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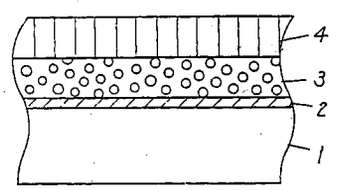
(54) A reversible thermosensitive recording material and a recording medium using the same.

(57) A reversible thermosensitive recording material capable of recording and erasing information by heat is provided. Also, a recording medium which comprises a substrate, a recording layer made of the above-mentioned recording material, and a protective layer stacked in this order is provided. The recording material of the present invention is made of a composition comprising a matrix polymer and organic crystal particles dispersed therein. The organic crystal particles are melted by heating and a different crystalline state is obtained in accordance with a temperature in heating. The matrix polymer and the organic crystal particles respectively have a group capable of forming a hydrogen bond. The organic crystal particles can be micro-capsulated by a matrix polymer for capsulation. In order to improve endurance, the recording layer can comprise spacer particles. As the protective layer of the medium, polyimide excellent in heat resistance or a polymer which comprises ultra-fine particles of an oxide is used. If required, an adhesive layer is provided between the substrate and a recording layer.

Fig. 1



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BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a thermosensitive recording material capable of reversibly recording and erasing information by heat, and to a recording medium using the same. The present invention is used for a memory card capable of rewriting information and if desired, having a display function, the memory card being used as a season ticket, an ordinary ticket, a coupon ticket, and a prepaid card; an IC card; a recording sheet for facsimile; a thermosensitive recycle paper; an optical disk, etc.

2. Description of the Prior Art:

Examples of a reversible thermosensitive recording material include thermosensitive dye type recording materials which comprise a leuco dye, a developer, and an agent for erasing a color in combination, and which reversibly develop and erase a color; thermosensitive recording materials having organic crystal particles dispersed in a matrix polymer, and wherein the recording and erasing of information is conducted utilizing the change of transparency of the recording material in accordance with a melting and solidification of the particles in the matrix; and thermosensitive recording materials comprising a liquid crystal polymer such as a cholesteric liquid crystal, the transparency of the recording material being changed by changing the molecular orientation of the polymer by applying heat. Among the above-mentioned various kinds of reversible thermosensitive recording materials, in the case of the recording materials with organic crystal particles dispersed in a matrix polymer, recording and erasing of information is made by the change of transparency of the recording material in accordance with the melting and solidification conditions of the particles. That is, when the above-mentioned organic crystal particles are melted by heat, and then solidified by lowering the temperature, the particles achieve various types of solidified states, i.e., a polycrystalline state, a single crystalline state, an amorphous state, or a non-crystalline state, according to the melting and solidification conditions. Each state has different transparency characteristics. Thus, the recording and erasing of information is accomplished by utilizing this phenomenon.

For example, the transparent matrix polymer sheet comprising organic crystal particles in a polycrystalline state is opaque at ordinary temperature since the organic crystal particles scatter light. As is shown in Figure 3, when this polymer sheet is gradually heated and the temperature exceeds T_0 (which is approximately equal to the glass transition point (Tg) of the matrix polymer), the polymer sheet begins to change from an opaque state to a transparent state. When the temperature reaches T_1, the polymer sheet becomes completely transparent. At this point, the organic crystal particles are in a single crystalline state and are light transmissible. When the temperature is raised further to T_2 or more, the light transmissibility of the organic crystal particles gradually decreases, and the polymer sheet becomes semi-transparent at T_3 - (approximately corresponding to the melting point of the organic crystal particles). When the organic crystal particles that were previously heated to a temperature between T_1 and T_2 are cooled to room temperature, the organic crystal particles are light transmissible, and thus the polymer sheet remains transparent. When the organic crystal particles that were previously heated to T_3 or more are cooled to room temperature, the organic crystal particles scatter light, and thus the polymer sheet becomes opaque. Because of this, for example, the state of the transparent sheet which has been cooled to room temperature, after having been heated to a temperature between T_1 and T_2, is made an initial state. Information is written to the sheet at a temperature of T_3 or more, whereby information is recorded. In the alternative, the state in which the sheet is opaque is made an initial state, and information can be written to the sheet so that the sheet becomes transparent.

Japanese Laid-Open Patent Publication No. 54-119377 discloses the combination of the above-mentioned matrix polymer and the organic crystal particles. Examples of the materials for the organic crystal particles disclosed herein include aliphatic and aromatic alcohols, carboxylic acids, amines, and amides, and halides and sulfides thereof. Examples of the matrix polymer disclosed herein include polyesters, polyamides, polyacrylic acid, polystyrene, silicone resins, polyvinyl chloride, polyvinylidene chloride, and polyacrylonitrile. Improved recording materials which further comprise carbon black or an anti-oxidant are disclosed in Japanese Laid-Open Patent Publication Nos. 57-82087 and 57-82088.

Generally, in the reversible thermosensitive recording medium with the organic crystal particles dispersed in the above-mentioned matrix polymer, a reversible thermosensitive recording layer is formed onto a substrate by coating a recording material, and a hard protective layer is formed on the recording layer. This protective layer is provided so that the recording layer is not damaged due to contact with a thermal head for recording and erasing in order to protect the recording layer. More particularly, the

protective layer is provided so as to prevent the thermal deformation of the recording layer by contact with the head, the attachment of the melted matrix polymer to the head, and mechanical damage of the recording layer by the pressure of the head. Mechanical strength and flexibility as well as thermal stability are required of the protective layer. Moreover, transparency of the protective layer is required for satisfactory readout of information on the recording layer.

Generally, materials used for the protective layer include cellulose type resins, polystyrene or styrene copolymer resins, acrylic or methacrylic resins including homopolymers and copolymers, polyester resins, butyral resins, polyvinyl chloride, polyvinyl acetate, vinyl chloride-vinyl acetate copolymer resins, polyurethane resins, acrylate type radiation-setting resins, etc. The protective layer also prevents waste and dirt from adhering to the recording layer.

In this type of recording medium, there is a problem that waste and dirt adhere to the thermal head, whereby irregularities are caused on a recording image. In order to overcome this problem, Japanese Laid-Open Patent Publication No. 2-258287 describes a method for preventing waste and dirt from adhering to the thermal head by mixing fine particles in the protective layer. The particles form a minute unevenness having a roughness of 0.5 to 3 μm on the surface of the protective layer, and making waste and dirt move and eliminate from the surface of the protective layer in accordance with the movement of the recording medium.

As is described above, various reversible thermosensitive recording materials and recording media with organic crystal particles dispersed in the matrix polymer are known; however, they have the following drawbacks. In this type of recording medium, the relatively low temperature at which the organic crystal particles dispersed in the matrix are light transmissible is between approximately 70 °C and 75 °C, so that the medium is poor in stability for maintaining information. Moreover, since the temperature range (T_1 to T_2 in Figure 3) in which the particles are light transmissible is a relatively small number of degrees of centigrade in width, the temperature at which the particles become light transmissible should be strictly regulated.

For example, a conventional reversible thermosensitive recording material is obtained by using behenic acid as the material for the organic crystal particles and using a vinyl chloride-vinyl acetate copolymer as the matrix polymer. The behenic acid has 22 carbon atoms and a melting point of 80 °C, which is a representative saturated straight chain aliphatic acid which can provide high resolution and contrast. The temperature range of the material so obtained in which the particles are light transmissible is from about 68 °C to 74 °C. Thus, the relevant temperature range has a width of about 6 °C. Therefore, it is difficult to perform stable recording.

For improving such a low and narrow temperature range at which the particles become light transmissible, novel organic crystal particles have been investigated and the novel combination of the organic crystal particles and the matrix polymer have been studied. For example, Japanese Laid-Open Patent Publication Nos. 2-1363 and 3-2089 describe a method for forming an organic crystal particle by mixing an aliphatic dicarboxylic acid with a higher aliphatic acid having 16 or more carbon atoms. In Japanese Laid-Open Patent Publication No. 2-1363, it is described that a higher aliphatic acid is mixed with a dicarboxylic acid or derivatives thereof having 4 to 16 carbon atoms in a weight ratio of 95:5 to 20:80 to form organic crystal particles. When the obtained particles in a matrix polymer are heated, the higher aliphatic acid and the dicarboxylic acid are melted and mixed, resulting in an eutectic mixture, whereby the temperature range in which the particles are light transmissible is enlarged.

Japanese Laid-Open Patent Publication No. 3-2089 describes a higher aliphatic acid which is mixed with aliphatic dicarboxylic acid having 20 or more carbon atoms in a weight ratio of 95:5 to 50:50 to form organic crystal particles. When the obtained particles in a matrix polymer are heated, the higher aliphatic acid and the dicarboxylic acid are melted and mixed, resulting in an eutectic mixture, whereby the temperature range in which the particles are light transmissible is enlarged. However, the temperature (T_1 in Figure 3) at which the particles become light transmissible is 100 °C or less, and the width of the temperature range in which the particles are light transmissible is enlarged at most to about 20 °C. In order to perform stable recording and to maintain the recorded information, a material having a higher temperature at which the particles become light transmissible and a larger temperature range in which the material is transparent is required, particularly in view of the temperatures ordinarily used for recording or erasing information.

Moreover, in the conventional reversible thermosensitive recording material, the relationship between the crystallinity of the organic crystal particles and the compatibility, dispersibility, etc. of the particles with respect to the matrix polymer, and the relationship between the crystallinity and the recording characteristics have not been sufficiently clarified. Thus, there is a problem in that a recording having excellent contrast cannot be performed.

Moreover, in this type of reversible thermosensitive recording material, there are several other problems. For example, since the organic crystal particles are repeatedly melted and solidified as a result of recording and erasing information, the shape of particles begins to deteriorate during such repetition. As a result, the contrast between the recorded area and the unrecorded area is decreased, and recording stability in the course of repeated use is poor. Furthermore, the recording layer is deformed due to the pressure of the thermosensitive recording head. Thus, durability is low.

The above-mentioned protective layer helps prevent the mechanical and physical deterioration of the recording layer as is discussed above. However the protective layer itself is subjected to thermal stress such as thermal contraction due to the repetition of heating and cooling for recording and erasing information, and the surface of the protective layer becomes deformed. As a result, irregular optical reflection is caused on the surface of the protective layer, and therefore, recording and erasing cannot be satisfactorily performed.

In the protective layer having a minute unevenness on the surface of the layer described in the above-mentioned Japanese Laid-Open Patent Publication No. 2-258287, there is a problem in that waste and dirt is accumulated in a concave portion of the protective layer according to the scanning of the thermal head. As a result of waste and dirt thus accumulated, dropouts are produced in the recording by the thermal head. Because of this, further improvement in the durability of the surface of the protective layer is required.

SUMMARY OF THE INVENTION

The reversible thermosensitive recording material of this invention, which overcomes the above-discussed and numerous other disadvantages and deficiencies of the prior art, is made of a composition comprising a transparent matrix polymer and organic crystal particles dispersed therein;

wherein the crystalline state of the organic crystal particles is changeable in accordance with an applied temperature, resulting in a reversible change of transparency of the recording materials; and

the matrix polymer and the organic crystal particles respectively have a group capable of forming a hydrogen bond.

In a preferred embodiment, each of the organic crystal particles comprises at least one selected from the group consisting of a carboxyl group and a hydroxyl group, and is made of a compound having a melting point in the range of 60 °C to 120 °C, and

the matrix polymer is selected from the group consisting of polyesters having a hydroxyl group, partially saponified vinyl acetate-vinyl chloride copolymers, polyamides, polyurethanes, thermoplastic phenol resins, vinyl alcohol copolymers, acrylic copolymers, acrylamide copolymers, maleic copolymers, urea resins, epoxy resins, and melamine resins.

In a preferred embodiment, each of the organic crystal particles comprises at least one hydroxycarboxylic acid or derivatives thereof having a melting point in the range of 60 °C to 120 °C.

In a preferred embodiment, the hydroxycarboxylic acid is an α-hydroxyalkylcarboxylic acid.

In a preferred embodiment, the organic crystal particles comprise at least one compound selected from the group consisting of an aliphatic amide compound and an aliphatic urea compound, and

each of the aliphatic amide compound and the aliphatic urea compound have at least one straight chain hydrocarbon group, respectively containing at least 10 carbon atoms, and a melting point of each of the compounds is in the range of 70 °C to 150 °C.

In a preferred embodiment, wherein each of the organic crystal particles comprises a compound having an amide or urea group and an aliphatic dicarboxylic acid; the compound having an amide or urea group is at least one selected from the group consisting of saturated aliphatic monocarboxamides with a hydrocarbon group having at least 12 carbon atoms, saturated aliphatic biscarboxamides with a hydrocarbon group having at least 12 carbon atoms, and ureas substituted with a hydrocarbon group having at least 12 carbon atoms; the aliphatic dicarboxylic acid is represented by the Formula $HOOC(CH_2)_{n8}COOH$ (wherein n8 is an integer from 14 to 24); and the ratio of the compound having an amide or urea group and the aliphatic dicarboxylic acid is in the range of 60:40 to 10:90 by weight.

In a preferred embodiment, the organic crystal particles comprise an aliphatic dicarboxylic acid having a melting point of at least 120 °C, and a straight chain aliphatic compound having at least one of a hydroxyl group, a carboxyl group, and an amide group and having a melting point in the range of 50 °C to 100 °C; and the ratio of the aliphatic dicarboxylic acid to the straight chain aliphatic compound is in the range of 3:7 to 8:2 by weight, and a width of the range in which the organic crystal particles are present in a light transmissible state is 20 °C or more.

In a preferred embodiment, the aliphatic dicarboxylic acid is represented by the formula $HOOC(CH_2)_{n9}COOH$, wherein n9 is an integer of 6 to 24.

In a preferred embodiment, the straight chain aliphatic compound is at least one compound selected from the group consisting of straight chain saturated higher alcohols, unsaturated aliphatic acid amide, and a straight chain saturated aliphatic acid, each having 12 or more carton atoms.

In a preferred embodiment, each of the organic crystal particles has a particle size of 0.1 μm or less.

In a preferred embodiment, each of the organic crystal particles is micro-capsulated with a transparent matrix polymer for capsulation.

A reversible thermosensitive recording medium of this invention comprises a substrate, a recording layer made of a the above-mentioned reversible thermosensitive material, and a protective layer stacked in this order.

In a preferred embodiment, the recording layer comprises a transparent spacer particle having a thickness approximately equal to that of the recording layer and a particle size less than the thickness of the recording layer in a proportion of 10% by weight.

In a preferred embodiment, the protective layer is made of a polyimide, and preferably, a soluble polyimide which is soluble in organic solvents.

In a preferred embodiment, the protective layer comprises ultra-fine particles made of an oxide whose primary particle has an average particle size of 100 nm or less.

In a preferred embodiment, the protective layer is made of a plurality of layers, a hardness of the plurality of layers successively becoming higher toward a direction of a surface layer from the substrate, and a protective layer of at least outermost surface layer comprises the ultra-fine particles made of an oxide whose primary particle has an average particle size of 100 nm or less.

In a preferred embodiment, the ultra-fine particles are made of silicon oxide, aluminium oxide or titanium oxide.

In a preferred embodiment, an adhesive layer is further disposed between the substrate and the recording layer.

In a preferred embodiment, the protective layer is made of at least one resin selected from the group consisting of polyethylene terephthalate, polymers containing fluorine, polysulfones, polyethylenenaphthalate, polyphenylenesulfide, polyarylates, polyimides, and polyamides.

In a preferred embodiment, a reflection layer is disposed between the substrate and the recording layer and information is recorded or erased by a laser beam.

Thus, the invention described herein makes possible the objectives of (1) providing a reversible thermosensitive recording material made of a composition comprising a matrix polymer and organic crystal particles dispersed therein, which is capable of recording and erasing information readily and reliably because the temperature at which the organic crystal particles become light transmissible is high, and the range of temperature in which the organic crystal particles are light transmissible is wide; (2) providing a reversible thermosensitive recording material which is excellent in recording resolution and gives a high contrast when information is recorded; (3) providing a reversible thermosensitive recording material which is excellent in durability and is capable of constantly maintaining recording characteristics even though information is repeatedly recorded and erased by a thermal head; and (4) providing a reversible thermosensitive recording medium which comprises a recording material having the above-mentioned excellent characteristics and which can be used for a card with a display function, a sheet for facsimile, and an optical memory device.

BRIEF DESCRIPTION OF THE DRAWINGS

This invention may be better understood and its numerous objects and advantages will become apparent to those skilled in the art by reference to the accompanying drawings as follows:

Figure **1** is a sectional view schematically illustrating an example of a reversible thermosensitive recording medium according to the present invention.

