

Description

The present invention relates to a magnetic recording material and, in particular, to a magnetic disk such as floppy disk.

Statement of Prior Art

As a substrate of a magnetic disk, a biaxially stretched polyethylene terephthalate (abbreviated as PET hereinafter) film has hitherto been used. Patent specification GB—A—1176482 describes a magnetic disk which in one version has a film of thin base material composed of PET and coated on one side with a magnetic material. Recently, with an increase in recording density, prolongation of recording time, and size reduction of a magnetic disk, a demand for a magnetic disk excellent in running characteristic and free of distortion in recording in spite of thinness thereof has been raised. Therefore, for maintaining the stiffness of a substrate disk, improvements in the quality of PET film material and in technology of film molding work are under examination.

As far as the film material is PET, however, a magnetic disk is short of mechanical strength when made thinner than a certain thickness and thus accompanied with drawbacks such as impaired running characteristic or distortion in recording. Further, because of a shortcoming of the biaxially stretched PET film which is insufficient in tensile strength, large in elongation, and inferior in dimensional stability due to high linear expansion coefficient against temperature and humidity, a new kind of material is demanded.

Summary of Invention

An object of the present invention is to provide a resinous base material which is excellent in mechanical strength and dimensional stability against variation in temperature and humidity and which can afford a magnetic disk with an increased information recording density by markedly reducing the thickness of a base film.

According to the invention there is provided a magnetic disk which comprises a magnetic layer on at least one surface of a layered substrate of polymer films, in which the major component of the layered substrate is a sheet of a liquid crystal polymer composition, said polymer being a polyester comprising constituent units selected from one or more aromatic hydroxy carboxylic acids, said units being employed alone or in combination with other aromatic or alicyclic constituent units.

It is preferable that the layered substrate is a laminate of a plurality of monoaxially oriented sheets, eventually being multiaxially oriented. The most practical embodiment of the substrate is a laminate of two monoaxially oriented sheets, laminated with each other so that one orientation direction of sheet may intersect that of the other with an angle of about 90°, said substrate being eventually biaxially oriented.

The resin material forming the layered substrate of a magnetic disk of the present invention is a thermoplastic polymer composition which shows optical anisotropy when melted and is capable of melt processing and generally categorized into thermotropic liquid crystal polymers.

A polymer which forms an anisotropic molten phase as mentioned above has a characteristic that the chains of polymer molecules have a regular, parallel arrangement. A state in which molecules have such an arrangement is often called a liquid crystal state or a nematic phase of a liquid crystal substance. Such a polymer is composed of monomers having a plurality of chain extending bonds which are slender, flat, fairly stiff along the longitudinal axis of the molecule, and generally in either coaxial or parallel relation with each other.

The nature of an anisotropic molten phase can be confirmed by the customary polarized light inspection method utilizing crossed polarizers. More precisely, confirmation of the anisotropic molten phase can be performed by the use of a Leitz polarizing microscope and the observation of a sample placed on a Leitz hot stage at 40 magnifications in an atmosphere of nitrogen. The above-described polymer is optically anisotropic. That is, the polymer is permeable to light when inspected between crossed polarizers. If a sample is optically anisotropic, it will permit the polarized light to pass therethrough even in a state of standstill.

As required for the liquid crystal polymers of the present invention the constituent units should essentially include:

(a) those composed of one or more aromatic hydroxy carboxylic acids.

The constituent units (a) can be used either alone or with other aromatic or alicyclic constituent units. The preferred other aromatic or alicyclic constituent units are as follows:

(b) those composed of one or more of aromatic hydroxy amines and aromatic diamines.

(c) those composed of one or more of aromatic dicarboxylic acids and alicyclic dicarboxylic acids, and

(d) those composed of one or more of aromatic diols, alicyclic diols and aliphatic diols.

Thus for the purposes of the present invention the preferred range of liquid crystal polymers is provided by those formed from the above constituent units in the following combinations:

(i) a polyester comprising (a) only;

(ii) a polyester comprising (a), (c) and (d);

(iii) a polyester amide comprising (a), (b) and (c); and

(iv) a polyester amide comprising (a), (b), (c) and (d).

Compounds which belong to components (a) to (d) mentioned above are as follows:

Aromatic dicarboxylic acids, such as terephthalic, 4,4'-diphenyldicarboxylic, 4,4'-triphenyldicarboxylic, 2,6-naphthalenedicarboxylic, diphenyl ether-4,4'-dicarboxylic, diphenoxyethane-4,4'-dicarboxylic, diphenoxybutane-4,4'-dicarboxylic, diphenylethane-4,4'-dicarboxylic, isophthalic, diphenyl ether-3,3'-dicarboxylic, diphenoxyethane-3,3'-dicarboxylic, diphenyl-ethane-3,3'-dicarboxylic, and naphthalene-1,6-dicarboxylic acids; and alkyl-, alkoxy-, or halogen-substituted derivatives of the abovesaid aromatic dicarboxylic acids such as chloroterephthalic, dichloroterephthalic, bromoterephthalic, methylterephthalic, dimethylterephthalic, ethylterephthalic, methoxyterephthalic, and ethoxyterephthalic acids.

Alicyclic dicarboxylic acids such as trans-1,4-cyclohexanedicarboxylic, cis-1,4-cyclohexanedicarboxylic, and 1,3-cyclohexanedicarboxylic acids; and alkyl-, alkoxy-, or halogen-substituted derivatives of the abovesaid alicyclic dicarboxylic acids such as trans-1,4-(1-methyl)cyclohexanedicarboxylic and trans-1,4-(1-chloro)cyclohexanedicarboxylic acids.

Aromatic diols such as hydroquinone, resorcinol, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxytriphenyl, 2,6-naphthalenediol, 4,4'-dihydroxydiphenyl ether, bis(4-hydroxyphenoxy)ethane, 3,3'-dihydroxydiphenyl, 3,3'-dihydroxydiphenyl ether, 1,6-naphthalenediol, 2,2-bis(4-hydroxyphenyl)propane, and 2,2-bis(4-hydroxyphenyl)methane; and alkyl-, alkoxy-, or halogen-substituted derivatives of the abovesaid aromatic diols such as chlorohydroquinone, methylhydroquinone, 1-butylhydroquinone, phenylhydroquinone, methoxyhydroquinone, phenoxyhydroquinone, 4-chlororesorcinol, and 4-methylresorcinol.

