Description

The present invention relates to an optical recording medium on which recording is carried out by the irradiation of light in near infrared region.

A heat-sensitive recording system is a direct recording system which does not require any development and fixing, and therefore it is excellent in operation and maintenance. For this reason, the heat-sensitive recording system is widely utilized in facsimiles and printers.

In this system, however, the recording is thermally made by bringing a thermal head or an exothermic IC pen into direct contact with a heat-sensitive recording paper, and hence melted colored substances adhere to the thermal head or the exothermic IC pen, so that troubles such as dregs adhesion and sticking take place, which brings about record obstruction and impairs record quality inconveniently.

In particular, when a line is depicted continuously in a recording direction as in the case of a plotter printer, it is impossible to avoid the trouble of the dregs adhesion.

Furthermore, when the recording is made by the thermal head, it is difficult to more heighten an image resolution of 8 dots/mm which is now employed.

Thus, as techniques by which troubles such as the dregs adhesion and the sticking are solved and by which the resolution is more improved, some non-contact recording systems using light have been suggested.

Japanese Patent Laid-open Publication No. 209594/1983 discloses an optical recording medium prepared by laminating at least one set of a near infrared absorbent layer having an absorption wave length in a near infrared region of 0.8 to 2 μm and a heat-sensitive color-developing material layer onto a substrate, and Japanese Patent Laid-open Publication No. 94494/1983 discloses a recording medium prepared by superposing, on a base material, a layer containing one or more kinds of heat-sensitive materials and a layer containing one or more kinds of near infrared absorbents comprising compounds having a maximum absorption wave length in near infrared rays of 0.7 to 3 μm.

These publications disclose the procedure of laminating or superposing the near infrared absorbent and the heat-sensitive color-developing material on the substrate or the base material. That is, the near infrared absorbent is mixed with the heat-sensitive color-developing material and the resulting mixture is then applied onto the substrate or the base material, or alternatively the heat-sensitive color-developing material is first applied on the substrate or the base material, and the near infrared absorbent is then applied on the heat-sensitive color-developing material layer.

In the above-mentioned publications, there are disclosed dyestuffs such as cyanine dyestuffs, thiol nickel complexes and squarylium as the near infrared absorbent.

In addition, as enumerated in "Near Infrared Absorption Dyestuffs", Chemical Industry, Vol. 43, May 1986, other dyestuffs are known which are, for example, nitroso compounds and their metal complexes, polymethine dyestuffs (cyanine dyestuffs), complexes of thiols and cobalt or palladium, phthalocyanine dyestuffs, triallylmethane dyestuffs, immonium dyestuffs, diimmonium dyestuffs and naphthoquinone dyestuffs.

When these conventional near infrared absorbent and heat-sensitive color-developing material are mixed and then applied on the substrate as disclosed in the above-mentioned publication, a desensitization phenomenon appears and a color development performance deteriorates. Furthermore, when the heat-sensitive color-developing material is first applied on the substrate, and the near infrared absorbent is then applied on this material layer, the deterioration in a ground color occurs inconveniently. In addition, all the conventional near infrared absorbents have relatively strong and wide absorption spectra in a visual region, and they are also intensively colored. Therefore, it is difficult to obtain the optical recording medium having a white ground color, which obstructs putting the optical recording medium into practice.

An object of the present invention is to provide an optical recording medium in which a ground color and a color development performance are improved.

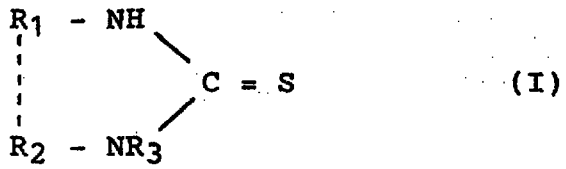
This object of the present invention can be achieved by providing an optical recording medium which comprises a substrate, a light-absorbing layer containing a near infrared absorbent, and a heat-sensitive color-developing layer, these layers being superposed upon the substrate, the aforesaid near infrared absorbent being prepared by heating a mixture of a thiourea derivative and a metallic compound.

Fig. 1 is a block diagram of an optical recording device which is used when an optical recording medium of the present invention is irradiated with a laser beam.

1: Laser diode collimator head
2: Shutter
3: Condenser
4: Optical recording paper

5: Power source
6: Paralleled laser beam
7: Condensed point
8: Operation distance

The present invention is directed to an optical recording medium which comprises a substrate, a light-absorbing layer containing a near infrared absorbent, and a heat-sensitive color-developing layer containing a basic colorless dye and an organic developer, these layers being superposed upon the substrate, the aforesaid near infrared absorbent being prepared by heating a mixture of a thiourea derivative represented by the formula (I)



(I)

wherein each of R_1, R_2 and R_3 is a monovalent group selected from the group consisting of hydrogen, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aralkyl group and a five-membered or six-membered heterocyclic residue, a pair of R_1 and R_2 or a pair of R_2 and R_3 may be linked together to form a ring, and each group of R_1, R_2 and R_3 may have one or more substituents of an amino group, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, a nitro group, a halogen atom, a hydroxyl group, an alkoxy group and an acyl group,
and a metallic compound represented by the formula (II)

$(R\text{-}X)_nM$ (II)

wherein R is hydrogen, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group and a heterocyclic residue, each group of R may have one or more substituents, X is -COO, $-SO_4$, $-SO_3$, $-PO_4$ or -O, n is an integer of 1 to 4, and M is a metal having an atomic weight of 40 or more except metals in the group IA and IIA of the periodic table
or a metallic compound selected from the group of chlorophyll M, M chlorophyllin sodium and bisacetylacetonate M.

The light-absorbing layer containing the near infrared absorbent may be used as an underlayer, and the heat-sensitive color-developing layer containing the basic colorless dye and the organic developer may be superposed upon the above-mentioned layer, and in this case, a maximum effect can be obtained.