Figures **2a** and **2b** are views schematically showing a crystalline state of organic crystal particles in the reversible thermosensitive recording material according to the present invention. In particular, Figure **2a** illustrates an organic crystal particle **6A** in a single crystalline state, where the particle is light transmissible. Figure **2b** shows an organic crystal particle **6B** in a polycrystalline state, where the particle can scatter light.

Figure **3** is a graph showing light transmissibility of the organic crystal particles as a function of the temperature of the reversible thermosensitive recording sheet according to the present invention.

Figure **4** is a view schematically showing an example of the reversible thermosensitive recording material according to the present invention.

Figures **5a** and **5b** are views schematically showing a crystalline state of an organic crystal particle in the

reversible thermosensitive recording material according to the present invention. Figure **5a** shows an organic crystal particle **70A** in a single crystalline state, where the particle is light transmissible. Figure **5b** shows an organic crystal particle **70B** in a polycrystalline state, where the particle can scatter light.

Figure **6** is a sectional view schematically showing an example of the reversible thermosensitive recording medium according to the present invention.

Figure **7** is a sectional view schematically showing an example of the reversible thermosensitive recording medium according to the present invention.

Figure **8** is a sectional view schematically showing an example of the reversible thermosensitive recording medium according to the present invention.

Figure **9** is a sectional view schematically showing an example of the reversible thermosensitive recording medium having an adhesion layer according to the present invention.

Figure **10** is view schematically illustrating a magnetic card which is an example of the recording medium using the reversible thermosensitive recording material according to the present invention.

Figure **11** is a graph showing recording characteristics of the reversible thermosensitive recording material obtained in Example **4** of the present invention.

Figure **12** is a graph showing recording characteristics of the reversible thermosensitive recording material obtained in Example **6** of the present invention.

Figure **13** is a sectional view schematically showing an example of the optical recording medium using the reversible thermosensitive recording material according to the present invention.

Figures **14a**, **14b**, and **14c** are graphs showing recording characteristics of the reversible thermosensitive sheets obtained in Example **11** of the present invention. Figure **14a** is a graph showing recording characteristics of the reversible thermosensitive recording material according to the present invention. Figure **14b** is a graph showing recording characteristics of the reversible recording material comprising eicosanedicarboxylic acid as a material for the organic crystal particles. Figure **14c** is a graph showing recording characteristics of the reversible thermosensitive recording material comprising docosanol as a material for the organic crystal particles.

Figure **15** is a sectional view schematically showing an other example of the reversible thermosensitive recording medium according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A matrix polymer used for the reversible thermosensitive recording material of the present invention has a group capable of forming a hydrogen bond. When this polymer is heated, bindings between the polymer and organic crystal particles dispersed therein can be varied. It is preferred that this polymer be transparent and colorless. Examples of suitable matrix polymers include polyesters, polyacrylates, polyvinyl chloride, polyvinyl chloride-vinyl acetate copolymers, cellulose acetate, polyvinyl butyral, polystyrene, and styrene-butadiene copolymers. More specifically, adhesive polyesters having a hydroxyl group, partially saponified vinyl acetate-vinyl chloride copolymers, polyamides, polyurethanes, thermoplastic phenol resins, vinyl alcohol copolymers, acrylic acid copolymers, acrylamide copolymers, maleic acid copolymers, urea resins, epoxy resins, melamine resins, and the like are preferred. In the recording material of the present invention, this matrix polymer is used as a thin film, so that excellent transparency can be obtained.

Among the above matrix polymers, as to the copolymers having vinyl chloride repeating units and vinyl acetate repeating units, when the recording medium to be obtained is heated, a temperature at which organic crystal particles dispersed therein become light transmissible and the width of the temperature range in which the particles are light transmissible can be regulated in accordance with the difference of a ratio of the above-mentioned units in the copolymer. Moreover, a vinyl acetate component is partially saponified to form vinyl alcohol units, resulting in a copolymer having three components including vinyl chloride, vinyl acetate, and vinyl alcohol. Thus, the proportion of a group capable of forming a hydrogen bond of the matrix polymer is regulated, whereby the above-mentioned temperature and the width of the temperature range can be regulated.

The organic crystal particles used in the present invention are made of a compound having a group capable of forming a hydrogen bond. Examples of the group capable of forming a hydrogen bond includes a carboxyl group, a hydroxyl group, an amino group, an amide group, etc. The above-mentioned compound has at least one of these groups, and the organic crystal particles have a melting point in the range of 60 °C to 120 °C.

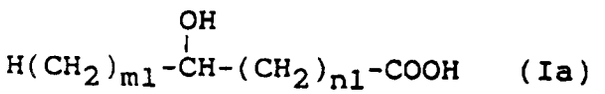
Examples of the compound which can be a material for the organic crystal particles include alkanols, alkanediols, alkylamines, alkylenediamines, mono- or dicarboxylic acids, amides, and sulfides and halides thereof. These compounds can be used alone or in combination. Moreover, when these compounds are

mixed together with other compounds such as higher alcohols, aliphatic acids, alkylamines, hydroxycarboxylic acids, dicarboxylic acids, diamines, and alkylene glycols, an eutectic crystal or a complex is formed, whereby crystal particles having a melting point of 60 °C to 120 °C can be formed. The number of carbon atoms of the above-mentioned higher alcohols, aliphatic acids, and the like which can form an eutectic crystal or a complex is preferably 10 to 30. Among such compounds, examples of the aliphatic acids include lauric acid, dodecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, nonadecanoic acid, arachic acid, behenic acid, and oleic acid. Examples of the higher alcohols include hexadecyl alcohol, heptadecyl alcohol, octadecyl alcohol, eicosanol, and docosanol.

A compound for forming the organic crystal particles, which has an unsaturated group at a straight-chain hydrocarbon in its molecule, is preferred for the following reasons. When the compound for forming organic crystal particles is dissolved in an organic solvent together with the matrix polymer and a recording layer is formed by coating the resulting mixture on a substrate, solubility of the compound with respect to the organic solvent is particularly satisfactory. Moreover, the compound has good compatibility against the matrix polymer, so that the crystal line state of the particles can be discretely changed, resulting in a satisfactory contrast of the recording medium that contains the particles.

As especially preferred materials for the organic crystal particles according to the present invention, there are (i) hydroxycarboxylic acids or derivatives thereof; (ii) aliphatic amides or aliphatic ureas; (iii) a mixture of an aliphatic dicarboxylic acid and at least one aliphatic compound having an amide group or a urea group selected from the group consisting of saturated aliphatic monoamides, saturated aliphatic bisamides, and hydrocarbon-substituted ureas; and (iv) a mixture of a dicarboxylic acid and an aliphatic straight-chain compound having a group capable of forming a hydrogen bond.

The hydroxycarboxylic acid which is a first material for the organic crystal particles is also called a hydroxy acid, and has at least one hydroxyl group and at least one carboxyl group in its molecule, each group being capable of forming a hydrogen bond. As the hydroxycarboxylic acid, compounds represented by the following Formulas Ia - Ie are especially preferred:



$$H(CH_2)_{m1}-\underset{\displaystyle OH}{\underset{|}{CH}}-(CH_2)_{n1}-COOH \qquad (Ia)$$

wherein m_1 and n_1 are respectively integers, and the total of m_1 and n_1 is 6 to 24;

$$HO\text{-}Ph\text{-}(CH_2)_{n2}\text{-}COOH \qquad (Ib)$$

wherein Ph is a phenylene group, and n_2 is an integer in the range of 0 to 18;

$$HO\text{-}Ph\text{-}COO(CH_2)_{n3}\text{-}COOH \qquad (Ic)$$

wherein Ph is a phenylene group, and n_3 is an integer in the range of 1 to 18.

$$HO\text{-}Ph\text{-}OCO(CH_2)_{n4}\text{-}COOH \qquad (Id)$$

wherein Ph is a phenylene group, and n_4 is an integer in the range of 1 to 18; and

$$HO\text{-}Ph\text{-}COO(CH_2)_{n5}\text{-}H \qquad (Ie)$$

wherein Ph is a phenylene group, and n_5 is an integer in the range of 1 to 18.

The compound represented by Formula Ia is a hydroxyalkylcarboxylic acid. The compound represented by Formula Ib is an alkylphenol in which the alkyl group is carboxylated, the position of the carboxyl group being arbitrary. The compound represented by Formula Ic is an ester of hydroxybenzoic acid and a hydroxyalkylcarboxylic acid. The compound represented by Formula Id is an ester of hydroquinone and an alkylenedicarboxylic acid. The compound represented by Formula Ie is a hydroxybenzoic ester. These compounds represented by Formulas Ia-Ie are the material used for antiseptics, food additives, and plasticizers for industrial purposes. Because of its low toxicity, it is particularly suitable for use in a recording material which is likely to be brought into direct contact with consumers. An eutectic crystal and a complex can be formed by mixing these hydroxycarboxylic acids together with other compounds such as higher alcohols, aliphatic acids, alkylamines, other hydroxycarboxylic acids, dicarboxylic acids, diamines,

and alkylene glycols, whereby organic crystal particles having a melting point in the range of 60 to 120 °C can be obtained by the use of the above-mentioned mixture. Examples of such hydroxycarboxylic acids include gallic acid, mandelic acid, tropic acid, malic acid, tartaric acid, and citric acid, and their derivatives.

In the hydroxycarboxylic acid, a hydroxyl group and a carboxyl group in a molecule, each being capable of forming a hydrogen bond, greatly influence behavior of the organic crystal particles in their melting and crystallization. This hydroxycarboxylic acid has two groups capable of forming a hydrogen bond, so that its crystallinity is high and the strength of the crystal is high. Most of the hydroxycarboxylic acids have an appropriate melting point of 60 °C to 120 °C and their melting and crystallization behavior is highly reliable. In contrast, alkylenediamines, alkylenedicarboxylic acids, and alkylene glycols, are molecules which have two groups capable of forming a hydrogen bond in their molecule. However, these molecules are not suitable for the present invention because the melting point is varied depending upon whether the number of carbons in their alkyl chain is even or odd, and the melting point is low compared with that of the hydroxycarboxylic acid.

The crystallization of the hydroxycarboxylic acid particles in the matrix polymer is substantially influenced by the hydrogen bond that is present at the interface between the matrix polymer and each of the hydroxycaroboxylic acid particles. Therefore, the number of the group capable of forming a hydrogen bond present at the interface between the crystal particles and the matrix polymer determine behavior of the crystallization. Also, the features of the group capable of forming a hydrogen bond determine behavior of the crystallization.

The aliphatic amide compound which is a second material for the organic crystal particles is represented by the following Formulas IIa, IIb, or IIc:

$$R^1\text{-}CONH\text{-}R^2 \qquad \text{(IIa)}$$

wherein R^1 is a straight chain hydrocarbon group having 1 to 25 carbon atoms, R^2 is hydrogen, a straight chain hydrocarbon group having 1 to 26 carbon atoms, or a methylol group, and at least one of R^1 and R^2 is a straight chain hydrocarbon group having at least 10 carbon atoms;

$$R^3\text{-}CONH\text{-}(CH_2)_{n6}\text{-}NHCO\text{-}R^3 \qquad \text{(IIb)}$$

wherein R^3 is a straight chain hydrocarbon group having 10 to 25 carbon atoms, and n_6 is an integer of 1 to 8;

$$R^4\text{-}NHCO\text{-}(CH_2)_{n7}\text{-}CONH\text{-}R^4 \qquad \text{(IIc)}$$

wherein R^4 is a straight chain hydrocarbon group having 10 to 25 carbon atoms, and n_7 is an integer of 1 to 8.

The aliphatic urea, which is also a second material for the organic crystal particles, is represented by the following Formula III:

$$R^5\text{-}NHCONH\text{-}R^6 \qquad \text{(III)}$$

wherein R^5 and R^6 are independently hydrogen or a straight chain hydrocarbon group having 1 to 26 carbon atoms, and at least one of R^5 and R^6 is a straight chain hydrocarbon group having at least 10 carbon atoms.

These compounds have an amide group or a urea group as a group capable of forming a hydrogen bond. The amide group has two portions capable of forming a hydrogen bond because of its structure of -NHCO-; thus, the amide group creates a strong association between the molecules. The strength of this association influences the melting point of the compound (e.g., the melting point of the organic crystal particles), crystallinity of the compound, (it relates to recording characteristics, especially a contrast when information is recorded) and dispersibility of the compound in the matrix. The urea group has a structure of -NHCONH-, which includes one more portion capable of forming a hydrogen bond compared with the amide group. Therefore, it creates a stronger association between the molecules. The amide compound represented by Formula IIb or IIc has portions capable of forming a hydrogen bond, which are twice as much as the compound represented by Formula IIa, so that the compound represented by Formula IIb or IIc exhibits a stronger association than that of the compound represented by Formula IIa. Because of these characteristics, the organic crystal particles have a high melting point in the range of 70 to 150 °C As a result, satisfactory crystallinity can be obtained. These groups capable of forming a hydrogen bond have a strong

interaction with respect to the matrix polymer and improve reversible thermosensitive recording characteristics. These groups capable of forming a hydrogen bond associate with long chain hydrocarbon groups which are present in the aliphatic amide compound or the aliphatic urea compound. The long chain hydrocarbon portion influences the compatibility between the matrix polymer and the molecule of the compound, and the melting point of the molecule of the compound. In particular, when the aliphatic hydrocarbon portion is a hydrocarbon chain having 10 or more carbon atoms, the organic crystal particles are readily dispersed in the matrix polymer in fine particles. Thus, this case is preferred. As described above, most of these compounds have a high melting point in the range of 70 to 150 °C, and their behavior in melting and crystallization is reliable, so that these compounds are preferred.

A mixture, which is obtained by adding at least one selected from the group consisting of higher alcohols, aliphatic acids, alkylamines, dicarboxylic acids, alkylenediols, alkylenediamines, alkylene glycols, hydroxycarboxylic acids, derivatives of alkyl benzoate, carboxyalkylphenols, aminoalkylphenols, and aminoalkyl alcohols to the aliphatic amide or the aliphatic urea compound, exhibits excellent characteristics.

A third material for the organic crystal particles is a mixture of an aliphatic dicarboxylic acid and an aliphatic compound containing an amide group or a urea group. The aliphatic dicarboxylic acid used in the present invention is $HOOC(CH_2)_{n8}COOH$ (wherein n_8 is an integer in the range of 14 to 24). The aliphatic compound containing an amide group or a urea group includes saturated aliphatic monoamides having a hydrocarbon group with at least 12 carbon atoms, saturated aliphatic biscarboxamides having a hydrocarbon group with at least 12 carbon atoms, or ureas substituted by a hydrocarbon group with at least 12 carbon atoms. Examples of the saturated aliphatic monocarboxamides include lauramide (mp. 86 °C), palmitamide (mp. 100 °C), stearamide (mp. 101 °C), behenamide (mp. 110 °C), hydroxystearamide (mp. 110 °C), N-stearylstearamide (mp. 94 °C), N-stearyloleamide (mp. 67 °C), oleylstearamide (mp. 74 °C), methylolstearamide (mp. 111 °C), and methylolbehenamide (mp. 110 °C). Examples of the saturated aliphatic bisamide include methylenebisstearamide (mp. 143 °C), ethylenebislauramide (mp. 157 °C), ethylenebisstearamide (mp. 143 °C), ethylenebishydroxystearamide (mp. 144 °C), hexamethylenebisstearamide (mp. 146 °C), N,N'-distearyladipamide (mp. 144 °C), m-xylenebisstearamide (mp. 123 °C), and N,N'-distearylisophthalamide (mp. 129 °C). Examples of the urea substituted by a hydrocarbon group include N,N'-distearylurea (mp. 114 °C), stearyl urea (mp. 109 °C), xylenebisstearylurea (mp. 163 °C), and diphenylmethanebisstearylurea (mp. 210 °C).

The aliphatic dicarboxylic acid has a carboxyl group at both terminals of its hydrocarbon chain, and this carboxyl group contributes a hydrogen bond between the molecules. Because of this, the aliphatic dicarboxylic acid itself has satisfactory crystallinity and a high melting point of 120 °C. Moreover, when the organic crystal particles are produced and mixed with the matrix polymer, the temperature at which the particles become light transmissible is relatively high. The length of the hydrocarbon chain of the aliphatic dicarboxylic acid is appropriately determined in view of the melting point of the organic crystal particles, the interaction of molecules in the organic crystal particles, solubility of the organic crystal particles into the matrix polymer, and the dispersibility of the organic crystal particles into the matrix polymer.

