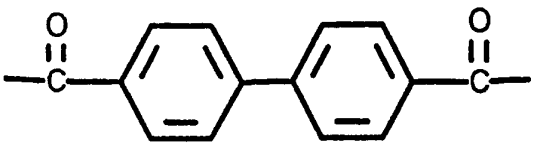




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(54) Title: IMPROVED BIAXIALLY ORIENTED COPOLYESTER FILM FOR MAGNETIC RECORDING MEDIA (57) Abstract Disclosed herein is a biaxially oriented mono- or multilayer copolyester film wherein the two surfaces of the film have different surface roughness, characterized in that at least one layer essentially consists of PENBB and the first surface of the film has large protrusions with a diameter of 0.2 to 2 μm and the second surface has either no protrusions or small protrusions with a diameter smaller than those of the large protrusions on the first surface. PENBB as mentioned herein is a copolyester containing units of formula (I).  (I)		

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IMPROVED BIAXIALLY ORIENTED COPOLYESTER FILM FOR MAGNETIC RECORDING MEDIA

5 Background Of The Invention

1) Field Of The Invention

This invention relates to an improved biaxially oriented copolyester film for thin metallic magnetic recording media. More specifically, this invention relates to a biaxially oriented copolyester film which has a smooth surface and
10 excellent running characteristics onto which a magnetic recording layer can be coated to form a thin film magnetic recording media. The copolyester employed contains at least 25 mole percent of its diester or diacid being 4,4'-bibenzoic acid. The remainder of the copolyester may be formed from other diacids or diesters as is known in the art.

15 2) Prior Art

Improving the signal emanating from magnetic tape has been the goal of every producer. In particular, background noise, hiss or drop-outs are to be limited to as low a level as possible. From the viewpoint of noise, the surface of the substrate is preferably as smooth as possible. On the other
20 hand, from the viewpoint of processability and handling of the substrate, particularly winding and unwinding, the smoothness of the film surface is a detriment. In particular, smoothness of the film surface results in poor slipperiness between film surfaces and causes the phenomenon of blocking. Accordingly, the surface of the substrate support is required to be smooth on
25 the side that will carry the magnetic recording layer and rough on the surface which will contact adjacent surfaces upon winding. PET (polyethylene terephthalate) substrates with improved surfaces are disclosed for instance in European Patent Application 0 203 604 or German Patent Application 34
14 310, but these films have inherent problems with other demands on
30 improved tape substrates.

Another demand associated with the magnetic tape industry is the desire to create thinner and thinner magnetic recording media tape. This will

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permit more and more information to be stored in the same space or in a smaller volume, while allowing better images for video tape and more crisp sounds in audio tape. Good mechanical properties of the substrate are desirable so that the magnetic recording film can be reduced in thickness.

5 Accordingly, there is a demand for high stiffness (tensile modulus) and strength so that the thinness of the film can be decreased.

As one solution to increasing the strength of tapes, especially PET tapes, a "super-tensilized" process can greatly increase the strength of the magnetic recording media especially in the longitudinal "machine direction".

10 However, such film has poor transverse directional strength which may cause the film to fold upon itself resulting in increased jamming in the recorder, which ruins the tape. Moreover, as magnetic recording media become thinner, skewing can occur where the magnetic tape was pulled beyond its physical limits. Skewed tapes also result in a loss of recorded information.

15 Another problem associated with magnetic recording tape is thermal stability. It is not unusual in the summer for the interior of a car to achieve a temperature in excess of 65°C. Magnetic recording tapes that shrink are undesirable. Shrinkage can occur when the magnetic recording media is exposed to elevated temperatures such as those present in the summer inside
20 automobiles. (For the purposes of measurement, higher temperatures are often chosen to make differences in substrates more pronounced.)

It is an object of the present invention to produce a film having superior mechanical properties, including high Young's modulus properties, good tensile strength, and low shrinkage.

25 Another aim of the present invention is to produce a smooth surface on a substrate with excellent running characteristics and good abrasion resistance such that the substrate can be further processed to make excellent magnetic recording film.

30 Other aims, objects and aspects of this invention, along with its advantages will become apparent upon the following detailed description.

