10 | 0.6                                                            | 4.9                                                            | 7.5                                           |
| Ex. 11 | 0.6                                                            | 4.9                                                            | 7.5                                           |
| Ex. 12 | 0.6                                                            | 4.9                                                            | 7.5                                           |
| Ex. 13 | 0.6                                                            | 4.9                                                            | 7.5                                           |
| Ex. 14 | 0.6                                                            | 4.9                                                            | 7.5                                           |

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(continued)

|              | Average transmittance at the wavelength of 300 nm to 400 nm(%) | Average transmittance at the wavelength of 380 nm to 495 nm(%) | Transmittance at the wavelength of 470 nm (%) |
|--------------|----------------------------------------------------------------|----------------------------------------------------------------|-----------------------------------------------|
| Ex. 15       | 4.5                                                            | 14.8                                                           | 25.6                                          |
| Comp. Ex. 1  | 6.0                                                            | 74.8                                                           | 86.5                                          |
| Comp. Ex. 2  | 6.0                                                            | 74.8                                                           | 86.5                                          |
| Comp. Ex. 3  | 6.0                                                            | 74.8                                                           | 86.5                                          |
| Comp. Ex. 4  | 6.0                                                            | 74.8                                                           | 86.5                                          |
| Comp. Ex. 5  | 6.0                                                            | 74.8                                                           | 86.5                                          |
| Comp. Ex. 6  | 16.0                                                           | 21.8                                                           | 39.1                                          |
| Comp. Ex. 7  | 3.4                                                            | 34.9                                                           | 40.9                                          |
| Comp. Ex. 8  | 22.3                                                           | 11.1                                                           | 10.4                                          |
| Comp. Ex. 9  | 1.8                                                            | 15.0                                                           | 17.3                                          |
| Comp. Ex. 10 | 18.1                                                           | 7.2                                                            | 6.6                                           |

Table 1-2

|        | Absorbance of wavelength 980 nm |                         |                                                                | Unersased density after light irradiation |
|--------|---------------------------------|-------------------------|----------------------------------------------------------------|-------------------------------------------|
|        | Initial                         | After light irradiation | After irradiation followed by being left to stand for 24 hours |                                           |
| Ex. 1  | 0.66                            | 0.70                    | 0.68                                                           | 0.035                                     |
| Ex. 2  | 0.69                            | 0.73                    | 0.71                                                           | 0.036                                     |
| Ex. 3  | 0.67                            | 0.70                    | 0.69                                                           | 0.010                                     |
| Ex. 4  | 0.67                            | 0.69                    | 0.69                                                           | 0.006                                     |
| Ex. 5  | 0.67                            | 0.68                    | 0.68                                                           | 0.005                                     |
| Ex. 6  | 0.68                            | 0.68                    | 0.68                                                           | 0.009                                     |
| Ex. 7  | 0.65                            | 0.70                    | 0.70                                                           | 0.020                                     |
| Ex. 8  | 0.60                            | 0.71                    | 0.70                                                           | 0.025                                     |
| Ex. 9  | 0.68                            | 0.69                    | 0.69                                                           | 0.004                                     |
| Ex. 10 | 0.67                            | 0.68                    | 0.68                                                           | 0.005                                     |
| Ex. 11 | 0.68                            | 0.69                    | 0.69                                                           | 0.006                                     |
| Ex. 12 | 0.68                            | 0.68                    | 0.68                                                           | 0.002                                     |
| Ex. 13 | 0.67                            | 0.68                    | 0.68                                                           | 0.005                                     |

(continued)

|             | Absorbance of wavelength 980 nm |                         |                                                                | Unerased density after light irradiation |
|-------------|---------------------------------|-------------------------|----------------------------------------------------------------|------------------------------------------|
|             | Initial                         | After light irradiation | After irradiation followed by being left to stand for 24 hours |                                          |
| Ex. 14      | 0.69                            | 0.69                    | 0.69                                                           | 0.002                                    |
| Ex. 15      | 0.67                            | 0.69                    | 0.69                                                           | 0.009                                    |
| Comp.Ex. 1  | 0.66                            | 0.81                    | 0.68                                                           | 0.034                                    |
| Comp.Ex. 2  | 0.67                            | 0.82                    | 0.69                                                           | 0.031                                    |
| Comp.Ex. 3  | 0.68                            | 0.80                    | 0.80                                                           | 0.010                                    |
| Comp.Ex. 4  | 0.65                            | 0.85                    | 0.85                                                           | 0.018                                    |
| Comp.Ex. 5  | 0.62                            | 1.01                    | 1.00                                                           | 0.020                                    |
| Comp.Ex. 6  | 0.66                            | 0.75                    | 0.74                                                           | 0.133                                    |
| Comp.Ex. 7  | 0.67                            | 0.77                    | 0.77                                                           | 0.011                                    |
| Comp.Ex. 8  | 0.68                            | 0.78                    | 0.77                                                           | 0.155                                    |
| Comp.Ex. 9  | 0.67                            | 0.68                    | 0.67                                                           | 0.245                                    |
| Comp.Ex. 10 | 0.66                            | 0.67                    | 0.67                                                           | 0.323                                    |

**[0340]** It was found from the results of Table 1 that an increase in the absorbance of light having a wavelength of 980 nm after light irradiation, which was due to an increased in the absorbance of the metal oxide, was suppressed in Examples 1 to 15, as the thermosensitive recording media thereof each use the light-blocking layer with which the average transmittance to light in the wavelength range of 300 nm to 400 nm was 5% or less, and the average transmittance to light in the wavelength range of 380 nm to 495 nm was 20% or less. As the light-blocking layer, whose average transmittance to light in the wavelength range of 380 nm to 495 nm was 10% or less was used in Examples 4 to 8 and 10 to 14, moreover, an increase in the absorbance of light having the wavelength of 980 nm was prevented even after light irradiation. Especially in Examples 5 to 6 and 10 to 14, the tungsten oxide compound was used as the metal oxide having absorbance in the near infrared region, and the light-blocking layer whose transmittance to light having a wavelength of 470 nm was 10% or less was used, the absorbance at the wavelength of 980 nm hardly changed after light irradiation. Furthermore, as oxygen was sufficiently blocked in Examples 3 to 15, the unerased density after light irradiation was low, and the image could be sufficiently erased.