The aliphatic compound having an amide group or a urea group has a hydrocarbon chain with almost the same length as that of the aliphatic dicarboxylic acid. When a mixture of this compound and the aliphatic dicarboxylic acid is heated to be eutectic, the interaction between the molecules is increased, resulting in the formation of an association or a complex, whereby a composite such as a mixed crystal and an eutectic is formed. In this way, plural forms of crystalline are formed, and the range of temperature in which the particles are light transmissible can be widened due to the difference in temperature characteristics of each form. In addition, a plurality of complicated fine crystals are present, so that the degree of white turbidity of the recording material when the particles scatter light is high. As a result, it is considered that high contrast can be obtained. Furthermore, it is considered that the aliphatic compound having an amide group or a urea group is present as ultra-fine particles dispersed in each of the organic crystal particles, and those ultra-fine particles serve as a crystal core in the organic crystal particle. Since the melting point of the crystal core is high, it functions as a core during the steps of melting and crystallization of the organic crystal particle even at higher temperatures. As a result, the organic crystal particles having a high melting point and a wide range of temperature in which the particles are light transmissible can be obtained. Also, since the matrix polymer has a group capable of forming a hydrogen bond, more remarkable effects are exhibited due to the strong interaction between the matrix and the organic crystal particles, and excellent recording characteristics are exhibited.

The dicarboxylic acid and the compound having an amide group and a urea group are mixed in a ratio in the range of 60:40 to 10:90 by weight. When the aliphatic dicarboxylic acid is in an excess amount, the aliphatic dicarboxylic acid is not effectively eutectic in order to be complexed with the aliphatic compound having an amide group or a urea group. An excess amount of dicarboxylic acid causes a great interaction

with the matrix polymer, and thus, the excess amount of the dicarboxylic acid is migrated from the organic crystal particles and dispersed in the matrix. As a result, the recording medium obtained does not provide high contrast. In contrast, when the compound having an amide group or a urea group is in an excess amount, the excess amount of the compound is migrated from the organic crystal particles and mixed in the matrix, and becomes nonuniform. As a result, the recording medium obtained does not provide high contrast and the temperature range in which the particles are light transmissible becomes narrow.

A fourth material for the organic crystal particles is a mixture of an aliphatic dicarboxylic acid and a straight-chain aliphatic compound. The aliphatic dicarboxylic acid is represented by $HOOC(CH_2)_{n9}COOH$ (where n_9 is an integer in the range of 6 to 24), and its melting point is 120 °C or more. The straight-chain aliphatic compound is a straight-chain compound having at least one of a hydroxyl group, a carboxyl group, or an acid amide group, which is capable of forming a hydrogen bond, and its melting point is in the range of 50 °C to 100 °C. Preferable examples of the straight-chain aliphatic compound include straight-chain saturated higher alcohols such as stearyl alcohol (mp. 50 °C), eicosanol (mp. 66 °C), and docosanol (mp. 70 °C); unsaturated aliphatic amides such as oleamide (mp. 70 °C) and erucamide (mp. 81 °C); and straight-chain saturated aliphatic acids such as palmitic acid (mp. 62 °C), stearic acid (mp. 70 °C), eicosanic acid (mp. 75 °C), and behenic acid (mp. 80 °C).

The above-mentioned aliphatic dicarboxylic acid is similar to that used as the third material for the organic crystal particles, and it functions in a similar way. It is preferred that the number of carbon atoms of the straight-chain aliphatic compound be the same or approximately the same as that of the aliphatic dicarboxylic acid. The number of carbon atoms is preferably 12 or more. It is considered that this straight-chain aliphatic compound functions in a similar way as that of the aliphatic compound having an amide group or a urea group, and this straight-chain aliphatic compound forms a complex together with the dicarboxylic acid. As a result, in a similar way as in the third organic crystal particles, particles for a recording material having a high melting point and a wide temperature range (20 °C or more) in which the particles are light transmissible can be obtained. The recording contrast obtained in the case when this recording medium is used is also high.

The dicarboxylic acid and the straight-chain aliphatic compound are mixed in a ratio in the range of 10:90 to 90:10, and preferably 30:70 to 80:20 by weight. When the aliphatic dicarboxylic acid is in an excess amount, in the same way as in the case that the aliphatic dicarboxylic acid is in an excess amount in the third organic crystal particles, high contrast cannot be obtained. In contrast, when the straight-chain aliphatic compound is in an excess amount, effects of the aliphatic dicarboxylic acid cannot be obtained, so that the range of temperature where the particles are light transmissible becomes narrow (e.g., less than 20 °C).

The particle size of the organic crystal particles made of the above-mentioned first to fourth materials is 0.1 μm or less, and usually 0.01 to 2 μm. As described below, these organic crystal particles are obtained by dissolving the above-mentioned materials and the matrix polymer in a protonic organic solvent, and by coating the mixture so obtained onto a substrate, thereby forming dispersed particles in the matrix polymer. For example, a recording layer **12** including organic crystal particles dispersed therein is formed on the substrate **11** in this manner, and then a protective layer **13** (described below) is formed on its surface, whereby a recording medium as shown in Figure **6** is obtained. Alternatively, the recording medium can be formed by dispersing the organic crystal particles in an organic solvent solution of the matrix polymer and coating this dispersion onto the surface of the substrate, followed by drying to form a recording layer, and then forming a protective layer on the recording layer.

As is shown in Figure **4**, it is advantageous that the organic crystal particles **7** are micro-capsulated with a matrix polymer **8** being different from a matrix polymer **9** in which the organic crystal particles are dispersed. A material for the matrix polymer **8** (hereinafter, referred to as a matrix polymer for capsulation) used for micro-capsulation is appropriately selected from the group of polymers which are used as the matrix polymer in which the organic crystal particles are dispersed. As the matrix polymer for capsulation, compounds having appropriate compatibility with the material for organic crystal particles and matrix polymer are selected. As described above, even in the case where compatibility between the compound forming the organic crystal particles and the matrix polymer is relatively poor, the compatibility can be increased by interposing the matrix for capsulation therebetween. Therefore, the micro-capsulated organic crystal particles enable highly reliable and stable crystalline characteristics.

For example, when the organic crystal particles are a compound having a group capable of forming a hydrogen bond and either an alkyl group or an alkylene group having 10 or more carbon atoms, and the matrix polymer is a polymer having repeating units with an alkylene component having 10 or more carbon atoms, as the matrix polymer for capsulation, styrene-butadiene copolymers, ethylene-vinyl acetate copolymer, ethylene-acrylic ester copolymers, olefin type copolymers, and the like are preferred. When the

capsulation is effected with such a polymer, the compound forming a core portion of the organic crystal particles and the matrix polymer for capsulation form a micell of an opposite type of hydrogen bonds due to the affinity of the alkylenes. On the other hand, the matrix polymer for capsulation and the matrix polymer form a hydrogen bond. As a result, the capsulated organic crystal particles and the matrix polymer have appropriate affinity (i.e., compatibility) with each other, whereby the above-mentioned effects are obtained.

The microcapsule can be produced by a micelle formed by an aqueous type or non-aqueous type coacervation method. As the coacervation method, there are a simple coacervation method in which a polymer solution and either a non-solvent or an electrolyte are used in combination, and a complex coacervation method in which electrical phase separation, e.g., the phase separation of polycations and polyanions, is effected. Examples of the method for producing a microcapsule by the coacervation method include chemical production methods such as an interface polymerization method, an in-situ polymerization method, and an interface curing coating method in which a hardening agent is used. And physical production methods such as a method utilizing a phase separation, a spray-drying method, and a fluid coating method.

The particle size of the microcapsule obtained is usually 0.5 to 50 μm, and the thickness of the coating layer is 0.1 to 5 μm. The content of the microcapsule **70** in the matrix polymer **9** is 10% to 70% by weight based on the total weight of the matrix polymer **9** and the microcapsule **70**, and preferably is 20% to 40% by weight, although the content may be varied depending upon the size of the microcapsule and the thickness of the coating layer of the microcapsule. When the content of the microcapsule exceeds this range, binding strength of the recording layer is decreased. As a result, a uniform recording layer cannot be obtained. In contrast, when the content of the matrix polymer is increased, the content of the microcapsule is decreased, so that the contrast of recording is degraded.

A colored recording medium can be obtained by using a colored polymer containing a coloring matter as the matrix polymer for capsulation in preparing the above-mentioned microcapsule. A multi-color recording medium can be obtained by using several kinds of microcapsules each having different colors, respectively. For example, a reversible thermosensitive recording material of the present invention comprising plural kinds of microcapsules variously colored is formed on a substrate (e.g., a polymer sheet) **1** on which a reflection layer **2** is formed as shown in Figure **1**, and a protective layer **4** is provided thereon, whereby a multi-color recording sheet which is optically scattered in various colors due to the opaqueness caused by thermal writing.

As is shown in Figure **15**, it is possible that spacer particles **43** are contained in a recording layer **42** so as to improve the durability of the recording medium of the present invention. The spacer particles **43** are light transmissible particles which have a particle size nearly equal to and less than the thickness of the recording layer **42**. It is desired that the spacer particles are formed of spherical particles which are made of glass or a polymer and have an average particle size of 1 to 100 μm with a narrow particle size distribution. As a material for the copolymer particles, melamine resins, acrylic resins, nylons, polycarbonates and the like can be used. The spacer particles are contained in the recording layer in an amount of 10% by weight or less. The material, particle size, and content of the spacer particles are selected in view of the material for the matrix polymer used in the recording medium and precision of recording. As shown in Figure **15**, when the spacer particles are contained in the recording layer, even though the recording material is likely to be thermally deformed, the hard spherical particles function as a pillar in the recording layer and resist the pressure of a thermal head. Thus, the recording layer is not deformed while being melted in the recording, and durability is substantially improved. As is described above, according to the present invention, a problem in that the recording material is deformed due to the melting of the recording layer, which cannot be avoided by this type of recording, can readily be overcome by a simple method.

The organic crystal particles (also including the micro-capsulated organic crystal particles) are contained in an amount of 5 to 50 parts by weight, preferably 15 to 40 parts by weight based on 100 parts by weight of the matrix polymer. When the content of the organic crystal particles exceeds the above amount, the binding strength of each component forming the recording layer is decreased and it becomes difficult to form a uniform recording layer by coating. In contrast, when the content of the matrix polymer is increased, the amount of the organic crystal particles is decreased, so that it becomes difficult to opacify the recording layer and the contrast of recording is degraded.

Examples of the material for the substrate used in the recording medium according to the present invention include polymers, metals, and ceramics. There is, however, no special limit. Examples of the polymers include polyester resins, polycarbonate resins, and acrylic resins. Examples of the metal include aluminium and stainless steel. An example of the ceramics includes glass. The polymer material usually used is in a sheet shape, and the substrate is selected based on characteristics such as strength and rigidity of the material. Plastics such as nylon, cellulose acetate type resins, polystyrene, polyethylene,

polypropylene, polyesters, polyimides, polycarbonates, and polyvinyl chloride are used alone or in combination. Polyesters and polyvinyl chloride are preferred. As to a sheet structure, sufficient thickness is required in order to maintain the configuration of the substrate. The thickness is preferably about 0.005 to 5 mm.

The reversible thermosensitive recording medium of the present invention is obtained by successively forming a recording layer **12** and a protective layer **13** (described below) on a base material **11** as shown in Figure **6**. As described above, the recording layer is formed by dissolving the above-mentioned materials capable of forming the organic crystal particles and the matrix polymer in the organic solvent; adding, if required, the above-mentioned spacer particles, a plasticizer, a leveling agent, a dispersant, a crystal core agent having a group capable of forming a hydrogen bond, an antioxidant, etc.; coating the mixture on a substrate **11**, and followed by drying. It is also desired that the crystal core agent and the antioxidant have a group capable of forming a hydrogen bond. Because of this, a recording medium can be obtained which has a high temperature for crystallization of the organic crystal particles and a wide temperature range in which particles are light transmissible, and which provides excellent contrast when information is recorded. As the antioxidant, phenol type antioxidants are preferred. Examples of methods for coating the mixture include ordinary coating methods such as gravure coating, bar coating, and screen coating. The reversible thermosensitive recording medium of the present invention can be prepared in various types of configurations in accordance with its intended use. For example, in order to increase contrast when information is recorded, a reflection layer **2** (described below) is provided between the substrate **1** and the recording layer **3** (Figure **1**). Other examples of the recording medium of the present invention are shown in Figures **7** to **9**.

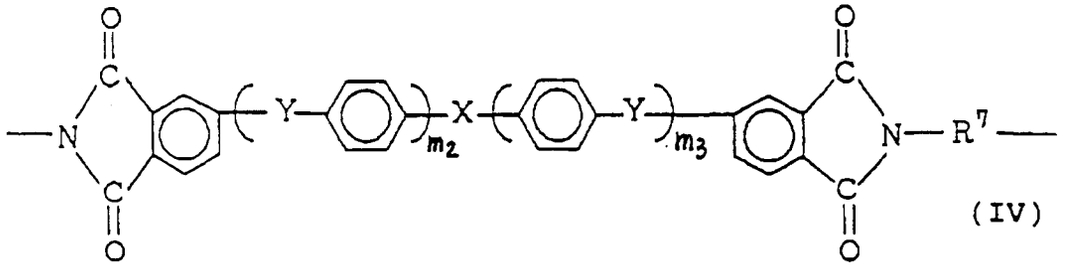
In the recording medium, as is shown in Figure **1** or **4**, the organic crystal particles are dispersed in the matrix polymer. The organic crystal particles are present in two kinds of crystalline states as shown in Figures **2a**, **2b** and **5a**, **5b**. Figures **2a** and **5a** show a single crystalline state in which the particles are light transmissible. Figures **2b** and **5b** show a polycrystalline state in which the particles can scatter light. A recording layer containing the organic crystal particles which can scatter light appears opaque as a whole.

As shown in Figure **3**, when the recording layer is gradually heated and the temperature exceeds $\mathbf{T}_0$ - (with $\mathbf{T}_0$ almost corresponding to a glass transition point (**Tg**) of the matrix polymer), the recording layer begins to change from an opaque state to a transparent state; and when the temperature reaches $\mathbf{T}_1$, the recording layer becomes completely transparent. At this point, the organic crystal particles are in a single crystalline state and are light transmissible. When the temperature is further raised to $\mathbf{T}_2$ or more, the light transmissibility of the organic crystal particles gradually decreases, and the recording layer becomes semi-transparent at $\mathbf{T}_3$ ($\mathbf{T}_3$ approximately corresponding to the melting point of the organic crystal particles). When the organic crystal particles heated to a temperature between $\mathbf{T}_1$ and $\mathbf{T}_2$ are cooled to room temperature, the organic crystal particles are light transmissible, and therefore the recording layer remains transparent. When the organic crystal particles heated to $\mathbf{T}_3$ or more are cooled to room temperature, the organic crystal particles scatter light, and therefore the recording layer becomes opaque.

Recording is made by setting the above-mentioned transparent state or opaque state as an initial state and changing the state as described above. For example, at first, a recording medium having a recording layer containing organic crystal particles is heated to a temperature in the range of $\mathbf{T}_1$ to $\mathbf{T}_2$, thereby obtaining a transparent recording layer. Then, as shown in Figure **7**, information can be written to the recording layer by using a means for heating **19** at a temperature of $\mathbf{T}_3$ or more. With appropriate materials selected for the organic crystal particles and the matrix polymer, the recording speed can be controlled due to the delay in the change of the crystal structure in a supercooled portion at the time when the recording layer is cooled after being heated. As the means for heating **19**, a thermal head, a heat roller, and laser beam are used; however, various other means may be employed without limitation.

In the recording medium of the present invention, in order to protect the surface of the recording layer, the protective layer is provided. As this protective layer, any transparent film can be used as long as it has the appropriate strength and rigidity for supporting the recording layer and abrasion resistance. Examples of materials for the protective layer include polyethylene terephthalate, polymers containing fluorine, polysulfones, polyethylene naphthalate, polyphenylenesulfide, polyarylates, polyimides and polyamides. The thickness of the protective layer should be determined so that the heat for recording or erasing information, which is generated by the means for heating, is transmitted to the recording layer. Preferably, the thickness of the protective layer is about 0.001 to 0.05 mm.

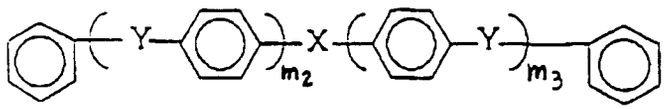
As the protective layer according to the present invention, a protective layer made of a soluble polyimide, or a protective layer made of a polymer comprising ultra-fine particles of an oxide whose primary particle has an average particle size of 10 nm or less is preferred. The soluble polyimide refers to a polyimide which is soluble in an organic solvent and is a polymer having a repeating unit represented by the following Formula IV:



(IV)

wherein X is 0, CO, $C(CF_3)_2$ or a single bond; Y is 0, CO, $C(CF_3)_2$, or a single bond; R^7 is a group having an aromatic ring; and m_2 and m_3 are independently 0, 1, or 2.