Moreover, a transparent protective layer may be disposed on the heat-sensitive color-developing layer, and a small amount of a conventional known near infrared absorbent dye may be contained in the protective layer or the underlayer, or on or under this layer, or alternatively a synthetic resin pigment having a high near infrared reflectivity is contained in the color-developing layer or the light-absorbing layer. According to this constitution, the more excellent optical recording medium can be obtained.

The feature of the present invention resides in that the optical recording medium comprises the light-absorbing layer containing the light absorbent and the heat-sensitive color-developing layer, and the light absorbent is the near infrared absorbent which can be prepared by heating the mixture of the thiourea derivative and the metallic compound.

This near infrared absorbent has relatively uniform and strong absorption spectra all over the near infrared region of 0.8 to 2.8 μm, and has relatively weak absorption spectra in a visible region. In addition, the near infrared absorbent can convert the absorbed near infrared rays into heat rapidly and effectively and then can release the heat. Therefore, this absorbent is suitable for the present invention.

The near infrared absorbent used in the present invention can be prepared by the method disclosed in Japanese Patent Application Nos. 145262/1988 and 232075/1988 filed by the same inventors as in the present application and regarding the near infrared absorption material which comprises the thiourea derivative and the copper compound or lead compound. That is, the near infrared absorbent used in the present invention can be prepared by mixing the thiourea derivative and the metallic compound, and then heating the resulting mixture. This preparation can be achieved by any of the following processes: A process in which the thiourea derivative is mixed with the metallic compound, and immediately the resulting mixture is then heated; a process in which both the materials are dispersed in a dispersant, and the resulting dispersion is then heated; a process in which each of the materials is separately dispersed in the

dispersant, and the resulting dispersions are then mixed, followed by heating; and a process in which the dispersant is removed from the above-mentioned dispersion by drying or the like, and heating is then carried out. In each of these processes, the mixing and heating steps may be effected simultaneously.

Other materials which do not impair the near infrared absorbency of the absorbent, i.e., a binder, a dispersant and a dispersing medium may be added to the mixture of the above-mentioned materials, if necessary.

In the heating treatment for generating the near infrared absorbency, any means can be used, so long as it can supply a thermal energy by which the two components are reacted to obtain a near infrared absorbing power. Examples of such a means include an electric heater, induction heating, melt molding of a film, a thermal head, a semiconductor laser and an infrared lamp. The heating operation can be carried out under an optional atmosphere such as the atmosphere or an inert atmospheric gas, but usually under the atmosphere.

A heating temperature is usually in the range of 40 to 400 °C, preferably 50 to 350 °C. A heating time is usually in the range of milliseconds to tens minutes. Furthermore, it is preferred to add stirring, rotation or vibration so as to increase the contact frequency of the materials, to uniform the transmission of heat energy and to thereby accelerate the reaction, and to uniform a mixing state.

In the present invention, a blend ratio of the thiourea derivative to the metallic compound depends upon kinds of both materials themselves, but usually the amount of the thiourea compound is 0.01 to 50 parts, preferably 0.1 to 10 parts with respect to 1 part of the metallic compound.

Typical examples of the thiourea derivative of the formula (I) which is one of the constitutional components of the near infrared absorbent used in the present invention include 1,3-diphenylthourea, 1,3-dibenzylthiourea, 1,3-dilaurylthiourea, 1,3-diethylthiourea, di-m-chlorophenylthiourea, 1-(2-thiazolyl)-3-phenylthiourea, 1-benzyl-3-morpholinothiourea, and other compounds enumerated in Japanese Patent Application No. 145262/1988.

Typical examples of the metallic compound which is the other constitutional component of the near infrared absorbent in the present invention include organic acid salts, alkoxides and hydroxides of Y, Ti, Zr, V, Nb, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Sn and Pb.

Examples of the organic acid include the following compounds, but they are not limited.

Stearic acid, palmitic acid, oleic acid, behenic acid, lauric acid, capric acid, caproic acid, valeric acid, isobutyric acid, butyric acid, propionic acid, acetic acid, formic acid, benzoic acid, orthotoluic acid, metatoluic acid, paratoluic acid, paratertiary butylbenzoic acid, orthochlorobenzoic acid, metachlorobenzoic acid, parachlorobenzoic acid, dichlorobenzoic acid, trichlorobenzoic acid, p-bromobenzoic acid, p-iodobenzoic acid, p-phenylbenzoic acid, o-benzoylbenzoic acid, p-nitrobenzoic acid, anthranyl acid, p-aminobenzoic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, monoester phthalic acid, naphthenic acid, naphthalenecarboxylic acid, tartaric acid, diphenylamine-2-carboxylic acid, 4-cyclohexylbutyric acid, gluconic acid, octylic acid, alkylbenzenesulfonic acid, p-toluenesulfonic acid, naphthalinesulfonic acid, naphthylaminesulfonic acid, n-dodecylbenzenesulfonic acid, dodecylsulfuric acid, 2,5-dimethylbenzenesulfonic acid, 2-carbomethoxy-5-methylbenzenesulfonic acid, α-naphtylphosphoric acid, stearylphosphoric acid, laurylphosphoric acid, di-2-ethylhexylphosphoric acid and isodecylphophoric acid.

Examples of the alcohol include alcohols corresponding to the above-mentoned organic acids.

Among others, the metallic compounds of V, Ni, Co, Fe, Ag, Cu and Pb are preferable as the near infrared absorbents, because they have uniform and intensive absorption spectra all over the near infrared region. In particular, the near infrared absorbent in which the copper compound or lead compound is used is more preferable, because when such a kind of absorbent is used, the light-absorbing layer having a white ground color can be obtained.

The absorbency of the near infrared rays depends upon kinds of the thiourea derivative and the metallic compound and can be optionally regulated by adjusting a ratio of the thiourea derivative to the metallic compound, the heating temperature and heating time.