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Summary Of The Invention

The present invention relates to a biaxially oriented mono- or multilayer copolyester film wherein the two surfaces of the film have different surface roughness, characterized in that at least one layer essentially consists of
5 PENBB and the first surface of the film has large protrusions with a diameter of 0.2 to 2 μm and the second surface has either no protrusions or small protrusions with a diameter smaller than the ones of the large protrusions on the first surface.

In a preferred embodiment the invention relates to a biaxially oriented
10 PENBB film (B) having fine particulate filler media incorporated therein to provide surface roughness. One or both sides of the film may carry a cover layer (layer A and optional layer C), which modifies the roughness of the surface. One side of this film (A) is smoother than the other (side B or C), the smoother side A being suitable for coating with high density magnetic
15 recording layers such as of the metallic type. Layer C, if present, serves to improve the abrasion resistance.

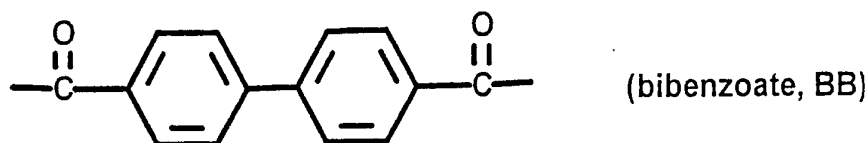
In the broadest sense, the present invention relates to a biaxially oriented PENBB film, wherein one surface (A) is smooth and the other surface (B or C) has large protrusions with an average diameter of 0.2 to 2 μm and an
20 average height of 2 to 20 nm arranged at a density of least 10^3 but less than $10^6/\text{mm}^2$; and optional small protrusions with a diameter of 10 to 100 nm and an average height of 1 to 10 nm distributed at a density of from 10^6 to $10^9/\text{mm}^2$; and having the summation of the Young's modulus in the machine direction and the Young's modulus in the transverse direction being greater
25 than or equal to 12 GPa with a shrinkage in each direction being less than 1 percent at 150°C at 15 minutes.

Description Of The Preferred Embodiments

Suitable copolyesters for the present invention must contain at least 25
30 mole percent of the diester or diacid of 4,4'-bibenzoic acid or 4,4'-dimethyl-

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naphthalate, containing the following repeat unit:



For the purpose of this invention such BB-containing copolyesters are called PENBB.

5 The remainder 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, sebacic acid, malonic acid, adipic acid, azelaic acid, glutaric acid, suberic acid, succinic acid, and the like, or mixtures of these. Naphthalene-2,6-dicarboxylic acid or
10 its ester equivalent is the preferred portion for the remainder of the copolyester.

 Suitable diols employed in the present invention include ethylene glycol, diethylene glycol, polyethylene glycol, butane diol, 1,5 pentane diol, 1,6-
15 hexane diol, naphthalene glycol, 1,10-dexane diol, 1,4-cyclohexane dimethylol, and the like. Ethylene glycol is the preferred glycol.

 Useable PENBB copolyester of the present invention can comprise, for example, polyethylene terephthalate/4,4'-bibenzoate, polybutylene terephthalate/4,4'-bibenzoate, polypropylene terephthalate/4,4'-bibenzoate,
20 polyethylene naphthalate/4,4'-bibenzoate, polyethylene terephthalate/azelaate/4,4'-bibenzoate, polyethyleneterephthalate/adipate/4,4'-bibenzoate, polyethylene terephthalate/ 4,4'-bibenzoate, and the like.

 In a preferred embodiment, the PENBB comprises a copolyester prepared from ethylene glycol and a mixture of roughly equimolar amounts
25 (i.e. molar ratio 6:4 to 4:6) of the dialkyl esters of 4,4'-bibenzoic acid and 2,6-naphthalene dicarboxylic acid or the dicarboxylic acids themselves. It may be advantageous to employ an excess amount of glycol in order to influence the reaction kinetics. After reaction of the diacids or diesters with glycol, a polycondensation reaction is carried out according to known

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processes. The diacids or their ester equivalents and the glycols are mixed uniformly and heated to approximately 200°C in the presence of a transesterification catalyst, as is well known in the art. The reaction yields oligomeric or low molecular weight polyester which is subsequently subjected to the polycondensation reaction in the presence of polycondensation catalysts. Additionally, stabilizers, antioxidants, delustrants, pigments, fillers, and antistatic agents, may be uniformly mixed with the raw materials or copolyester.

