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(54) **THERMOPLASTIC COMPOSITE MATERIAL AND OPTICAL ELEMENT**

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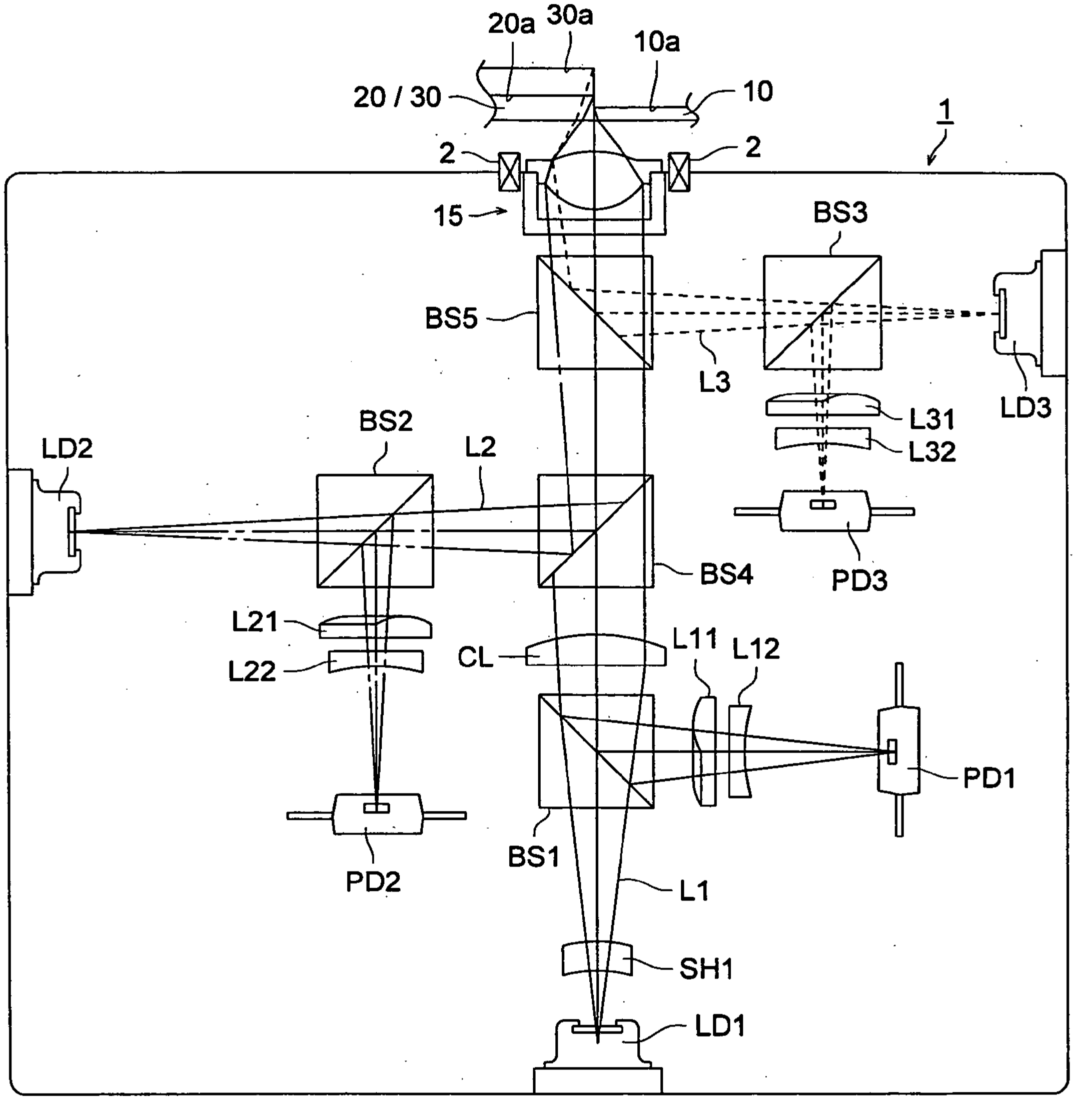
(57) **ABSTRACT**

A thermoplastic composite material comprising: (i) a thermoplastic resin comprising an organic polymer; and (ii) particles having an average diameter of 1-30 nm dispersed in the thermoplastic resin, wherein the particles contain two or more kinds of inorganic particles having different refractive indexes.