The thus obtained near infrared absorbent has weak absorption spectra in the visible region, and therefore the absorption spectra in the near infrared portion of 1 μm or less are weaker than in the other portions. This tendency is noticeable, when a small amount of the near infrared absorbent is used. On the other hand, most of the conventional known near infrared absorption dyestuffs have absorption peaks in the region of 1 μm or less. Accordingly, when the near infrared absorbent and the known near infrared absorption dyestuff are used together adjusting amounts of these absorbents, the functionally balanced light-absorbing layer can be formed which can absorb the near infrared rays uniformly in the wide region.

The thus obtained near infrared absorbent is mixed with and dispersed in the material constituting the light-absorbing layer, and the light-absorbing layer containing the absorbent is applied onto the substrate by

means of spray, coating or printing. Alternatively, the preparation of the near infrared absorbent and the preparation of the light-absorbing layer may be carried out simultaneously by separately dispersing the thiourea compound or the metallic compound with the material constituting the light-absorbing layer to form slurries; mixing these slurries; applying the mixture on the substrate by means of spray, coating or printing; drying the applied material to remove a used dispersing medium therefrom; and heating the same.

The material of the substrate is not limited at all, but papers, synthetic papers and plastic films are usually used.

The material constituting the light-absorbing layer is composed of auxiliaries such as a binder, a white pigment and a near infrared absorption dyestuff.

The binder can be selected from conventional binders for the heat-sensitive color-developing layer which will be described.

The white pigment is effective to hide the color of the near infrared absorbent and to whiten the whole optical recording medium, and in addition, the pigment has functions of scattering the incident near infrared rays so as to increase the probability that the scattered near infrared rays hit against the near infrared absorbent, and to thereby heighten heat generation efficiency.

The white pigment works to reflect the visible rays intensively on the average, and usually it reflects the near infrared rays and visible rays similarly. Examples of the usable white pigment include clay, calcium bicarbonate, sedimentary calcium carbonate, titanium oxide, calcium sulfate, barium sulfate, zinc sulfate, satin white, talc, basic magnesium carbonate, zinc oxide, alumina, white carbon, silica gel, colloidal silica and plastic pigments. Preferable are white pigments having a porous state or a large specific surface area, such as silica gel, colloidal silica, ultrafine alumina and plastic pigments.

In particular, the hollow plastic pigments are preferable for the following reason: These hollow plastic pigments are excellent in reflection properties of the near infrared rays and insulating properties, and therefore they can inhibit the diffusion of the heat generated from the near infrared rays absorbed by the near infrared absorbent.

The near infrared absorption dyestuff which ensures the effect of the near infrared absorbent used in the present invention is relatively easily soluble in a solvent such as water, an alcohol and toluene, and its solubility is preferably 5% or more. Typical examples of such dyestuffs include polymethine dyestuffs (cyanine dyestuffs), azulenium dyestuffs, pyrylium dyestuffs and mercaptophenol dyestuffs which are mentioned as soluble near infrared absorbents in Japanese Patent Application No. 272702/1988 regarding an optical recording medium using a solvent-insoluble dispersible near infrared absorbent and filed by the same inventors as in the present application.

This near infrared absorption dyestuff can be contained in layers other than the heat-sensitive color-developing layer of the optical recording medium, i.e., in the light-absorbing layer and/or a protective layer or between these layers.

The thus obtained light-absorbing layer is superposed upon the heat-sensitive color-developing layer comprising a basic colorless dye, an organic developer and a binder, and if necessary, quality regulators such as a sensitizer and a filler, thereby obtaining the optical recording medium.

The heat-sensitive color-developing layer is all the same as a color-developing layer for a heat-sensitive recording paper containing a known electron-donating colorless dye and an electron-receiving organic developer by way of color development components, and all the known techniques regarding this color-developing layer for the heat-sensitive recording paper can be applied hereto.

Examples of the basic colorless dye include a triphenylmethane leuco dye such as crystal violet lactone, a fluoran leuco dye such as 3-diethylamino-6-methyl-7-anilinofluoran, an azaphthalide leuco dye such as 3-(4-diethylamino-2-ethoxyphenyl)-3-(1-ethyl-2-methylindole-3-yl)-4-azaphthalide and a fluorhein leuco dye such as 3,6,6'-tris(dimethylamino)spiro[fluorhein-9,3'-phthalide].

Furthermore, examples of the organic developer include bisphenol A's, 4-hydroxybenzoic acid esters, 4-hydroxyphthalic acid diesters, phthalic acid monoesters, bis(hydroxyphenyl) sulfides, 4-hydroxyphenylaryl sulfones, 4-hydroxyphenylarylsulfonates, 1,3-di[2-(hydroxyphenyl)-2-propyl]-benzenes, 4-hydroxybenzoyloxybenzoic acid esters and bisphenol sulfones.

Examples of the binder include completely saponified polyvinyl alcohol having a polymerization degree of 200 to 1900, a modified polyvinyl alcohol such as amide-modified polyvinyl alcohol, hydroxyethyl cellulose and styrenebutadiene copolymer.

Usually, fatty amide and montan wax can be used as sensitizers or quality regulators, and clay, calcium carbonate and plastic pigments which are generally used in the paper coating field can also be used as fillers. In particular, the hollow plastic pigments are preferable because of excellent reflecting properties to the near infrared rays and because of good heat retaining properties.

As these materials used in the heat-sensitive color-developing layer, basic colorless dyes, organic developers, binders, sensitizers, fillers and quality regulators mentioned in Japanese Patent Application No. 272702/1988 filed by the same inventors as in the present case can also be used in the present invention.

Kinds and amounts of the organic developer, the basic colorless dye, the binder, the sensitizer, the filler and other components in the color-developing layer used in the present invention depend upon desired performance and recording properties, and they are not particularly limited. Usually, the suitable amount of the organic developer is from 3 to 12 parts (weight parts of the solid), that of the sensitizer is from 3 to 12 parts, that of the filler is 1 to 20 parts with respect to 1 part of the basic colorless dye, and the suitable amount of the binder is from 10 to 25 parts in the whole solids in the color-developing layer.