In a polymer comprising the above-mentioned repeating unit of Formula IV, as the molecular structure of an aromatic portion of the tetracarboxylic acid anhydride component, that is:



there are biphenyl, biphenyl ether, benzophenone, and di(trifluoro)diphenylmethane; and as the structure (-N-R^7-N-) of aromatic diamine, there are phenylenediamine, oxydianiline, methylenedianiline, diaminobiphenyl, and tolidine. A soluble polyimide resin obtained by the combination of these components and a soluble polyimide resin which is a copolymer comprising these components and other components such as pyromellitic acid anhydride can be used for the protective layer. These polyimides are formed by polycondensation of aromatic tetracarboxylic acid anhydride and aromatic diamine. These polyimides are dissolved in a solvent capable of dissolving the polyimide and being coated onto the recording layer as described above. As organic solvents capable of dissolving these soluble polyimide resins, demethylformamide, dimethylacetamide, N-methylpyrrolidone, dimethylsulfoxide, and cresol are suitable. However, any organic solvents capable of dissolving polyimide resins can be used for the formation of the protective layer. A solvent capable of dissolving a soluble polyimide resin is selected as an organic solvent for production of the soluble polyimide by polymerization, whereby a polyimide resin solution can be obtained. In addition, there is another method for obtaining a polyimide resin solution in which polyamic acid as a precursor is taken out by reprecipitation from a reaction mixture. The polyamic acid thus obtained is subjected to heat treatment to obtain an imide, and then dissolved in an organic solvent.

The recording medium of the present invention, as shown in Figure **6**, is obtained by forming a recording layer **12** made of a matrix polymer comprising organic crystal particles on a substrate **11**, and then coating a solution comprising a soluble polyimide thereon, followed by drying. When the protective layer made of the above-mentioned polyimide resin is formed, the protective layer is excellent in heat resistance and mechanical strength, so that the repeatable characteristics of highly reliable recording and erasing can be obtained. As to the temperature for thermal deformation of the protecting layer caused by degradation due to the thermal head, in the case of polyethylene terephthalate, it is 230 °C; while in the case of polyimides, it is 300 °C or more which is an excellent characteristic as will be appreciated. When polyimide is used for the protective layer, a decrease in recording conditions due to the repetition of heating in the process of recording and erasing, and mechanical damages caused by the thermal head can be avoided. As a result, reversible thermosensitive recording with satisfactory repeating characteristics can be realized.

In the process of preparing a recording medium of the present invention which uses a soluble polyimide resin as a protective layer, a solution of the soluble polyimide resin is coated onto the recording layer. In this process, a step for applying heat for imidation is not required. In this process, heating at a relatively low temperature and the reducing of pressure for removing the organic solvent are only required. Thus, the deterioration of the matrix polymer of the recording layer can be prevented. Moreover, condensed water caused by the imidation is not generated, and thus, a void is not likely to occur, and a uniform protective layer can be produced.

Furthermore, according to the preferred embodiment in which the soluble polyimide resin comprises a repeating unit represented by Formula IV, deterioration in recording conditions due to the repetition of

heating during the recording and erasing and mechanical damages caused by the thermal head can be avoided. As a result, the reversible thermosensitive recording with satisfactory repeating characteristics can be realized.

On the other hand, in the case where poly(pyromellitic)imide, commercially available as "Kapton" (Trade Name, manufactured by Dupont Co., Ltd.), is formed into a protective layer, heat treatment is required for the following reasons. As poly(pyromellitic) imide is insoluble in organic solvents, polyamic acid which is the precursor of the imide and soluble in organic solvents is coated on the recording layer as an organic solvent solution, and the coated layer is heat-treated to form a polyimide. In this case, in order to sufficiently effect the imidation reaction, a temperature of 300 °C or more is required, so that it is necessary to pay close attention to the thermal degradation of the recording layer caused during the heat treatment. Moreover, there is a problem in that a void is formed by water generated during a condensation reaction of the imidation, and thus a uniform film cannot readily be produced.

In another preferred embodiment of the protective layer, the protective layer is made of a polymer comprising ultra-fine particles of an oxide whose primary particle has an average particle size (i.e., diameter) of 100 nm or less. As a resin which is to be the matrix of this protective layer, thermosetting resins such as acrylic resins, epoxy type resins, and unsaturated polyester resins are preferred since they have high hardness. Since, ultra-fine particles of an oxide are contained, thermoplastic resins such as polyester resins or polyamide type resins can also be used. Among them, when an energy beam curable acrylic resin is used, the resin can readily be cured with an energy beam after being coated, so that the productivity is satisfactory. The obtained protective layer has sufficient transparency. As an energy beam curable acrylic resin, transparent resins having an acryloyl group or a methacryloyl group are suitable; for example, urethaneacrylate resins, epoxyacrylate resins, acrylate resin oligomers, methacrylate resins and acrylate resins can be used alone or in combination. As a method for curing with an energy beam, ordinary methods such as UV irradiation and electron beam irradiation can be used.

The material of ultra-fine particles of an oxide contained in the protective layer is a metal oxide or silicon oxide. Such a material includes silicon oxide, aluminium oxide, titanium oxide, chromium oxide, zinc oxide, tantalum oxide, niobium oxide and manganese oxide. Among them, silicon oxide, aluminium oxide and titanium oxide are preferred since they are white and have satisfactory compatibility with the resin of the protective layer. Particles having a narrow size distribution are preferred, and they can be readily produced. Particles of silicon oxide, aluminium oxide, or titanium oxide having a narrow particle size distribution can be produced by, for example, hydrolysis of a metal halide gas at a high temperature.

As the ultra-fine particles of an oxide, particles whose primary particle has an average particle size of 100 nm or less are used, and especially particles whose primary particle has an average particle size of 20 nm or less are preferred.

When the ultra-fine particles of an oxide are contained in the protective layer, (1) durability of the protective layer is increased, and a flat configuration of the surface of the protective layer is maintained; and (2) reduced friction is provided between the means for providing heat energy (e.g., the thermal head) and the surface of the protective layer. The ultra-fine particles used in the present invention are fine particles which have high hardness and do not abrade by themselves. Since the average particle size of primary particles of the ultra-fine particles is 100 nm or less preferably, the surface of the protective layer is flat and its durability is increased. However, even though the primary particles are small, a very fine unevenness of less than 100 nm is formed on the surface of the protective layer. Because of this unevenness, the contact area between the thermal head and the protective layer is decreased, so that friction between the thermal head and the protective layer is decreased. As a result, mechanical and thermal damage can be prevented. Moreover, since the ultra-fine particles are made of inorganic oxide which are heat resistant, the apparent heat resistance of the protective layer itself is improved. The ultra-fine particles of an oxide can satisfactorily transmit the heat generated from the thermal head. Furthermore, since the ultra-fine particles are used, light scattering due to the unevenness on the surface hardly occurs. As a result, the transparency of the protective layer can be maintained. Moreover, the fine particles present on the surface of the protective layer regulate surface energy, so that the surface is not likely to become dirty and waste and dust are not likely to adhere thereto.

The ultra-fine particles of an oxide are contained in the protective layer in an amount of 0.1 to 50% by weight, preferably about 10% by weight or less. When the ultra-fine particles of an oxide are contained in an amount of 5% by weight, the dispersibility is especially satisfactory, and the unevenness on the surface of the protective layer becomes 50 nm or less, whereby the flat surface is obtained.

Furthermore, in order to improve slipperiness and abrasion resistance of the surface of the ultra-fine particles of an oxide, it is possible to form an organic chemical adsorption film on the surface of the fine particles to provide a water repellant property, a lipophilic property, and a soil resistance property thereon.

As a chemical adsorbent used for forming such a film, a silane coupling agent having a hydrocarbon chain and/or a fluorocarbon chain can be used. When the surface of the ultra-fine particles of an oxide are treated with this kind of chemical adsorbent, an organic chemical adsorption film is formed on the surface. In this adsorbent film, an alkyl group, perfluoroalkyl group, and/or partially fluorinated alkyl group with various chain lengths derived from the chemical adsorbent are present. These groups are chemically bonded to the ultra-fine particles of an oxide via a siloxane group, an ether group, or the like. When the ultra-fine particles of an oxide which are treated as described above are used; for example, in the case of the lipophilic organic chemical adsorbent film, the compatibility between the film and the resin of the protective layer is improved and the binding strength there-between is increased. Also, in the case of a fluorine type organic chemical adsorbent film, particularly excellent slipperiness can be provided on the surface of the ultra-fine particles of an oxide so that damage caused by the thermal head can be prevented and excellent durability performance can be achieved. Moreover, the surface can be prevented from dirt, waste, and dust, so that an image irregularity does not arise. In addition, the compatibility between the organic chemical adsorption film and the resin of the protective layer, and the soil resistance of the surface of the ultra-fine particles can be regulated by designing and selecting a hydrocarbon chain and a group which binds to the hydrocarbon chain in the organic chemical absorption agent.

In order to improve the durability of the protective layer, it is preferred that two or more protective layers are laminated. In this case, a structure in which hardness of the layer is increased toward the outermost surface layer of the protective layer is desired, and the ultra-fine particles of an oxide are contained at least in the outermost surface layer. When the protective layer is made a multi-layer structure, hardness is increased toward the outermost surface layer by selecting a desired resin or desired mixing ratio of resins for the respective layers.

In the recording medium of the present invention, for example as shown in Figures **1** and **7**, it is possible to provide a reflection layer **2** or **15** between the base material and the recording layer in order to increase contrast between transparent and an opaque portions when information is recorded. As to this reflection layer, a metal exhibiting a high reflection index in a visible light region, such as Al, Au, and Te, can be directly used in a sheet shape. Alternatively, a layer in which their powders are dispersed in a binder resin can be used in a sheet shape. Organic thin films having metallic gloss, for example, methine dyes or xanthene dyes can be used. This reflection layer can directly be produced on a support sheet by vacuum deposition or sputtering, or coated thereon by casting or plating. It is also possible to use a reflection sheet (shown by the reference numeral **29** in Figure **9**) in which a reflection layer is formed on the surface of a support sheet. The support sheet is made of any material that can be used for a substrate.

In the recording medium provided with the reflection layer, clear recording with high resolution can readily be performed. Therefore, excellent high density optical recording or erasing of information by laser beam can be performed. This recording medium can be used as a low cost optical disk in which information can be rewritten.

In the recording medium of the present invention, it is recommended that an adhesion layer be provided between the recording layer and the substrate so as to prevent the deterioration of performance due to the deformation of the recording layer caused by repeated recording and erasing of information. In the case in which the reflection layer is provided between the recording layer and the substrate, the adhesion layer can be provided between the substrate and the reflection layer and/or between the reflection layer and the recording layer. Examples of the adhesive used for the adhesion layer include thermosetting resins such as phenol resins and epoxy resins; thermoplastic resins such as polyamide resins, polyurethane resins, vinyl chloride-vinyl acetate copolymer resins, and butyral resins; and elastmers such as butadieneacrylonitrile rubber.

Next, a recording medium having an adhesion layer and a recording medium having an adhesion layer and a reflection layer will be described with reference to Figures **8** and **9**. Figure **8** shows a recording medium in which an adhesion layer **22** is provided between a substrate **23** and a recording layer **21**. This recording medium is obtained, for example, by laminating a recording sheet **24**, in which a reversible thermosensitive recording layer **21** is formed on a protective layer **20** by coating, on a substrate **23** having an adhesion layer **22** so that the surface of the recording layer **21** faces that of the adhesion layer **22**.

Figure **9** shows a structure in which the adhesion layer **27**, a reflection sheet **29**, a silane coupling agent layer **28**, an adhesion layer **22**, and a protective layer **24** are successively laminated on a substrate **23**. The silane coupling agent layer **28** is provided in order to improve the adhesion between a reflection layer **25** of the reflection sheet **29** and the adhesion layer **22**. The silane coupling agent can be, for example, represented by the following Formula V:

$$Y\text{-}(CH_2)_{n11}\text{-}Si(R^8)_{3-m4}(X)_{m4} \qquad (V)$$

wherein Y is a functional group which can react with an adhesive material in the adhesion layer. For example, Y is an amino group, a vinyl group, an epoxy group, a mercapto group, a chlorine atom, or a lipophilic methyl group. Furthermore, n_{11} is an integer in the range of 0 to about 30. R^8 is an inactive group such as a methyl group or an ethyl group. X is a functional group which can be hydrolyzed and can react with a material of the reflection layer. For example, X is a methoxy group, an ethoxy group, or a chloro group. The term m4 is an integer in the range of 1 to 3.

The recording medium in Figure **9** can be produced, for example, as follows. First, a reflection layer made of aluminium or the like is formed on a support sheet **26** by vapor deposition to obtain a reflection sheet **29**. The surface of the reflection layer of this reflection sheet is treated with a silane coupling agent and is adhered to the substrate **23** via an adhesion layer **27**. Separately, a polymer sheet which serve as the protective layer is provided, and on the surface of the sheet, a recording layer **21** made of a matrix polymer comprising organic crystal particles is formed. The polymer sheet having the recording layer **21** so obtained is laminated on the surface of the base material **23** having the reflection sheet so that the recording layer **22** is in contact with the reflection layer **25** via the adhesion layer **22**, whereby the recording medium is obtained.

As is described above, the recording mediums shown in Figures **8** and **9** are excellent in durability because of the formation of the adhesion layer. By using these mediums, recording with high contrast can be performed because of the presence of the reflection layer.

In general, as in the description of the prior art, the following items have been required for reversible thermosensitive recording materials which comprises organic crystal particles dispersed in a matrix polymer: (1) a temperature, at which the particles are heated in order to be light transmissible, is high, and a temperature range in which the particles are in a light transmissible state which is wide; (2) a contrast between transparent regions and opaque regions which is high when information is recorded; and (3) stability for maintenance and repeating characteristics are excellent. The inventors have studied the above-mentioned items and they have found that the melting point of the organic crystal particles and the strength of interaction generated between the compound constituting the organic crystal particles and the matrix polymer are important. In particular, it has been found that in order to obtain satisfactory recording characteristics and contrast, the kind and number of groups capable of forming a hydrogen bond in the organic crystal particles and the matrix polymer are important.

In the reversible thermosensitive recording material of the present invention, each of the organic crystal particles and the matrix polymer is made of a compound having a group capable of forming a hydrogen bond. As a result, they have compatibility with each other, and their melting and solidification characteristics are affected by their interaction. In the recording material of the present invention, crystallization behavior which is highly reliable is exhibited, and the above-mentioned requirements can be satisfied. Also, the organic crystal particles and the matrix polymer are not substantially separated from each other and large crystal particles and cracking are not generated.

In the recording material of the present invention, the compatibility between the matrix polymer and the organic crystal particles is appropriate, so that the size of the crystal particles is not varied when heating and cooling (i.e., recording and erasing) steps are repeated, and a recording material with high resolution and excellent lifetime performance can be provided.

Examples

Hereinafter, the present invention will be described by way of illustrating examples.

Example 1

First, as a recording material, 2 g of 16-hydroxyhexadecanoic acid, 0.1 g of a phenol type antioxidant, and 8 g of partially saponified vinyl chloride-vinyl acetate copolymer having a hydroxyl group were dissolved in 100 ml of tetrahydrofuran. The solution thus obtained was coated onto a reflection layer **2** formed by vapor deposition of aluminium on a polyester sheet (substrate **1**) with a thickness of 0.2 mm and dried, thereby forming a recording layer **3** with a thickness of 13 μm. Then, a UV-curable acrylic resin prepolymer was coated on the recording layer **3** to a thickness of 10 μm. After that, the prepolymer was irradiated with ultraviolet rays to be cured, whereby a protective layer **4** was formed (see Figure **1**). Thus, a reversible thermosensitive recording sheet was obtained. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation

and by using a Macbeth densitometer. The temperature range was found to be from about 73 °C to 95 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 100 °C and erased from the recording layer at 90 °C.

The opaque region of the recording layer where information was recorded, and the transparent region of the recording layer where information was erased, were analyzed by X-ray diffraction, and the diffraction peaks were observed in both of the regions. It was found that in both of the regions, fine crystalline particles were present. It was found that the particles in the transparent region were in a single crystalline state. This state is schematically shown as **6A** in Figure **2a**. It was also found that the particles in the opaque region were in a polycrystalline state. This state is schematically shown as **6B** in Figure **2b**. Moreover, observation of these regions using a scanning electron microscope revealed that the interface between the organic crystal particles and the matrix polymer was not clear and cracks were not observed. Furthermore, observation of the organic crystal particles using the scanning electron microscope revealed that the particle has a size of 0.1 μm or less.

The recording sheet was cut as shown in Figure **10**, and a magnetic recording layer **30** and the recording sheet **31** were formed on a part of a substrate such that a recording card with a display function was produced.