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

U.S. Patent No. 3,008,934 discloses copolyesters containing as acid derived units 4,4'-biphenylate 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 and dimensional stability in comparison to PET film are not disclosed in U.S. Patent No. 3,008,934.

The PENBB film of the present invention can be manufactured by an extrusion process. 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.

The copolyester resin is first heated to a molten stage 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 copolyester. The cast sheet is removed

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from the casting drum and axially stretched in one direction, either in the direction of the film travel (machine direction) or perpendicular to the machine direction (transverse direction), while being heated to a temperature between the glass transition temperature and about 30°C above the cold crystallization temperature (both temperatures being easily measured by differential scanning colorimetry, DSC).

The PENBB film of this invention is biaxially oriented (stretched in both machine direction and the transverse direction). The total stretch ratio in the machine direction and the transverse direction lie between 1:2 and 1:10, preferably between 1:2.5 and 1:5. The product of the total stretch ratios should be between 1 - 30 and preferably between 5 - 20. Biaxial drawing is performed such that the birefringence is < 0.2 , preferably < 0.1 to ensure adequately isotropic properties. Birefringence 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 step occurs at a temperature between the cold crystallization temperature and the melt temperature of the copolyester composition. After heat setting, the film may be wound on a roll.

It is desirable for the film to have a final total thickness between 2 and 15 μm , preferably between 4 and 12 μm .

The main feature of the biaxially oriented PENBB film of this invention is that the surface of the rougher side (B or C) contains:

- (a) many large protrusions with a diameter of 0.2 to 2 μm , and a height from about 2 to 20 nm; and
- (b) optionally many small protrusions with a diameter of about 10 to about 100 nm and a height of about 1 to 10 nm.

The other (smoother) side A may contain such small protrusions but should contain no large ones. On this Surface A, it is contemplated that a thin metallic film as a magnetic recording layer is to be applied.

The density of the distribution of the large and small protrusions is also

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important. The density of distribution for the large protrusions is at least 10^3 but at less than $10^6/\text{mm}^2$. The density of distribution for the small protrusions is from 10^6 to $10^9/\text{mm}^2$. If these large and small protrusions on the surfaces of the copolyester substrate satisfy these conditions, noise in resulting magnetic metal recording layer applied to side A is drastically reduced, and the resultant magnetic film has markedly superior noise level with excellent running properties, thermal stability, and appropriate thickness reduction.

Preferably, the large protrusions have a diameter of 0.5 to 2 μm , especially 0.5 to 1.5 μm and a height of 5 to 20 nm, especially 7 to 15 nm, and the density of this distribution is from 10^4 to $10^5/\text{mm}^2$. The small protrusions preferably have a diameter of 50 to 100 nm and a height from about 1 to 10 nm, especially 2 to 7 nm, and the density of distribution of small protrusions is from 10^7 - $10^8/\text{mm}^2$.

The diameter, height and distribution density of the large and small protrusions on the surface of the PENBB film of the present invention are measured by the following methods.

For the diameter of the large protrusions, the film surface is photographed through a differential interference microscope and the diameters of the protrusions are measured on the basis of the photograph at a magnification of about 400 X with an average value being calculated.

In the case of the optional small protrusions, the surface is photographed with a scanning electron microscope at a magnification of about 45,000 X. The average diameter is calculated from that of 20 protrusions.

To measure the height of the large protrusions, the distance from the peak to the bottom of the protrusions is measured by the use of a profilometer having a high precision stylus contacting the surface of the biaxially oriented PENBB film of the present inventions.

In the case of the optional smaller protrusions, the height is measured with a scanning electron microscope using a magnification of about 80,000 X in the planar direction and about 800,000 to 2,400,000 X in the vertical direction. The average height is calculated from 10 protrusions.

To determine distribution density of the protrusions for both the large

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and small protrusions, 5 photographs of the film surface of the type used to determine the large or small protrusion diameter are taken and the number of protrusions determined from the photograph and their density of distribution is calculated per square millimeter of film surface. Generally, for the large protrusions measuring both the diameter and the density distribution the photographs are taken at about 400 X. For determining the diameter of the small protrusions, the scanning electron microscope is generally about 45,000 X. For determining the height and distribution density of the small protrusions, the scanning electron microscope is at about 80,000 X.

