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(54) **Thermal recording materials**

(57) A thermal recording material possessing high sensitivity comprises a support having thereon in sequence an interlayer containing at least one polymer selected from nitrocellulose, brominated polyhydroxystyrene and chlorinated rubber, and a recording layer containing a metal as an essential component.

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SPECIFICATION

Thermal recording materials

This invention relates to thermal recording materials on which the storage of information is effected by scanning the material with a beam of high intensity radiation, such as a laser beam, to cause deformation of a recording layer.

Recording materials utilizing high-intensity light beams, such as lasers are known, for instance the thermal recording materials described below and silver salt conrtaining light-sensitive materials. The former type of thermal recording material has a recording layer of high optical density which, when struck by an incident beam of light having high energy density, produces a local increase of temperature which causes thermal deformation, for example, fusion, evaporation, aggregation and so on. By the additional procedure of removing the exposed areas of the recording layer, there result differences in optical density between the exposed areas and the unexposed areas which enable information to be recorded. Thermal recording materials of this type possess several advantages: they do not, in general, require any development and subsequent fixing processings; they make a dark room unnecessary because of their insensitivity to ordinary indoor light; they provide images of high contrast; and they make it possible to add information onto the record, such addition being known as "add-on".

Many processes for recording information on a thermal recording material as described above include transforming the information to be recorded into electrical, time series signals, and scanning the recording material with a laser beam the amplitude of which is modulated according to such signals. Such processes have the advantage that the images can be recorded in real time.

The recording layers of the above-described thermal recording materials are generally metals, dyes, plastics and the like, and it is usually possible to choose inexpensive materials. Thermal recording materials are described in more detail in, for example, M. L. Levene, et al., *Electron, Ion and Laser Beam Technology,* transactions of 11th symposium (1969); *Electronics,* March 18, 1968, page 50; D. Maydan, The Bell System Technical Journal, vol. 50 (1971), page 1761;C. O. Carlson *Science*, vol. 154 (1966), page 1550; etc. Of these materials, those which utilize metal recording layers wherein thin layers of metals such as Bi, Sn, In and the like are laminated on supports, possess excellent properties and images can be recorded thereon with high resolving power and with high contrast. However, many of the recording materials utilizing metallic thin layers as recording layers suffer from the defect that 50% or more of the laser beam employed for recording is reflected from the metallic thin layer. As a result the energy of the laser beam is not used efficiently and a high intensity laser beam is required to effect recording. In the case of rapid scanning still more power is required from the light source of the laser beam and consequently, the apparatus is large in size and expensive.

Under such circumstances, recording materials having high recording sensitivity have been studied. As an example thereof, U.S. Patent No. 3,560,994 proposes a recording material comprising a thin layer of Se and Bi with a very thin layer of Ge thereon to reduce reflectance. However, the use of Se and other metals is undesirable because they are apt to cause pollution problems and, further, the quality of the images recorded are not entirely acceptable.

Another example of a recording material which has a reflection preventing layer is described in Japanese Patent Application (OPI) No. 74632/'76, in which a reflection preventing layer capable of absorbing light in the wavelength region of the laser beam employed for recording is provided on the metal recording layer. However, it is very difficult to eliminate light reflection completely by providing a reflection preventing layer on the metal layer. Even if it were possible to eliminate light reflection completely, a high power light source for the laser beam would be required in order to induce thermal deformation such as fusion, evaporation, aggregation or the like in the metallic thin layer. Such being the case, recording materials possessing higher sensitivity are desired.