Example 2

First, as a recording material, 2 g of 1,16-hexadecanediol, 0.1 g of a phenol type antioxidant, 2 g of an adhesive polyester (Vyron, manufactured by Toyobo Co., Ltd,), and 5 g of polyurethane were dissolved in 100 ml of tetrahydrofuran. The solution thus obtained was coated onto a reflection layer **2** made of aluminium formed on a substrate **1** and dried, thereby forming a recording layer **3** with a thickness of 20 μm. Then, a protective layer **4** made of a UV-cured urethane acrylate resin was formed on the recording layer **3** so as to have a thickness of 5 μm, thereby obtaining a reversible thermosensitive recording sheet (Figure **1**). The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was the heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 65 °C to 95 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 100 °C and erased from the recording layer at 90 °C. As a result, satisfactory recording characteristics using the sheet were obtained.

Example 3

First, as a recording material, 2 g of α-hydroxystearic acid, 0.1 g of an phenol type antioxidant, and 8 g of partially saponified vinyl chloride-vinyl acetate copolymer having a hydroxyl group were dissolved in 100 ml of tetrahydrofuran. The solution thus obtained was coated onto a reflection layer formed by vapor deposition of alminium on a polyester sheet and dried, thereby forming a recording layer with a thickness of 13 μm. Then, a protective layer made of an oligomer containing an acrylic ester in both terminals of the molecule as its component, which was cured with ultraviolet rays, was formed on the recording layer, thereby forming a reversible thermosensitive recording sheet. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 90 °C to 110 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 120 °C and erased from the recording layer at 100 °C.

Example 4

First, as a recording material, 2.5 g of butyl p-hydroxybenzoate, 0.1 g of a hindered phenol type antioxidant, and 7.5 g of vinyl chloride-vinyl acetate-acrylamide copolymer were dissolved in 100 ml of tetrahydrofuran. The solution thus obtained was coated to a thickness of 20 μm on a blue-colored layer formed on the surface of a hard polyvinylchloride sheet (1 mm thickness), thereby forming a recording layer. Then, a protective layer made of a urethane acrylate resin, which was cured with ultraviolet rays, was formed on the resulting recording layer to a thickness of 5 μm, thereby obtaining a reversible thermosensitive recording sheet. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 70 °C to 90 °C. The recording characteristics measured by a Macbeth densitometer are shown in Figure **11**. It was found that the width of the temperature range was large and the sheet provided high contrast during the recording.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. After that, this sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 100 °C and erased from the recording layer at 80 °C.

Example 5

First, as a recording material, 1 g of stearamide (melting point: 101 °C) having a saturated hydrocarbon chain with 17 carbon atoms, and 3 g of partially saponified vinyl chloride-vinyl acetate copolymer were dissolved in 15 g of tetrahydrofuran. The solution thus obtained was coated onto a reflection layer **2** formed by vapor deposition of alminium on a polyester sheet **1** with a thickness of 0.188 mm as shown in Figure **1** and dried, thereby forming a recording layer **3** with a thickness of 10 μm. Then, a UV-curable acrylic resin prepolymer was coated on the recording layer **3** to a thickness of 8 μm. After that, the resulting recording layer **3** was irradiated with ultraviolet rays in order to be cured, whereby a protective layer **4** was formed. As a result, a reversible thermosensitive recording sheet was obtained. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 80 °C to 105 °C, and thus the width of the temperature range was about 26 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 120 °C and erased from the recording layer at 95 °C.

Example 6

First, as a recording material, 2 g of erucamide (melting point: 81 °C) with a hydrocarbon chain which had one unsaturated bond and 21 carbon atoms, and 4 g of partially saponified vinyl chloride-vinyl acetate copolymer (copolymerization ratio: vinyl chloride/vinyl acetate = 97/13) were dissolved in 15 g of tetrahydrofuran. Then, a reversible thermosensitive recording sheet was obtained by using this solution in the same way as in Example **5**, except that the thickness of the recording layer **3** was made 15 μm. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 68 °C to 81 °C, and thus the width of the temperature range was 14 °C. The recording characteristics measured by a Macbeth densitometer are shown in Figure **12**. It was found that the width of the temperature range was large, and the contrast between the recorded region and the unrecorded region was high after the recording.

Next, 2 g of erucamide and 4 g of partially saponified vinyl chloride-vinyl acetate copolymer (copolymerization ratio: vinyl chloride/vinyl acetate = 50/50) were dissolved in 15 g of tetrahydrofuran, thereby producing a reversible thermosensitive recording sheet in the same way as the above-mentioned process by using this solution. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 57 °C to 81 °C. Since the number of

hydroxyl groups of the copolymer used here was larger than that of the above-mentioned copolymer, the hydroxy group was likely to be bonded to the amide group of erucamide (which is an aliphatic carboxamide) by a hydrogen bond. Because of this, the width of the temperature range became large (25 °C). Due to the large temperature range, recording conditions can widely be set.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range (i.e., 68 °C to 81 °C) and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 90 °C and erased from the recording layer at 70 °C. At this time, a clear display was obtained. Furthermore, the measurement of lifetime by the repetition of the above recording and erasing steps revealed that the reversible thermosensitive recording sheet could stand 500 or more repetitions.

Example 7

First, as a recording material, 1.5 g of N,N'-dioctadecylurea (melting point: 114 °C) with two hydrocarbon chains each having 18 carbon atoms and 4 g of partially saponified vinyl chloride-vinyl acetate copolymer were dissolved in 15 g of tetrahydrofuran. Then, a reversible thermosensitive recording sheet was obtained by using this solution in the same way as in Example 5. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 90 °C to 120 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 130 °C (the recorded portion was opaque) and erased from the recording layer at 100 °C (the erased portion was transparent). As a result, satisfactory recording characteristics were obtained.

Example 8

First, as a recording material, 2 g of erucamide (melting point: 81 °C), 1 g of docosanol (melting point: 69 °C), and 8 g of partially saponified vinyl chloride-vinyl acetate copolymer were dissolved in 20 g of tetrahydrofuran. Then, a recording layer **33** with a thickness of 20 μm was formed on a glass substrate **32** with a thickness of 1.2 mm by using the solution thus obtained. On the recording layer **33**, a carbon film having a thickness of 0.1 μm was formed as a layer **34** which becomes heated due to absorbing light. As a reflection layer **35** on the layer **34**, aluminium was vapor-deposited to a thickness of 0.2 μm, thereby resulting in a reversible thermosensitive recording sheet as shown in Figure **13**. Information was recorded in or erased from the recording layer by irradiation provided from a semiconductor laser beam **37** having an oscillation wavelength of 780 nm through an actuator lens **36** from the side of the glass substrate **32**. The temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 60 °C to 80 °C. Under these conditions, heat provided by the layer **34** was regulated by controlling the power of the semiconductor laser beam such that the temperature of the recording layer was varied. As a result, information was recorded in the recording layer at 100 °C and erased from the recording layer at 70 °C. Observation of the spot formed by the irradiating light revealed that satisfactory bit recording with a clear spot edge was performed.

Example 9

First, as an organic crystal particle material, 0.6 g of eicosanedicarboxylic acid ($HOOC(CH_2)_{18}COOH$, melting point: 127 °C), which is an aliphatic dicarboxylic acid, and 0.4 g of stearamide (melting point: 101 °C) were added to 15 g of tetrahydrofuran. Then, 3 g of partially saponified vinyl chloride-vinyl acetate copolymer (the number of the hydroxy groups based on the total number of the hydroxy groups and the acetoxy groups being about 5%) was added as a matrix polymer to the mixture so obtained, whereby a solution was provided. As is shown in Figure **1**, a substrate **1** made of a polyester sheet having a thickness of 0.2 mm on which an reflection layer **2** was formed by vapor deposition of aluminium was provided. The tetrahydrofuran solution was coated onto the surface of the reflection layer and dried in an isothermal bath

at 150 °C, thereby forming a recording layer **3** having a thickness of 14 μm. A UV-curable acrylate resin prepolymer was coated on the recording layer **3** to a thickness of 10 μm, and after that the resulting recording layer **3** was irradiated with ultraviolet rays in order to be cured, whereby a protection layer **4** was formed and a reversible thermosensitive recording sheet was obtained. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual obsarvation and by using a Macbeth densitometer. The temperature range was found to be from about 80 °C to 110 °C. And thus the width of the temperature range was about 30 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range (i.e., 80 °C to 110 °C) and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 115 °C (the recorded portion was opaque) and erased from the recording layer at 100 °C (the erased portion was transparent). As a result, satisfactory recording characteristics were obtained. Using the Macbeth densitometer, it was found that the contrast between the recorded region and unrecorded region was 0.73, and satisfactory recording was performed. The repetition of the recording and erasing above steps revealed that the sheet withstood 500 or more repetitions.

As a comparative example, a reversible thermosensitive recording sheet comprising organic crystal particles formed from 0.7 g of eicosanedicarboxylic acid and 0.3 g of stearamide was prepared. The temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 80 °C to 85 °C, and thus width of the temperature range was 6 °C. Thus, the transparency of the recording layer was unsatisfactory and the sheet withstood only 10 repetitions.

Example 10

First, as an organic crystal particle material, 0.7 g of octadecanedicarboxylic acid ($HOOC(CH_2)_{16}COOH$, melting point: 125 °C), which is an aliphatic dicarboxylic acid, 0.3 g of m-xylenebisstearylurea (melting point: 163 °C), and 0.3 g of docosanol (melting point: 70 °C) were mixed. This mixture was added to 15 g of tetrahydrofuran, and 3 g of partially saponified vinyl chloride-vinyl acetate copolymer (the number of the hydroxy groups based on the total number of hydroxy groups and the acetoxy groups being about 5%) was added as a matrix polymer to the mixture so obtained, whereby the mixture was dissolved to prepare a solution of a recording material. A substrate **1** made of a polyester sheet having a thickness of 0.2 mm on which an reflection layer **2** was formed by vapor deposition of aluminium was provided, and the tetrahydrofuran solution was coated onto the surface of the reflection layer **2** and dried in an isothermal bath at 150 °C, thereby forming a recording layer **3** having a thickness of 15 μm. A protective layer **4** made of urethane acrylate resin cured with ultraviolet rays was formed on the recording layer **3** to produce a reversible thermosensitive recording sheet. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 78 °C to 110 °C, thus the width of the temperature range was about 33 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 115 °C (the recorded portion was opaque) and erased from the recording layer at 100 °C (the erased portion was transparent). As a result, satisfactory recording characteristics were obtained.

Example 11

First, as an organic crystal particle material, 0.6 g of eicosanedicarboxylic acid ($HOOC(CH_2)_{18}COOH$, melting point: 127 °C), which is an aliphatic dicarboxylic acid, and 0.4 g of docosanol (melting point: 70 °C) were added to 15 g of tetrahydrofuran. Then, 3 g of partially saponified vinyl chloride-vinyl acetate copolymer (the number of the hydroxyl groups based on the total number of the hydroxyl groups and the acetoxy groups being about 12%) was added as a matrix polymer to the mixture so obtained, whereby a solution was obtained. In the same way as in Example **9**, a reversible thermosensitive recording sheet was produced. The recording layer of the reversible thermosensitive recording sheet was opaque at room

temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 70 °C to 110 °C, thus the width of the temperature range was about 40 °C. The recording characteristics measured by the Macbeth densitometer are shown in Figure **14a**. The Macbeth optical density, which was a standard of contrast, was 1.48 when the recording layer was transparent, and was 0.6 when the recording layer was opaque. Such contrast was found to be satisfactory. Moreover, the measurement of lifetime characteristics by the repetition of the above recording and erasing steps revealed that the sheet withstood 500 or more repetitions.

As a comparative example, eicosanedicarboxylic acid or docosanol was used alone as an organic crystal particle material, whereby a reversible thermosensitive recording sheet was formed (thickness of a recording layer was about 10 μm). The results obtained by measuring the Macbeth optical density are shown in Figures **14b** and **14c**. From Figures **14b** and **14c**, when the eicosanedicarboxylic acid was used, the temperature range in which the recording layer was transparent was found to be from about 80 °C to 120 °C, and thus the width of the temperature range was about 40 °C. However, the Macbeth optical density was about 0.8 and the transparency of the recording layer was relatively high when the recording layer was opaque, and the recognition property of the recording was not high. In contrast, when docosanol was used, the Macbeth optical density was 0.6 or less when the recording layer was opaque, and the contrast between the recorded region and the unrecorded region was high. However, the temperature range in which the recording layer was transparent was found to be from about 61 °C to 69 °C, and thus the width of the temperature range was 9 °C. As a result, the temperature range available when recording was small and recording conditions could not be widely set.

Example 12

First, as an organic crystal particle material, 0.5 g of eicosanedicarboxylic acid ($HOOC(CH_2)_{18}COOH$, melting point: 127 °C), which is an aliphatic dicarboxylic acid, and 0.5 g of erucamide (melting point: 81 °C) were mixed. This mixture was added to 15 g of tetrahydrofuran. Then, 3 g of partially saponified vinyl chloride-vinyl acetate copolymer (the number of the hydroxyl groups based on the total number of hydroxyl groups and the acetoxy groups being about 5%) was added as a matrix polymer to the mixture so obtained so as to provide a solution. The solution was coated onto a substrate and dried in an isothermal bath at 150 °C, thereby forming a recording layer having a thickness of 10 μm. Moreover, a protective layer made of an oligomer containing an acrylic ester in both terminals of the molecule as its component cured with ultraviolet rays was formed, whereby a reversible thermosensitive recording sheet was produced. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 67 °C to 110 °C, and thus the width of the temperature range was about 44 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 120 °C (the recorded portion was opaque) and erased from the recording layer at 100 °C (the erased portion was transparent). As a result, satisfactory recording characteristics were obtained. Moreover, the repetition of the above recording and erasing steps revealed that the sheet withstood 500 or more repetitions.

Example 13

First, as an organic crystal particle material, 0.3 g of sebacic acid ($HOOC(CH_2)_8COOH$, melting point: 134 °C), which is an aliphatic dicarboxylic acid, 0.3 g of oleamide (melting point: 70 °C), and 0.4 g of behenic acid (melting point: 81 °C) were mixed. This mixture was added to 15 g of tetrahydrofuran. Then, 3 g of an adhesive polyester resin (having a hydroxyl group) was added as a matrix polymer to the mixture so produced, whereby a solution was obtained. The solution so obtained was coated onto a reflection layer which was formed by vapor deposition of aluminium on a polyester sheet having a thickness of 0.2 mm and dried in an isothermal bath at 150 °C, thereby forming a recording layer having a thickness of 15 μm. Moreover, a protective layer made of urethane acrylate resin cured with ultraviolet rays was formed on the recording layer, whereby a reversible thermosensitive recording sheet was produced. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated

using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 65 °C to 98 °C, and thus the width of the temperature range was about 34 °C.

Then, starting with the sheet in an initial, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 110 °C (the recorded portion was opaque) and erased from the recording layer at 90 °C (the erased portion was transparent). As a result, satisfactory recording characteristics were obtained. Moreover, the repetition of the above recording and erasing steps revealed that the sheet withstood 500 or more repetitions.

Example 14

First, 4.5 g of microcapsules having an average particle size of 20 μm including the organic crystal particles having a composition of Example **12** as a core and a cross-linked polyurethane as a coating layer, and 6 g of polyvinyl alcohol were added to 100 ml of ethyl alcohol, whereby the microcapsules were dispersed and the polyvinyl alcohol was dissolved. Then, this mixture was coated onto the surface of a reflection layer which was formed on a polyester sheet having a thickness of 0.2 mm by vapor deposition of aluminium. A UV-curable acrylate resin prepolymer was coated onto the recording layer to a thickness of 15 μm and cured with ultraviolet rays, whereby a protective layer was formed. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 70 °C to 110 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 120 °C (the recorded portion was opaque) and erased from the recording layer at 100 °C (the erased portion was transparent). As a result, satisfactory recording characteristics were obtained. Moreover, the repetition of the above recording and erasing steps revealed that the sheet withstood 740 or more repetitions.

Example 15

First, 1.5 g each of microcapsules of three colors including an organic crystal particle made of 2-hydroxypalmitic acid (melting point: 86 °C) as a core and a modified ethylene-vinyl acetate copolymer which is colored with a coloring matter as a coating layer, and 5 g of polyvinylbutyral were added to 100 ml of ethyl alcohol. As a result, the microcapsules were dispersed and the polyvinylbutyral was dissolved. Then, the ethyl alcohol mixture was coated onto a coating layer having thickness of 0.02 μm which was formed by vapor deposition of gold on a sheet made of hard polyvinyl chloride and having a thickness of 1 mm, whereby a recording layer having a thickness of 25 μm was formed. A UV-curable acrylate resin prepolymer was coated onto the recording layer to a thickness of 10 μm and cured with ultraviolet rays to form a protective layer. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 65 °C to 85 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a semiconductor laser, and information was recorded in and erased from the recording layer.

