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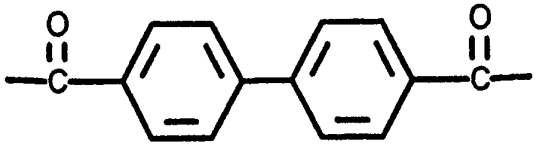
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(54) Title: IMPROVED BIAXIALLY ORIENTED COPOLYESTER FILM FOR MAGNETIC RECORDING MEDIA

(57) Abstract

The present invention provides an improved substrate film for magnetic tapes. The base film is a biaxially oriented PENBB film, i.e. a biaxially oriented copolyester film containing the structural unit (I) (bibenzoate, BB). Such particle containing films exhibit improved modulus in the machine and transverse direction and show surface protrusions such that their height crosses the line of $\log_{10} y = -18x + 3.7$ twice.



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IMPROVED BIAXIALLY ORIENTED COPOLYESTER FILM FOR MAGNETIC RECORDING MEDIA

Background Of The Invention

1) Field Of The Invention

This invention relates to a biaxially oriented PENBB copolyester film suitable as a base film for a magnetic recording medium. More specifically, this invention relates to a biaxially oriented copolyester film having a high Young's modulus in both the MD and TD directions and being useful as a base film for the production of a magnetic record medium having excellent electromagnetic conversion characteristics as well as improved mechanical strength.

2) Prior Art

Magnetic recording media having a polyethylene terephthalate (PET) film as a base have found wide use, for example, in video tapes audio tapes, computer tapes, and floppy disks. In such applications, there has been increasing demand for high density recording in small sizes, and accordingly, the polyester based film should have a flat surface, good slip, excellent processability, and thin film thickness. In portable magnetic recording devices such as an 8 mm video tape, the tape is frequently exposed to high temperatures outdoors or inside vehicles. Therefore, the tape for such applications must have both dimensional stability and thermal stability.

Generally, when the PET base film requires a reduction in thickness, it is the usual practice to draw it at a higher ratio in the machine direction (MD) and thus increase its Young's modulus so that the tape has the appropriate strength, but only in the MD direction. Such base film based on polyethylene terephthalate has reduced stiffness in the transverse direction (TD), which makes the tape susceptible to edge damage, folding and/or difficulties with close contact of the reading head to the tape.

In recent years, magnetic recording media have increasingly been required to permit long-time recording (or high density recording) and be of

reduced thickness. Therefore, the substrate films must have higher Young's modulus to permit smaller thicknesses and higher density recording. A higher Young's modulus is necessary to thinner films because of the lower stiffness of thinner film. Unless a film has a higher Young's modulus, a tape prepared from such film encounters trouble in traveling or traversing the various heads and cannot withstand repeated brunting. In the case of a video tape, its contact with a rotating cylinder head is not good with the result that the electromagnetic signal is not read properly.

European Patent Application No. 199,244 to Teijin Limited discloses a polyethylene terephthalate based film for magnetic recording media. This application discloses stretching the PET film at a high ratio only in the machine direction and thus the resultant product has reduced stiffness in the TD direction and is susceptible to edge damage and uniform contact with the reading head cannot be achieved.

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 and dimensional stability in comparison to PET film are not disclosed in U.S. Patent No. 3,008,934.

It is the general object of this invention to overcome such problems and to develop a biaxially oriented copolyester base film which has a high Young's modulus in both the MD and TD, as well a flatness, dimensional stability, and thermal stability thereby producing magnetic recording media of high quality.

An aim of the present invention is to provide a biaxially oriented copolyester base film having many fine protrusions on its surface, which:

(1) has sufficient strength to permit thickness reduction of the magnetic recording media

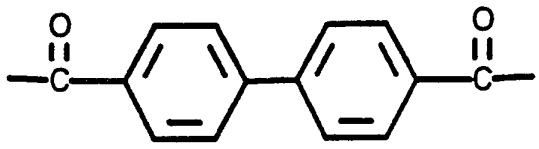
(2) has a magnetic recording medium having excellent thermal and dimensional stability; and

(3) has a flat surface with no large protrusions;

Other objects of this invention along with its advantages will become apparent from the following detailed description.

Summary Of The Invention

The present invention employs a PENBB copolyester having at least 25 mole percent of its diacid or diester content of 4,4'-bibenzoic acid (or 4,4'-dialkylbibenzoate; alkyl being C_1-C_4-alkyl)



(bibenzoate, BB)

with the remainder of the diacid part of the copolyester being produced from other dicarboxylic acids or their ester equivalents.