In addition, the recording layers of the thermal recording materials described above, especially metal layers, are liable to be scratched. Therefore, to provide a protective layer on the recording layer is effective from the standpoint of improving its durability, mechanical strength and keeping stability, all of which are requisite properties for a recording material. The characteristics which are indispensable for the protective layer are high transmittance with respect to the light beam of high energy density used, high mechanical strength, low reactivity with the recording layer, good coating properties, facility in preparation and so on. Substances suitable for the protective layer may be inorganic or organic compounds. As examples of inorganic compounds, there are known transparent compounds such as Al_2O_3, SiO_2, SiO, MgO, ZnO, MgF_2 and CuF_2. On the other hand, the use of organic compounds as the protecting layer is an excellent technique, which is disclosed in, for example, each of Japanese Patent Applications (OPI) Nos. 96716/'74; 59626/'76; 75523/'76;88024/'76 and 134633/'76. However, recording materials in which the protective layers possess effective strength suffer from the defect of a sharp decrease in recording sensitivity as compared with those which do not have any protective layers. Thus, it is desirable to produce thermal recording materials which can exhibit high sensitivities even when the protective layers are provided thereon.

According to the present invention there is provided a thermal recording material which comprises a support having thereon in sequence a layer containing at least one high polymer selected from nitrocellulose, brominated polyhydroxystyrene and chlorinated rubber and a recording layer containing a metal as a main component. While the basis for the improvement in sensitivity attained in the present invention is not completely clear, it may be that the interlayer facilitates deformation of the recording layer for example by facilitating the aggregation of the recording layer upon local heating.

Specific examples of supports which may be employed in the present invention include those which have generally been used for this type of recording material, such as plastics like polyethylene terephthalate and polycarbonate, glass, sheets of paper, plate-form or foil-form metals and so on. Of these materials, a polyethylene terephthalate film is particularly preferred as the support for its excellent adhesion to the interlayer.

The recording layer used in the present invention is a layer possessing high optical density, and is preferably formed of a substance that can exhibit high covering power in a thin layer. Typical examples of such substances are metals. In addition, the recording layer may include another layer laminated thereon to increase the recording sensitivity, or it may be a layer in which a metal is mixed with another substance in order to increase the recording sensitivity. Naturally the recording layer can consist of the substance possessing covering power, i.e., be a metal layer.

The recording layer is the layer principally responsible for the change in optical transmittance or reflectance which results upon thermal deformation in the areas irradiated with a laser beam or the like. A wide variety of layer constructions and substances can be chosen for the recording layer. Specific examples of the metals which may be employed for the recording layer include Mg, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Ge, Te, Pb, Po, Sn, As, Sb, Bi, Se and Te, and these metals may be used alone or in combinations of two or more. Preferably the metals employed in the present invention have low toxicity, require small energy for fusion or evaporation and form films with ease. The most preferred metals are Sn, Bi and In.

The metals are provided on a support or a subbing layer or other layers in the form of a thin layer constructed from a single layer or a plurality of layers by vacuum evaporation, sputtering, ion plating, electroplating, nonelectrolytic plating or other treatment, alone, as mixtures of two or more, or as alloys. Moreover, these metals may be present as a physical mixture in a layer formed by, for example, co-deposition with substances used for increasing the sensitivity, as described below.

The metal layer should have a thickness sufficient to provide the optical density required of the images formed. For instance, a thickness ranging from about 300 Å to 1,500 Å is generally required in order to attain an optical density (transmission) of 2, and the thickness depends upon the kind of metal used. In addition, the thickness necessary to attain a desirable optical density varies from one case to the next because the layer structure of the metal layer varies with a number of factors relating to its deposition such as the kind of support used, the temperature of the support during deposition, the pressure inside the vacuum line used for deposition, the deposition speed and so on, even when the same metal is used for forming the metal layer on the support by vacuum deposition, sputtering, ion plating, etc.

Further, it is preferred to use substances for increasing the recording sensitivity in combination with the above-described metals. They may be laminated in a separate layer on the recording layer or mixed with the metals in the recording layer. These substances increase the recording sensitivity by, for example, preventing reflection.