Alicyclic diols such as trans-1,4-cyclohexanediol, cis-1,4-cyclohexanediol, trans-1,4-cyclohexanedimethanol, cis-1,4-cyclohexanedimethanol, trans-1,3-cyclohexanediol, cis-1,2-cyclohexanediol, and trans-1,3-cyclohexanedimethanol; and alkyl-, alkoxy-, or halogen-substituted derivatives of the abovesaid alicyclic diols such as trans-1,4-(1-methyl)cyclohexanediol and trans-1,4-(1-chloro)cyclohexanediol.

Aliphatic diols including straight-chain and branched aliphatic diols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, and neopentyl glycol.

Aromatic hydroxycarboxylic acids such as 4-hydroxybenzoic, 3-hydroxybenzoic, 6-hydroxy-2-naphthoic, and 6-hydroxy-1-naphthoic acids; and alkyl-, alkoxy-, or halogen-substituted derivatives of the aromatic hydroxycarboxylic acids such as 3-methyl-4-hydroxybenzoic, 3,5-dimethyl-4-hydroxybenzoic, 2,6-dimethyl-4-hydroxybenzoic, 3-methoxy-4-hydroxybenzoic, 3,5-dimethoxy-4-hydroxybenzoic, 6-hydroxy-5-methyl-2-naphthoic, 6-hydroxy-5-methoxy-2-naphthoic, 3-chloro-4-hydroxybenzoic, 2-chloro-4-hydroxybenzoic, 2,3-dichloro-4-hydroxybenzoic, 3,5-dichloro-4-hydroxybenzoic, 2,5-dichloro-4-hydroxybenzoic, 3-bromo-4-hydroxybenzoic, 6-hydroxy-5-chloro-2-naphthoic, 6-hydroxy-7-chloro-2-naphthoic, and 6-hydroxy-5,7-dichloro-2-naphthoic acids.

Aromatic hydroxy amines and aromatic diamines such as 4-aminophenol, N-methyl-4-aminophenol, 1,4-phenylenediamine, N-methyl-1,4-phenylenediamine, N,N'-dimethyl-1,4-phenylenediamine, 3-aminophenol, 3-methyl-4-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 4-amino-1-naphthol, 4-amino-4'-hydroxydiphenyl, 4-amino-4'-hydroxydiphenyl ether, 4-amino-4'-hydroxydiphenylmethane, 4-amino-4'-hydroxydiphenyl sulfide, 4,4'-diaminodiphenyl sulfide (thiodianiline), 4,4'-diaminodiphenyl sulfone, 2,5-diaminotoluene, 4,4'-ethylenedianiline, 4,4'-diaminodiphenoxyethane, 4,4'-diaminodiphenylmethane (methylenedianiline), and 4,4'-diaminodiphenyl ether (oxydianiline).

The above-listed polymers (i) to (iv) composed of the above components include those which can form an anisotropic molten phase and those which can not according to the kind of component, compositional ratio in the polymer, and sequence distribution, and only those polymers which can form an anisotropic molten phase among the above-listed polymers can be used in the present invention.

Polyesters (i) and (ii) and polyester amides (iii) and (iv) as polymers forming an anisotropic molten phase and suitable for use in the present invention can be produced by various methods of ester formation comprising a reaction among organic monomer compounds, each having a functional group which can form required repeating units by condensation. Such a functional group includes, for example, carboxyl, hydroxyl, ester, acyloxy, acyl halide, and amine groups. The abovesaid organic monomer compound can be reacted by melt acidolysis method in the absence of heat exchange fluid. According to this method, monomers are heated together first to form a melt of the reactants. With the proceeding of the reaction, solid polymer particles become suspended in the melt. For easy removal of volatile substances (e.g., acetic acid or water) formed as by-products at the final stage of the condensation, the reaction system may be evacuated.

The slurry polymerization, too, is applicable to the formation of fully aromatic polyester preferably used in the present invention. Solid products obtained by this method are in a state of suspension in the medium for heat exchange.

In any of the processes employing the abovesaid melt acidolysis and slurry polymerization, organic monomeric reactants leading to a fully aromatic polyester can take part in the reaction in the modified form, i.e. as a lower acyl ester, obtained by esterification of the hydroxyl group of said monomer at an ordinary temperature. The lower acyl group has preferably two to four carbon atoms. Acetates of such organic monomeric reactants are preferably used in the reaction.

Typical examples of catalysts usable in any of the melt acidolysis and slurry methods are dialkyltin oxide (e.g., dibutyltin oxide), diaryltin oxide, titanium dioxide, antimony trioxide, alkoxytitanium silicate, titanium alkoxide, alkali and alkaline earth metal salts of carboxylic acids (e.g., zinc acetate), Lewis acid

(e.g., BF_3), and gaseous acid catalyst such as hydrogen halide (e.g. HCl). The amount of the catalyst is generally about 0.001 to 1% by weight, particularly, about 0.01 to 0.2% by weight of the total monomers.

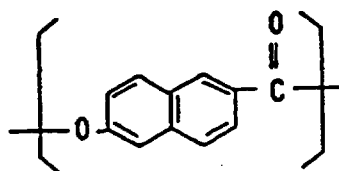
Fully aromatic polymers suitable for use in the present invention tend to be substantially insoluble in common solvents and therefore are unsuitable for solution processing. However, as described above, such polymers are readily amenable to ordinary melt processing. Particularly preferable fully aromatic polymers are somewhat soluble in pentafluorophenol.