In the broadest sense of the present invention, a biaxially oriented PENBB copolyester film suitable for use as a magnetic recording medium has the following mechanical properties, namely:

- a Young's modulus in the machine direction of greater than or equal to 6.5 GPa

$$E_{MD} \geq 6.5 \text{ GPa}$$

In preferred aspects of the invention, the oriented copolyester film has - in addition to the above E_{MD} value - the following characteristics:

- the sum of the Young's modulus values in the machine direction (E_{MD}) and the transvers direction (E_{TD}) are greater than or equal to 12 GPa

$$E_{MD} + E_{TD} \geq 12 \text{ GPa}$$

and preferably greater than or equal to 14 GPa

$$E_{MD} + E_{TD} \geq 14 \text{ GPa}.$$

- a distribution curve representing the relationship between the number of protrusions per surface area (y/mm^2) and the height of the protrusions (x μm), such that the portion of the curve above 20 protrusions/mm^2 crosses the line of

$$\log_{10} y = -18\,x + 3.7$$

twice (c.f. figure 1);

- less than 20 protrusions per mm^2 on the film surface have a height greater than 0.13 μm;
- a surface roughness (R_a) of not more than 12 nm;
- a heat shrinkage in the longitudinal direction of not more than 0.1 % when heat treated at 70 °C for one hour under no load.

Brief Description Of The Drawing

Figure 1 shows a graph of the number of protrusions per mm^2 versus the height of the protrusions in μm with the distribution curve of the composition disclosed in Examples 1 and 2, along with the line of $\log_{10} y = 18x + 3.7$.

Description Of The Preferred Embodiments

The biaxially stretched copolyester (PENBB) base film of the present invention can be produced by reacting an aromatic diacid or its diester equivalent with a diol as is known in the art for making polyesters. The copolyester composition (PENBB composition) must contain at least 25 mol-% (based on the total diacid derived components) of the diester or diacid of 4,4'-dialkylbenzoate, preferably 4,4'-dimethylbenzoate or 4,4'-benzoic acid. The remainder diacid derived portion of the copolyester may be formed from other dicarboxylic acids or their ester equivalents, such as terephthalic acid, isophthalic acid, phthalic acid, naphthalene-2,6-dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, di-(4-phenyl) acetylene dicarboxylic acid, 1,2 di-(4-phenyl) ethene dicarboxylic acid, sebacic acid, malonic acid, adipic acid, azelaic, glutaric acid, suberic acid, succinic acid, and the like, or mixtures of these can be employed in the present invention. Naphthalene-2,6-dicarboxylic acid is the preferred remainder diacid for the copolyester.

Suitable diols employed in the present invention include ethylene glycol, diethylene glycol, polyethylene glycol, butane diol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,10-decanediol, cyclohexane dimethanol, and the like. Ethylene glycol is the preferred glycol.

Suitable copolyesters of the present invention can comprise, for example, polyethylene terephthalate/4,4'-bibenzoate, polybutylene terepht-

halate/4,4'-bibenzoate, polypropylene terephthalate/4,4'-bibenzoate, polyethylene naphthalate/4,4'-bibenzoate, polyethylene terephthalate/isophthalate/4,4'-bibenzoate, polyethylene terephthalate/adipate/4,4'-bibenzoate, polyethylene terephthalate/sulfoisophthalate/4,4'-bibenzoate, and the like.

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.

In a preferred embodiment, a polyethylene naphthalate/4,4'-bibenzoate copolyester comprises roughly equimolar (i.e. from about 40 : 60 to 60 : 40 molar ratio) portions of the esters of 2,6-dinaphthalate and 4,4'-bibenzoate, or the diacids of naphthalene-2,6-dicarboxylic acid and 4,4'-bibenzoic acid. The copolyester is obtained by polycondensation of the reaction product of the diacids or diesters with the diol or glycol. The reaction yields monomer or low molecular weight polyester which is subsequently subjected to the polycondensation reaction in the presence of a catalyst an optionally stabilizers, antioxidants, delusterants, pigments, antistatic agents, etc.

Suitable catalysts may be antimony, manganese, cobalt, magnesium, zinc, calcium, etc., as are well known in the art. The preferred transesterification catalyst, where employed, would be manganese and/or cobalt. The preferred polycondensation catalyst would be antimony compounds. Such catalysts are well known and conventional in the prior art.