The organic developer, the basic colorless dye and the sensitizer are ground separately or, if necessary and if accepted, together with materials to be added, by means of a mill such as a ball mill, an attritor, a sand grinder or a suitable emulsifier until the particle diameter of each component has been at a level of microns or less. Afterward, the binder and, when desired, various quality regulators are further added thereto in order to prepare a coating solution.

The thus obtained coating solution is applied onto the substrate or the optical recording layer, thereby preparing the heat-sensitive color-developing layer.

When the heat-sensitive color-developing layer is superposed upon the optical recording layer, the color of the optical recording layer is further hidden, so that the optical recording medium having a preferable appearance is prepared.

It is a preferable way to dispose a protective layer on the surface of the heat-sensitive color-developing layer so as to diminish or inhibit the contamination by moisture, gases, water, solvents and oily substances.

The protective layer must be permeable to the visible rays and must not have a bad influence on the heat-sensitive color-developing layer. Usually, the protective layer is formed by coating with one or more selected from the binders which are used in the heat-sensitive color-developing layer. When the soluble near infrared absorbent is contained in the protective layer or between the protective layer and the heat-sensitive color-developing layer, the sensitivity of the optical recording medium can be further heightened.

A light source necessary in an optical recording operation must contain a wave length in the near infrared region of 0.7 to 2.5 μm, and examples of such a light source include a semiconductor laser, a diode pumping YAG laser, a Xe flashlamp, a quartz flashlamp and a halogen lamp, from which preferable one can be selected in compliance with its use purpose.

As discussed above, recording is performed by irradiating, with the near infrared rays, the optical recording medium of the present invention which comprises the substrate, the light-absorbing layer containing the near infrared absorbent prepared by mixing and heating the thiourea derivative and the metallic compound, the heat-sensitive color-developing layer containing the basic colorless dye and the organic developer, these layers being superposed upon the substrate.

The near infrared absorbent in the light-absorbing layer absorbs the near infrared rays of any wave length contained in the irradiation light and converts into heat effectively. The generated heat rapidly transfers to the heat-sensitive color-developing layer which lies on or under the light-absorbing layer, and then causes a reaction between the basic colorless dye and the organic developer in the heat-sensitive color-developing layer. An image can be recorded on the optical recording medium substantially simultaneously with the irradiation of the light.

Since the near infrared absorbent has weak absorption spectra in the visible region, the ground color of the light-absorbing layer is good. In particular, when the light-absorbing layer is disposed under the heat-sensitive color-developing layer, the ground color is better, and in addition, the near infrared absorbent is separated from the heat-sensitive color-developing layer, so that any desensitization does not occur in the color-developing layer.

Now, the present invention will be described in detail in reference to examples, but the scope of the present invention should not be limited to these examples. In the examples, parts and percent are on weight.

Optical recording papers in the undermentioned examples and comparative examples were evaluated in points of image density and ground color. Measurements were carried out as follows, and the results are set forth in Table 1.

Density of developed color: An image density was measured with a Macbeth densitometer by a light irradiation.

Ground color: A white paper portion was measured by means of a Macbeth densitometer.

Examples 1 to 21

[Light-absorbing layer]

Each of a thiourea derivative and a metallic compound shown in Table 1 was used in the form of the following composition.

Solution A	
Thiourea derivative	50 parts
10% Aqueous polyvinyl alcohol solution	25 parts
Water	125 parts
Total	200 parts

Solution B	
Metallic compound	50 parts
10% Aqueous polyvinyl alcohol solution	25 parts
Water	125 parts
Total	200 parts

Each solution of the above-mentioned composition was wet-ground by an attritor until the average particle diameter of each component was about 3 μm.

A filler was used in the form of the following dispersion, i.e., solution C.

Solution C: Filler-containing slurry	
Silica	40 parts
Water	60 parts
Total	100 parts

Silica was dispersed in the solution C by a stirrer.

The solution A (thiourea derivative dispersion) was mixed with the solution B (metallic compound dispersion) in each blend ratio shown in Table 1, and the mixture was then added to a filler-containing slurry prepared by adding 100 parts of a 10% aqueous polyvinyl alcohol solution to 250 parts of the solution C, the amount of the mixture being described in the column of "amount of composition for near infrared absorption" in Table 1, whereby a light-absorbing layer coating solution was prepared.

A fine paper having a basis weight of 60 g/m^2 was coated with the thus prepared light-absorbing layer coating solution by the use of a meyer bar so that a coating weight might be 5 g/m^2. After drying, a heat treatment was then carried out at 150 °C to obtain a heat conversion under sheet having the light-absorbing layer.

[Heat-sensitive color-developing layer]

Solution E (basic colorless dye dispersion)	
Basic colorless dye shown in Table 1	2.0 parts
10% Aqueous polyvinyl alcohol solution	3.4 parts
Water	1.27 parts
Total	6.67 parts

In Table 1, ODB, S-205 and ODB-2 in the column of "Dye" are indicative of the following compounds:
ODB: 3-Diethylamino-6-methyl-7-anilinofluoran
S-205: 3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilinofluoran
ODB-2: Dibutylamino-6-methyl-7-anilinofluoran

Solution F (developer dispersion)	
Developer shown in Table 1	6.0 parts
P-Benzylbiphenyl	4.0 parts
10% Aqueous polyvinyl alcohol solution	12.5 parts
Water	2.5 parts
Total	25.0 parts

In Table 1, BPA, BPS and POB in the column of "Developer" are indicative of the following compounds:
BPA: Bisphenol A
BPS: Bisphenol S
POB: p-Hydroxybenzoic acid benzyl ester

Solutions E and F having the above-mentioned compositions were separately wet-ground for 1 hour by a sand grinder for tests.

Next, 6.67 parts of the solution E (dye dispersion), 25 parts of the solution F (developer dispersion) and 11.76 parts of a 42.5% hollow pigment (trade name ROPAQUE OP-48J; made by Rohm & Haas Co.) were mixed in order to prepare a heat-sensitive color-developing coating solution.