**[0341]** On the other hand, in Comparative Examples 1 to 5, the absorbance at the wavelength of 980 nm was significantly increased after light irradiation, as the thermosensitive recording media of Comparative Examples 1 to 5 did not contain the compound that absorbed, reflected, or scattered light in the wavelength range of 500 nm or shorter. If the absorbance of laser light having a wavelength of 980 nm is increased in the aforementioned manner, an image printing quality of a bar code is degraded as in the following evaluations of Comparative Examples 1 to 3.

**[0342]** Moreover, oxygen could be sufficiently blocked in Comparative Examples 3 to 5, and therefore the increased absorbance at the wavelength of 980 nm stayed the same even after leaving to stand for 24 hours after light irradiation.

**[0343]** Since light in the wavelength range of 500 nm or shorter was insufficiently blocked in Comparative Examples 6 to 8, the absorbance at the wavelength of 980 nm was largely increased after light irradiation. Especially in Comparative Examples 6 and 8, the unerased density after light irradiation was large, as the average transmittance to light in the wavelength range of 300 nm to 400 nm was significantly greater than 5%. Moreover, light in the wavelength range of 380 nm to 495 nm was sufficiently blocked in Comparative Example 10, but the unerased density after light irradiation

was significantly large, as the average transmittance to light in the wavelength range of 300 nm to 400 nm was significantly greater than 5%.

**[0344]** As an oxygen barrier layer was not provided to the thermosensitive recording medium of Comparative Example 9, moreover, the absorbance at the wavelength of 980 nm hardly changed after light irradiation, as oxygen was supplied. However, the unerased density after light irradiation was significantly large, as oxygen could not be blocked.

<Evaluation of Image Printing Quality of Bar code>

**[0345]** A bar code was recorded on an initial state of each of the thermosensitive recording media of Examples 1 to 2, and 5, and Comparative Examples 1 to 3 under the aforementioned laser recording conditions. As for the evaluation of the image printing quality of the bar code, the bar code image was read by a one-dimensional bar code reader (WEBSCANTruCheck 401-RL, manufactured by WEBSCAN) to thereby measure a grade of the bar code. As a result, the bar codes recorded on the thermosensitive recording media of Examples 1 to 2, and 5, and Comparative Examples 1 to 3 were all grade C. Note that, as for the grade of the bar code, the grade D or better is typically regarded as readable by a bar code reader. When the grade is F, it is determined it cannot be read by a bar code reader.

**[0346]** Subsequently, each of the thermosensitive recording media of Examples 1, 2, and 5, and Comparative Examples 1 to 3 was irradiated with light by means of a solar simulator manufactured by SERUC., Ltd. for 14 days at 30°C, 80%RH, with 80 klx. Thereafter, a bar code was recorded on each of the thermosensitive recording media of Examples 1, 2, and 5 and Comparative Examples 1 to 3, which had been irradiated with light, under the aforementioned laser recording conditions. As for the evaluation of the image printing quality of the bar code, the bar code image was read by a one-dimensional bar code reader (WEBSCANTruCheck 401-RL, manufactured by WEBSCAN) to thereby measure a grade of the bar code. As a result, the bar codes recorded on the thermosensitive recording media of Examples 1 to 2, and 5 were grade C. This is because the absorbed quantity of laser light did not change, as the absorbance at the wavelength of 980 nm hardly changed, and as a result, the thermosensitive recording medium was not excessively heated, and a writing line width did not change. On the other hand, the bar codes recorded on the thermosensitive recording media of Comparative Examples 1 to 3 were grade F, and the bar codes could not be read. This is because the absorbed quantity of laser light increased due to the increase in the absorbance at the wavelength of 980 nm to excessively heat the thermosensitive recording medium, and thus the writing line width widened, and the bar code readability was degraded. Furthermore, a bar code was recorded on each of the thermosensitive recording media of Comparative Examples 1 to 3, which had been left to stand for 24 hours after the light irradiation, under the aforementioned laser recording conditions. In Comparative Examples 1 to 2, the increased absorbance at the wavelength of 980 nm as returned back, as therefore the thermosensitive recording medium was not excessively heated, and the grade of the bar code was grade C as measured by the one-dimensional bar code reader. In Comparative Example 3, the increased absorbance at the wavelength of 980 nm stayed the same even after being left for 24 hours after the light irradiation, and thus the grade of the bar code was still grade F, and the bar code could not be read. Note that, Examples 1, 2, and 5, and Comparative Examples 1 to 3 in the evaluation of the image printing quality of the bar code are corresponded to Examples and Comparative Examples applied for a write-only thermosensitive recording medium.

**[0347]** The thermosensitive recording medium of the present invention contains: a layer containing, as a photothermal converting material, metal oxide having absorbance in the near infrared region; an oxygen barrier layer; and a light-blocking layer, with which the average transmittance to light in a wavelength range of 300 nm to 400 nm is 5% or less, and the average transmittance to light in a wavelength range of 380 nm to 495 nm is 20% or less, and therefore, a high-contrast image can be repeatedly recorded and erased in a non-contact manner with the thermosensitive recording medium being attached to a container, such as a cardboard box, and a plastic container, and changes in the image recording sensitivity and image erasing sensitivity over time can be prevented even when the thermosensitive recording medium is left outside and irradiated with light, such as sun light, for a long period. Accordingly, the thermosensitive recording medium of the present invention is particularly suitably used for a physical distribution or delivery system.

**[0348]** The embodiments of the present invention are, for example, as follows:

<1> A thermosensitive recording medium, including:

- a support;
  - an image recording layer, which is provided on the support, and contains a leuco dye, a color developer, and a metal oxide having absorbance in the near infrared region;
  - an oxygen barrier layer; and
  - a light-blocking layer,
- wherein the oxygen barrier layer and the light-blocking layer are provided a surface of the image recording layer, which is an opposite side to a surface thereof where the support is provide, and
- wherein an average transmittance of the light-blocking layer to light in a wavelength range of 300 nm to 400

nm is 5% or less, and an average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 20% or less.