The polyester film of the present invention can be manufactured by an extrusion process. The polyester resin is first heated to a molten state and then extruded through a wide slot die in the form of an amorphous sheet onto a polished, revolving casting drum. The amorphous sheet extrudate is rapidly cooled or "quenched" to form a cast sheet of polyester. The cast polyester sheet is removed from the casting drum and axially stretched in one direction, either in the direction of the film travel (machine direction, MD) or perpendicular to the machine direction (transverse direction, TD), while being heated to a temperature between the glass transition temperature and about 30°C

above the cold crystallization temperature (both temperatures can easily be measured on the films by differential scanning colorimeter (DSC).

The copolyester film of the present invention is biaxially oriented, i.e. stretched in both the machine direction and the transverse direction. The total stretch ratio in the machine direction and the transverse direction is between 1:2 and 1:10, preferably between 1:2.5 and 1:5. The product of the total stretch ratio should be between 1 to 30 and preferably and between 5 to 20. Biaxial drawing is performed such that the birefringeance is < 0.2, preferably < 0.1 to ensure adequate 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.

After orientation of the film, a heat setting step occurs to lock in the properties of the film. The heat setting occurs at a temperature between the cold crystallization temperature and the melt temperature of the copolymer composition.

After heat setting, the film may be wound on a roll, or in some cases surface treatment of the film such as corona treatment, plasma or flame treatment may be employed before winding the film on the roll, particularly where the film will be further coated with a primer coating, for example.

It is desirable for the film to have a final total thickness of between 1 and 15 μm, preferably between 2 and 12 μm, still more preferably between 3 and 6 μm.

According to the present invention, biaxially oriented PENBB copolyester film is characterized by the following properties, namely:

- a Young's modulus in the machine direction of greater than or equal to 6.5 GPa

$$E_{MD} \geq 6.5 \text{ GPa}$$

The following preferred embodiments provide further improvement in the performance as a magnetic tape substrate. In these preferred embodiments, the film has the characteristics:

- the sum of the Young's modulus values in the machine direction (E_{MD})

and the transverse direction (E_{TD}) are greater than or equal to 12 GPa

$$E_{MD} + E_{TD} \geq 12 \text{ GPa},$$

and preferably greater than or equal to 14 GPa

$$E_{MD} + E_{TD} \geq 14 \text{ GPa}$$

- a distribution curve representing the relationship between the number of protrusions per surface area (y/mm^2) and the height of the protrusions (x μm), such that the portion of the curve above 20 protrusions/mm^2 crosses the line of

$$\log_{10} y = -18 x + 3.7$$

twice (c.f. figure 1);

- less than 20 protrusions per mm^2 on the film surface have a height greater than 0.13 μm;
- a surface roughness (R_a) of not more than 12 nm;
- a heat shrinkage in the longitudinal direction of not more than 0.1 % when heat treated at 70 °C for one hour under no load; and
- a birefringeance of less than 0.2 and an IV of the copolyester greater than 0.5 dl/g.

The copolyester film of this invention has been surface-roughened by the inclusion of many fine inert particles being incorporated into the molten polymer to impart good slip.

It has been found in accordance with this invention that a copolyester film having a Young's modulus in the longitudinal direction of at least 6.5 GPa, preferably at least 7 GPa, especially preferably at least 7.5 GPa is suitable as a base for electromagnetic recording media.

In order to prevent edge damage to the increasingly thinner tape, it is also important to have a high Young's modulus in the transverse (TD) direction. Therefore, the sum of the Young's modulus in the machine direction plus Young's modulus in the transverse direction should be greater than or equal to 12, and preferably greater than or equal to 14 GPa. The use of the copolyester of the present invention (PENBB) allows these high values to be attained much more easily, with much less risk of breakage during production than with PET film. Also, with PET film higher machine draw ratios are required to impart a higher MD modulus.