Substances employed for such a purpose can, for example, accelerate the thermal deformation of the above-described metals by preventing reflection, etc. Specific examples include oxides such as PbO, WO_3, TiO_2, SiO, SiO_2 and ZrO_2; chalcogen compounds of Ge, In, Sn, Cu, Ag, Fe, Bi, Al, Si, Zn and V; halogenides such as PbX_2, AgX, SnX_2, SbX_5 and SbX_3 (wherein X represents fluorine, chlorine, bromine or iodine); As, Sb, P, Ge, Si and Te. Characteristics desirable for such substances are low toxicity; reduced deterioration with time due to moisture absorption, deliquescence, dark reaction with metals; and the ability to produce films with ease. For the above-described purpose, GeS, SnS, PbI_2 and the like are particularly preferred.

The thickness of the films made of these substances varies with the kind of metal used, the thickness of the metal layer and so on. However, a thickness within the range of 50 Å to 1,000 Å is generally preferable.

Nitrocellulose, brominated polyhydroxystyrene or chlorinated rubber form the interlayer between the support and the recording layer in the recording material of the present invention. They may be used independently or in a combination of two or more. The above polymers are preferred in order of brominated polyhydroxystyrene, nitrocellulose and chlorinated rubber. These polymers should have a weight average molecular weight of about 2,000 to 100,000. The nitrocellulose preferably has a nitrogen substitution degree of 8 to 12.5 %, and most preferably 10 to 12 %. The brominated polyhydroxystyrene preferably contains 0.3 to 2, preferably 0.5 to 1.5, bromine atoms per hydroxystyrene unit. The chlorinated rubber desirably has 0.3 to 1.5 chlorine atoms per monomer unit.

The interlayer can increase sensitivity when its thickness is about 0.05 μ or more, and within this range the increase in sensitivity is for the most part independent of its thickness. However, if the interlayer is too thick cracking is apt to occur upon bending of the sensitive material and additives such as a plasticizer may be required. In general, a thickness of 0.05 μ to 10 μ is adequate.

The interlayer may be formed by coating a solution of the aforesaid polymers on a support using a conventional coating technique. As solvents for the polymers forming the interlayer, mention may be made of known solvents such as toluene, xylene, ethyl acetate, butyl acetate, "Cellosolve" acetate ("Cellosolve" is a Registered Trade Mark), methyl ethyl ketone, 1,2-dichloroethane, methyl isobutyl ketone, cyclohexanone, tetrahydrofuran, ethyl ether, dioxane, methanol, ethanol, isopropyl alcohol, butanol and the like. In addition, mixed solvents in which two or more of the above solvents are mixed or a portion of the above-described solvents is replaced by nonsolvents such as cyclohexane and the like can also be employed.

As indicated above plasticizers may be added to the interlayer to prevent cracking. Conventional plasticizers can be used such as phosphate type plasticizers, e.g. tricresyl phosphate or triphenyl phosphate; and phthalate type plasticizers, e.g. dibutyl phthalate, diethyl phthalate or diheptyl phthalate. The amount of the plasticizers varies depending upon the kind of plasticizer and can easily be determined by one skilled in the art.

In accordance with some embodiments of the present invention a protective layer is provided on the recording layer made of either inorganic or organic substances. Transparent inorganic layers such as Al_2O_3, SiO_2, SiO, MgO, ZnO, MgF_2, CuF_2 layers and the like are desirable. The protective layer is formed by subjecting these substances to vacuum deposition, sputtering, a reactive deposition such as ion plating, etc.

On the other hand, excellent results are obtained using organic substances for the protective layer. High molecular materials possessing film forming ability can be used. Specific examples of high molecular materials suitable for this purpose include various polymers such as styrene polymers, e.g., polystyrene and styrene-maleic anhydride copolymer; vinyl acetate polymers, e.g., poly-vinyl acetate, polyvinyl alcohol, polyvinyl butyral and polyvinyl formal; methacrylic acid ester resins, e.g., polyisobutylmethacrylate and polymethylmethacrylate; amide polymers, e.g., polydiacetone acrylamide and polyacrylamide; cellulose or derivatives thereof, e.g., ethyl cellulose, cellulose acetate butyrate, cellulose nitrate and diacetyl cellulose; halogenated polyolefins, e.g., polyvinyl chloride, chlorinated polyethylene and chlorinated polypropylene; phenolic resins; soluble polyesters; soluble nylons; gelatins; and copolymers thereof. These macromolecular materials are dissolved in an appropriate solvent and applied to the recording layer using known coating techniques.