10 Said large and small protrusions in the surface of the film are conveniently produced by the inclusion of larger and smaller inert solid fine particles in the surface layer of the film.

While there is no limitation on the inert solid fine particles to be included in the copolyester, so long as they do not except any deleterious effects on the physical and chemical properties of the copolyester, suitable particles to provide good handling and winding properties of the film are as follows. Such fine particles can be:

- (a) silicon dioxide (including its hydrate, diatomaceous earth, silica sand and quartz);
- 20 (b) alumina;
- (c) silicates containing at least 30 % by weight of SiO_2 [for example, amorphous or crystalline clay minerals, aluminosilicates (including calcined products or hydrates), chrysotile, zirconium, flyash, etc.];
- 25 (d) oxides of metals such as Mg, Zn, Zr and Ti;
- (e) sulfates of Ca, Mg and Ba;
- (f) phosphates of Li, Na and Ca (including monohydrogen salts or dihydrogen salts);
- (g) benzoates of Li, Na and K;
- 30 (h) terephthalates of Ca, Ba, Zn and Mn;
- (i) titanates of Mg, Ca, Ba, Zn, Cd, Pb, Sr, Mn, Fe, Co and Ni;
- (j) chromates of Ba and Pb;

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- (k) carbon (such as carbon black and graphite);
- (l) glass (glass powder and glass beads);
- (m) carbonates of Ca and Mg;
- (n) fluorspar;
- 5 (o) sulfides of Zn and Mo;
- (p) powders of organic polymeric substances such as polytetrafluoroethylene polyethylene; and
- (q) talc, lithium fluoride, and any organic acids salts of Ca, Ba, Zn and Mn.

10

It is also possible to use fine particles made of cross-linked polymers such as polystyrenes, polyacrylates or polymethacrylates. Particles may be of one type or mixtures of several types. The shape of the particles can be irregular, flaky, spherical or elongated. The inert solid fine particles preferably

15 have average diameter of 0.05 to 2 μm , especially 0.05 to 1 μm . The above-described surface topography is produced by incorporating the larger inert solid fine particles in the base layer of the biaxially oriented PENBB film (layer B) and the optional smaller inert solid fine particles in the cover layers (A and C). The cover layers make up between 0.05 and 20 % of the total thickness

20 of the film, wherein the required thickness depends on the type of the larger inert fine particles in use and can be determined by simple experimentation.

The larger inert solid fine particles should not contain more than 5% by weight, and especially not more than 2% by weight of particles more than 1 μm in diameter. The amount of the larger inert fine particles to be incorporated

25 into the copolyester is generally 0.005 to 1 % by weight, preferably 0.005 to 0.5% by weight, based on the weight of the copolyester.

The larger inert solid fine particles can be dispersed within the copolyester by a variety of known methods. For example, the inert solid fine particles can be added in the form of glycol slurry during the ester interchange

30 or transification reaction. Also, the particles can be added to the reaction chamber just before or during the polycondensation reaction such that the particles are uniformly dispersed throughout the copolyester. Incorporation

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of the inert solid fine particles produces the larger protrusions on the film surface in layer B or C after stretching and heat setting the PENBB film.

The optional smaller protrusions are produced by including smaller inert fine particles in the cover layers A and C. Such optional smaller fine particles generally have an average diameter of 10 to 100 nm, preferably 50 to 100 nm. Because the cover layers A and C are relatively thin, it is essential that the optional smaller fine particles do not contain an excessive amount of larger particles, i.e. the amount of particles larger than 0.3 μm should make up less than 5 weight-% of the total smaller fine particles.

The cover layers A or C can be produced by either of two methods, coating the film, preferably in-line, with a polymeric dispersion or solution or by coextruding the base film with layers of other polymer(s), preferably a polyester and more preferably a copolyester. The smaller fine particles are optionally contained in the coating dispersion or solution or the coextruded polymer. In the case of the coextruded polymer, they are preferably dispersed in a method similar to that used for the larger fine inert particles in layer B.