<2> A thermosensitive recording medium, containing:

a support;  
 an image recording layer containing a leuco dye and a color developer;  
 a photothermal conversion layer containing a metal oxide having absorbance in the near infrared region;  
 an oxygen barrier layer; and  
 a light-blocking layer,  
 wherein the image recording layer and the photothermal conversion layer are provided on the support, and the oxygen barrier layer and the light-blocking layer are provided on a surface of the image recording layer or the photothermal conversion layer, which is an opposite side to a surface thereof where the support is provided, and wherein an average transmittance of the light-blocking layer to light in a wavelength range of 300 nm to 400 nm is 5% or less, and an average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 20% or less.

<3> The thermosensitive recording medium according to <1> or <2>, wherein the average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 10% or less.

<4> The thermosensitive recording medium according to any one of <1> to <3>, wherein a transmittance of the light-blocking layer to light having a wavelength of 470 nm is 10% or less.

<5> The thermosensitive recording medium according to any one of <1> to <4>, wherein the light-blocking layer contains an ultraviolet ray-blocking layer and a blue light-blocking layer.

<6> The thermosensitive recording medium according to any one of <1> to <5>, wherein the metal oxide having absorbance in the near infrared region is a tungsten oxide compound, indium-doped tin oxide, or antimony-doped tin oxide, or any combination thereof.

<7> The thermosensitive recording medium according to any one of <1> to <6>, wherein the metal oxide having absorbance in the near infrared region is a tungsten oxide compound.

<8> The thermosensitive recording medium according to any one of <1> to <7>, wherein the oxygen barrier layer is composed of a first oxygen barrier layer and a second oxygen barrier layer, and wherein the first oxygen barrier layer is provided on a surface of the image recording layer or the photothermal conversion layer, which is an opposite side to a surface thereof where the support is provided, and the second oxygen barrier layer is provided between the image recording layer and the support, or on a surface of the support, which is an opposite side to a surface thereof where the image recording layer is provided, or both therebetween and thereon.

<9> An image processing method, containing:

irradiating the thermosensitive recording medium according to any one of <1> to <8> with light to perform image recording, or image erasing, or both.

<10> The image processing method according to <9>, wherein light with which the thermosensitive recording medium is irradiated is near infrared laser light in a wavelength range of 700 nm to 2,000 nm.

## Claims

1. A thermosensitive recording medium, comprising:

a support;  
 an image recording layer, which is provided on the support, and contains a leuco dye, a color developer, and a metal oxide having absorbance in the near infrared region;  
 an oxygen barrier layer; and  
 a light-blocking layer,  
 wherein the oxygen barrier layer and the light-blocking layer are provided a surface of the image recording layer, which is an opposite side to a surface thereof where the support is provide, and wherein an average transmittance of the light-blocking layer to light in a wavelength range of 300 nm to 400 nm is 5% or less, and an average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 20% or less.

2. A thermosensitive recording medium, comprising:

a support;

an image recording layer containing a leuco dye and a color developer;

a photothermal conversion layer containing a metal oxide having absorbance in the near infrared region;

an oxygen barrier layer; and

a light-blocking layer,

wherein the image recording layer and the photothermal conversion layer are provided on the support, and the oxygen barrier layer and the light-blocking layer are provided on a surface of the image recording layer or the photothermal conversion layer, which is an opposite side to a surface thereof where the support is provided, and wherein an average transmittance of the light-blocking layer to light in a wavelength range of 300 nm to 400 nm is 5% or less, and an average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 20% or less.

3. The thermosensitive recording medium according claim 1 or 2, wherein the average transmittance of the light-blocking layer to light in a wavelength range of 380 nm to 495 nm is 10% or less.

4. The thermosensitive recording medium according to any one of claims 1 to 3, wherein a transmittance of the light-blocking layer to light having a wavelength of 470 nm is 10% or less.

5. The thermosensitive recording medium according to any one of claims 1 to 4, wherein the light-blocking layer comprises an ultraviolet ray-blocking layer and a blue light-blocking layer.

6. The thermosensitive recording medium according to any one of claims 1 to 5, wherein the metal oxide having absorbance in the near infrared region is a tungsten oxide compound, indium-doped tin oxide, or antimony-doped tin oxide, or any combination thereof.

7. The thermosensitive recording medium according to any one of claims 1 to 6, wherein the metal oxide having absorbance in the near infrared region is a tungsten oxide compound.

8. The thermosensitive recording medium according to any one of claims 1 to 7, wherein the oxygen barrier layer is composed of a first oxygen barrier layer and a second oxygen barrier layer, and wherein the first oxygen barrier layer is provided on a surface of the image recording layer or the photothermal conversion layer, which is an opposite side to a surface thereof where the support is provided, and the second oxygen barrier layer is provided between the image recording layer and the support, or on a surface of the support, which is an opposite side to a surface thereof where the image recording layer is provided, or both therebetween and thereon.

9. An image processing method, comprising:

irradiating the thermosensitive recording medium according to any one of claims 1 to 8 with light to perform image recording, or image erasing, or both.

10. The image processing method according to claim 9, wherein light with which the thermosensitive recording medium is irradiated is near infrared laser light in a wavelength range of 700 nm to 2,000 nm.

