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(71) Applicants *(for all designated States except US)*: HOECHST AKTIENGESELLSCHAFT [DE/DE]; Postfach 80 03 20, D-65296 Frankfurt am Main (DE). HOECHST CELANESE CORPORATION [US/US]; Route 202-206 North, Somerville, NJ 08876 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: BENNETT, Cynthia [US/DE]; Mainstrasse 22, D-6200 Wiesbaden (DE). CHOE, E-Won [US/US]; 130 Radtke Road, Randolph, NJ 07869 (US). FLINT, John, Anthony [GB/US]; 150 Lenape Lane, Berkeley Heights, NJ 07922 (US). KUHMANN, Bodo [DE/DE]; Lindenstrasse 5, D-6258 Runkel 5 (DE).

(74) Agents: CLEMENTS, Gregory, N. et al.; Hoechst Celanese Corporation, Patent Dept., 4000 Barclay Downs Drive, Charlotte, NC 28232-2414 (US).

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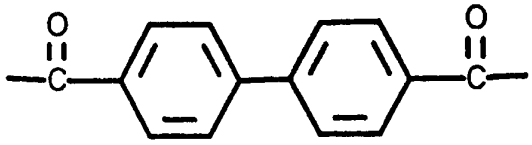
(54) Title: BIAXIALLY ORIENTED COPOLYESTER FILM FOR MAGNETIC RECORDING DISKS AND MAGNETIC RECORDING DISKS MADE THEREFROM



(I)

(57) Abstract

Disclosed herein is a biaxially oriented PENBB film for magnetic recording disks having low water absorption, low shrinkage and high modulus. The film typically is 60-100 microns thick. One surface of the film preferably is very smooth. PENBB as mentioned herein is a copolyester containing units of formula (I).

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BIAXIALLY ORIENTED COPOLYESTER FILM FOR MAGNETIC RECORDING DISKS AND MAGNETIC RECORDING DISKS MADE THEREFROM

Scope of the Invention

This invention relates to the use of a high melting, high strength biaxially oriented PENBB copolyester film for the manufacture of superior performing magnetic recording disks, and the disks made therefrom.

Background

Increased demand for electronic storage media that contain more information in a given volume has produced a need for substitute materials upon which magnetic recording coatings may be deposited. The requirements for the substrate include a need for a super-smooth surface upon which the recording media (e.g. magnetic oxide coatings or thin film metal depositions) may be laid down with lush smoothness and purity are required to prevent drop-outs of recorded information. For optimal reading of recorded information, it is important that the disk be stiff enough to prevent distortion by bending. On the other hand, a lightweight disk material is desirable, so increasing thickness is not a viable solution. Thus, there is a need for a film substrate material with a tensile modulus - which correlates with stiffness towards bending - that is uniform over the plane of the film. In addition, the disks made from the substrate are subject to severe centrifugal stress in use, which may result in distortion of the disks from perfect circularity. Such distortion causes alterations in the recording tracks and mis-location of the recorded information. While this may be compensated for electronically, it results in increased cost for disk drives.

Similarly, environmental changes, such as in temperature and humidity, can result in dimensional changes of the substrate, and also result in signal loss or distortion. These dimensional changes may result from inherent polymer expansion coefficients, or from relief of any residual stresses in the film that occur as a result of the film manufacturing process.

The trend in information recording is toward smaller equipment, this results in higher operating temperature due to the heat generated by the equipment. The higher temperatures may produce or exacerbate the dimensional changes described above. Thus there is a need for a product with greater dimensional stability. Similar problematic dimensional changes may be caused by a hygroscopic expansion shrinkage upon changes in ambient humidity. Hence, a product with reduced water pick-up from the environment is needed.

Description of Invention

This invention relates to the use of PENBB copolyester biaxially oriented film as a base for magnetic recording disks. PENBB resin may be extruded and formed into film using conventional biaxial orientation systems. The film product is higher melting than polyethylene terephthalate film, has a higher glass transition temperature, and higher inherent modulus and tensile properties. PENBB as mentioned herein is a copolyester containing acid-derived units of which at least 25 mole percent are bibenzoate units. The remainder of the acid-derived units are difunctional units such as 2,6-dicarboxy naphthalate, which is preferred or terephthalate, isophthalate, adipic acid or poly-functional units such as trimellitic acid, pyromellitic acid, and p-hydroxy benzoic acid. The diol units of the copolyester may be chosen from ethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, 1,4-cyclohexane dimethanol, and p-xylene glycol.

The preferred copolyester would contain 4,4'-bibenzoate as acid derived units in the range 40 to 60 mole percent and 2,6-dinaphthoic acid in the range 60 to 40 percent. The diol component preferably comprises at least 80 mole percent ethylene glycol-derived units by weight, more preferably 95 to 100 percent.