In the case that the small protrusions on surface A and optionally C of the PENBB film are formed by coating, a coating composition composed of inorganic or organic smaller inert solid fine particles and organic polymeric binder is applied to one or both the first surfaces of the film which has been stretched in at least one direction, preferably between the draws for biaxially orienting the PENBB film. The inert solid fine particles incorporated or uniformly blended with the copolyester referred to above may also be employed for the coating composition, however, the size restrictions for the smaller inert fine particles noted above apply.

The coating composition may be solvent-based or aqueous-based. Preferably, an aqueous based coating composition is employed. Consequently, the polymeric binder is preferably water soluble or water dispersable. Known aqueous-based coating compositions based on modified polyester copolymers, acrylates, methacrylates, melamine resin, polyvinylalcohol, polyethers, starches, cellulose, etc. are acceptable. Solvent based coatings employing polyurethane, polyvinylalcohol, melamine resin, epoxy resins, as are

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conventional and known in the art are also satisfactory.

The amount of smaller inert solid fine particles in the organic polymeric binder may vary depending upon the degree of biaxial orientation employed. Generally, a suitable amount of smaller inert solid fine particles is 0 to 50 parts by weight and more preferably 20 to 30 parts by weight, per 100 parts by weight of the organic polymeric binder employed. The coating composition may also contain suitable additives such as cross-linking agents, polymerization catalysts, heat stabilizers or UV absorbers, anti-static agents, surface active agents or filler dispersion or lubricants in effective amounts. The suitable amount of the organic polymeric binder is generally 1 to 20% by weight of the coating composition and preferably 2 to 10% by weight of the coating composition. The coating thickness on the surface of the biaxially oriented PENBB film, on a dry weight basis is generally 1 to 5 mg/m², and preferably 1 to 2.5 mg/m². The coating composition can be applied by means of roll coating, gravure coating, air knife coating, meniscus coating, reverse gravure coating, or dipping. Drying and curing the coated film may be carried out at a temperature sufficient to quickly evaporate the solvent or aqueous portion of the coating composition. When the coating is applied between draws of the biaxially oriented film, generally the last draw and the heatsetting stage of the process for producing the biaxially oriented PENBB film is sufficient to evaporate the solvent and the water.

In the case that the surface topography of sides A and C of the biaxially oriented PENBB film is produced by coextrusion, melts of these layers, optionally containing the above-mentioned smaller solid inert fine particles, are supplied to multimanifold coextrusion die, where they are combined with the melt for layer B, and the combined melt layers are extruded onto a chill roll.

The coextruded polymer may be any thermoplastic polymer which will survive the film making and drawing processes of the biaxially oriented copolyester film, and exhibit sufficient adhesion to the copolyester layer B. Preferably, polyesters and copolyesters are used for coextruded layers A and C, particularly those with a melting point lower than that of the copolyester of layer B. Such polyesters and copolyesters may be, for example, poly-

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ethylene terephthalate and its copolymers with other diacids, such as isophthalic acid, 5-sodium sulfoisophthalic acid, phthalic acid, adipic acid, sebacic acid, naphthalene 2,6-dicarboxylic acid and/or 4,4'-bibenzoic acid, etc. and/or other diols such as propylene glycol, butylene glycol, p-xylylene diol and/or 1,4-cyclohexane-dimethylol, etc., poly-1,4-cyclohexanedimethylene terephthalate and its copolymers, polybutylene terephthalate, polyethylene-2,6-naphthalate and its copolymers and polyethylene 2,6-naphthalate/4,4'-bibenzoate and copolymers thereof. The amount of the smaller inert fine particles contained in the coextruded layers may range from 0 to 50 % by weight of the total layer. Layers A and optional layer C may be made up of the same or different polymers with the same or different particle content. Layer C, if present, preferably is thinner than layer A.

After coextrusion with layer A and optional layer C, the drawing and heat-setting of the coextruded, biaxially oriented PENBB film proceeds as described hereinbefore.

Desireably, the coated or coextruded smooth surface A of the biaxially oriented PENBB film has a surface roughness value R_a not greater than 5 nm and R_z not greater than 100 nm.

The rougher surface B or C of the coated or coextruded biaxially oriented PENBB film of the present invention has a surface roughness (R_a) generally from 2 to 100 nm, and preferably from 3 to 20 nm. The average of the difference between the highest peaks and lowest valleys (R_z) of the surface is generally from 20 to 1,000 nm and preferably from 30 to 200 nm.