Weight-average molecular weights of the fully aromatic polyesters suitable for use in the present invention range from about 2,000 to 200,000, preferably about 10,000 to 50,000, and more desirably about 20,000 to 25,000. On the other hand, molecular weights of preferable fully aromatic polyester amides are generally between about 5,000 and 50,000, preferably about 10,000 and 30,000, for example, 15,000 and 17,000. These molecular weights can be measured by gel permeation chromatography and other standard methods not causing dissolution of polymers, for example, determination of terminal groups by the infrared spectrophotometry of a compression-formed film. The molecular weights can be measured by preparing a pentafluorophenol solution and using light scattering method.

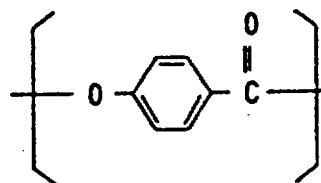
The abovesaid fully aromatic polyester and polyester amide, when dissolved in pentafluorophenol at a concentration of 0.1 wt % at 60°C , generally show a logarithmic viscosity (I.V.) of at least about 2.0 dl/g, for example, from about 2.0 to 10.0 dl/g.

Polyesters forming an anisotropic molten phase particularly suitable for use in the present invention contain repeating units containing naphthalene moieties, such as 6-hydroxy-2-naphthoic acid, 2,6-dihydroxynaphthalene, and 2,6-dicarboxynaphthalene in quantities larger than about 10 mol %. Preferable polyester amides contain repeating units of the abovesaid naphthalene moieties and the other moieties comprising 4-aminophenol or 1,4-phenylenediamine. More specifically, these amides are as follows:

(1) Polyester essentially composed of the following repeating units I and II:



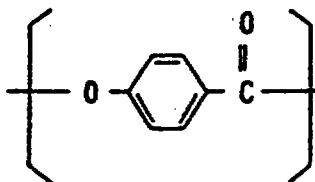
I



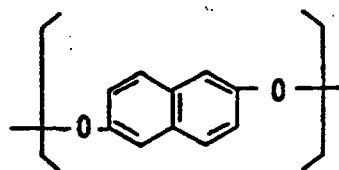
II

This polyester contains about 10 to 90 mol % of unit I and about 10 to 90 mol % of unit II. In one embodiment, unit I is present in a quantity ranging from about 65 to 85 mol %, preferably about 70 to 80 mol % (e.g., about 75 mol %). In another embodiment, unit II is present in a quantity of as small as about 15 to 35 mol %, preferably 20 to 30 mol %. In some cases, at least part of hydrogen atoms bonded to the ring may be substituted by a substituent selected from among an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and a combination of these components.

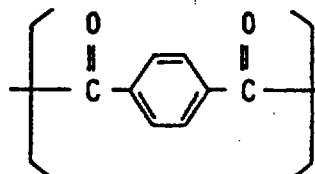
(2) Polyester essentially composed of the following repeating units I, II, and III:



I



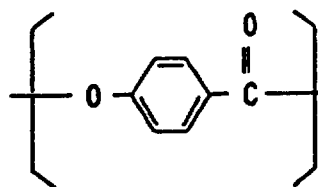
II



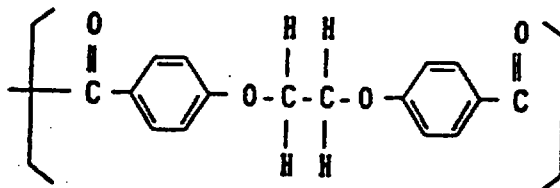
III

This polyester contains unit I in a quantity of about 30 to 70 mol % and preferably composed of about 40 to 60 mol % of unit I, about 20 to 30 mol % of unit II and about 20 to 30 mol % of unit III. In some cases, at least part of hydrogen atoms bonded to the ring may be substituted by a substituent selected from among an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and a combination of these components.

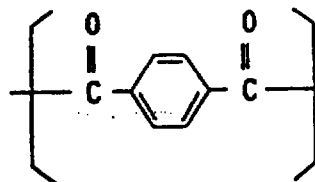
(3) Polyester essentially composed of the following repeating units I, II, III, and IV:



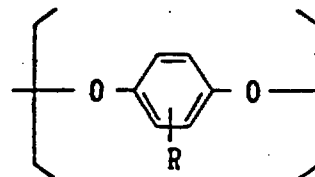
I



II



III

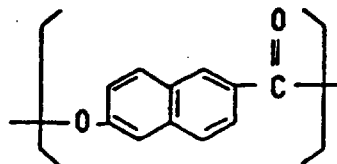


IV

(In the above formulas, R stands for methyl, chloro, bromo, or the combination thereof, which is a substituent for the hydrogen atom on the aromatic ring.) This polyester is composed of about 20 to 60 mol % of unit I, about 5 to 18 mol % of unit II, about 5 to 35 mol % of unit III and about 20 to 40 mol % of unit IV, preferably, about 35 to 45 mol % of unit I, about 10 to 15 mol % of unit II, about 15 to 25 mol % of unit III and about 25 to 35 mol % of unit IV. The total molar concentration of units II and III is substantially equal to that of unit IV. In some cases, at least part of hydrogen atoms bonded to the ring may be substituted by a substituent selected from among an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and a combination of these components. This fully aromatic polyester generally shows a logarithmic viscosity of at least 2.0 dl/g, for example, 2.0 to 10.0 dl/g, when dissolved in pentafluorophenol at a concentration of 0.3 w/v% at a temperature of 60°C.

(4) Polyester essentially composed of the following repeating units I, II, III, and IV:

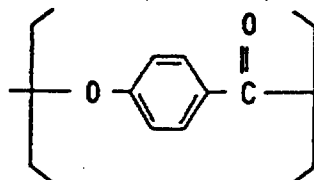
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I

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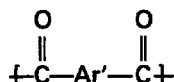
II

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III Dioxyaryl unit represented by the general formula --O--Ar--O-- (wherein Ar represents a bivalent group containing at least one aromatic ring).

IV Dicarboxyaryl unit represented by the general formula

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(wherein Ar' represents a bivalent group containing at least one aromatic ring).