FIG. 1A

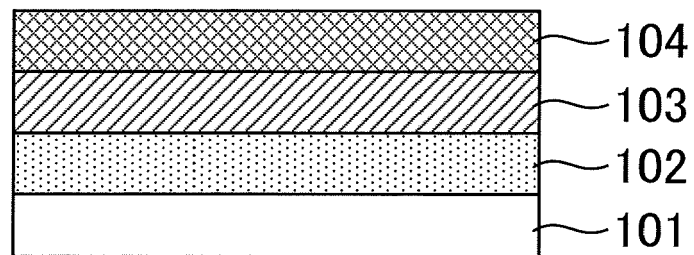


FIG. 1B

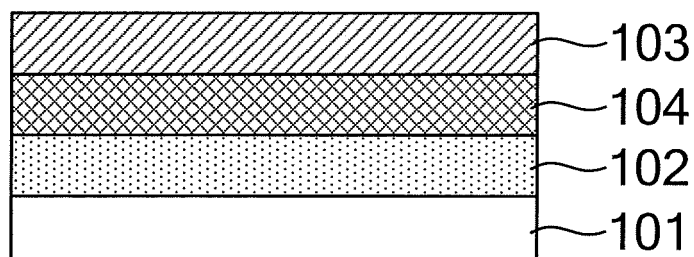


FIG. 2A

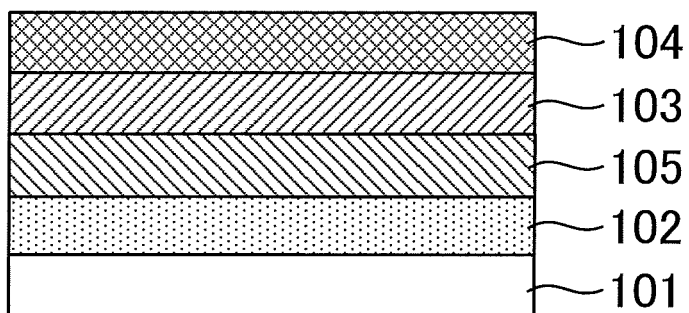


FIG. 2B

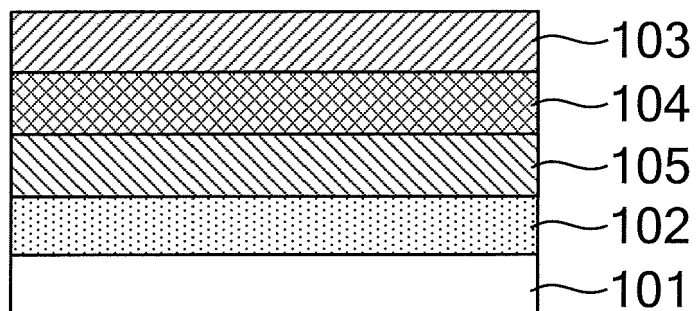


FIG. 2C

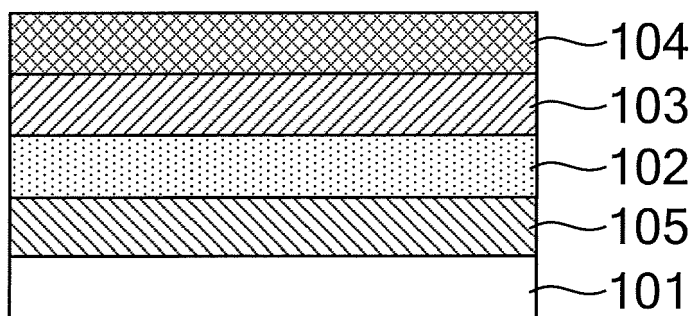


FIG. 2D