The following examples serve to illustrate the invention. In these examples, the following measurement methods are employed:

The average center line surface roughness

R_a is measured by using a high precision surface roughness tester - profilometer. A sample of film approximately 1.25 cm in length is employed and the profilometer is drawn across the surface of the film under a load 30 mg with a cut-off of 0.08 mm using a stylus with a radius of 2 μ m. Usually, the surface roughness is an average of at least 4 measured values.

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The average surface roughness

The peak-to-valley average surface roughness (R_z) is measured using the profilometer, load, stylus, and cut-off previously mentioned. The average of the difference between the high peaks and low valleys is generally the average of 5 measurements.

Tensile properties

Tensile properties were determined in a tensile testing machine produced by Zwick GmbH of Ulm, Germany, using the following parameters:

10	sample dimensions	:	150 x 15 mm
	testing length	:	100 mm
	draw rate (modulus)	:	10 mm/min
	draw rate (tensile strength) and elongation	:	100 mm/min

15 Heat shrinkage

Heat shrinkage was determined by measuring the dimensional change of a 100x100 mm square film sample after 15 minute exposure to 150 °C in a forced-air oven.

EXAMPLE 1

20 (preparation of neat copolyester)

306 parts by weight of dimethyl 2,6-naphthalene dicarboxylate, 303 parts by weight of dimethyl 4,4'-bibenzoate, 368 parts by weight of ethylene glycol and 0.7 parts of manganese acetate tetrahydrate are introduced into a conventional polycondensation reactor provided with a blanketing gas line (N_2), pressure equalization, a thermometer, a condenser, a vacuum line and stirred for 2.5 hours, during which time methanol distills off. 0.675 parts by weight of triphenyl phosphate and 0.2259 parts of antimony trioxide are then added as polycondensation catalysts and 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 granulated. The granules are white, opaque and crystalline. An IV value of 0.56 dl/g is determined for the granules (measured

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at a concentration of 0.1 g/ml in pentafluorophenol/hexafluoroisopropanol [weight ratio 1:1] at 25 °C).

The granules are further condensed for 20 hours at 240 °C under vacuum in the solid phase. After this treatment the IV value is 1.1 dl/g. The
5 melting point (T_m) is 270 °C.

EXAMPLE 2

(preparation of copolyester with larger inert fine particles)

The same procedure as in Example 1 is followed, except that 289 parts
by weight of dimethyl 2,6-naphthalene dicarboxylate and 322 parts by weight
10 of dimethyl-4,4'-bibenzoate are employed and 23 parts of a slurry of BaSO_4
particles in ethylene glycol is added to the transesterified mixture just before
adding the triphenyl phosphate and antimony trioxide. This slurry is prepared
by dispersing 10 parts by weight of BaSO_4 with an average particle diameter
of 1.0 μm in 30 parts by weight of ethylene glycol. The resulting copolyester
15 contains 0.3 wt.-% BaSO_4 particles and melts at 281 °C.

EXAMPLE 3

The copolyesters prepared according to examples 1 and 2 are each
melted in separate extruders, sent to a multimanifold slot die via 2 gear
pumps, combined to form a two-layer film, where the polymer from example
20 1 forms the layer A and the polymer of example 2 forms the base layer B, and
cooled on a chill roll to 20 °C. The thus obtained amorphous film is heated
to 125 °C and drawn by a factor of 3.5 in MD, then by 3.5 in TD. The film
is then heat set under restraint at 260 °C for 10 seconds to afford a two-
layer biaxially oriented PENBB film 8 μm thick with a rough and a smooth side,
25 which can be wound with no difficulty. The thickness of layer A is 0.5 μm
and that of layer B is 7.5 μm .

The mechanical properties are:

	MD	TD	Unit
tensile modulus	9.2	8.0	GPa
tensile strength	240	180	MPa

30

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	MD	TD	Unit
elongation at break	25	7	%

The R_a values of each side are:

rough side (B)	15	nm
smooth side (A)	4	nm

The shrinkage, measured after 25 min. treatment in a forced-air oven at 150 °C is 0.3 % in both MD and TD. The water pickup of the film at 50 % r.h. and 25 °C is 0.04 %.