This polyester is composed of about 20 to 40 mol % of unit I, from more than 10 up to about 50 mol % of unit II, from more than 5 up to about 30 mol % of unit III, and from more than 5 up to about 30 mol % of unit IV, preferably about 20 to 30 mol % (for example, about 25 mol %) of unit I, about 25 to 40 mol % (for example, about 35 mol %) of unit II, about 15 to 25 mol % (for example, about 20 mol %) of unit III and about 15 to 25 mol % (for example, about 20 mol %) of unit IV. In some cases, at least part of hydrogen atoms bonded to the ring may be substituted by a substituent selected from among an alkyl group 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, phenyl, substituted phenyl, and a combination of these components.

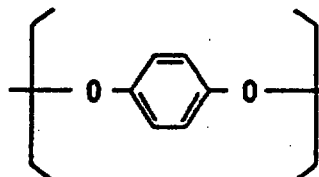
35

The units III and IV are preferably symmetrical in the sense that bivalent bonds which bond these units to other units on both sides in main chains of polymers are positionally symmetrical on one or two aromatic rings (for example, these units are in positions of para with each other or on the diagonal ring when present on the naphthalene ring). However, non-symmetrical units such as those derived from resorcinol or isophthalic acid are also usable.

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A preferable dioxyaryl unit III is

45

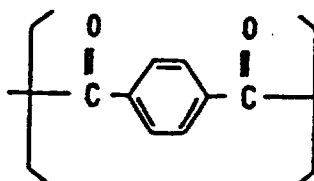


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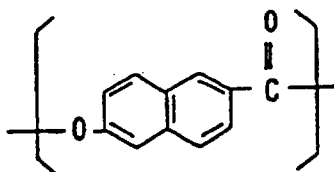
and a preferable dicarboxyaryl unit IV is

60



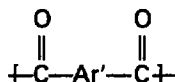
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(5) Polyester essentially composed of the following repeating units I, II, and III:



II Dioxyaryl unit represented by the general formula --O--Ar--O-- (wherein Ar represents a bivalent group containing at least one aromatic ring).

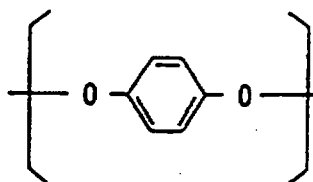
III Dicarboxyaryl unit represented by the general formula



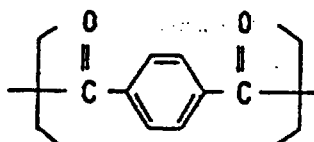
(wherein Ar' represents a bivalent group containing at least one aromatic ring).

This polyester is composed of about 10 to 90 mol % of unit I, 5 to 45 mol % of unit II and 5 to 45 mol % of unit III, preferably about 20 to 80 mol % of unit I, about 10 to 40 mol % of unit II and about 10 to 40 mol % of unit III. More desirably, this polyester is composed of about 60 to 80 mol % of unit I, about 10 to 20 mol % of unit II and about 10 to 20 mol % of unit III. In some cases, at least part of hydrogen atoms may be substituted by a substituent selected from among an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, and substituted phenyl.

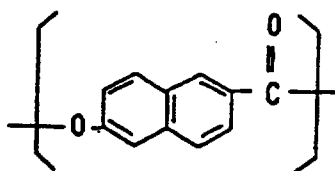
A preferable dioxyaryl unit II is



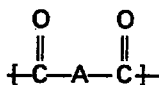
and a preferable dicarboxyaryl unit III is



(6) Polyester amide essentially composed of the following repeating units I, II, III, and IV:



II A unit represented by the general formula



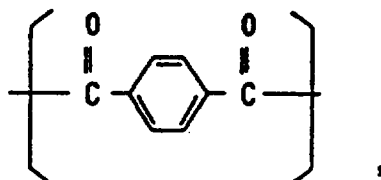
(wherein A represents a bivalent group containing at least one aromatic ring or a bivalent trans cyclohexane group).

III A unit represented by the general formula --Y--Ar--Z-- (wherein Ar represents a bivalent group containing at least one aromatic ring; Y represents O, NH, or NR; Z represents NH or NR, and R represents

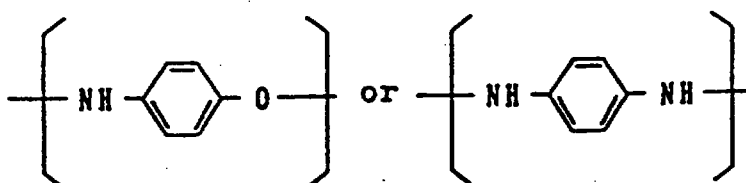
alkyl group of 1 to 6 carbon atoms or an aryl group).

IV A unit represented by the general formula $[-O-Ar'-O-]$ (wherein Ar' represents a bivalent group containing at least one aromatic ring). This polyester amide is composed of about 10 to 90 mol % of unit I, about 5 to 45 mol % of unit II, about 5 to 45 mol % of unit III and about 0 to 40 mol % of unit IV. In some cases, at least part of hydrogen atoms bonded to the ring may be substituted by a substituent selected from among an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, halogen, phenyl, substituted phenyl, and a combination of these components.

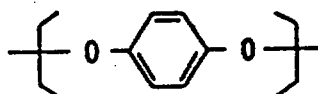
A preferable dicarboxyaryl unit II is



a preferable unit III is



and a preferable dioxyaryl unit IV is



Polymers which form an anisotropic molten phase according to the present invention include one wherein one part of a high-molecular chain is composed of a segment of a polymer forming an anisotropic molten phase as described above and the other part is composed of a segment of a thermoplastic resin not forming an anisotropic molten phase.

The polymer composition forming an anisotropic molten phase and capable of melt processing to be used in the present invention may further contain one or more of ① other polymers forming an anisotropic molten phase, ② thermoplastic resins not forming an anisotropic molten phase, ③ thermosetting resins, ④ low-molecular organic compounds, and ⑤ inorganic substances. The polymer part forming an anisotropic molten phase may be or may not be thermodynamically compatible with the other part of the composition.