As previously mentioned, the inclusion of fine particles in the film produces protrusions in the surface of the film, which prevent the film from sticking or blocking when run over rollers or wound on a roll. While good slip is required for a tape, excessive roughness is detrimental to the recording characteristics, most especially in higher density recording, where large protrusions cause defects and drop-outs in the recording. Therefore, the surface topography of the film, i.e. the size and distribution of the surface protrusions, is important for the performance of the tape substrate. A plot of the number of surface protrusions (y/mm^2) versus the height of these protrusions (x in μm) is a useful description of the surface topography (whereby the portion of the curve having less than 20 protrusions per mm^2 is disregarded). Such a plot always has a peak value at the protrusion height corresponding to the most common protrusions. If that portion of this height distribution curve with protrusions heights higher than those of the abovementioned peak value does not fall below the line described by the equation

$$\log_{10} y = -18x + 3.7,$$

then the surface of the film is excessively rough, and the chance of the existence of protrusions higher than 0.13 μm, which are especially detrimental, is too high. Such films do not make good magnetic tape, especially not for high density recording.

On the other hand, if the peak value of the height distribution curve does not lie above the line

$$\log_{10} y = -18x + 3.7,$$

then the film surface is too smooth and has poor running characteristics (blocking, sticking, wrinkles, creases).

Thus, the height distribution curve must cross the line

$$\log_{10} y = -18x + 3.7$$

twice, once before the peak value and once after.

The height (x) of the protrusions and the number of the protrusions (y/mm^2) are obtained by measuring in accordance with the described procedures below.

A three-dimensionally image of the profile of protrusions on the film surface is made with a three-dimensional roughness tester (Hommel tester) under the following conditions:

stylus diameter	: 2 μm
stylus pressure	: 30 mg
measuring length	: 1 mm
sampling pitch	: 2 μm
cutoff	: 0.25 mm
magnification in the longitudinal direction	: 20,000
magnification in the transverse direction	: 200
scanning	: 150 lines.

The standard level (0 level) of the plane of the profiles is determined in accordance with European Patent Application No. 199,244.

It is also critical that the film of the present invention have a surface roughness (R_a) of not more than 12 nm as stated previously. If the surface roughness (R_a) of the copolyester based film is larger than 12 nm, the surface of the magnetic recording media applied to the copolyester film cannot retain the sufficient electromagnetic conversion characteristics. The preferred surface roughness should not be more than 10 nm, and especially preferred surface roughness is between 8 to 4 nm.

The surface roughness (R_a) of the film is measured by the procedure described in European Patent Application No. 199,244 with the equipment previously described.

It has been found in accordance with the present invention that the use of the copolyester PENBB allows the production of film with suitable low shrinkage values without the use of special MD relaxation techniques and procedures. Longitudinal shrinkage of less than or equal to 0.1 percent after exposure at 70°C under no load can be obtained, which gives high quality magnetic recording media. Low shrinkage in both the MD and TD directions as well as high Young's modulus in both the MD and TD directions result in a highly dimensionally stable film having a substantial reduction in edge damage or distortion of the magnetic recording media.

In order to provide good handling and winding properties, the film composition must be such that the surface is rough. This can be achieved by incorporating fine inert insoluble particles into the film. By "inert", it is meant any particle which does not react with the monomer, polymer or coating during the manufacture of the polymer, the film or the tape.

The addition of fine particles to the monomers before or during polycondensation or to the polymer before extrusion is the typical procedure known in the art. Such inert fine particles, either in agglomerated form, or finely dispersed form can be kaolin, talc, silica, carbonates of magnesium, calcium, or barium; sulfates of calcium, or barium; phosphates of lithium, calcium, or magnesium; oxides of aluminum, silicone, titanium, or zirconium, or mixtures of these; lithium fluoride, carbon black, and the organic acid salts of calcium, barium, zinc, and manganese. It is also possible to employ fine particles made of crosslinked polymers such as polystyrenes, polyacrylates, and polymethacrylates. The particles may be all of one type or mixtures of several types. The shape of the particles can be irregular, flaky, spherical, or elongated, preferably spherical. The hardness, density, and color of the particles is immaterial. The average size of the particles should be less than 10 μm preferably less than 3 μm, still more preferably less than 2 μm. Silicone dioxide, titanium dioxide and calcium carbonate are especially preferred. The inert solid fine particles preferably have an average particle diameter of 0.05 to 0.6 mm, especially 0.08 to 0.4 mm. The amount of inert solid fine particles to be incorporated into the copolyester is generally 0.01 to 1.5 percent by weight, preferably 0.03 to 1 percent by weight, especially preferably 0.05 to 0.6 percent by weight, based on the weight of the copolyester.

The copolyester film of the present invention generally has a thickness of 2 to 12 μm and contains many fine protrusions on its surface. However, no large protrusions exist and the high Young's modulus and excellent dimensional stability produce a superior film for magnetic recording media of high quality.