The solvent employed to coat the protective layer can be selected from various solvents depending upon the polymeric substance used. Specific examples of such solvents include acetone, methyl ethyl ketone, methyl isobutyl ketone, diacetone alcohol, methyl "Cellosolve", ethyl "Cellosolve", butyl "Cellosolve", methyl "Cellosolve" acetate, ethyl "Cellosolve" acetate, butyl "Cellosolve" acetate, hexane, cyclohexane, ethylene chloride, methylene chloride, benzene, chlorobenzene, methanol, ethanol, propanol, isopropyl alcohol, butanol, petroleum ether, dimethyl formamide, thinner and so on.

Various additives such as pigments, matting agents, plasticizers, lubricants and so on can be added to a polymeric protective layer depending on the purpose or the end-use of the recording material. In particular, it is effective to add higher fatty acids having 11 or more carbon atoms or acid amides thereof in an amount of 0.1 to 10 % by weight to the macromolecular substance. An optimum thickness is selected taking into account the mechanical strength of the film, keeping stability, recording sensitivity and other properties each of which is indispensable for the recording material.

Preferred thicknesses of the protective layer range, in general, from 0.5 μ to 15 μ.

A double layer construction is desirable for the protective layer to enable the protective layer to possess sufficient mechanical strength with only a slight drop in the sensitivity of the recording layer, as disclosed in Japanese Patent Application Nos. 77268/'78 and 79072/'78 (corresponding to U.S. Patent Application Serial Nos. 52,511 (filed June 26, 1979) and (filed June 26, 1979), respectively). Therein, the lower layer, which is in contact with the recording layer, is made up of a soft macromolecular substance having a low softening point, while the upper layer is made up by a macromolecular substance possessing high mechanical strength, which can be selected without concern for the softening point.

The present invention will now be illustrated in greater detail by reference to the following Example.

Example

Each of three compositions having the following formulae was coated on a polyethylene terephthalate film having a thickness of 100 μ at a dry coverage of 0.3 μ to prepare an interlayer.

Formulation I:

Nitrocellulose (trade name; RC 1/8 products of Dai-Nippon Celluloid Co., Ltd.)	2 g
Methyl ethyl ketone	70 cc
Methyl "Cellosolve" acetate	30 cc

Formulation II:

Brominated polyhydroxystyrene (trade name; RESIN MB a product of Maruzen Petro-Chemical Co., Ltd.)	2 g
Methyl ethyl ketone	70 cc
Methyl "Cellosolve" acetate	30 cc

Formulation III:

Chlorinated rubber (trade name; CR-10, products of Asahi Denka Kogyo K.K.)	2 g
Methyl ethyl ketone	70 cc
Methyl "Cellosolve" acetate	30 cc

Next, onto a polyethylene terephthalate film or each of the above-described interlayers (corresponding to the Formulations I, II and III, respectively) the metals and the compounds shown in Table 1 were evaporated successively in thin layers to form a recording layer. The recording material obtained by forming the recording layer directly on a polyethylene terephthalate film was labelled A, and the recording materials in which the recording layers were formed on the interlayers of the Formulations I, II and III were labelled B, C and D, respectively. The above-described recording layer was formed by evaporating Sn, In or Bi in a thin metal film 350 Å thick under reduced pressure of 5×10^{-5} Torr, and thereon was formed a reflection preventing layer by evaporating one of various compounds in a thin layer 200 Å thick onto the thin metal film. Each of the thus-obtained recording materials had an optical density (transmission) within the range of 1 to 2.

Recording was carried out by scanning each of these recording materials with an argon ion laser beam (wavelength 5145 Å), which had a maximum output of 2 W and was focused by a lens into a spot of 25 μ diameter. The scanning speed of the laser beam was 19 m/sec and irradiation was carried out from the side of the recording layer. The sensitivities of the recording materials obtained were evaluated relatively by changing the output power of the laser beam to irradiate each of the recording materials and determining the value of the output required for production of a recorded spot having a diameter of 10 μ, followed by comparison of the values obtained. It is apparent from Table 1 that each of the recording materials, B, C and D prepared in accordance with embodiments of the present invention has higher sensitivity, compared with the Sample A prepared for comparison.