The thermoplastic resins ② include, for example, polyethylene, polypropylene, polybutylene, polybutadiene, polyisoprene, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polystyrene, acrylic resin, ABS resin, AS resin, BS resin, polyurethane, silicone resin, fluororesin, polyacetal, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, aromatic polyester, polyamide, polyacrylonitrile, polyvinyl alcohol, polyvinyl ether, polyether imide, polyamide imide, polyether ether imide, polyether ether ketone, polyether sulfone, polysulfone, polyphenylene sulfide, and polyphenylene oxide.

The thermosetting resins ③ include, for example, phenolic, epoxy, melamine, urea, unsaturated polyester and alkyd resins.

The low-molecular organic compounds ④ include, for example, additives for common thermoplastic and thermosetting resins, such as plasticizer, light-resistant and weather-proof stabilizers such as antioxidant and ultraviolet absorber, nucleator, antistatic agent, fireproofing compound, coloring agent such as dyestuff and pigment, foaming agent, as well as crosslinking agents such as divinyl compound, peroxide, and vulcanizer, and low-molecular organic compound used as lubricant for improving fluidity and mold releasability.

The inorganic substances ⑤ include, for example, additives for common thermoplastic and thermosetting resins, that is, ordinary inorganic fibers such as glass, carbon, metallic, ceramic, and boron fibers and asbestos; powdery substances such as calcium carbonate, highly dispersive silicic acid, alumina, aluminium hydroxide, talcum powder, mica, glass flake, glass bead, quartz powder, siliceous sand, various metal powders, carbon black, barium sulfate, and calcium sulfate; inorganic compounds such as silicon carbide, alumina, boron nitrate, and silicon nitride; and whisker and metallic whisker.

In the polymer composition of the present invention, the polymer chains, when being melted, are highly orderly oriented even in a static state and demonstrate a high degree of orientation because of the flow of the melt in melt molding, thereby showing a higher degree of orientation in a two-dimensional article such as a thin molding. Accordingly, the polymer composition of the present invention fully satisfies the requirements including dimensional stability, various mechanical properties, and heat resistance demanded for the base resin as a substrate of a magnetic disk. However, for a magnetic disk used as a floppy disk shaped circular for convenience of use, not only excellent dimensional stability, that is, low linear expansion coefficients in all directions in the circular shape against temperature and humidity, but also isotropy in these values are desired.

Japanese patent laid-open No. 31718/1983 has proposed a multiaxially oriented high-performance laminated composed of laminated monoaxially oriented sheets of a thermotropic liquid crystal polymer and this polymer is preferably used as a substrate in the present invention.

The abovesaid patent has disclosed a method of manufacturing a multiaxially oriented laminate having desirable mechanical properties and excellent resistance to heat and chemicals, comprising the steps of (a) preparing at least two sheets of substantially one-directionally oriented polymers capable of forming an anisotropic molten phase; and (b) exposing said at least two sheets to heat bonding conditions in such a way that axial directions of the two sheets may intersect each other at a certain degree of angle to compose a multiaxially oriented laminate while maintaining substantial one-directional orientation in each sheet. In embodying the present invention, a laminate film obtained by heat-pressing two sheets of polymers as described above which are disposed to intersect each other at an angle of about 90° is preferably used.

Thus, formation of a biaxially oriented laminate film from the polymer composition forming an anisotropic molten phase make it possible to obtain a disk substrate having a desirable isotropic linear expansion coefficient.

A magnetic layer for a magnetic disk of the present invention is not specific and any layer composed of known magnetic material is applicable. Particular examples of the layer include those composed of γ - Fe_2O_3 - CrO_3 , iron oxide doped with Co, metals such as Fe, Co, or Ni, and alloys of these metals and, particularly, a magnetic layer substantially free of thin film type of organic polymer is preferable.

In a method of manufacturing a magnetic disk according to the present invention, polymers forming an anisotropic molten phase can be made into a film by employing film processing techniques generally applied to thermoplastic resins, for example, T-die method or inflation method as the process for non-stretched or stretched film.

When required, heat-treatment of the film thus produced enables further improvement in the mechanical strength of the film. An appropriate condition for heat treatment includes a temperature range of 200 and 270°C.

The monoaxially oriented films thus obtained are laminated into a multiaxially oriented film by a method as disclosed in the aforesaid patent laid-open No. 31718/1983.

In forming biaxially and multiaxially oriented sheets with the application of lamination, adhesives may be used if desired. Applicable adhesives are of hot melt type, reactive type, organic solvent type, and emulsion type, which are used in the manufacture of ordinary laminate films, among which a hot melt type of adhesive is desirable because of easiness in processing and polyester, polyamide, polyacrylic, polyvinyl acetate and their copolymers are used for this purpose.

A magnetic layer is formed on the disk substrate thus obtained. Various known methods of layer formation are applicable. They include, for example, coating with a solution prepared by dissolving powders of γ - Fe_2O_3 - Cr_2O_3 , iron oxide doped with Co, metals such as Fe, Ni, or Co, and alloys composed of these metals together with resin binders such as copolymer of vinyl chloride and vinyl acetate, polyurethane, polybutadiene, polyepoxy, polyacrylic, or phenolic resin, and additives such as various stabilizers, dispersant, antistatic agent, and lubricant in a solvent, and direct formation of a layer of the desired metal by sputtering, vapor deposition, or ion plating. The known corona-discharge treatment (in the air, nitrogen, or carbonic acid gas) prior to formation of the above-said magnetic layer onto a substrate film, lamination of other kinds of polymers for imparting adhesiveness, slipperiness, or surface smoothness, or covering by the use of other kinds of compounds may be applicable. In this way, the manufacture of a disk of either coating type or vapor deposition type is possible.

Addition of inorganic or organic additives such as antioxidant, heat stabilizer, ultraviolet ray absorber, nucleator, or surface projection forming agent in normal quantities within the range not interfering with the object of the present invention to a film to be used as a substrate according to the present invention is allowable.