Example 16

First, 2 g of 12-hydroxystearic acid, 0.1 g of a phenol type antioxidant, and 8 g of partially saponified vinyl chloride-vinyl acetate copolymer having a hydroxyl group were dissolved in 100 ml of tetrahydrofuran. Then, 0.8 g of glass beads having an average particle size of 15 μm was dispersed in the mixture. As is shown in Figure **15**, the above dispersion solution was coated onto a reflection layer **41** which was formed on a substrate **40** (a polyester sheet) having a thickness of 0.2 mm by vapor deposition of aluminium and

dried. As a result, a recording layer **42** having a thickness of 13 μm was formed. A UV-curable acrylate resin was coated onto the recording layer **42** to a thickness of 10 μm and cured with ultraviolet rays to form a protective layer **44**. Thus, a reversible thermosensitive recording sheet was obtained. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 70 °C to 90 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 100 °C (the recorded portion was opaque) and erased from the sheet at 80 °C (the erased portion was transparent). As a result, no deterioration of recording image quality due to the glass beads was visually observed. Moreover, the endurance test by repetition of the above recording and erasing revealed that the sheet withstood 1,500 or more repetitions. The lifetime is about 7 times that obtained in the case where there is no addition of glass beads.

Example 17

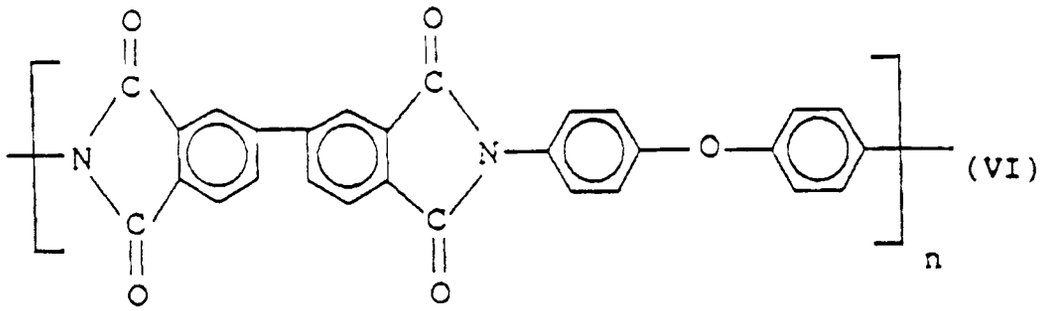
First, 2 g of the organic crystal particles of the composition in Example **12**, 0.1 g of a phenol type antioxidant, 2 g of an adhesive polyester (Vyron, manufactured by Toyo Boseki Co., Ltd.), and 5 g of polyurethane were dissolved in 100 ml of tetrahydrofuran. Moreover, 0.3 g of melamine resin having an average particle size of 20 μm was dispersed therein. The above dispersion solution was coated onto a reflection layer which was formed on a substrate (a polyester sheet) having a thickness of 0.2 mm by vapor deposition of aluminium and dried, whereby a recording layer having a thickness of 20 μm was formed. In the same way as in Example **16**, a UV-curable acrylate resin prepolymer was coated onto the recording layer to a thickness of 10 μm and cured with ultraviolet rays to form a protective layer, whereby a reversible thermosensitive recording sheet was obtained. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recoding layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 90 °C to 110 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 120 °C (the recorded portion was opaque) and erased from the recording layer at 100 °C (the erased portion was transparent). As a result, satisfactory recording characteristics were obtained. Moreover, the lifetime characteristics as determined by the repetitions of the above recording and erasing steps revealed that the sheet withstood 1800 repetitions.

Example 18

As a substrate **11** shown in Figure **6**, a white polyethylene terephthalate sheet having a thickness of 200 μm was used, on which a magnetic recording layer showing a dark brown color of γ -Fe_2O_3 was formed. A recording layer **12** was formed by coating the dispersion solution including the reversible thermosensitive recording material of the composition in Example **12** on the substrate so that the thickness after being dried would be 12 μm.

As a soluble polyimide resin used for a protective layer **13**, a polyimide (Upilex R, manufactured by Ubekosan Co., Ltd.) represented by the following Formula VI was used:



wherein n is about 5 or more.

Next, 5 g of the polyimide was dissolved in 100 ml of m-cresol, and the solution thus obtained was coated onto the surface of the recording layer **12** to a thickness of 8 μm to form a pale yellow and transparent protective layer **13**. Then, the solvent was removed at 120 °C for 5 hours, and for another **12** hours in a vacuum drier, thereby resulting in a reversible thermosensitive recording sheet as shown in Figure **6**. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 75 °C to 110 °C.

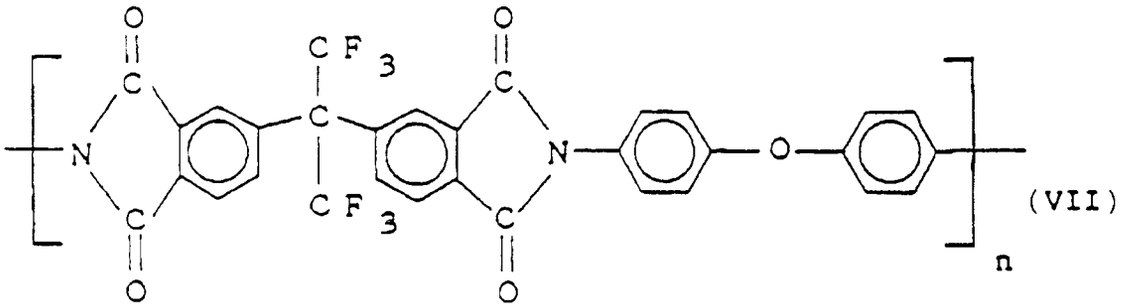
Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. The images of the figures **0** to **9** were recorded in the recording layer at a temperature of more than 110 °C. As a result, the figures were displayed in a white color on the dark brown surface of the magnetic recording layer and were satisfactorily recognized. The figures were repeatedly recorded in and erased from the sheet. The sheet withstood 3,000 or more repetitions. Moreover, on the surface of the protective layer **13** contacting the thermal head, residual figures usually caused by thermal or mechanical damage were not observed after the figures had been erased.

As a comparative example, a reversible thermosensitive recording sheet was produced in the same way as the above-mentioned recording medium, except a material of the protective layer was changed. A UV-curable acrylate resin prepolymer was coated on the recording layer to a thickness of 10 μm and cured with ultraviolet rays to form a protective layer **13**, whereby a reversible thermosensitive recording was obtained. Images of letters were repeatedly recorded in and erased from the recording layer, and the sheet withstood 1,000 or more repetitions. However, residual letters having a white color were observed on the surface of the protective layer **13**. This was apparently caused by the irregular reflection due to the mechanical abrasion by the thermal head, or due to the surface distortion of the recording layer itself caused by thermal stress thereof or that of the protective layer caused by thermal contraction thereof.

Example 19

As the substrate **11** shown in Figure **6**, a white polyethylene terephthalate sheet having a thickness of 180 μm on which a reflection layer having a thickness of 0.2 μm was formed by the vapor deposition of aluminium was used. As a compound capable of forming organic crystal particles, 2.5 g of p-dodecyloxybenzoic acid and 1.5 g of erucamide were used; as an antioxidant, 0.1 g of an phenol type antioxidant was used; and as a matrix polymer, 10 g of vinyl chloride-vinyl acetate-maleic acid copolymer was used. The materials were uniformly dissolved in 100 ml of tetrahydrofuran. The solution thus obtained was coated onto the reflection layer on the substrate **11** to form a recording layer having a thickness of 20 μm.

As a soluble polyimide resin for a protective layer with heat resistance, a polyimide resin containing a fluorine atom represented by the following Formula VII was used:



(VII)

wherein n is about 5 or more.

This polyimide resin was dissolved in N-methylpyrolidone, and the solution was coated to the surface of the recording layer **12** to a thickness of 10 μm. After that, the resulting recording layer **12** was heat-treated at 150 ° C for 30 minutes and dried in vacuo for another 12 hours to obtain a reversible thermosensitive recording sheet having a protective layer **13**. A void was not present in the protective layer of the sheet thus produced. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 70 ° C to 95 ° C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, and information was recorded in the recording layer at 100 ° C and erased from the recording layer at 75 ° C.

This sheet was cut to the size of a telephone card (54 mm x 86 mm), and the repetition of recording and erasing was evaluated by using a card reader and writer. The sheet withstood 5,000 or more repetitions of recording and erasing. Moreover, on this sheet, residual information was not observed after being erased.

Example 20

The present example will be described with reference to Figure **7**.

A recording layer **16** was formed on the surface of a reflection layer **15** which was disposed on a substrate **14**. Then, on the surface of the recording layer **16**, a protective layer **17** was formed by using a recording material of the composition in Example **12**. This protective layer **17** was obtained by thoroughly mixing 5 g of urethane acrylate which was an energy beam-curable resin, 5 g of acrylate resin oligomer, 0.5 g of photopolymerization initiator and, as ultra-fine particles **18**, 0.8 g of titanium dioxide powder whose primary particle had an average particle size of about 21 nm; thereafter coating, as a prepolymer, the mixture thus obtained on the surface of the recording layer **16** to a thickness of 3 μm; and curing the mixture with ultraviolet ray.

The protective layer **17** so produced was a transparent hard coating layer, and its surface had an average roughness of 50 nm. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head **19** and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 70 ° C to 110 ° C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head **19** and information was recorded in the recording layer at 120 ° C (the recorded portion was opaque) and erased from the recording layer at 90 ° C (the erased portion was transparent). The endurance test was performed by the repetition of recording and erasing, and it revealed that the sheet withstood 1,800 or more repetitions. The operating lifetime was thus about three times that found in the case where the ultra-fine particles of an oxide **18** were not added to the protective layer **17**.

Separately, as ultra-fine particles of an oxide **18**, 3 g of titanium dioxide whose primary particle had an average particle size of 100 nm was dispersed in the resin component similar to the above to produce the similar reversible thermosensitive recording sheet. The protective layer **17** had an average roughness of 90 nm. When a similar endurance test of this reversible thermosensitive recording sheet was performed,

satisfactory recording characteristics were obtained as above, and this sheet withstood 1,000 times repetitions. The reason for the difference in recording characteristics between this case and the above is not made clear; however, it is considered that this is due to the increase in the unevenness pitch of the surface of the protective layer **17** rather than the increase of the average roughness of the surface of the protective layer **17**. Even though titanium dioxide having an average particle size of 100 nm was used, the lifetime was about two times that of the prior art.

Example 21

As a recording material, 2 g of erucamide with a hydrocarbon chain having one unsaturated bond with 21 carbon atoms, and 4 g of vinyl chloride-vinyl acetate-acrylamide copolymer were dissolved in 15 g of tetrahydrofuran. This solution was coated onto a reflection layer **15** which was formed a substrate **14** made of a polyethylene terephthalate having a thickness of 0.2 mm by vapor deposition of aluminium. The solution was dried to form a recording layer **16** having a thickness of 15 μm. A protective layer **17** was formed on the recording layer **16** as follows.

Next, 7 g of urethane acrylate as an energy beam-curable resin, 3 g of oligomer containing an acrylic ester in both terminals of the molecule as its component and 0.5 g of photopolymerization initiator. As a prepolymer, this mixture was coated onto the surface of a recording layer **16** to a thickness of 3 μm. After that, the resulting recording layer **16** was cured with ultraviolet rays to form a first protective layer. Then, 5 g of urethane acrylate as an energy beam-curable resin, 5 g of oligomer containing an acrylic ester in both terminals of the molecule as its component, 0.5 g of photopolymerization initiator, and as ultra-fine particles of an oxide **18**, 0.7 g of silica powders whose primary particle had an average particle size of 12 nm, the surface of which was treated with perfluorooctyltrichrolosilane, were thoroughly mixed.

This mixture was coated, as a prepolymer, onto the first protective layer to a thickness of 3 μm and cured with ultraviolet rays to form a second protective layer. The protective layer having a two layered structure thus formed was a transparent hard coating layer, and its surface had an average roughness of 50 nm. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 68 °C to 81 °C, and thus the width of the temperature range was 14 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. This sheet, in which the recording layer was then transparent, was provided with energy using a thermal head **19** and information, was recorded in the recording layer at 90 °C and erased from the recording layer at 75 °C. A clear display was performed without image irregularity due to the stain of the thermal head caused by the stain of the surface. The endurance test performed by the repetition of recording and erasing revealed that this sheet withstood 2,000 or more repetitions. Such lifetime was about three or more times that found in the case where the ultra-fine particles of an oxide **18** were not added to the second protective layer.

Example 22

The present example will be described with reference to Figure **8**.

As a substrate **23**, a white polyethylene terephthalate sheet having a thickness of 200 μm was used, on which a magnetic recording layer showing a dark brown color of γ -Fe_2O_3 on its surface was formed. A transparent polyethylene terephthalate film having a thickness of 15 μm was used as a protective sheet 20. The recording material having the same composition as that in Example 12 was coated onto the transparent sheet 20 to a thickness of 12 μm, thereby obtaining a recording sheet **24** having a recording layer **21**. As an adhesion layer **22**, a polyester resin adhesive was coated onto the surface of the recording layer **21** of the recording sheet **24** to a thickness of about 1 μm. After that, the magnetic recording layer of the substrate **23** and the recording layer **21** of the recording sheet **24** were laminated so that the respective surfaces faced each other, whereby a reversible thermosensitive recording sheet as shown in Figure **8** was formed. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 65 °C to 81 °C.

Images representing the alphabet were recorded in the recording layer of the reversible thermosensitive recording sheet. As a result, the alphabet was displayed in a white color on the dark brown surface of the

magnetic recording layer, and **26** alphabetical letters could satisfactorily be recognized.

The alphabet was repeatedly recorded in and erased from the recording layer, and it was found that the sheet withstood 3,000 or more repetitions. Moreover, on the surface of the transparent sheet contacting the thermal head, no residual letters caused by thermal or mechanical damage were observed after the letters had been erased.

Example 23

As a substrate **23**, a white polyethylene terephthalate having a thickness of 180 μm was used. As a transparent thin sheet **20** with abrasion resistance and as a sheet **26** for supporting a reflection layer, a polyethylene terephthalate with a thickness of 15 μm was used.

Then, 2 g of eicosanedicarboxylic acid, 2 g of erucamide, 0.5 g of docosanol, 0.1 g of a phenol type antioxidant as an antioxidant, and 10 g of vinyl chloride-vinyl acetate-acrylamide copolymer as a matrix polymer were uniformly dissolved in 100 ml of tetrahydrofuran. This solution was coated onto the transparent sheet **20** for a protective layer so as to have a thickness of 12 μm after being dried, thereby obtaining a recording sheet **24** having a recording layer **21**.

Next, a method for producing a reflection sheet **29** will be described. A reflection layer **25** made of aluminium was formed to a thickness of 0.2 μm on the sheet **26** by vapor deposition. Then, γ - glycidoxypropyltrimethoxysilane (a silane coupling agent) in isopropyl alcohol was chemically adsorbed into the reflection layer **25** to form a monomolecular layer. This layer **28** made from a silane coupling agent improves the adhesion between an adhesive layer **22** and the reflection sheet **29**. An epoxy resin adhesive was coated, as an adhesive layer **27**, onto the surface of the sheet **26** of the reflection sheet **29** to a thickness of about 1 μm. After that, the reflection sheet **29** was laminated on the substrate **23** via the adhesive layer **27**. Then, an epoxy resin adhesive was coated, as the adhesive layer **22**, to a thickness of about 1 μm onto the reflection layer **25** which was treated with the silane coupling agent, and then the recording layer **21** of the recording sheet **24** and the adhesive layer **22** were laminated so that the respective surfaces faced each other to form a reversible thermosensitive recording sheet as is shown in Figure **9**. The recording layer of the reversible thermosensitive recording sheet was opaque at room temperature. The sheet was heated using a thermal head and the temperature range in which the recording layer was transparent was determined by visual observation and by using a Macbeth densitometer. The temperature range was found to be from about 70 °C to 110 °C.

Then, starting with the sheet in an initial state, in which the recording layer was opaque at room temperature, the sheet was heated to a temperature in the above-mentioned range and cooled to room temperature. The sheet, in which the recording layer was then transparent, was provided with energy using a thermal head, information was recorded in the recording layer at 115 °C (the recorded portion was opaque), and erased from the recording layer at 85 °C (the erased portion was transparent).