The light-absorbing heat conversion under sheet was then coated with this coating solution by the use of a meyer bar so that a coating weight might be 3.0 g/m^2, followed by drying, in order to obtain an optical recording paper.

(Protective layer)	
10% Aqueous polyvinyl alcohol solution	100 parts
Glyoxal (40%)	5 parts
Total	105 parts

The above-mentioned optical recording paper was coated with this protective layer coating solution by the use of a meyer bar so that a coating weight might be 2 g/m^2, followed by drying, in order to obtain an optical recording paper with the protective layer.

Comparative Examples 1, 7, 8 and 9

Each fine paper having a basis weight of 60 g/m^2 was coated with a filler-containing slurry prepared by mixing 250 parts of the solution C used in Examples 1 to 21 with 100 parts of a 10% aqueous polyvinyl alcohol solution by the use of a meyer bar so that a coating weight might be 5 g/m^2, followed by drying. Next, a heat treatment was carried out at 150 °C in order to obtain a filler-containing sheet containing no near infrared absorbent. This sheet was then coated with a coating material in which the dye and developer in Table 1 were blended as in Examples 1 to 21, by the use of a meyer bar so that a coating weight might be 3.0 g/m^2, followed by drying, in order to obtain recording papers of Comparative Examples 1, 7, 8 and 9.

Comparative Examples 2, 3, 4, 5, 6 and 10

Solutions A and B were prepared from thiourea derivatives or metallic compounds of Comparative Examples 2, 3, 4 and 5 in Table 1 in the same manner as in Example 1. Then, 20 parts of each of the solutions A and B was mixed with the filler-containing slurry used in Comparative Example 1 in order to form an undercoating solution. A fine paper having a basis weight of 60 g/m^2 was coated with this undercoating solution by a meyer bar so that a coating weight might be 5 g/m^2, followed by drying. A heat treatment was then carried out at 150 °C in order to obtain under sheets containing only one component of the near infrared absorbent regarding Comparative Examples 2, 3, 4 and 5. Each sheet was then coated with a coating material in which ODB and BPA were blended as a dye and developer by the same

procedure as in Examples 1 to 21, by the use of a meyer bar so that a coating weight might be 3.0 g/m^2, followed by drying, in order to obtain recording papers of Comparative Examples 2, 3, 4 and 5.

ODB and BPA were used as a dye and a developer in the same manner as in Examples 1 to 21 in order to form a heat-sensitive color-developing coating material. The thus prepared heat-sensitive color-developing coating material was then mixed with 20 parts of 1,3-diphenylthiourea dispersion formed by the same procedure as in the case of the solution A in Examples 1 to 21. The filler-containing sheet obtained in Comparative Example 1 was then coated with the resulting mixture, followed by drying, whereby a recording paper having the heat-sensitive color-developing layer regarding Comparative Example 6 was obtained.

The heat-sensitive color-developing layer of this recording paper regarding Comparative Example 1 was coated with a coating material which had been prepared by mixing 20 parts of 1,3-diphenylthiourea dispersion formed in the same manner as in the case of the solution A of Examples 1 to 21 with 105 parts of the protective layer coating solution used in Examples 1 to 21, by the use of a meyer bar so that a coating weight might be 2.0 g/m^2, followed by drying, in order to obtain a recording paper of Comparative Example 10.

The optical recording mediums thus obtained in Examples 1 to 12 and Comparative Examples 1 to 10 were then irradiated with light from a strobo flash Auto 433D (made by Sun Pack Co., Ltd.) for cameras under conditions that an emission window was stopped to 5% in order to perform recording.

As is apparent from Table 1, in the comparative examples regarding the optical recording mediums which do not contain the near infrared absorbent used in the present invention or which comprise the under layer containing either of the thiourea compound or the metallic compound and the heat-sensitive color-developing layer, any color is not developed at all, when irradiated with the light. On the contrary, with regard to the optical recording papers of the examples in which the heat-sensitive color-developing layer is superposed upon the light-absorbing layer containing the near infrared absorbent obtained by mixing and then heating the thiourea derivative and the metallic compound, a high image density and a white ground color can be obtained, and therefore the optical recording papers regarding the present invention are practical.

Furthermore, the optical recording medium in which the protective layer is superposed upon the heat-sensitive color-developing layer is substantially equal in the image density and the ground color to the other medium in which no protective layer is disposed. When the surface of the optical recording medium having the protective layer was rubbed with a wet finger of a man, it did not peel off, which means that the optical recording medium of the present invention is excellent in water resistance and wear resistance.

Table 1 (I)

	Protective Layer	Amount of Composition for Near Infrared Absorption	Light-absorbing Layer Thiourea Derivative (I)
Example 1	Absent	20 (parts)	1,3-diphenylthiourea
Example 2	Absent	20	1,3-diphenylthiourea
Example 3	Absent	20	1,3-diphenylthiourea
Example 4	Present	20	1,3-diphenylthiourea
Example 5	Absent	20	1,3-diphenylthiourea
Example 6	Absent	20	1,3-diphenylthiourea
Example 7	Absent	20	1,3-diphenylthiourea
Example 8	Absent	20	di-m-chlorophenylthiourea
Example 9	Absent	20	di-m-chlorophenylthiourea
Example 10	Absent	20	1,3-diphenylthiourea
Example 11	Absent	20	1,3-diphenylthiourea
Example 12	Absent	20	1,3-distearylthioure
Example 13	Absent	20	1,3-distearylthiourea
Example 14	Absent	20	1,3-diphenylthiourea
Example 15	Absent	20	1,3-dibenzylthiourea
Example 16	Absent	20	1,3-dibenzylthiourea

Table 1 (II)