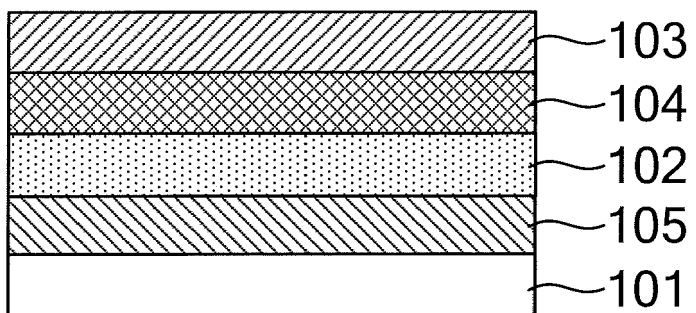


FIG. 2E

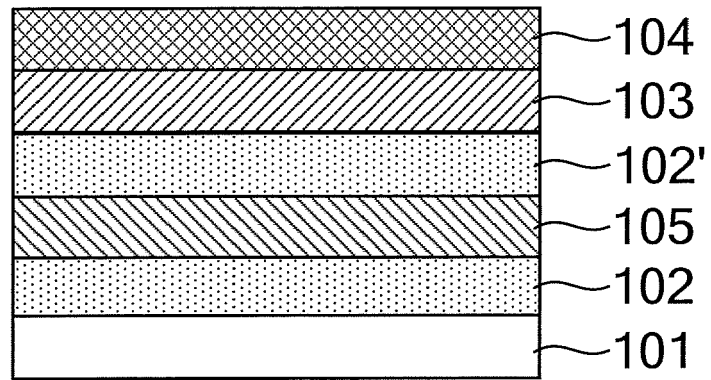


FIG. 3A

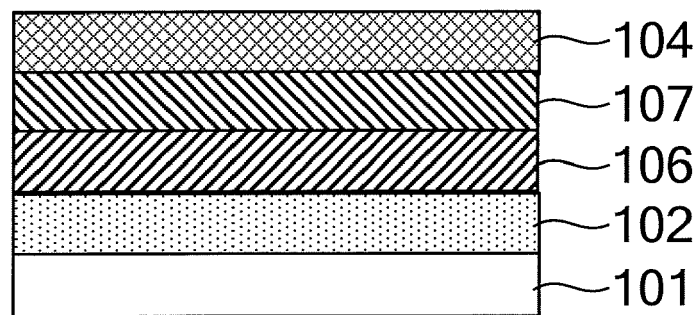


FIG. 3B

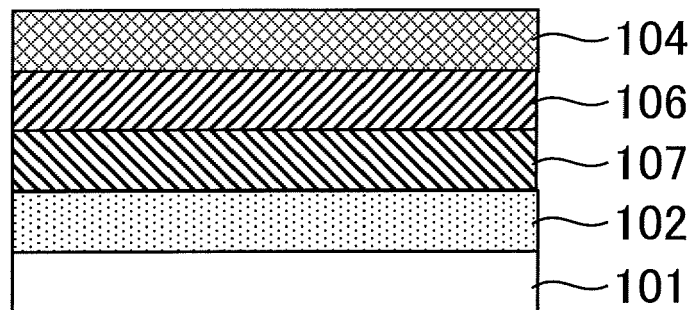


FIG. 3C

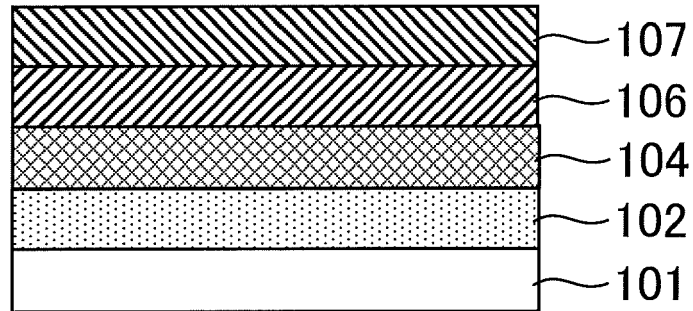


FIG. 3D

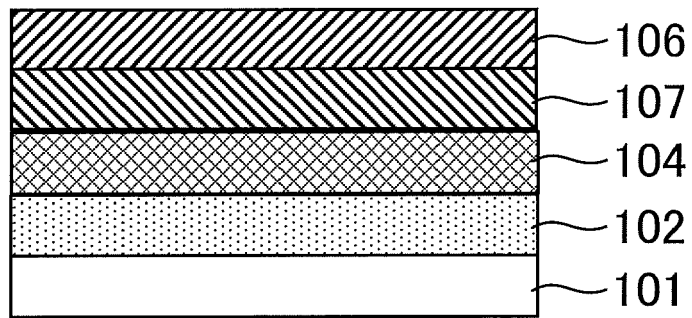