This reversible thermosensitive recording sheet was cut into the size of a telephone card (i.e., 54 mm x 86 mm). Recording and erasing of information was repeated by using a card reader and writer having a thermal head. It was found that the sheet withstood 2,000 or more repetitions with stable performance and, moreover, residual information was not observed.

It is understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the scope and spirit of this invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to description as set forth herein, but rather that the claims be construed as encompassing all the features of patentable novelty that reside in the present invention, including all features that would be treated as equivalents thereof by those skilled in the art to which this invention pertains.

Claims

1. A reversible thermosensitive recording material made of a composition comprising a transparent matrix polymer and organic crystal particles dispersed therein;

   wherein the crystalline state of the organic crystal particles is changeable in accordance with an applied temperature, resulting in a reversible change of transparency of the recording material; and

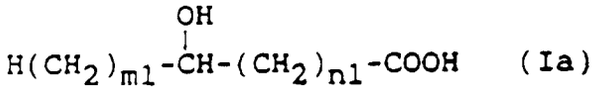
   the matrix polymer and the organic crystal particles respectively have a group capable of forming a hydrogen bond.

2. A recording material according to claim 1, wherein each of the organic crystal particles comprises at least one selected from the group consisting of a carboxyl group and a hydroxyl group, and is made of a compound having a melting point in the range of 60 °C to 120 °C, and

the matrix polymer is selected from the group consisting of polyesters having a hydroxyl group, partially saponified vinyl acetate-vinyl chloride copolymers, polyamides, polyurethanes, thermoplastic phenol resins, vinyl alcohol copolymers, acrylic copolymers, acrylamide copolymers, maleic copolymers, urea resins, epoxy resins, and melamine resins.

3. A recording material according to claim 2, wherein each of the organic crystal particles comprises at least one hydroxycarboxylic acid or derivatives thereof having a melting point in the range of 60 °C to 120 °C.

4. A recording material according to claim 3, wherein the hydroxycarboxylic acid is at least one selected from the group of compounds represented by the following Formulas Ia, Ib, Ic, Id, and Ie:



$$H(CH_2)_{m1}\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}(CH_2)_{n1}\text{-}COOH \qquad (Ia)$$

wherein m_1 and n_1 are respectively integers, and the total of m_1 and n_1 is 6 to 24;

$$HO\text{-}Ph\text{-}(CH_2)_{n2}\text{-}COOH \qquad (Ib)$$

wherein Ph is a phenylene group, and n_2 is an integer in the range of 0 to 18;

$$HO\text{-}Ph\text{-}COO(CH_2)_{n3}\text{-}COOH \qquad (Ic)$$

wherein Ph is a phenylene group, and n_3 is an integer in the range of 1 to 18;

$$HO\text{-}Ph\text{-}OCO(CH_2)_{n4}\text{-}COOH \qquad (Id)$$

wherein Ph is a phenylene group, and n_4 is an integer in the range of 1 to 18; and

$$HO\text{-}Ph\text{-}COO(CH_2)_{n5}\text{-}H \qquad (Ie)$$

wherein Ph is a phenylene group, and n_5 is an integer in the range of 1 to 18.

5. A recording material according to claim 4, wherein the hydroxycarboxylic acid is an α-hydroxyalkylcarboxylic acid.

6. A recording material according to claim 1, wherein the organic crystal particles comprise at least one compound selected from the group consisting of an aliphatic amide compound and an aliphatic urea compound, and

each of the aliphatic amide compound and the aliphatic urea compound have at least one straight chain hydrocarbon group, respectively containing at least 10 carbon atoms, and a melting point of each of the compounds is in the range of 70 °C to 150 °C.

7. A recording material according to claim 6, wherein the aliphatic amide compound is at least one selected from the group consisting of the compounds represented by the following Formulas IIa, IIb, and IIc:

$$R^1\text{-}CONH\text{-}R^2 \qquad (IIa)$$

wherein R^1 is a straight chain hydrocarbon group having 1 to 25 carbon atoms, R^2 is hydrogen, a straight chain hydrocarbon group having 1 to 26 carbon atoms, or a methylol group, and at least one of

R^1 and R^2 is a straight chain hydrocarbon group having at least 10 carbon atoms;

R^3-CONH-$(CH_2)_{n6}$-NHCO-R^3 (IIb)

wherein R^3 is a straight chain hydrocarbon group having 10 to 25 carbon atoms, and n_6 is an integer in the range of 1 to 8; and

R^4-NHCO-$(CH_2)_{n7}$-CONH-R^4 (IIc)

wherein R^4 is a straight chain hydrocarbon group having 10 to 25 carbon atoms, and n_7 is an integer in the range of 1 to 8.

8. A recording material according to claim 6, wherein the aliphatic urea compound is represented by the following Formula III:

R^5-NHCONH-R^6 (III)

wherein R^5 and R^6 are independently hydrogen or a straight chain hydrocarbon group having 1 to 26 carbon atoms, and at least one of R^5 and R^6 is a straight chain hydrocarbon group having at least 10 carbon atoms.

9. A recording material according to claim 1, wherein each of the organic crystal particles comprises a compound having an amide or urea group and an aliphatic dicarboxylic acid; the compound having an amide or urea group is at least one selected from the group consisting of saturated aliphatic monocarboxamides with a hydrocarbon group having at least 12 carbon atoms, saturated aliphatic biscarboxamides with a hydrocarbon group having at least 12 carbon atoms, and ureas substituted with a hydrocarbon group having at least 12 carbon atoms; the aliphatic dicarboxylic acid is represented by the Formula $HOOC(CH_2)_{n8}COOH$ (wherein n_8 is an integer from 14 to 24); and the ratio of the compound having an amide or urea group and the aliphatic dicarboxylic acid is in the range of 60:40 to 10:90 by weight.

10. A recording material according to claim 1, wherein the organic crystal particles comprise an aliphatic dicarboxylic acid having a melting point of at least 120 °C, and a straight chain aliphatic compound having at least one of a hydroxyl group, a carboxyl group, and an amide group and having a melting point in the range of 50 °C to 100 °C; and the ratio of the aliphatic dicarboxylic acid to the straight chain aliphatic compound is in the range of 3:7 to 8:2 by weight, and a width of the range in which the organic crystal particles are present in a light transmissible state is 20 °C or more.

11. A recording material according to claim 10, wherein the aliphatic dicarboxylic acid is represented by the formula $HOOC(CH_2)_{n9}COOH$, wherein n9 is an integer of 6 to 24.

12. A recording material according to claim 10, wherein the straight chain aliphatic compound is at least one compound selected from the group consisting of straight chain saturated higher alcohols, unsaturated aliphatic acid amide, and a straight chain saturated aliphatic acid, each having 12 or more carton atoms.

13. A recording material according to claim 1, wherein each of the organic crystal particles has a particle size of 0.1 μm or less.

14. A recording material according to claim 1, wherein the composition comprises an antioxidant having active hydrogen.

15. A recording material according to claim 1, wherein the composition comprises crystalline particles of a compound having a group capable of forming a hydrogen bond.

16. A recording material according to claim 1, wherein each of the organic crystal particles is microcapsulated with a transparent matrix polymer for capsulation.

17. A recording material according to claim 16, wherein the transparent matrix polymer for capsulation comprises a coloring matter.

18. A reversible thermosensitive recording medium comprising a substrate, a recording layer made of a reversible thermosensitive material of claim 1, and a protective layer stacked in this order.

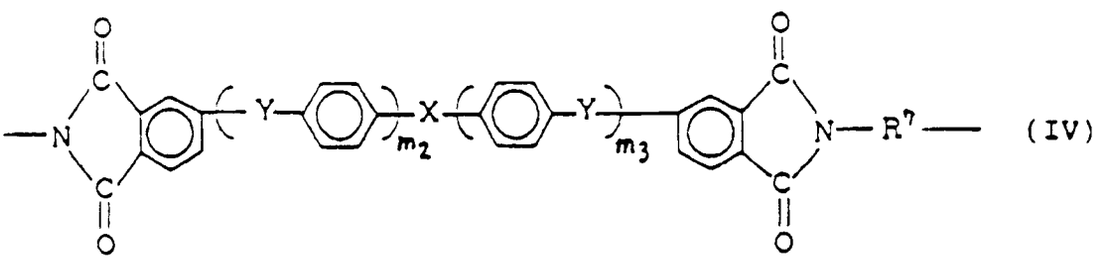
19. A recording medium according to claim 18, wherein the recording layer comprises a transparent spacer particle having a thickness approximately equal to that of the recording layer and a particle size less than the thickness of the recording layer in a proportion of 10% by weight.

20. A recording medium according to claim 19, wherein the spacer particle is made of glass or a polymer and is a spherical particle with an average particle size of 1 to 100 μm and with a narrow particle size distribution.

21. A recording medium according to claim 18, wherein the protective layer is made of a polyimide.

22. A recording medium according to claim 21, wherein the polyimide is a soluble polyimide which is soluble in organic solvents.

23. A recording medium according to claim 22, wherein the soluble polyimide has a repeating unit represented by the following Formula IV:



(IV)

wherein X is 0, CO, $C(CF_3)_2$ or a single bond, Y is 0 CO, $C(CF_3)_2$, or a single bond, R^7 is a group having an aromatic ring, and m_2 and m_3 are independently 0, 1, or 2.

24. A recording medium according to claim 18, wherein the protective layer comprises ultra-fine particles made of an oxide whose primary particle has an average particle size of 100 nm or less.

25. A recording medium according to claim 18, wherein the protective layer is made of a plurality of layers, a hardness of the plurality of layers successively becoming higher toward a direction of a surface layer from the substrate, and a protective layer of at least outermost surface layer comprises the ultra-fine particles made of an oxide whose primary particle has an average particle size of 100 nm or less.

26. A recording medium according to claim 18, wherein the protective layer is an energy beam-curable acrylic type resin.

27. A recording medium according to claim 24, wherein the ultra-fine particles are made of silicon oxide, aluminium oxide or titanium oxide.

28. A recording medium according to claim 27, wherein each of the ultra-fine particles is a particle made of silicon oxide, aluminium oxide or titanium oxide which has been subjected to a surface treatment with an organic chemical adsorption agent.

29. A recording medium according to claim 18, wherein an adhesive layer is further disposed between the substrate and the recording layer.

30. A recording medium according to claim 29, wherein the protective layer is made of at least one resin selected from the group consisting of polyethylene terephthalate, polymers containing fluorine, polysul-

fones, polyethylenenaphthalate, polyphenylenesulfide, polyarylates, polyimides, and polyamides.

31. A recording medium according to claim 18, wherein a reflection layer is disposed between the substrate and the recording layer and information is recorded or erased by a laser beam.