	Protective Layer	Amount of Composition for Near Infrared Absorption	Light-absorbing Layer Thiourea Derivative (I)
Example 17	Absent	15 (parts)	1,3-diphenylthiourea
Example 18	Absent	30	1,3-diphenylthiourea
Example 19	Absent	50	1,3-diphenylthiourea
Example 20	Absent	20	1-benzyl-3-morpholino-thiourea
Example 21	Absent	20	1,3-diphenylthiourea
Comp. Ex. 1	Absent	0	-
Comp. Ex. 2	Absent	20	1,3-diphenylthiourea
Comp. Ex. 3	Absent	20	-
Comp. Ex. 4	Absent	20	di-m-chlorophenylthiourea
Comp. Ex. 5	Absent	20	
Comp. Ex. 6	Absent	20	1,3-distearylthiourea
Comp. Ex. 7	Absent	0	-
Comp. Ex. 8	Absent	0	-
Comp. Ex. 9	Absent	0	-
Comp. Ex. 10	Present	20	1,3-diphenylthiourea

Table 1 (III)

	Light-absorbing Layer		Layer*		Evaluation	
	Metallic Compound (II)	(I):(II)	Developer	Dye	Color Density	Ground Color
Example 1	copper p-chlorobenzoate	5:1	BPA	ODB	1.35	0.12
Example 2	lead p-chlorobenzoate	5:1	BPA	ODB	1.34	0.13
Example 3	copper p-chlorobenzoate	1:1	BPA	ODB	1.35	0.16
Example 4	copper p-chlorobenzoate	1:1	BPA	S-205	1.32	0.13
Example 5	copper stearate	5:1	BPA	ODB	1.32	0.14
Example 6	copper p-chlorobenzoate	5:1	POB	ODB	1.32	0.12
Example 7	lead p-chlorobenzoate	5:1	POB	ODB	1.32	0.13
Example 8	copper p-chlorobenzoate	5:1	BPS	ODB	1.20	0.14
Example 9	lead p-chlorobenzoate	5:1	BPS	ODB	1.19	0.15
Example 10	copper hydroxide	5:1	BPA	ODB	1.40	0.12
Example 11	lead hydroxide	5:1	BPA	ODB	1.32	0.13
Example 12	copper hydroxide	5:1	BPA	ODB-2	1.34	0.13
Example 13	lead hydroxide	5:1	BPA	ODB	1.21	0.12
Example 14	copper hydroxide	5:1	POB	ODB	1.33	0.13
Example 15	copper benzoate	5:1	BPA	ODB	1.34	0.14
Example 16	lead benzoate	5:1	BPA	ODB	1.32	0.13

* Layer: Heat-sensitive color-developing layer

Table 1 (IV)

	Light-absorbing Layer		Layer*		Evaluation	
	Metallic Compound (II)	(I):(II)	Developer	Dye	Color Density	Ground Color
Example 17	copper p-chlorobenzoate	5:1	BPA	ODB	1.05	0.11
Example 18	copper p-chlorobenzoate	5:1	BPA	ODB	1.35	0.14
Example 19	copper p-chlorobenzoate	5:1	BPA	ODB	1.40	0.23
Example 20	copper p-chlorobenzoate	5:1	BPA	ODB	1.35	0.13
Example 21	cobalt hydroxide	5:1	BPA	ODB	1.35	0.15
Comp. Ex. 1	-	0:0	BPA	ODB	0.07	0.08
Comp. Ex. 2	-	100:0	BPA	ODB	0.07	0.07
Comp. Ex. 3	copper p-chlorobenzoate	0:100	BPA	ODB	0.09	0.09
Comp. Ex. 4	-	100:0	BPA	ODB	0.07	0.07
Comp. Ex. 5	lead p-chlorobenzoate	0:100	BPA	ODB	0.10	0.10
Comp. Ex. 6	-	100:0	BPA	ODB	0.07	0.07
Comp. Ex. 7	-	0:0	BPS	ODB	0.09	0.09
Comp. Ex. 8	-	0:0	POB	ODB	0.06	0.06
Comp. Ex. 9	-	0:0	BPA	S-205	0.07	0.07
Comp. Ex. 10	-	100:0	BPA	ODB	0.09	0.09

Example 22

Optical recording was carried out by irradiating the optical recording paper obtained in Example 1 with a laser beam by the use of a device shown in Fig. 1 in which a semiconductor laser head (laser diode

collimator head LDC-8330-CINC; made by Applied Optic Co., Ltd., central wave length 830 nm, output 30 nW) was used as a light source and a condenser (MDPLAN 5 made by Olympus Optical Co., Ltd., 0.1) was also used. An irradiation time was 1/500 second. A colored spot was measured by the use of a densitometer (PDM-5 made by Konishiroku Photo Industry Co., Ltd.), and the measured value was converted into a Macbeth density, whereby it was definite that the colored spot was an extremely black color image having a Macbeth density of 1.35. On the contrary, when the optical recording papers of Comparative Examples 1 to 10 were irradiated with the laser beam under the same conditions, any image was not recorded at all. Thus, the irradiation was further made for 10 minutes, but any color was not developed at all.

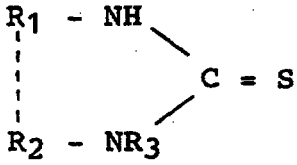
Example 23

Optical recording was carried out by irradiating the optical recording paper obtained in Example 1 with a laser beam for 1 second by the use of a device shown in Fig. 1 in which an He-Ne laser head (Model 105-1 made by Spectra Physics Co., Ltd., central weve length 632.8 nm, output 5 mW) was used as a light source and a beam collimator (BC-5 made by Nippon Kagaku Engineering Co., Ltd.) was also used. A colored spot was measured by the use of a densitometer (PDM-5 made by Konishiroku Photo Industry Co., Ltd.), and the measured value was converted into a Macbeth density, whereby it was definite that the colored spot was a completely colored image having a Macbeth density of 1.33. On the contrary, when the optical recording papers of Comparative Examples 1 to 10 were irradiated with the laser beam under the same conditions, any image was not recorded at all. Thus, the recording papers were further irradiated for a long time of 10 minutes, but any color was not developed at all.