FIG. 3E

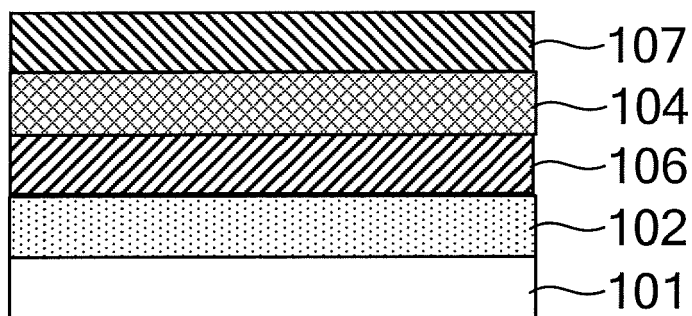


FIG. 4A

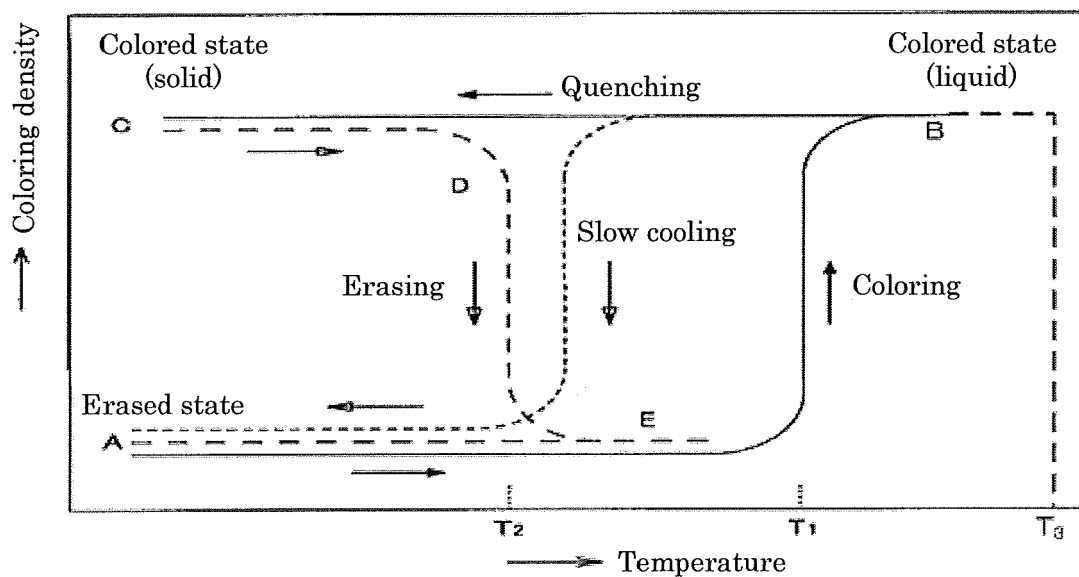


FIG. 4B

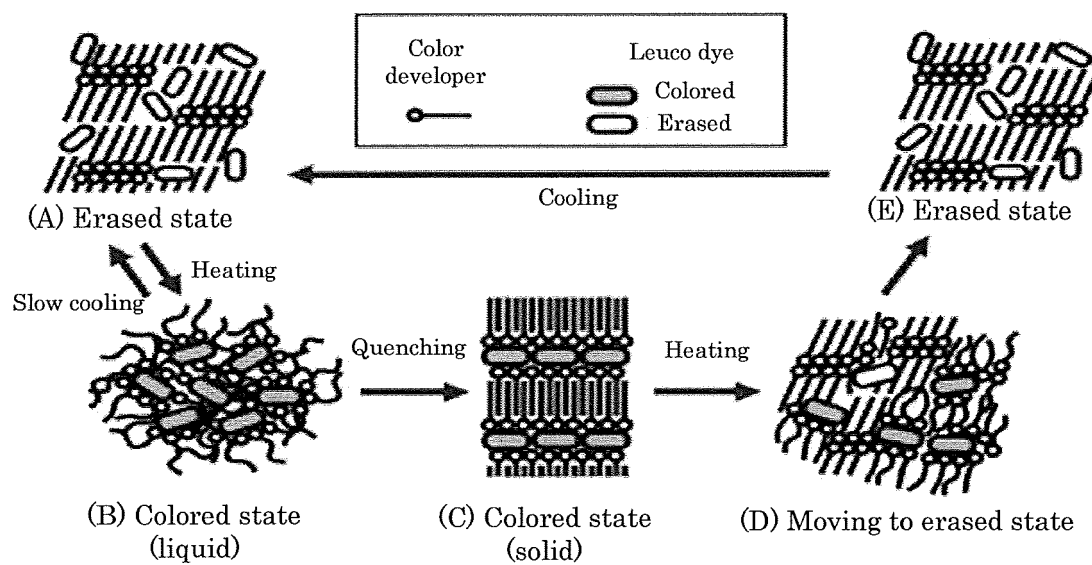


FIG. 5

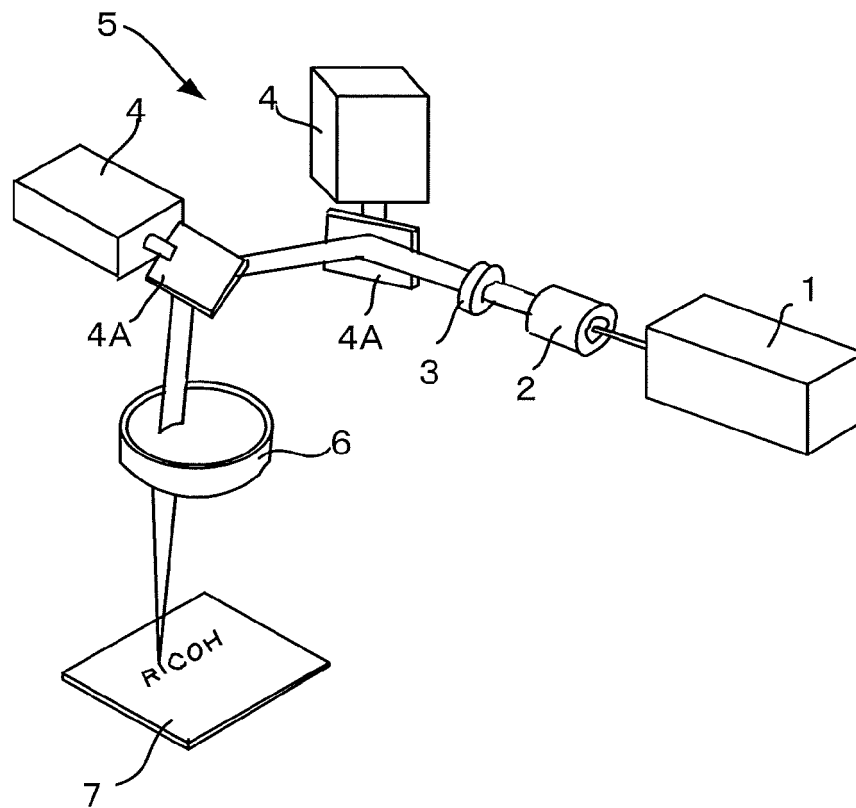


FIG. 6

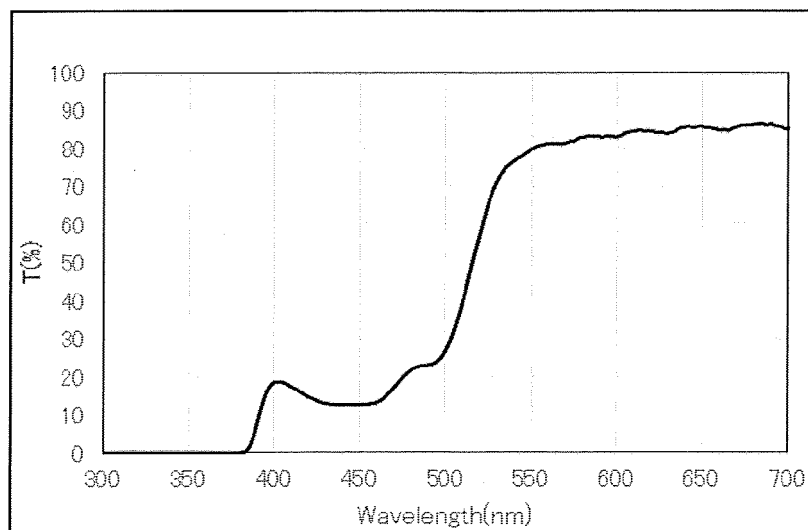