FIG. 1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THERMOPLASTIC COMPOSITE MATERIAL AND OPTICAL ELEMENT

[0001] This application is based on Japanese Patent Application No. 2004-358369 filed on Dec. 10, 2004 in Japanese Patent Office, the entire content of which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to a thermoplastic composite material which has small thermal variation ratio in the refractive index and is suitably applied for a lens, filter, grating, optical fiber and planar light conducting path, and an optical element using the material.

BACKGROUND OF THE INVENTION

[0003] An optical pickup is installed in information apparatus such as a player, a recorder and a drive for leading out or recording information from or to an optical information recording medium, referred also to as simply a medium, such as an MO, CD and DVD. The optical pickup apparatus has an optical element such as a lens for irradiating light generated from a light source having a prescribed wavelength to the medium, and for receiving the reflected light by a light receiving element unit, and a lens for condensing the light on the reflective surface of the medium or the light receiving element.

[0004] A plastic is preferably applied for the material of the optical element of the optical pickup apparatus because the optical element can be produced with low cost by a means such as an injection molding. A copolymer of a cyclic olefin and an α-olefin is known as the plastic capable for applying the optical element (for example, refer to Patent Document 1).

[0005] In an information apparatus capable of leading and writing information to plural kinds of recording media such as a CD/DVD player, it is necessary that the optical pickup has a constitution capable of corresponding to the wavelength of the light to be applied to each of the media and the shape thereof. In such the case, the optical element is preferably one commonly applicable to both of the media from the viewpoint of cost and picking up property.

[0006] In the optical element unit using plastic as a material, it is desirable that the plastic is a material having optical stability similar to that of a glass lens. The optical plastic material such as the cyclic olefin, for example, has sufficiently improved stability in the refractive index with respect to humidity, but the improvement in the stability of the refractive index is not fully sufficient in the present stage.

[0007] Various methods have been proposed for compensating the refractive index of such the plastic lens by using a particle filler.

[0008] The particle filler is employed for compensating the refractive index of the optical plastic. The plastic can hold sufficient transparency for the lens without light scattering caused by the filler by the use of the filler of sufficiently small particle size. Technology for enhancing the refractive index of the plastic by the addition of the particles is described in Non-patent Documents 1 and 2, for example.

materials are lighter in the weight and lower in the cost when compared with glass. However, the plastic is inferior to the glass in the stability in the refractive index against changes in temperature and humidity. Therefore, improvement is desired in this point of view for the plastic materials.

[0010] The refractive index of an organic polymer decreases with increasing temperature almost without exception (temperature dependency of the refractive index: $dn/dT<0$). As described below, for example, dn/dT of organic polymer materials (thermoplastic resins) to be applied for the optical use is generally almost -10^{-4}/K.

[0011] A method for reducing the absolute value of dn/dT has been proposed, in which a substance having a dn/dT of more than 0 is mixed in the thermoplastic resin host material which has a dn/dT of less than 0. Among inorganic substances, known are the ones showing a dn/dT of more than 0, which is a result of the variation in the intramolecular coordination with varing temperature. It has been expected that the absolute value of dn/dT is reduced by mixing an organic polymer thermoplastic resin of which a dn/dT is less than 0 with inorganic particles having a dn/dT of more than 0. Accordingly, an optical product reduced in thermal sensitivity of an optical property, containing a thermal sensitive thermoplastic polymer resin and particles dispersed therein has been proposed in Patent Documents 2 through 8, for example.

[0012] Various proposals have been submitted regarding the composite materials each containing inorganic particles. Composite materials containing particles of a semi-conductive substance and a resin composition in which semi-conductive particles are bonded with the polymer chain by a covalent bond are disclosed, for example, in Patent Document 9, and a resin composition containing zinc sulfide particles is disclosed, for example, in Patent Document 10.