Fig. 1

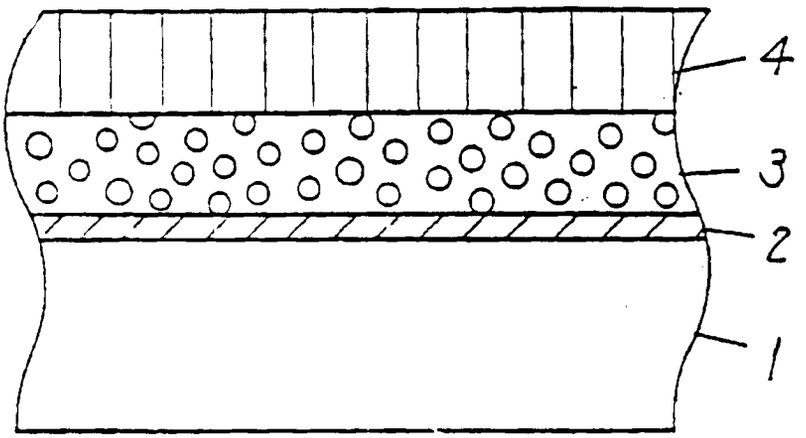


Fig. 2a

Fig. 2b

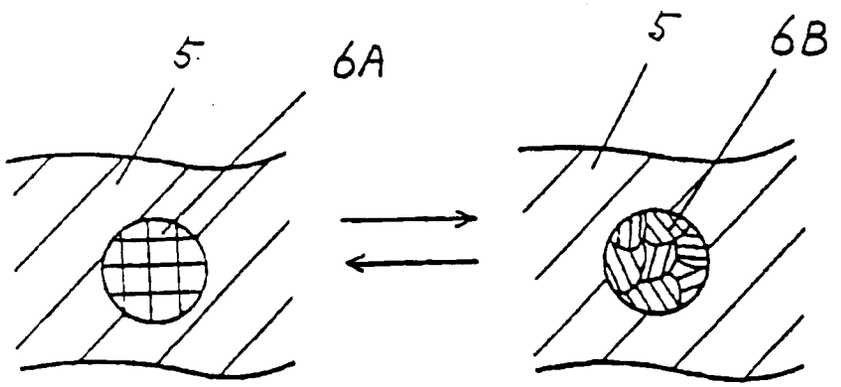


Fig. 3

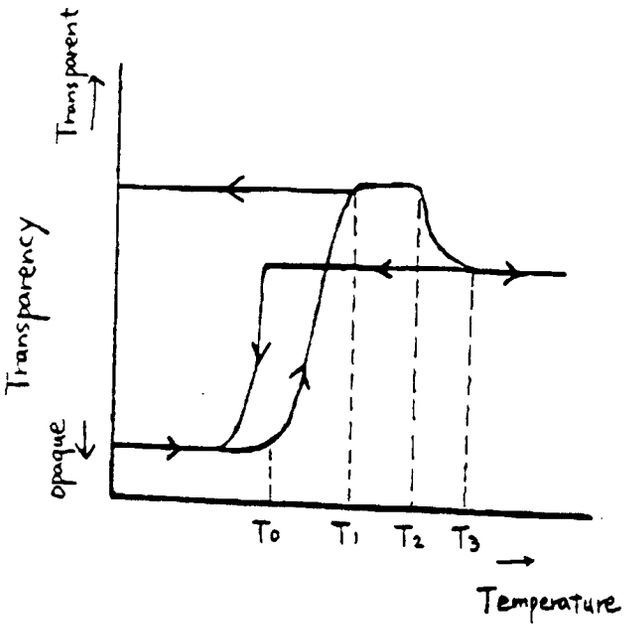


Fig. 4

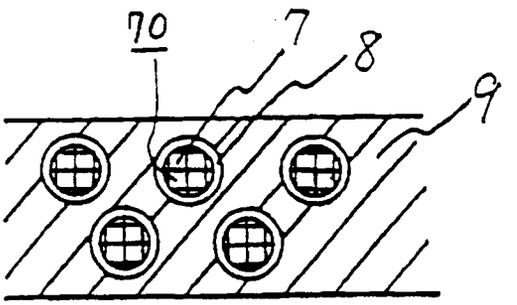


Fig. 5a

Fig. 5b

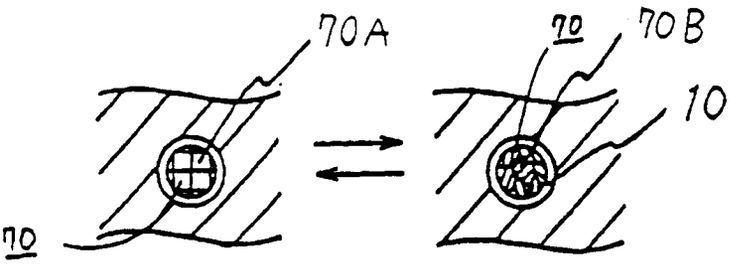


Fig. 6

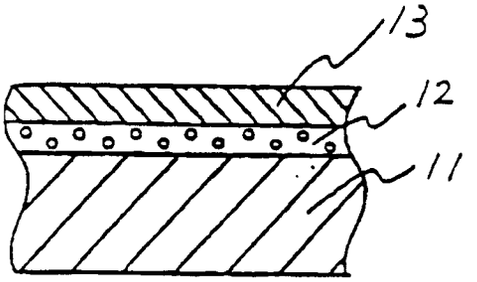


Fig. 7

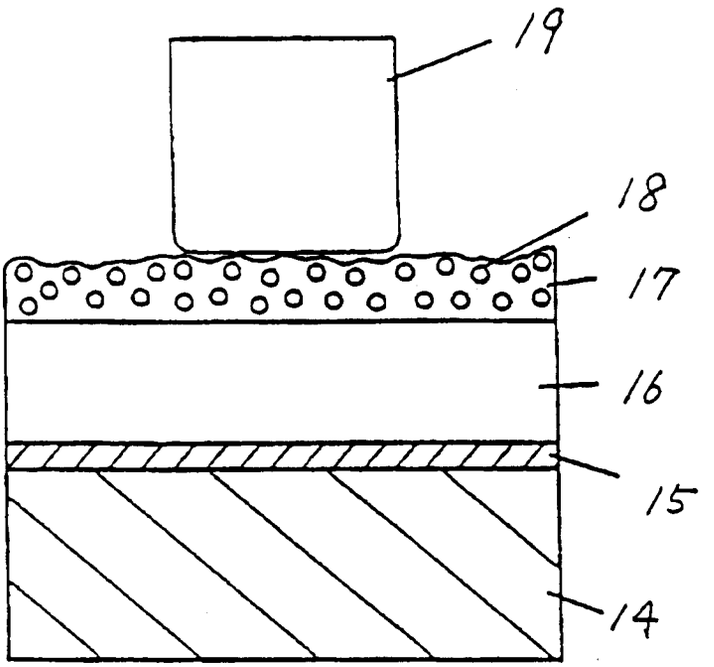


Fig. 8

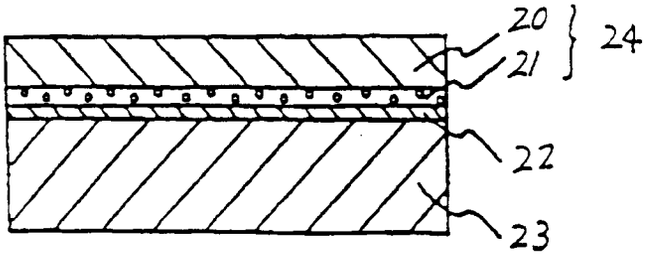


Fig. 9

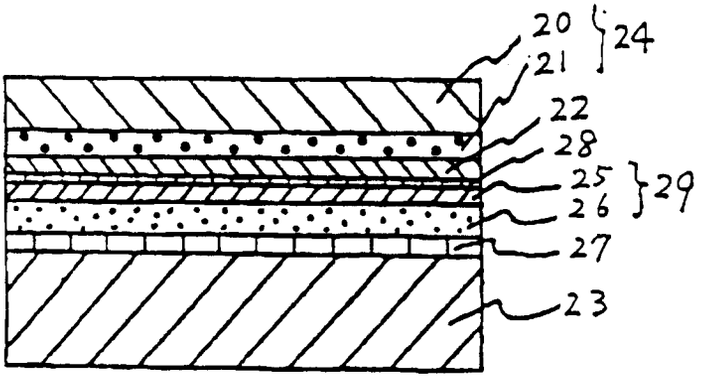


Fig. 10

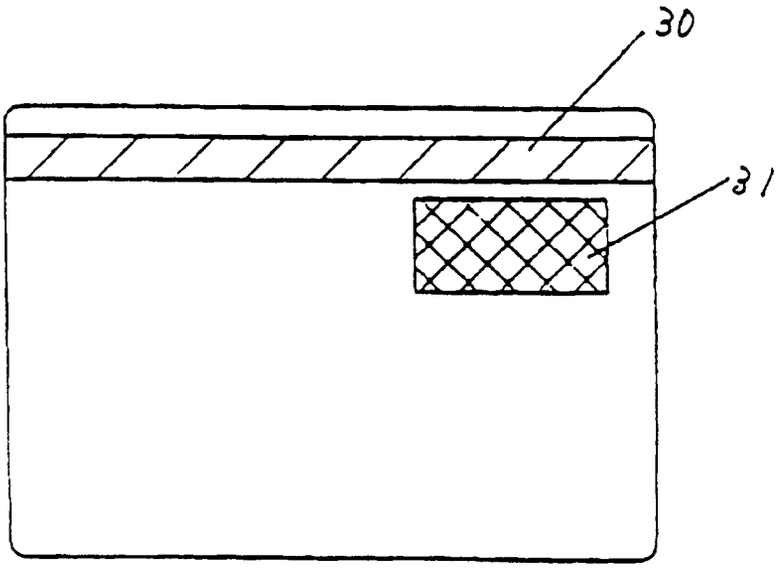


Fig. 11

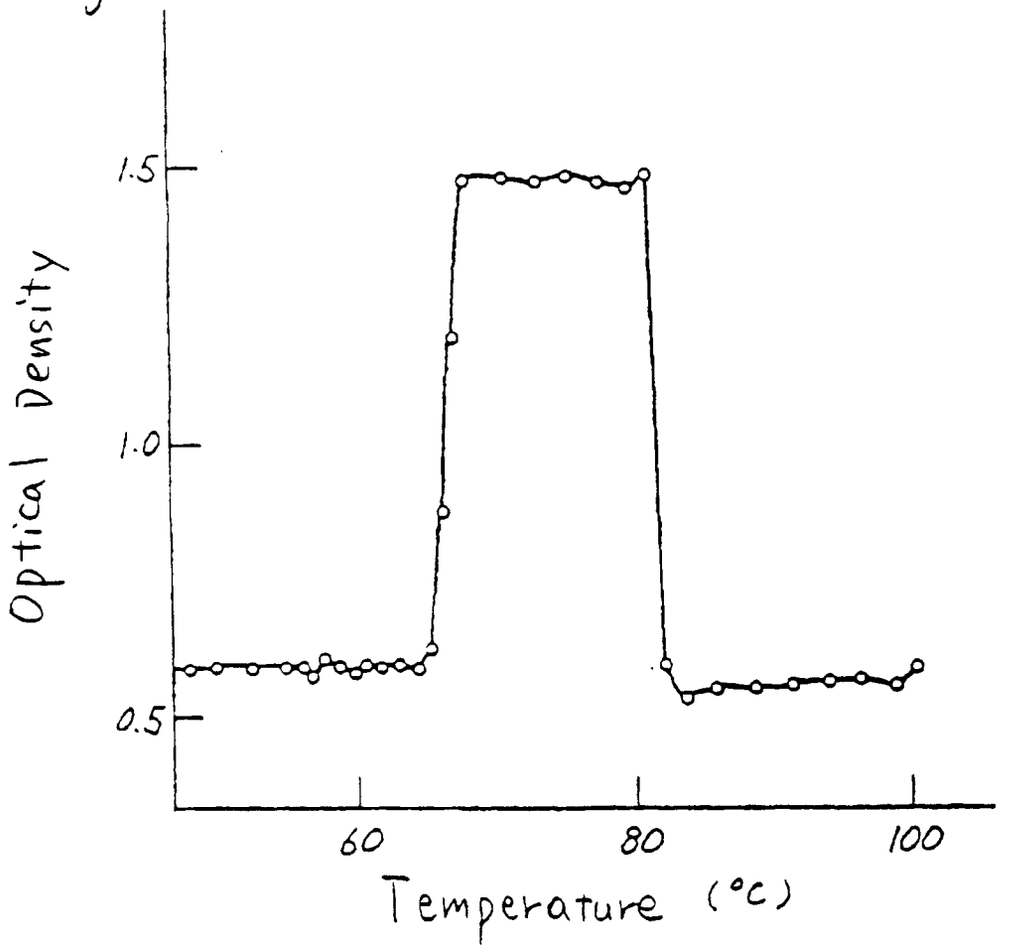
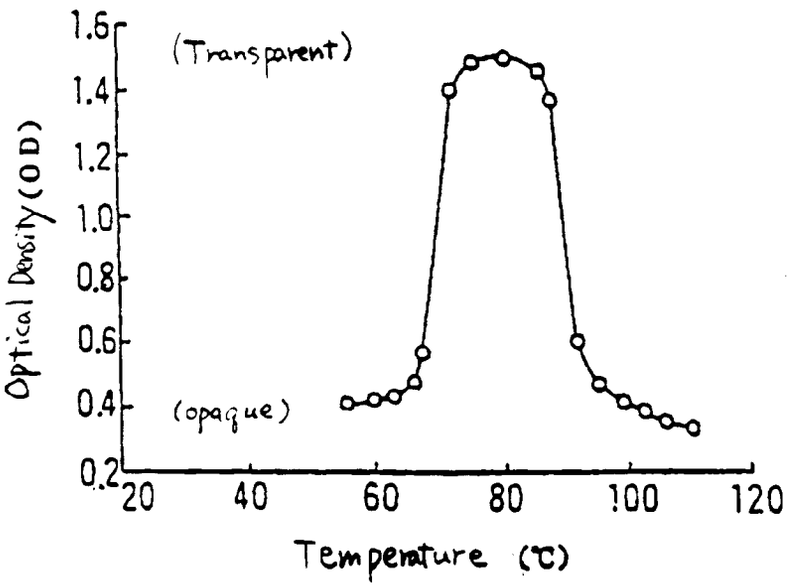

Optical Density
1.5
1.0
0.5
60
80
100
Temperature (°C)

Fig. 12


(Transparent)
(opaque)
Optical Density (OD)
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1.4
1.2
1.0
0.8
0.6
0.4
0.2
20
40
60
80
100
120
Temperature (°C)

Fig. 13

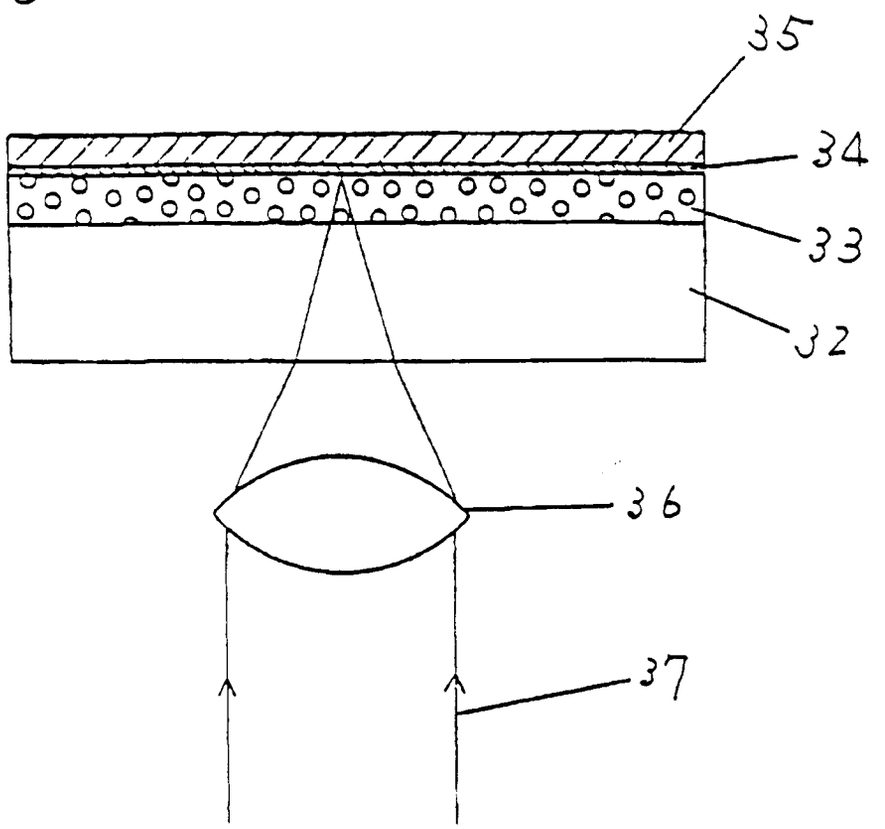


Fig.14a

Fig.14b

Fig.14c

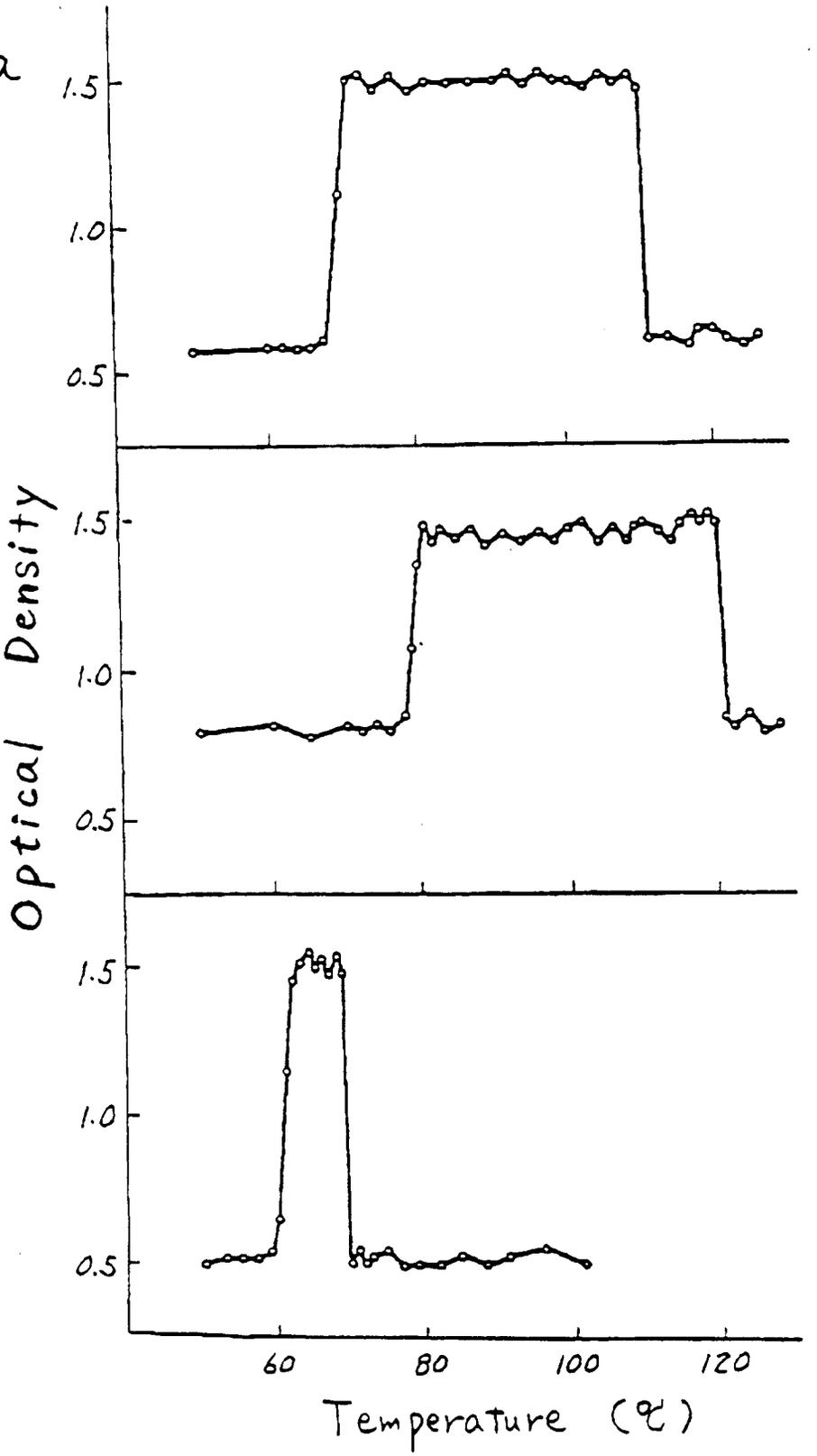
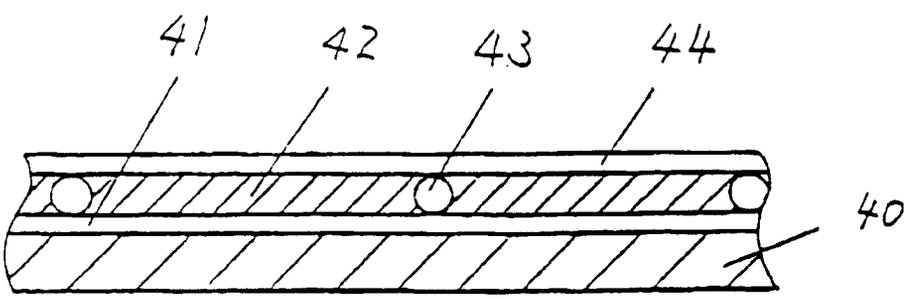


Fig. 15



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 5309

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-4 019 683 (RICOH K.K.) * page 4, line 46 - page 5, line 53 * ---	1-31	B41M5/36
X	DE-A-4 017 640 (RICOH K.K.) * page 3, line 63 - page 4, line 30; claims 4,5 *	1	
A	* the whole document * ---	2-31	
X	EP-A-0 014 826 (TIPP-EX TECHNIK WOLFGANG DABISCH) * page 10, line 34 - page 12, line 20; claims 3,6 *	1	
A	* the whole document * ---	2-31	
X	EP-A-0 302 374 (HOECHST AG.) * column 1, line 17 - line 23 * * column 2, line 9 - line 25 * * column 2, line 31 - line 52 *	1	
A	* the whole document * ---	2-31	
P,X	EP-A-0 429 010 (OKI ELECTRIC INDUSTRY K.K.) * page 2, line 39 - line 48 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
P,A	* the whole document * -----	2-31	B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 JUNE 1992	BACON A.J.

CATEGORY OF CITED DOCUMENTS

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