[Effect of the Invention]

The present invention, as has been described above, provides a magnetic disk having a magnetic layer formed on at least one surface of a film composed of specified polymers and excellent in physical properties and, therefore, can exhibit superior effects as follows:

(1) A magnetic disk low in heat contraction, excellent in running characteristic even with a reduced thickness, and free of distortion in recording can be obtained and, as a result, reduction in film thickness, reduction in size, and increase in recording density of the magnetic disk is made possible.

(2) The magnetic disk can afford a magnetic recording material excellent in adhesiveness between the disk substrate and the magnetic layer and, accordingly, entirely free of distortion in recording.

(3) The magnetic disk is excellent in mechanical strength and dimensional stability and exhibits high performance as a magnetic disk because of an isotropic low linear expansion coefficient thereof resulting from the use of biaxially oriented laminated film.

A magnetic disk of the present invention is usable as a floppy disk for all kinds of magnetic recording.

[Embodiment]

The way of embodying the present invention will now be described with reference to examples to which, however, the present invention is not limited.

Reference Examples 1 to 4:

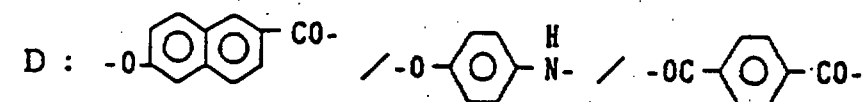
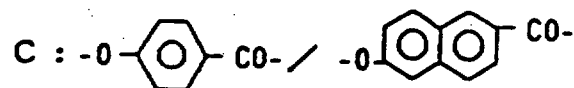
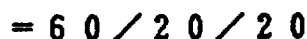
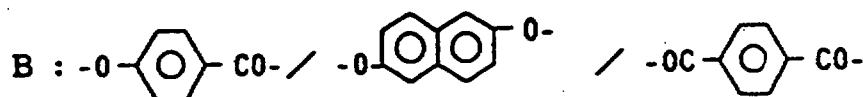
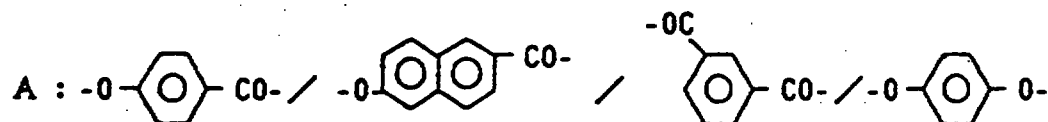
Pellets containing polymers A, B, C, and D forming an anisotropic molten phase which will be described later were extrusion-molded by means of a film extruder provided with a slit dice at extrusion temperatures of 310, 320, 315, and 320°C, respectively, with a drawing speed of 5 m/min, when 82 mm wide and 0.15 mm thick films were obtained. The films were made up by laminating two sheets of films of the same kind in such an arrangement that the longitudinal axis of one film perpendicularly intersects that of the other and by hot-pressing the laminated film at 300°C. Characteristics of these laminated films are shown in Table 1.

Mechanical properties of these films were measured in accordance with ASTM, D-882, and linear expansion coefficients were measured by the constant load elongation tester (made by Nippon Jido Seigyo K. K.).

Reference Comparative Example 1:

Chips of polyethylene terephthalate were extruded by an extruder provided with a T-die while melted at 290°C and then wound around a quenching drum for solidifying the molten product into a non-stretched film. The obtained film was heated to 80°C by a pre-heating roll and, while being subjected to rapid heating from both sides with a silicon carbide heating element heated to 1000°C, stretched 3.7 times lengthwise and then 3.8 times widthwise at 110°C, a film of 0.20 mm in thickness was obtained. Characteristics of this film, too, are listed in Table 1.

The polymers A, B, C, and D forming an anisotropic molten phase and used as resins for film formation are composed of the following structural units:



EP 0 206 599 B1

A detailed method of preparing the above resins A, B, C, and D will now be described.

[Resin A]

1081 parts by weight of 4-acetoxybenzoic acid, 460 parts by weight of 6-acetoxy-2-naphthoic acid, 166 parts by weight of isophthalic acid, and 194 parts by weight of 1,4-diacetoxybenzene were fed into a reactor equipped with an agitator, a nitrogen inlet tube, and a distilling tube, and heated to 260°C in a nitrogen stream. While distilling off acetic acid from the reactor, the mixture was vigorously agitated for 2.5 hours at 260°C and further for 3 hours at 280°C. Then, the temperature was raised to 320°C and, after the suspension of introduction of nitrogen, the pressure in the reactor was gradually decreased to 0.1 mmHg with the lapse of 15 minutes. The mixture was agitated for 1 hour at the same temperature and pressure.

The obtained polymer showed a concentration of 0.1 wt % and specific viscosity of 5.0 as measured in pentafluorophenol at 60°C.

[Resin B]

1081 parts by weight of 4-acetoxybenzoic acid, 489 parts by weight of 2,6-diacetoxynaphthalene, and 332 parts by weight of terephthalic acid were fed into a reactor equipped with an agitator, a nitrogen inlet tube, and a distilling tube, and heated to 250°C in a nitrogen stream. While distilling off acetic acid from the reactor, the mixture was vigorously agitated for 2 hours at 250°C and further for 2.5 hours at 280°C. Then, the temperature was raised to 320°C and, after the suspension of introduction of nitrogen, the pressure in the reactor was gradually decreased to 0.2 mmHg with the lapse of 30 minutes. The mixture was agitated for 1.5 hours at the same temperature and pressure.

The obtained polymer showed a concentration of 0.1 wt % and specific viscosity of 2.5 as measured in pentafluorophenol at 60°C.

[Resin C]

1261 parts by weight of 4-acetoxybenzoic acid and 691 parts by weight of 6-acetoxy-2-naphthoic acid were fed into a reactor equipped with an agitator, a nitrogen inlet tube, and a distilling tube, and heated to 250°C in a nitrogen stream. While distilling off acetic acid from the reactor, the mixture was vigorously agitated for 3 hours at 250°C and further for 2 hours at 280°C. Then, the temperature was raised to 320°C and, after the suspension of introduction of nitrogen, the pressure in the reactor was gradually decreased to 0.1 mmHg with the lapse of 20 minutes. The mixture was agitated for 1 hour at the same temperature and pressure.