U.S. Patent No. 3,008,934 discloses copolyesters containing as acid derived units 4,4'-bibenzoate and a host of other dicarboxylates including 2,6-naphthalic dicarboxylate. It also discloses oriented fibers and films prepared from these copolyesters, however, biaxially oriented PENBB films are not

disclosed or envisioned. In particular, those films with improved stiffness (tensile modulus) and tensile strength in both MD and TD as well as thermostability, UV stability, hydrophobicity, dimensional stability and impermeability toward gases in comparison to PET film are not disclosed in U.S. Patent No. 3,008,934.

The copolyester is obtained by polycondensation of the corresponding diacid or lower dialkyl diester and the corresponding diol. Both components should normally be employed in equimolar ratios. It may, however, be advantageous to employ one of the components -- especially the diol -- in excess during the synthesis, for instance in order to influence the reaction kinetics or to serve as a solvent. The polycondensation is carried out according to known processes used, e.g., in the production of polyethylene terephthalate (PET). Usually about 100 mole percent of the dicarboxylic acid or dialkyldicarboxylate mixture are mixed with > 100 mole percent of the corresponding diol(s). This mixture is then heated to about 200°C, preferably in the presence of a transesterification catalyst, until sufficient lower alkyl alcohol or water has been removed from the mixture via distillation. This reaction yields an oligomer or a low molecular weight polyester, which is subsequently subjected to polycondensation, preferably in the presence of a stabilizer and/or catalyst. Useful stabilizers and catalysts can be polyphosphates, triorganyl phosphates, antimony trioxide or tetraalkoxy titanate(IV) or mixtures of triphenylphosphate and antimony trioxide. A preferred process for the production of such copolyesters is described in U.S. Patent Application Serial No. 07/735,553 which is incorporated herein by reference. A further increase in molecular weight can be achieved by solid phase polycondensation at a temperature just below the melting point, under vacuum, or in a stream of dry air or inert gas. In order to achieve the desired mechanical properties in the biaxially oriented PENBB film it is recommended that the IV value (inherent viscosity, as measured in a 1 : 1 weight-ratio mixture of pentafluorophenol and hexafluoroisopropanol at a concentration of 0.2 g/dl and a temperature of 25 °C) of the PENBB polymer after extrusion be > 0.5 dl/g and preferably > 0.55 dl/g.

To produce the film, the polymer melt is extruded through a die onto a chill roll where it solidifies, biaxially oriented, heat set, optionally post treated, and then wound on a roll. The solidified film as extruded on the chill roll should be obtained in an essentially amorphous state. To achieve this, the melt film must be pinned to the chill roll by a known method such as electrostatic pinning, vacuum, air knife or the like.

The biaxial orientation of the film is achieved by stretching the film at elevated temperature in the machine direction (MD) and transverse direction (TD). This stretching can be either simultaneous or sequential. In the case of sequential stretching the first stretching step can be in either MD or TD, followed by stretching in the other direction. The orientation in MD can also be achieved in several steps, either one after another prior to stretching in TD, or before and after the TD stretching. Preferred temperatures for stretching lie between the glass transition temperature and about 30°C above the cold crystallization temperature of the PENBB copolymer composition in use (both temperatures can easily be measured on amorphous films by DSC). Suitable total stretch ratios in MD and TD lie between 1 to 2 and 1 to 10, preferably between 1 to 2.5 and 1 to 5. The product of the MD and TD total stretch ratios should be between 1 and 30 preferably between 5 and 20. Biaxial drawing is performed such that the birefringeance is < 0.2, preferably < 0.1 to ensure adequately isotropic properties. Birefringeance as mentioned herein is the absolute value of the difference between the maximum and minimum refractive indices in the plane of the film, as measured on common instruments such as Abbé refractometer, optical bench or compensators.

To achieve film properties that are desirable for use in magnetic recording disks, it is necessary to modify the resin and film to provide the optimum balance of slip and handling characteristics with the very smooth surface required for the high density storage of information. The modification may include one or more of the following techniques:

Inclusion of fine particles within the polymer. Such particles may be added during the polymer manufacturing process, formed by precipitation of

catalyst residues during polymerization, and/or added in heavily loaded master batches to the extrusion melt stream.

Use of coatings applied to the base film, preferably during the film manufacturing process said coatings, either as continuous or discontinuous layers, may provide surface protrusions, or combinations of protrusions and depressions, sufficient to provide good slip and handleability without negatively impacting electronic records properties. These coatings may also contain inert particulate matter to provide the proper surface character.

Use of multilayers of polymers in the film by means of co-extrusion or lamination. Such multilayers may be all of PENBB or may contain layers of other polymers such as polyethylene terephthalate, PEN, etc. It is preferred that at least one of these layers contain means to provide a surface rough enough to provide good ship. This may be achieved by added particles or by coatings.

At least one surface should be smooth to provide an excellent base for the magnetic susceptible layer. It is preferred that any protrusions on this surface be less than 0.75 μm. This may be best achieved by having at least one layer of the PENBB either free from added particles or only containing particles that are very small. For example, a slip coating could be applied to only one surface layer of the disk whereas the other surface layer has no such coating and is smooth enough for magnetic recording.