[0013] Patent Document 6, for example, describes that the mixing of 40% by weight or more of aluminum oxide or magnesium oxide is necessary to reduce by 50% of the dn/dT of the thermoplastic resin.

[0014] However, when a composite material contains inorganic particles having high refractive index in such the high ratio, the following problems may occur, for example, (i) transparency of the composite material largely decreases; and (ii) the property of the composite material varies during prolonged storage due to coagulation of the inorganic particles dispersed in the resin. Accordingly, composite materials suitable for practical use as an optical element have hardly been obtained.

[0015] In the methods disclosed in Patent Documents 9 and 10, particles having high refractive index, namely semi-conductive particles are added to increase the refractive index of the resin composition. However, a sufficiently high transparency as an optical element cannot be obtained in the resin composition obtained by such a method. These Patent Documents do not describe the use of two or more kinds of particles having different refractive indexes such as that described in the present invention, and no composite material having high transparency and small temperature dependency in the refractive index as obtained in the present invention has been known until now.

on thermoplastic nanocomposites with surface-modified silica nanoparticles", SPIE Proceedings, July 1998, vol. 3469, p.p. 88-98

[0017] Non-patent Document 2: B. Braune, P. Mueller and H. Schmidt, "Tantalum oxide nanomers for optical applications", SPIE Proceedings, July 1998, vol. 3469, p.p. 124-132

[0018] Patent Document 1: Japanese Patent Publication Open to Public Inspection (hereafter referred to as JP-A) No. 2002-105131, (p. 4)

[0019] Patent Document 2: JP-A No. 2002-207101, (Claims)

[0020] Patent Document 3: JP-A No. 2003-240901, (Claims)

[0021] Patent Document 4: JP-A No. 2002-241560, (Claims)

[0022] Patent Document 5: JP-A No. 2002-241569, (Claims)

[0023] Patent Document 6: JP-A No. 2002-241592, (Claims)

[0024] Patent Document 7: JP-A No. 2002-241612, (Claims)

[0025] Patent Document 8: JP-A No. 2002-303701, (Claims)

[0026] Patent Document 9: JP-A No. 2002-105325, (Claims)

[0027] Patent Document 10: JP-A No. 2003-73563, (Claims)

SUMMARY OF THE INVENTION

[0028] An object of the present invention is to provide a thermoplastic composite material having considerably small thermal variation in the refractive index and an optical element employing the composite material.

[0029] One of the aspects of the present invention to attain the above object is a thermoplastic composite material containing: (i) a thermoplastic resin containing an organic polymer; and (ii) particles having an average diameter of 1-30 nm dispersed in the thermoplastic resin, wherein the particles contain two or more kinds of inorganic particles having different refractive indexes.

BRIEF DESCRIPTION OF THE DRAWING

[0030] **FIG. 1** shows a schematic drawing of constitution of optical pickup apparatus **1**.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0031] The above object of the present invention is achieved by the following structures.

[0032] (1) A thermoplastic composite material containing:

[0033] (i) a thermoplastic resin containing an organic polymer; and

wherein the particles contain two or more kinds of inorganic particles having different refractive indexes.

[0035] (2) The thermoplastic composite material of Item (1), wherein

[0036] nh and np**1** satisfy Formula (A), provided that nh represents a refractive index of the thermoplastic resin and np**1** represents a smallest refractive index among refractive indexes of the two or more kinds of inorganic particles.

$$nh-0.1 \leqq np1 \leqq nh+0.1 \quad \text{Formula (A)}$$

[0037] (3) The thermoplastic composite material of Item (2), wherein

[0038] np**1** and np**2** satisfy Formula (B), provided that np**2** represents one of the refractive indexes of the two more kinds of inorganic particles other than np**1**.

$$0.1 \leqq np2-np1 \leqq 1.0 \quad \text{Formula (B)}$$

[0039] (4) The thermoplastic composite material of Item (3), wherein

[0040] a weight content of inorganic particles having the refractive index of np**1** is not less than a content of inorganic particles having the refractive index of np**2**.