In the production of magnetic recording medium, a magnetic recording layer can be formed on the base film and by any of the well known techniques

and materials known in the prior art. Producing magnetic recording media from the copolyester based film of the present invention is not a part of the present invention.

The Young's modulus was determined by obtaining a film sample 15 mm wide and 15 cm long was stretched by a Zwick universal tensile tester with an interchuck distance of 100 mm at a head speed of 10 mm per minute. The modulus of the sample was calculated from a tangent to the rising part of the load-elongation curve generally taken between 0.4 to 0.6 percent of the elongation.

The following examples illustrate the present invention in greater detail. However, the examples are not intended to limit the present invention. The various alternatives, modifications and variations apparent to those skilled in the art from the following examples are intended to be within the scope of the present invention.

EXAMPLE 1

10 parts of silica (average particle diameter 0.15 μm) is added to 90 parts of ethylene glycol and are mixed to form a slurry.

289 parts by weight of dimethyl 2,6-naphthalene dicarboxylate, 322 parts by weight of dimethyl 4,4'-bibenzoate, 368 parts by weight of ethylene glycol and 0.7 parts of manganese acetate tetrahydrate are initially introduced into a conventional polycondensation reactor provided with a blanket gas (nitrogen) with pressure equalization, a thermometer, a condenser, a vacuum connection, and a stirrer. The mixture is heated at 220°C for 2.5 hours, during which time methanol is distilled off. 15 parts of the silica/ethylene glycol slurry are added along with 0.675 parts by weight of triphenyl phosphate and 0.226 parts of antimony trioxide are added as polycondensation catalysts. The mixture is heated to 270°C with stirring. Vacuum is applied and the temperature is raised to 285°C and maintained for 2.5 hours.

The residual melt is pelletized. The pellets are white, opaque and crystalline. An inherent viscosity of 0.56 dl/g is determined for the pellets (measured at a concentration of 0.1 g/ml in pentafluorophenol/hexafluoroiso

propanol at a weight ratio of 1:1 at 25°C in an Ubbelohde capillary viscosimeter).

The pellets are further polycondensed for 20 hours at 240°C under vacuum in the solid phase. Thereafter, the inherent viscosity is 1.1 dl/g. As expected, no T_g or T_{cc} are discernable in the DSC recording for the crystalline granules. The melt point (T_m) temperature is 281°C.

EXAMPLE 2

The PENBB pellets from Example 1 containing 0.2 percent by weight silica particles are melted in an extruder at 280°C to 320°C and extruded through a die slot onto a chill roll at 30°C. A 120 μm thick amorphous film is removed from the chilled roll and stretched 3.5 times in the MD direction at 140°C, then stretched 3.5 times in the TD direction at 140°C. The copolyester film is subsequently heat set at 260°C for 10 seconds. The resulting mechanical properties of the resulting 10 μm thick film are:

TABLE 1

CHARACTERISTICS	MD	TD	UNITS
Tensile Modulus	9.1	8.0	GPa
Tensile Strength	220	190	MPa
Elongation At Break	27	17	%

The distribution of the heights of the protrusions and the number of protrusions on the film surface is as shown in curve A of Figure 1. The surface roughness (R_a) is about 8 nm.

EXAMPLE 3

Example 2 is repeated except that 0.3 percent by weight of titanium dioxide having an average particle diameter of 0.4 μm is added instead of the silica. To incorporate the proper amount of titanium dioxide into the polymer prepared as in Example 1, 23 parts of the titanium dioxide slurry are added.

The properties of the film are substantially the same as those set forth in Example 2. The distribution curve of the film is shown as curve B in Figure

1. Because of the larger average particle diameter of the titanium oxide, the film surface is coarser than the film of Example 1.

Thus, it is apparent that there has been provided, in accordance with the invention, an improved copolyester film for magnetic recording media that fully satisfies the objects, aims and aspects set forth above. While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations as falling within the sphere and broad scope of the present invention.