In addition, the values in parentheses in Table 1 correspond to the output power of the laser beam required to attain the equivalent recordings in recording materials having additionally the following protective layer on the respective recording layers. The protecting layer was formed by coating a composition of Formulation IV at a dry coverage of 0.4 μ and then, by coating another composition of the Formulation V at a dry coverage of 0.4 μ and further, by coating the other composition of the formulation VI at a dry coverage of about 0.05 μ.

Formulation IV :

Chlorinated polyethylene (trade name; 907HA, products of Sanyo Kokusaku Pulp Co., Ltd.)	2 g
Toluene	50 cc
Cyclohexane	50 cc

Formulation V :

Styrene-butadiene copolymer (trade name; Pliolite, products of Goodrich Co., Ltd.)	4 g
Cyclohexane	100 cc

Formulation VI :

Behenic acid	1 g
n-Hexane	1,000 cc

TABLE 1

Sample No.	Recording Layer		Laser Output (mW) Required for Recording			
	Metal Layer	Compound Layer	A	B	C	D
1	Sn	SnS	200 (275)	150 (225)	150 (225)	150 (225)
2	Sn	GeS	175 (250)	125 (200)	125 (200)	125 (200)
3	Sn	PbI_2	100 (200)	75 (125)	75 (125)	75 (125)
4	Sn	AgCl	100 (200)	75 (125)	75 (125)	75 (125)
5	Sn	CuI	100 (200)	75 (125)	75 (125)	75 (125)
6	Sn	SnI_2	100 (200)	75 (125)	75 (125)	75 (125)
7	In	GeS	175 (250)	125 (200)	125 (200)	125 (200)
8	Bi	PbI_2	100 (200)	75 (125)	75 (125)	75 (125)

As may be clearly seen from the results in Table 1, even when a protective layer is present, the interlayer of the present invention effectively increases the sensitivity of the thermal recording layer.

CLAIMS

1. A thermal recording material comprising a support having thereon in sequence an interlayer containing at least one polymer selected from nitrocellulose, brominated polyhydroxystyrene and chlorinated rubber, and a recording layer.
2. A material as claimed in Claim 1, wherein said interlayer is 0.05 microns or more thick.
3. A material as claimed in Claim 2, wherein said interlayer is from 0.05 to 10 microns thick.
4. A material as claimed in any preceding claim, wherein said support is a polyethylene terephthalate

film.

5. A material as claimed in any preceding claim, wherein said recording layer is a layer of a metal of a thickness sufficient to provide a suitable image density.

6. A material as claimed in Claim 5, wherein a suitable image density is a transmission density of at least 2.0.

7. A material as claimed in any preceding claim, wherein said recording layer or a layer deposited on said recording layer contains a substance capable of increasing the sensitivity of the recording material.

8. A material as claimed in Claim 7, wherein said substance capable of increasing sensitivity is PbO, WO_3, TiO_2, SiO, SiO_2 and ZrO_2; a chalcogen compound of Ge, In, Sn, Cu, Ag, Fe, Bi, Al, Si, Zn or V; PbX_2, AgX, SnX_2, SbX_5 and SbX_3, wherein X represents fluorine, chlorine, bromine or iodine; As, Sb, P, Ge, Si or Te.

9. A material as claimed in any preceding claim, which additionally comprises a protective layer on the recording layer.

10. A material as claimed in Claim 1 and substantially as herein described.

11. A thermal recording material substantially as herein described with reference to Samples Nos. 1 to 6 B-D.

12. A material as claimed in any preceding claim bearing a recorded image produced by imagewise exposure of the recording layer to a laser beam.

13. The features as herein disclosed, or their equivalents, in any novel selection.

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