FIG. 7

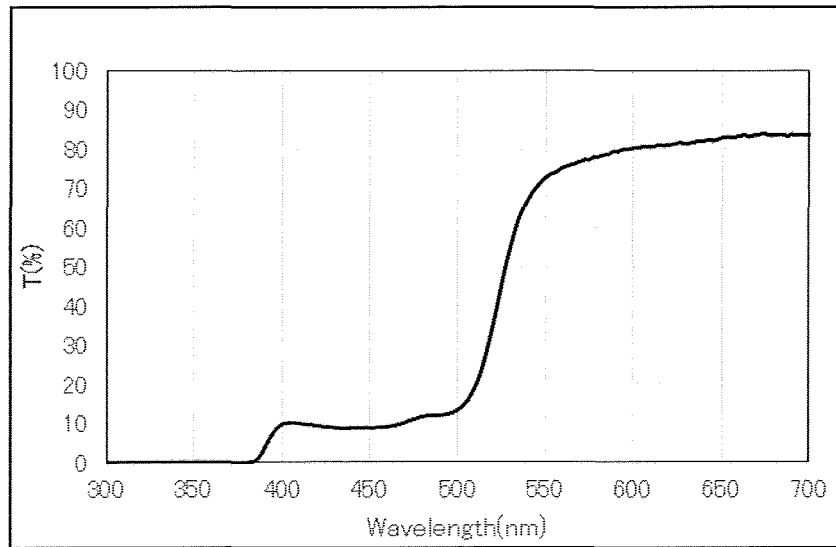


FIG. 8

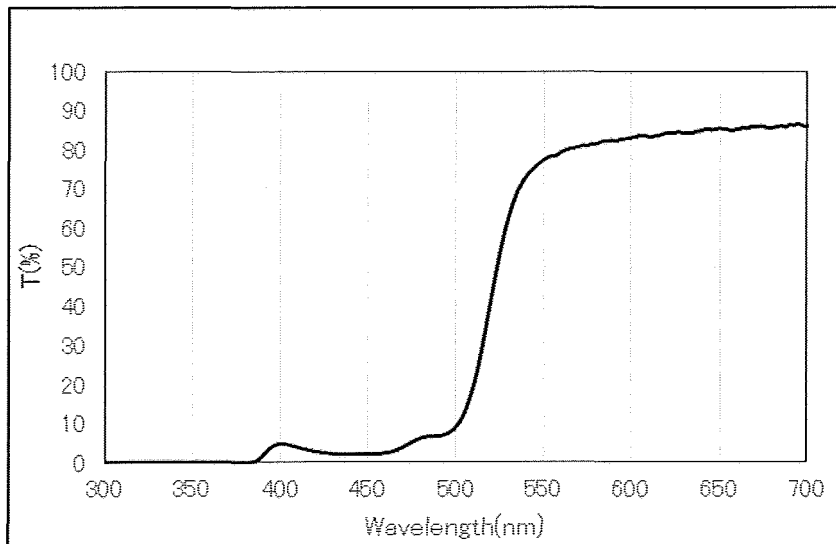


FIG. 9

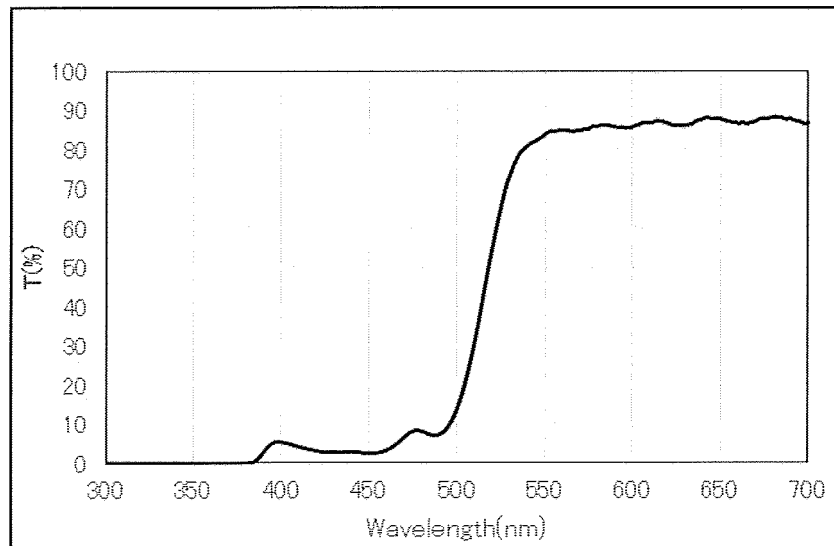


FIG. 10

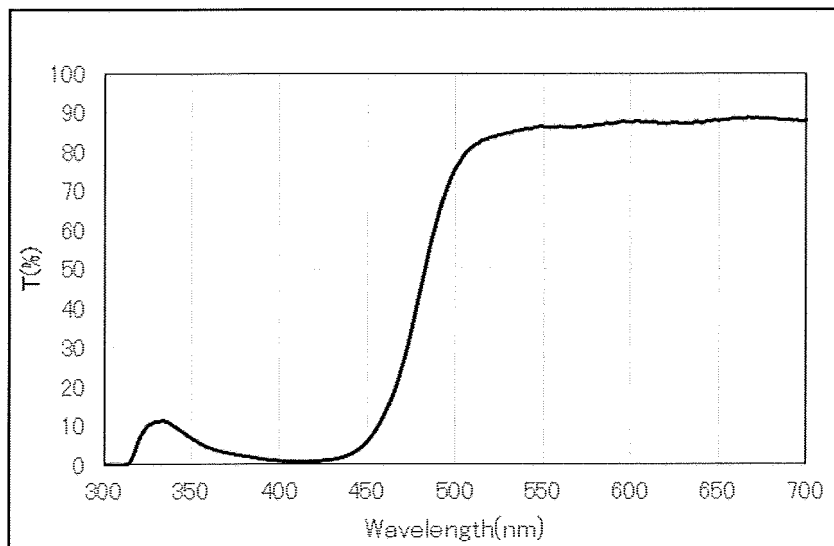


FIG. 11

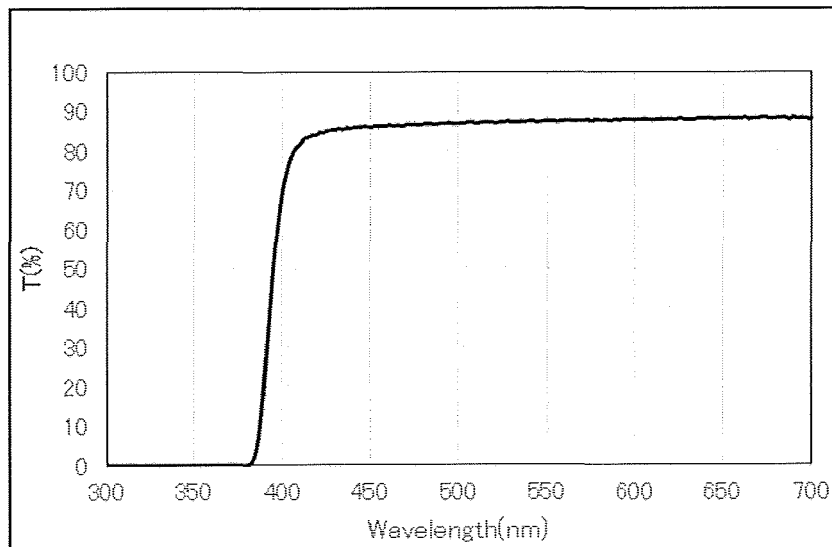


FIG. 12