THAT WHICH IS CLAIMED IS:

1. A biaxially oriented copolyester film having many fine protrusions on its surface comprising a copolyester having at least 25 mole percent of its diacid derived content of 4,4'-bibenzoate and having a Young's modulus in machine direction greater than or equal to 6.5 GPa

$$E_{MD} \geq 6.5 \text{ GPa.}$$

2. A biaxially oriented copolyester film according to claim 1, wherein the sum of the Young's modulus values in the machine direction (E_{MD}) and the transverse direction (E_{TD}) is greater than or equal to 12 GPa

$$E_{MD} + E_{TD} \geq 12 \text{ GPa.}$$

3. A biaxially oriented copolyester film according to claim 1 or 2, having a distribution curve representing the relationship between the number of protrusions per surface area (y/mm^2) and the height of the protrusions (x/μm), such that the portion of the curve above 20 protrusions/mm^2 crosses the line of

$$\log_{10} y = -18x + 3.7$$

twice.

4. A biaxially oriented copolyester fim according to claim 1, 2 or 3 with less than 20 protrusions per mm^2, having a height greater than 0.13 μm.

5. A biaxially oriented copolyester film according to any one or more of the previous claims with a surfce roughness (R_a) of not more than 12 nm.

6. A biaxially oriented copolyester film according to any one or more of the previous claims, having a heat shrinkage in the longitudinal direction of not more than 0.1 % at 70 °C for one hour under no load.

7. A biaxially oriented copolyester film according to any one or more of the previous claims, wherein the heat shrinkage in the transverse direction is

not more than 0.1 percent when heat treated at 70°C for 1 hour under no load.

8. A biaxially oriented copolyester film according to any one or more of the previous claims having a birefringeance of less than 0.2 and wherein the copolyester has an IV-value of greater than 0.5 dl/g.

9. A biaxially oriented copolyester film according to any one or more of the previous claims, wherein said copolyester includes other dicarboxylic acids or their ester equivalents including terephthalic acid, isophthalic acid, phthalic acid, naphthalene-2,6-dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, di-(4-phenyl) acetylene dicarboxylic acid, 1,2 di-(4-phenyl)-ethene dicarboxylic acid, sebacic acid, malonic acid, adipic acid, azelaic, glutaric acid, suberic acid, succinic acid and mixtures of these.

10. The biaxially oriented copolyester film of Claim 9, wherein said copolyester is formed from glycols including ethylene glycol, diethylene glycol, polyethylene glycol, butane diol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,10-decanediol and cyclohexane dimethanol.

11. The biaxially oriented copolyester film of any one or more of the preceeding claims, wherein the copolyester is selected from the group consisting of polyethylene terephthalate bibenzoate, polybutylene terephthalate bibenzoate, polypropylene terephthalate bibenzoate, polyethylene naphthalate bibenzoate, polyethylene terephthalate/isophthalate bibenzoate, polyethylene terephthalate/adipate/bibenzoate and polyethylene terephthalate/-sulfoisophthalate/bibenzoate.

12. The biaxially oriented copolyester film of Claim 11, wherein the copolyester is polyethylene naphthalate/bibenzoate.

13. A biaxially oriented copolyester film according to any one or more of the previous claims, wherein said copolyester film includes inert solid fine particles dispersed therein.