As discussed above, on the optical recording medium of the present invention, an image having a high resolution can be directly obtained by the irradiation of near infrared rays from a semiconductor laser or a strobo flash. When the near infrared absorbent comprising a less colored thiourea derivative and a metallic compound is used, light sources such as a semiconductor laser having optional near infrared wave lengths and a strobo flash having continuous near infrared wave lengths can be utilized effectively. In consequence, the near infrared absorbent used in the present invention has led to a successful result in putting a heat mode optical recording medium into practice.

Claims

1. An optical recording medium which comprises a substrate, a light-absorbing layer containing a near infrared absorbent, and a heat-sensitive color-developing layer containing a basic colorless dye and an organic developer, these layers being superposed upon said substrate, said near infrared absorbent being prepared by heating a mixture of a thiourea derivative represented by the formula (I)



(I)

wherein each of R_1, R_2 and R_3 is a monovalent group selected from the group consisting of hydrogen, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aralkyl group and a five-membered or six-membered heterocyclic residue, a pair of R_1 and R_2 or a pair of R_2 and R_3 may be linked together to form a ring, and each group of R_1, R_2 and R_3 may have one or more substituents of an amino group, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, a nitro group, a halogen atom, a hydroxyl group, an alkoxy group and an acyl group,
and a metallic compound represented by the formula (II)

$$(R\text{-}X)_nM \quad (II)$$

wherein R is hydrogen, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group and a heterocyclic residue, each group of R may have one or more substituents, X is -COO, $-SO_4$, $-SO_3$, $-PO_4$ or -O, n is an integer of 1 to 4, M is a metal having an atomic weight of 40 or more except metals in the group IA and IIA of the periodic table

collimator head LDC-8330-CINC; made by Applied Optic Co., Ltd., central wave length 830 nm, output 30 nW) was used as a light source and a condenser (MDPLAN 5 made by Olympus Optical Co., Ltd., 0.1) was also used. An irradiation time was 1/500 second. A colored spot was measured by the use of a densitometer (PDM-5 made by Konishiroku Photo Industry Co., Ltd.), and the measured value was converted into a Macbeth density, whereby it was definite that the colored spot was an extremely black color image having a Macbeth density of 1.35. On the contrary, when the optical recording papers of Comparative Examples 1 to 10 were irradiated with the laser beam under the same conditions, any image was not recorded at all. Thus, the irradiation was further made for 10 minutes, but any color was not developed at all.

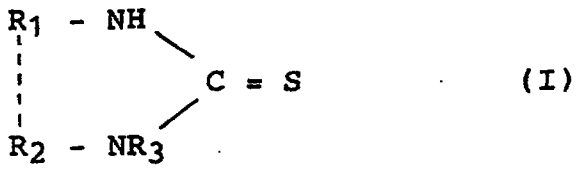
Example 23

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As discussed above, on the optical recording medium of the present invention, an image having a high resolution can be directly obtained by the irradiation of near infrared rays from a semiconductor laser or a strobo flash. When the near infrared absorbent comprising a less colored thiourea derivative and a metallic compound is used, light sources such as a semiconductor laser having optional near infrared wave lengths and a strobo flash having continuous near infrared wave lengths can be utilized effectively. In consequence, the near infrared absorbent used in the present invention has led to a successful result in putting a heat mode optical recording medium into practice.

Claims

1. An optical recording medium which comprises a substrate, a light-absorbing layer containing a near infrared absorbent, and a heat-sensitive color-developing layer containing a basic colorless dye and an organic developer, these layers being superposed upon said substrate, said near infrared absorbent being prepared by heating a mixture of a thiourea derivative represented by the formula (I)



(I)

wherein each of R_1, R_2 and R_3 is a monovalent group selected from the group consisting of hydrogen, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aralkyl group and a five-membered or six-membered heterocyclic residue, a pair of R_1 and R_2 or a pair of R_2 and R_3 may be linked together to form a ring, and each group of R_1, R_2 and R_3 may have one or more substituents of an amino group, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, a nitro group, a halogen atom, a hydroxyl group, an alkoxy group and an acyl group,
and a metallic compound represented by the formula (II)

$(R\text{-}X)_nM$ (II)

wherein R is hydrogen, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group and a heterocyclic residue, each group of R may have one or more substituents, X is -COO, $-SO_4$, $-SO_3$, $-PO_4$ or -O, n is an integer of 1 to 4, M is a metal having an atomic weight of 40 or more except metals in the group IA and IIA of the periodic table

or a metallic compound selected from the group of chlorophyll M, M chlorophyllin sodium and bisacetylacetonate M.

2. An optical recording medium according to Claim 1 wherein said light-absorbing layer is superposed upon said substrate, and said heat-sensitive color-developing layer is superposed upon said light-absorbing layer in turn.

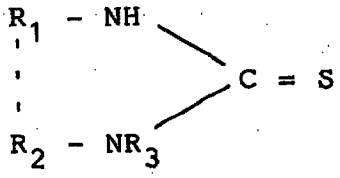
3. An optical recording medium according to Claim 1 or 2 wherein a transparent protective layer is disposed on said heat-sensitive color-developing layer.

4. An optical recording medium according to any one of Claims 1 to 3 wherein said metal of said metallic compound is copper and/or lead.

5. An optical recording medium according to any one of Claims 1 to 4 wherein said metallic compound is copper hydroxide and/or lead hydroxide, and said thiourea derivative is diphenylthiourea.