The obtained polymer showed a concentration of 0.1 wt % and specific viscosity of 5.4 as measured in pentafluorophenol at 60°C.

[Resin D]

1612 parts by weight of 6-acetoxy-2-naphthoic acid, 290 parts by weight of 4-acetoxyacetanilide, 249 parts by weight of terephthalic acid, and 0.4 parts by weight of sodium acetate were fed into a reactor equipped with an agitator, a nitrogen inlet tube, and a distilling tube, and heated to 250°C in a nitrogen stream. While distilling off acetic acid from the reactor, the mixture was vigorously agitated for 1 hour at 250°C and further for 3 hours at 300°C. Then, the temperature was raised to 340°C and, after the suspension of introduction of nitrogen, the pressure in the reactor was gradually decreased to 0.2 mmHg with the lapse of 30 minutes. The mixture was agitated for 30 minutes at the same temperature and pressure.

The obtained polymer showed a concentration of 0.1 wt % and specific viscosity of 3.9 as measured in pentafluorophenol at 60°C.

Table 1

Reference Example	Resin	Mechanical properties		Linear expansion coefficient	
		Tensile strength (MPa)	Elongation (%)	Temperature (/°C)	Humidity (/RH)
1	A	213	5.8	1×10^{-6}	1×10^{-6}
2	B	206	6.2	2×10^{-6}	3×10^{-6}
3	C	233	5.6	1×10^{-6}	2×10^{-6}
4	D	220	5.8	2×10^{-6}	2×10^{-6}
Comparative Example 1	Biaxially stretched PET	192	95	16×10^{-6}	13×10^{-6}

Examples 1 to 4 and Comparative Example 1:

The films prepared in accordance with the description of Reference Examples 1 to 4 and Reference Comparative Example 1 were coated with a coating agent containing $\gamma\text{-Fe}_2\text{O}_3$ powder (copolymer of vinyl chloride-vinyl acetate-vinyl alcohol and that of acrylonitrile-butadiene). The linear expansion coefficients of these films are shown in Table 2.

Examples 5 to 8 and Comparative Example 2:

The films prepared in accordance with the description of Reference Examples 1 to 4 and Reference Comparative Example 1 were coated with a coating agent containing Co- $\gamma\text{-Fe}_2\text{O}_3$ powder and respective magnetic disks were obtained (Examples 5 to 8 and Comparative Example 2). The linear expansion coefficients of these films are shown in Table 2.

Table 2

Example	Resin	Magnetic substance	Linear expansion coefficient	
			Temperature (/°C)	Humidity (/RH)
1	A	$\gamma\text{-Fe}_2\text{O}_3$	2×10^{-6}	2×10^{-6}
2	B	$\gamma\text{-Fe}_2\text{O}_3$	2×10^{-6}	4×10^{-6}
3	C	$\gamma\text{-Fe}_2\text{O}_3$	1×10^{-6}	2×10^{-6}
4	D	$\gamma\text{-Fe}_2\text{O}_3$	2×10^{-6}	2×10^{-6}
Comparative Example 1	Biaxially stretched PET	$\gamma\text{-Fe}_2\text{O}_3$	16×10^{-6}	14×10^{-6}

Table 3

Example	Resin	Magnetic substance	Linear expansion coefficient	
			Temperature (/°C)	Humidity (/RH)
5	A	Co- γ -Fe ₂ O ₃	2×10^{-6}	1×10^{-6}
6	B	Co- γ -Fe ₂ O ₃	2×10^{-6}	3×10^{-6}
7	C	Co- γ -Fe ₂ O ₃	1×10^{-6}	3×10^{-6}
8	D	Co- γ -Fe ₂ O ₃	2×10^{-6}	3×10^{-6}
Comparative Example 2	Biaxially stretched PET	Co- δ -Fe ₂ O ₃	17×10^{-6}	13×10^{-6}

As apparent from Tables 2 and 3, a laminated film composed of polymer films each forming an anisotropic molten phase prepared according to the present invention was provided with a magnetic layer excellent in adhesiveness, and a superior magnetic disk having an isotropic low linear expansion coefficient was obtained by employing the abovesaid film as a base film of the disk.

Claims

1. A magnetic disk which comprises a magnetic layer on at least one surface of a layered substrate of polymer films, in which the major component of the layered polymer substrate is characterized in that the layered polymer substrate is a sheet of a liquid crystal polymer composition, said polymer being a polyester comprising constituent units selected from one or more aromatic hydroxy carboxylic acids, said units being employed alone or in combination with other aromatic or alicyclic constituent units.

2. A magnetic disk as claimed in claim 1, in which the liquid crystal polymer is a polyester comprising constituent units selected from at least three of:

- (a) one or more aromatic hydroxy carboxylic acids,
- (b) one or more aromatic hydroxy amines and aromatic diamines,
- (c) one or more of aromatic dicarboxylic acids and alicyclic dicarboxylic acids, and
- (d) one or more of aromatic diols, alicyclic diols and aliphatic diols.

3. A magnetic disk as claimed in claim 1 or claim 2, in which the layered substrate comprises at least two monoaxially oriented sheets of a liquid crystal polymer.

4. A magnetic disk as claimed in claim 3, in which two monoaxially oriented sheets of a liquid crystal polymer are laminated so that the orientation direction of one sheet intersects that of the other at an angle of about 90°.

Patentansprüche

1. Magnetische Scheibe, umfassend eine magnetische Schicht auf wenigstens einer Oberfläche eines geschichteten Substrats aus Polymer-Folien, worin der Haupt-Bestandteil des geschichteten Polymer-Substrats dadurch gekennzeichnet ist, daß das geschichtete Polymer-Substrat eine Folie aus einer Flüssigkristall-Polymer-Zusammensetzung ist, wobei das Polymer ein Polyester ist, der konstituierende Einheiten umfaßt, die aus einer oder mehreren aromatischen Hydroxycarbonsäuren ausgewählt sind, wobei diese Einheiten allein oder in Kombination mit anderen aromatischen oder aliphatischen konstituierenden Einheiten eingesetzt werden.