[0041] (5) The thermoplastic composite material of Item (3), wherein

[0042] a weight content of inorganic particles having the refractive index of np**1** is not more than a content of inorganic particles having the refractive index of np**2**.

[0043] (6) The thermoplastic composite material of any one of Items (1) to (5), wherein

[0044] a total content of the two or more kinds of inorganic particles is in the range of 20-70% by weight based on a weight of the thermoplastic resin.

[0045] (7) An optical element formed by using the thermoplastic composite material of any one of Items (1) to (6).

[0046] A thermoplastic composite material having considerably small temperature dependence of the refractive index can be obtained by the present invention, and further an optical element having small temperature dependence of the refractive index and high light transmittance which is not degraded during storage for a prolonged period can be obtained by employing the thermoplastic composite material of the present invention.

[0047] Preferred embodiments of the present invention are described below. Though various technical limitations preferable for carrying out the present invention are described in the followings, the present invention is not limited thereto.

[0048] An optical element exhibiting small temperature dependence of the refractive index and high transparency which is not degraded during storage for a prolonged period can be realized by a thermoplastic composite material containing a thermoplastic organic polymer resin as a host material and particles having an average diameter of 1-30 nm dispersed in the thermoplastic organic polymer resin, wherein

[0049] (i) the particles contain two or more kinds of inorganic particles having different refractive indexes; and polymer resin and np**1** represents a refractive index of one of the two or more kinds of inorganic particles.

$$nh-0.1 \leqq np1 \leqq nh+0.1 \quad \text{Formula (A)}$$

[**0051**] The above mentioned effects of the present invention are further enhanced when the thermoplastic composite material containing particles having an average diameter of 1-30 nm dispersed in the thermoplastic organic polymer resin satisfy one of the following conditions (1) to (4):

[**0052**] (1) np**1** and np**2** satisfy Formula (B), wherein np**1** and np**2** represent refractive indexes of two kinds of inorganic particles and np**2** is larger than np**1**;

$$0.1 \leqq np2-np1 \leqq 1.0 \quad \text{Formula (B)}$$

[**0053**] (2) The content of inorganic particles having the refractive index of np**1** is not less than the content of inorganic particles having the refractive index of np**2**;

[**0054**] (3) The content of the inorganic particle having the refractive index of np**1** is not more than the content of the inorganic particle having the refractive index of np**2**; and

[**0055**] (4) The total content of the two or more kinds of inorganic particles is in the range of 20-70% by weight based on a weight of the thermoplastic organic polymer resin.

[**0056**] The embodiments of the present invention will now be described in detail below.

<<Inorganic Particle>>

[**0057**] The average size of the inorganic particles is preferably from 1 nm to 30 nm, more preferably 1 nm to 20 nm, and further preferably from 1 nm to 10 nm. When the average diameter is less than 1 nm, there is the possibility that the desired property cannot be obtained because the particles are difficultly dispersed. When the average diameter exceeds 30 nm, there is the possibility that the light transparency becomes less than 70% by the lowering in the transparency due to the turbid of the thermoplastic material composition. The average particle diameter is the value in the terms of the diameter of the sphere having the same volume.

[**0058**] Though the shape of the inorganic particle is not specifically limited, a spherical particle is preferably employed. The distribution of the particles is also not limited but ones having relatively narrow distribution are preferable than ones having relatively wide distribution for enhancing the effects of the present invention.

[**0059**] The dn/dT of the inorganic particle is preferably not less than 0, more preferably from 0 to 0.01, and specifically preferably from 5×10^{-5} to 5×10^{-3}.

[**0060**] As inorganic particles, oxide particles are employable, for example. In concrete, examples of the oxide include: silicon oxide, titanium oxide, zinc oxide, aluminum oxide, zirconium oxide, hafnium oxide, niobium oxide, tantalum oxide, magnesium oxide, calcium oxide, strontium oxide, barium oxide, yttrium oxide, lanthanum oxide, cerium oxide, indium oxide, tin oxide, lead oxide, and a double oxide composed of these oxides such as lithium niobate, potassium niobate and lithium tantalate. Phosphate, magnesium carbonate, calcium carbonate, strontium carbonate, zinc sulfate and copper sulfate are also preferably employed.