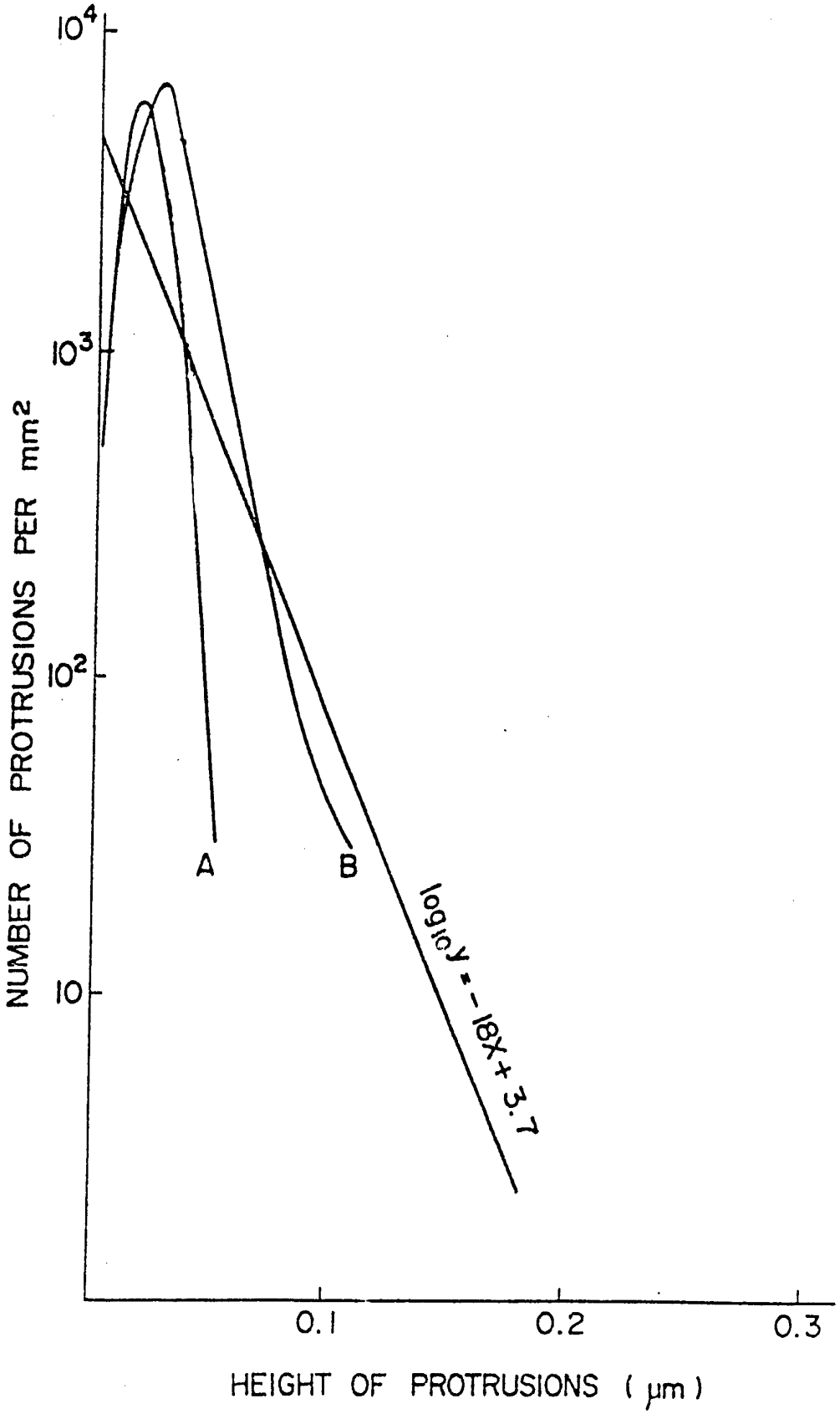
14. The biaxially oriented copolyester film of Claim 13, wherein said inert solid fine particles are selected from the class consisting of kaoline; talc; silica; carbonates of magnesium, calcium, barium; sulfates of calcium, barium; phosphates of lithium, calcium, magnesium; oxides of aluminum, silicone, titanium, zirconium; lithium fluoride; carbon black; organic acid salts of calcium, barium, zinc, manganese; crosslinked polymers, and mixtures thereof.

15. The biaxially oriented copolyester film of Claim 14, wherein said inert fine particles are silicone dioxide.

16. The biaxially oriented copolyester film of Claim 14, wherein said inert fine particles are titanium dioxide.

17. Use of a biaxially oriented copolyester film of Claim1 as a substrate for magnetic tapes.

Fig. 1


10^4
10^3
10^2
10
NUMBER OF PROTRUSIONS PER mm^2
A
B
$\log_{10} y = -18X + 3.7$
0.1
0.2
0.3
HEIGHT OF PROTRUSIONS (μm)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10711

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 33/00; DO6N 7/04
US CL :428/ 141, 143, 145, 323, 325, 446, 480, 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/ 141, 143, 145, 323, 325, 446, 480, 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.
Y	US, A, 4,568,599 (ONO) 04 FEBRUARY 1986, ENTIRE DOCUMENT	1-3
Y	US, A, 4,619,869 (KIRIYAMA) 28 OCTOBER 1986, ENTIRE DOCUMENT	1-3
Y	US, A, 4,833,024 (MUELLER) 23 MAY 1989, ENTIRE DOCUMENT	1-3
Y	US, A, 5,096,733 (SAKAMOTO) 17 MARCH 1992, ENTIRE DOCUMENT	1-3

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

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 24 FEBRUARY 1993	Date of mailing of the international search report 14 APR 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer ELIZABETH EVANS Telephone No. (703) 308-2351

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10711

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. [X] Claims Nos.: 17
because they relate to subject matter not required to be searched by this Authority, namely:

Claim 17 is directed to a "USE" PCT Article 17(2)(a)(i). "Use" claims not in method terminology is not search by this ISA.

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. [X] Claims Nos.: 4-16
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.