2. Magnetische Scheibe nach Anspruch 1, worin das Flüssigkristall-Polymer ein Polyester ist, der konstituierende Einheiten umfaßt, die aus wenigstens dreien von

- (a) einer oder mehreren aromatischen Hydroxycarbonsäuren,

Table 3

Example	Resin	Magnetic substance	Linear expansion coefficient	
			Temperature (/°C)	Humidity (/%RH)
5	A	Co- γ -Fe ₂ O ₃	2×10^{-6}	1×10^{-6}
6	B	Co- γ -Fe ₂ O ₃	2×10^{-6}	3×10^{-6}
7	C	Co- γ -Fe ₂ O ₃	1×10^{-6}	3×10^{-6}
8	D	Co- γ -Fe ₂ O ₃	2×10^{-6}	3×10^{-6}
Comparative Example 2	Biaxially stretched PET	Co- δ -Fe ₂ O ₃	17×10^{-6}	13×10^{-6}

As apparent from Tables 2 and 3, a laminated film composed of polymer films each forming an anisotropic molten phase prepared according to the present invention was provided with a magnetic layer excellent in adhesiveness, and a superior magnetic disk having an isotropic low linear expansion coefficient was obtained by employing the abovesaid film as a base film of the disk.

Claims

1. A magnetic disk which comprises a magnetic layer on at least one surface of a layered substrate of polymer films, in which the major component of the layered polymer substrate is characterized in that the layered polymer substrate is a sheet of a liquid crystal polymer composition, said polymer being a polyester comprising constituent units selected from one or more aromatic hydroxy carboxylic acids, said units being employed alone or in combination with other aromatic or alicyclic constituent units.

2. A magnetic disk as claimed in claim 1, in which the liquid crystal polymer is a polyester comprising constituent units selected from at least three of:

- (a) one or more aromatic hydroxy carboxylic acids,
- (b) one or more aromatic hydroxy amines and aromatic diamines,
- (c) one or more of aromatic dicarboxylic acids and alicyclic dicarboxylic acids, and
- (d) one or more of aromatic diols, alicyclic diols and aliphatic diols.

3. A magnetic disk as claimed in claim 1 or claim 2, in which the layered substrate comprises at least two monoaxially oriented sheets of a liquid crystal polymer.

4. A magnetic disk as claimed in claim 3, in which two monoaxially oriented sheets of a liquid crystal polymer are laminated so that the orientation direction of one sheet intersects that of the other at an angle of about 90°.

Patentansprüche

1. Magnetische Scheibe, umfassend eine magnetische Schicht auf wenigstens einer Oberfläche eines geschichteten Substrats aus Polymer-Folien, worin der Haupt-Bestandteil des geschichteten Polymer-Substrats dadurch gekennzeichnet ist, daß das geschichtete Polymer-Substrat eine Folie aus einer Flüssigkristall-Polymer-Zusammensetzung ist, wobei das Polymer ein Polyester ist, der konstituierende Einheiten umfaßt, die aus einer oder mehreren aromatischen Hydroxycarbonsäuren ausgewählt sind, wobei diese Einheiten allein oder in Kombination mit anderen aromatischen oder aliphatischen konstituierenden Einheiten eingesetzt werden.

2. Magnetische Scheibe nach Anspruch 1, worin das Flüssigkristall-Polymer ein Polyester ist, der konstituierende Einheiten umfaßt, die aus wenigstens dreien von

- (a) einer oder mehreren aromatischen Hydroxycarbonsäuren,



(b) einem oder mehreren aromatischen Hydroxyaminen und aromatischen Diaminen,
 (c) einer oder mehreren aromatischen Dicarbonsäuren und alicyclischen Dicarbonsäuren und
 (d) einem oder mehreren aromatischen Diolen, alicyclischen Diolen und aliphatischen Diolen
 ausgewählt sind.

3. Magnetische Scheibe nach Anspruch 1 oder Anspruch 2, worin das geschichtete Substrat
 wenigstens zwei monoaxial orientierte Folien eines Flüssigkristall-Polymers umfaßt.

4. Magnetische Scheibe nach Anspruch 3, worin zwei monoaxial orientierte Folien eines Flüssigkristall-
 Polymers so laminiert sind, daß die Orientierungsrichtung einer Folie diejenige der anderen unter einem
 Winkel von etwa 90° schneidet.

Revendications

1. Un disque magnétique qui comprend une couche magnétique sur au moins une surface d'un
 substrat stratifié de pellicules polymères, dans lequel le constituant principal du substrat polymère stratifié
 est caractérisé en ce que le substrat polymère stratifié est une feuille d'une composition de polymère à
 cristaux liquides, ledit polymère étant un polyester comprenant des motifs constitutifs choisis parmi un ou
 plusieurs acides hydroxycarboxyliques aromatiques, lesdits motifs étant employés seuls ou en
 combinaison avec d'autres motifs constitutifs aromatiques ou alicycliques.

2. Un disque magnétique selon la revendication 1, dans lequel le polymère à cristaux liquides est un
 polyester comprenant des motifs constitutifs choisis parmi au moins trois de

- (a) un ou plusieurs acides hydroxycarboxyliques aromatiques,
- (b) une ou plusieurs hydroxyamines aromatiques et diamines aromatiques,
- (c) un ou plusieurs acides dicarboxyliques aromatiques et acides dicarboxyliques alicycliques,
- (d) un ou plusieurs diols aromatiques, diols alicycliques et diols aliphatiques.

3. Un disque magnétique selon la revendication 1 ou la revendication 2, dans lequel le substrat stratifié
 comprend au moins deux feuilles monoaxialement orientées d'un polymère à cristaux liquides.

4. Un disque magnétique selon la revendication 3, dans lequel deux feuilles monoaxialement orientées
 d'un polymère à cristaux liquides sont stratifiées de façon que la direction d'orientation d'une des feuilles
 coupe celle de l'autre à un angle d'environ 90°.