[**0061**] As inorganic particles, particles of a semi-conductor crystal are also preferably utilized. Though the composition of the semi-conductor crystal is not specifically limited, desirable are those exhibiting no absorption, no light emission and no fluorescence within the range of the wavelength of light applying to the optical element. Examples of the composition include: elements of Group 14 of periodic table such as carbon, silicon, germanium and tin; elements of Group 15 of periodic table such as phosphorus (black phosphorous); elements of Group 16 of periodic table such as selenium and tellurium; compounds composed of elements of Group 14 of periodic table such as silicon carbide SiC; compounds composed of an element of Group 14 and that of Group 16 of periodic table such as tin oxide(IV) SnO_2, tin sulfide(II, IV) $Sn(II)Sn(IV)S_3$, tin sulfide (IV) SnS_2, tin(II) selenide SnSe, tin(II) telluride SnTe, lead(II) sulfide PbS, lead(II) selenide PbSe and lead(II) telluride PbTe; compounds of an element of Group 13 and that of Group 15 of periodic table (or semi-conductor compounds of Group III-V) such as boron nitride BN, boron phosphide BP, boron arsenide BAs, aluminum nitride AlN, aluminum phosphide AlP, aluminum arsenide AlAs, aluminum antimonide AlSb, gallium nitride GaN, gallium phosphide GaP, gallium arsenide GaAs, gallium antimonide GaSb, indium nitride InN, indium phosphide InP, indium arsenide InAs and indium antimonide InSb; compounds of an element of Group 13 and that of Group 16 of periodic table such as aluminum sulfide Al_2S_3, aluminum selenide Al_2Se_3, gallium sulfide Ga_2S_3, gallium selenide Ga_2Se_3, gallium telluride Ga_2Te_3, indium oxide In_2O_3, indium sulfide In_2S_3, indium selenide In_2Se_3 and indium telluride In_2Te_3; compounds of an element of Group 13 and that of Group 17 of periodic table such as thallium(I) chloride TlCl, thallium(I) bromide TlBr and thallium(I) iodide TlI; compounds of an element of Group 12 and that of Group 16 of periodic table (or semiconductor compounds of Group II to VI) such as zinc oxide ZnO, zinc sulfide ZnS, zinc selenide ZnSe, zinc telluride ZnTe, cadmium oxide CdO, cadmium sulfide CdS, cadmium selenide CdSe, cadmium telluride CdTe, mercury sulfide HgS, mercury selenide HgSe and mercury telluride; compounds of an element of Group 15 and that of Group 16 of periodic table such as arsenic(III) sulfide As_2S_3, arsenic(III) selenide As_2Se_3, arsenic(III) telluride As_2Te_3, antimony(III) sulfide Sb_2S_3, antimony selenide Sb_2Se_3, antimony(III) telluride Sb_2Te_3, bismuth(III) sulfide Bi_2S_3, bismuth(III) selenide Bi_2Se_3 and bismuth(III) telluride Bi_2Te_3; compounds of an element of Group 11 and that of Group 16 of periodic table such as copper(I) oxide Cu_2O and copper(I) selenide Cu_2Se; compounds of an element of Group 11 and that of Group 17 of periodic table such as copper(I) chloride, copper(I) bromide CuBr, copper(I) iodide CuI, silver chloride AgCl and silver bromide AgBr; compounds of an element of Group 10 and that of Group 16 of periodic table such as nickel(II) oxide NiO; compounds of an element of Group 9 and that of Group 16 of periodic table such as cobalt(II) oxide CoO and cobalt(II) sulfide CoS; compounds of an element of Group 8 and that of Group 16 of periodic table such as iron(II) diiron(III) oxide Fe_3O_4 and iron(II) sulfide FeS; compounds of an element of Group 7 and that

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