Patentansprüche

1. Optisches Aufzeichnungsmedium, welches ein Substrat, eine Licht absorbierende Schicht enthaltend ein mittleres-Infrarot-Absorptionsmittel und eine wärmeempfindliche farbentwickelnde Schicht enthaltend einen basischen farblosen Farbstoff und einen organischen Entwickler umfaßt, wobei diese Schichten auf diesem Substrat übereinander abgelagert sind und dieses mittleres-Infrarot-Absorptionsmittel hergestellt ist durch Erhitzen eines Gemisches eines Thioharnstoffderivats, dargestellt durch die Formel (I)



(I)

worin R_1, R_2 und R_3 jeweils eine einwertige Gruppe sind, ausgewählt aus der Gruppe bestehend aus Wasserstoff, einer Alkylgruppe, einer Alkenylgruppe, einer Cycloalkylgruppe, einer Arylgruppe, einer Aralkylgruppe und einem fünfgliedrigen oder sechsgliedrigen heterocyclischen Rest, wobei ein Paar von R_1 und R_2 oder ein Paar von R_2 und R_3 zusammen verknüpft sein können, um einen Ring zu bilden, und jede Gruppe R_1, R_2 und R_3 einen oder mehrere Substituenten aus einer Aminogruppe, einer Alkylgruppe, einer Alkenylgruppe, einer Arylgruppe, einer Aralkylgruppe, einer Nitrogruppe, einem Halogenatom, einer Hydroxylgruppe, einer Alkoxygruppe oder einer Acylgruppe haben kann,
und einer Metallverbindung, dargestellt durch die Formel (II)

$(R\text{-}X)_nM$ (II)

worin R Wasserstoff, eine Alkylgruppe, eine Cycloalkylgruppe, eine Arylgruppe, eine Aralkylgruppe und ein heterocyclischer Rest ist, wobei jede Gruppe R einen oder mehrere Substituenten haben kann, X -COO, $-SO_4$, $-SO_3$, $-PO_4$ oder -O ist, n ist eine Zahl von 1 bis 4, M ist ein Metall mit einem Atomgewicht von 40 oder mehr, ausgenommen Metalle der Gruppen IA und IIA des Periodensystems, oder einer Metallverbindung ausgewählt aus der Gruppe von Chlorophyll M, Natrium-M-chlorophyllin und M-Bisacetylacetonat.

2. Optisches Aufzeichnungsmedium gemäß Anspruch 1, worin diese lichtabsorbierende Schicht auf diesem Substrat abgelagert ist und die genannte wärmeempfindliche farbentwickelnde Schicht ihrerseits auf der genannten lichtabsorbierenden Schicht abgelagert ist.

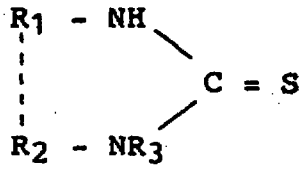
3. Optisches Aufzeichnungsmedium gemäß Anspruch 1 oder 2, worin eine transparente Schutzschicht auf der wärmeempfindlichen farbentwickelnden Schicht angeordnet ist.

4. Optisches Aufzeichnungsmedium gemäß einem der Ansprüche 1 bis 3, worin das genannte Metall der Metallverbindung Kupfer und/oder Blei ist.

5. Optisches Aufzeichnungsmedium gemäß einem der Ansprüche 1 bis 4, worin die genannte Metallverbindung Kupferhydroxid und/oder Bleihydroxid ist, und das genannte Thioharnstoffderivat Diphenylthioharnstoff ist.

Revendications

1. Un milieu d'enregistrement optique qui comprend un substrat, une couche absorbant la lumière contenant un absorbant de l'infrarouge proche et une couche thermosensible révélatrice chromogène contenant un colorant incolore basique et un révélateur organique, ces couches étant superposées sur ledit substrat, ledit absorbant de l'infrarouge proche étant préparé par chauffage d'un mélange d'un dérivé de thio-urée représenté par la formule (I)



(I)

dans laquelle chacun de R_1, R_2 et R_3 est un groupe monovalent choisi parmi l'hydrogène, un groupe alkyle, un groupe alcényle, un groupe cycloalkyle, un groupe aryle, un groupe aralkyle et un reste hétérocyclique pentagonal ou hexagonal, R_1 et R_2 ou R_2 et R_3 peuvent être liés ensemble pour former un cycle et chaque groupe représenté par R_1 R_2 et R_3 peut avoir un ou plusieurs substituants constitués d'un groupe amino, d'un groupe alkyle, d'un groupe alcényle, d'un groupe aryle, d'un groupe aralkyle, d'un groupe nitro, d'un atome d'halogène, d'un groupe hydroxyle, d'un groupe alcoxy et d'un groupe acyle,
et d'un composé métallique représenté par la formule (II)

$(R\text{-}X)_nM$ (II)

dans laquelle R est un hydrogène, un groupe alkyle, un groupe cycloalkyle, un groupe aryle, un groupe aralkyle ou un reste hétérocyclique, chaque groupe représenté par R peut avoir un ou plusieurs substituants, X est -COO, $-SO_4$, $-SO_3$, $-PO_4$ ou -O, n est un entier de 1 à 4, M est un métal ayant un poids atomique de 40 ou plus, à l'exception des métaux des groupes IA et IIA de la classification périodique,
ou d'un composé métallique choisi parmi chlorophylle-M, M-chlorophylline-sodium et bisacétylacétonate-M.

2. Un milieu d'enregistrement optique selon la revendication 1, dans lequel ladite couche absorbant la lumière est superposée audit substrat, et ladite couche thermosensible révélatrice chromogène est superposée à ladite couche absorbant la lumière.

3. Un milieu d'enregistrement optique selon la revendication 1 ou 2, dans lequel une couche protectrice transparente est disposée sur ladite couche thermosensible révélatrice chromogène.

4. Un milieu d'enregistrement optique selon l'une quelconque des revendications 1 à 3, dans lequel ledit métal dudit composé métallique est le cuivre et/ou le plomb.

5. Un milieu d'enregistrement optique selon l'une quelconque des revendications 1 à 4, dans lequel ledit composé métallique est l'hydroxyde de cuivre et/ou l'hydroxyde de plomb et ledit dérivé de la thio-urée est la diphénylthio-urée.