The biaxially oriented PENBB film of the instant invention is characterised by a heat shrinkage of < 0.5 % in both machine (MD) and transverse (TD) direction when measured at 150 °C for 30 minutes. Its tensile modulus is in the range of about 5 to 10 GPa in both machine (MD) and transverse (TD) direction as measured at 20 °C. The equilibrium water pick up is less than 0.1 % at 50% relative humidity and 23 °C. A film exhibiting the above described desirable combination of parameters is unique and was hitherto unknown.

EXAMPLE 1

Biaxially oriented film is produced from a PENBB copolyester made from 289 parts by weight of dimethyl 2,6-naphthalene dicarboxylate, 322 parts by weight of dimethyl 4,4'-dibenzoate and 368 parts by weight of ethylene glycol. Granules of this polymer, having a melting point of 281°C, are melted in a single screw extruder at a temperature of 280° - 320°C and extruded through a sheet die onto a cooling roll maintained at 30°C. The film obtained has a density of 1.31 g/cm^3. This film is sequentially biaxially oriented at draw ratios of 3x3. The film is heat set under restraint for 10 seconds at 260°C. The resulting film has unrestrained thermal shrinkage of 0.3% in MD and 0.3% in TD, measured at 150°C for 30 minutes. This film exhibits hardly any slip and winding or unwinding is very difficult.

EXAMPLE 2

Biaxially oriented film is produced from the same polymer as in Example 1, except that:

a master batch of 3% silica (Syloblock 44 from Grace GmbH, Worms, Germany), produced by adding the silica to the reaction mixture according to Example 1 after transesterification, is added to the PENBB co-polymer to give a diluted concentration of about 2000 ppm of silica in the extruded film. The biaxial orientation and heat setting are carried out under the same conditions as in Example 1 to give a film of substantially the same physical properties. However, it was found that this product had good slip and could readily be handled.

EXAMPLE 3

To produce a suitable base for magnetic recording disks, an A/B type co-extrusion of the filled (cf. Example 2) and un-filled (cf. Example 1) resins is made. The filled polymer layer is 25% by weight of the total film weights; the unfilled polymer layer is 75% by weight. At a total thickness of 75 μm of the finished oriented heat set co-extruded film, the filler particles in the filled polymer layer do not protrude through the surface of the unfilled layer.

This film shows good slip, and has excellent smoothness on the unfilled surface which is suitable for a magnetic susceptible coating.

EXAMPLE 4

Film from Example 1 is coated in-line between the forward draw stage and the transverse draw stage with a latex containing methyl methacrylic-ethyl acrylate-methacrylamide terpolymer and stearamidopropyl-dimethyl-B-hydroxy-ethylammonium nitrate, as described in U.S. Patent No. 4,302,506 at a coating weight of 15 mg/cm^2. This product has sufficient slip to be readily processable through magnetic coating equipment.

All films exhibit a heat shrinkage of < 0.5 % (in MD and TD); their tensile moduli are in the range of 5-10 GPa and their equilibrium water pick up is < 0.1 % at 50% r.h..

What is claimed is:

1. A biaxially oriented mono- or multilayer coated or uncoated copolyester film, wherein the copolyester is PENBB and wherein the heat shrinkage of the film is < 0.5 % in both machine and transverse direction when measured at 150 °C for 30 minutes.

2. A biaxially oriented copolyester film according to claim 1 which has a modulus of 5-10 GPa in both the machine and transverse direction as measured at 20°C.

3. A biaxially oriented copolyester film according to claim 1 or 2 which has an equilibrium water pick up of less than 0.1% at 50% relative humidity and 23°C.

4. A biaxially oriented copolyester film according to claim 1,2 or 3, wherein the film contains inert particulate material.

5. A biaxially oriented copolyester film according to claim 1,2,3 or 4 having at least one surface having no protrusions greater than 0.75 μm.

6. A biaxially oriented copolyester film according to any one or more of the preceeding claims having a thickness in the range of 60 to 100 μm.

7. A biaxially oriented copolyester film according to any one or more of the preceeding claims characterised in that the film is a mono-layered film.

8. A biaxially oriented copolyester film according to any one or more of claims 1 - 6 characterised in that the film is a bi-layered film.

9. A biaxially oriented copolyester film according to any one or more of the preceding claims wherein at least one surface of the film is coated.

10. A biaxially oriented copolyester film according to claim 9, wherein the coating is an acrylic coating.

11. A biaxially oriented copolyester film according to any one or more of the preceding claims, wherein the birefringeance of the film is < 0.2 and the IV of the PENBB is > 0.5 dl/g.

12. A magnetic recording medium comprising film according to claim 1.

13. A magnetic recording disk comprising a medium according to claim 11.

INTERNATIONAL SEARCH REPORT

Ir. ..ational application No.
PCT/US92/10687

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 9/00
US CL :428/483, 692, 910
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/483, 692, 910

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,590,119 (KAWAKAMI ET AL) 20 MAY 1986	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

In. .ational application No.
PCT/US92/10687

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-11 and 13
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.