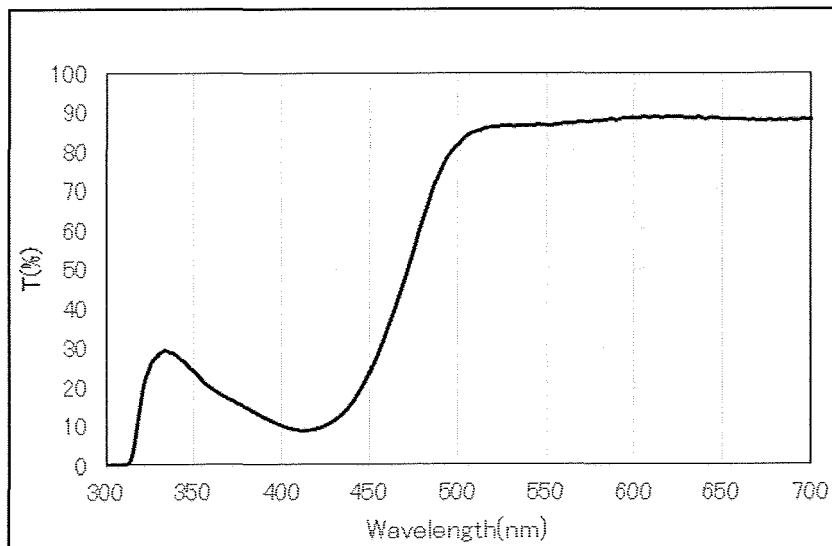


FIG. 13

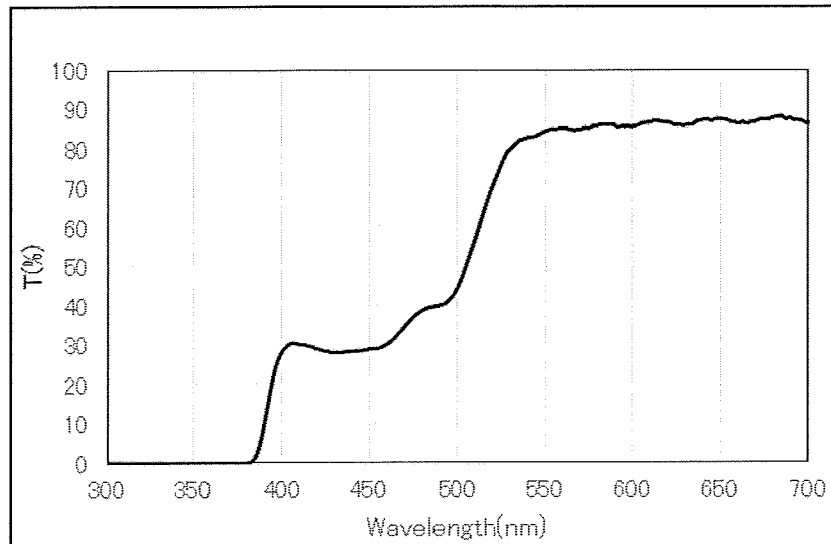


FIG. 14

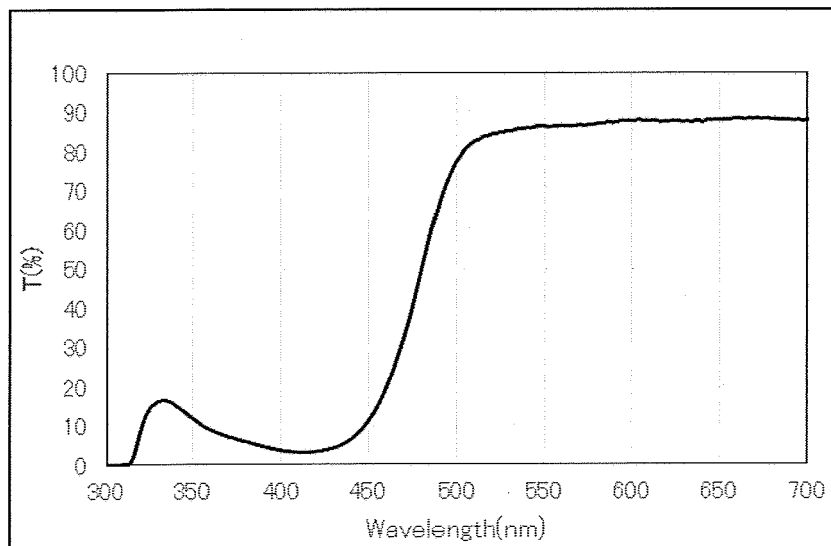
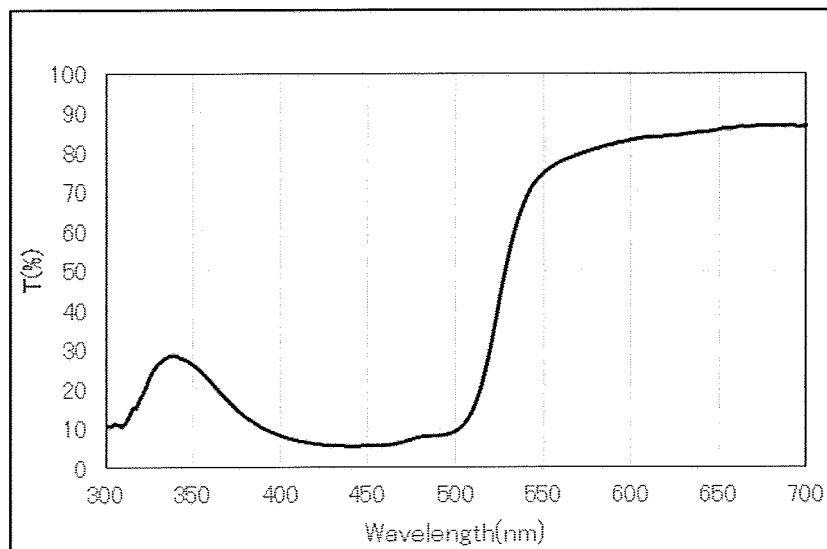


FIG. 15



**REFERENCES CITED IN THE DESCRIPTION**

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