EXAMPLE 4

(comparative)

A monolayer film is prepared from the copolyester according to Example 1 in a manner similar to example 3, except that only one extruder is used. After drawing, it is difficult to wind this film due to wrinkles and blocking.

The roughness R_a of a portion of the film is:

side A	4	nm
side B	4	nm

EXAMPLE 5

A copolyester is prepared similarly to example 2, except that instead of BaSO_4 , kaolin particles with an average diameter of 0.1 μm were added in amount to give a final concentration of 0.1 wt.-%.

An aqueous 2 wt.-% solids coating composition is prepared from aluminum acrylate, polyoxyethylene diol, polyoxyethylene diglycidyl ether, polyoxyethylene nonyl phenyl ether and colloidal silica with an average particle size of 75 nm in a weight ration of 10:5:2:1:9.

The copolyester is melted in an extruder at 310 °C and extruded as a

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monolayer film through a slot die onto a chill roll temperature controlled at 25 °C, using pinning to give an amorphous sheet. The amorphous sheet is stretched in the longitudinal direction by a factor of 3.5 at a temperature of 125 °C. The film is then coated on both sides of the film by means of
5 gravure rolls carrying different amounts of coating, whereupon the film is stretched in the transverse direction by a factor of 3.5 at 125 °C, and heat set at 260 °C, to provide a three-layer, biaxially oriented PENBB film with a total thickness of 8 μm . Layer A has a thickness of 20 nm and layer C a thickness of 2nm.

10 The film can be handled and wound easily without blocking, exhibiting excellent abrasion resistance. The R_a of surface A is 4 nm and that of surface C is 7 nm. The R_z of surface A is 60 nm and that of surface C is 80 nm. Surface C has 20,000/mm² large protrusions with an average height of 11 nm and average diameter of 0.8 μm and 4·10⁷/mm² small protrusions with an
15 average height of 4 nm and an average diameter of 70 nm.

Thus, it is apparent that there has been provided, in accordance with the invention, a biaxially oriented PENBB film useful as a magnetic tape substrate film, that fully satisfies the objects, aims, and aspects set forth above. While the invention has been described in conjunction with the
20 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 fall within the sphere and broad scope of the present invention.

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WHAT IS CLAIMED IS:

1. A biaxially oriented mono- or multilayer copolyester film wherein the two surfaces of the film have different surface roughness, characterized in that at least one layer essentially consists of PENBB and the first surface of the film has large protrusions with a diameter of 0.2 to 2 μm and the second surface has either no protrusions or small protrusions with a diameter smaller than the ones of the large protrusions on the first surface.
2. The biaxially oriented copolyester film according to Claim 1, wherein the first surface in addition to the large protrusions has small protrusions with a diameter of 10 to 100 nm.
3. The biaxially oriented copolyester film according to Claim 1 or 2, wherein the large protrusions have a height from 2 to 20 nm.
4. The biaxially oriented copolyester film according to any one or more of Claims 1 to 3, wherein the protrusions of the second surface are small protrusions with a diameter of 10 to 100 nm.
5. The biaxially oriented copolyester film according to any one or more of Claims 1 to 4, wherein the small protrusions have a height of 1 to 10 nm.
6. The biaxially oriented copolyester film according to any one or more of Claims 1 to 5, wherein the distribution density of the large protrusions is $> 10^3/\text{mm}^2$.
7. The biaxially oriented copolyester film according to any one or more of Claims 1 to 6, wherein the distribution density of the large protrusions is $< 10^6/\text{mm}^2$.
8. The biaxially oriented copolyester film according to any one or more of

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Claims 1 to 7, wherein the distribution density of the protrusions on the second surface is $\geq 10^6/\text{mm}^2$.

5 9. The biaxially oriented copolyester film according to any one or more of Claims 1 to 8, wherein the distribution density of the protrusions on the second surface is $\leq 10^9/\text{mm}^2$.

10 10. The biaxially oriented copolyester film according to any one or more of Claims 1 to 9, wherein the film contains particles.

11. The biaxially oriented copolyester film according to any one or more of Claims 1 to 10, wherein the film is a bilayer film consisting of a base layer B and a cover layer A or C.

15 12. The biaxially oriented copolyester film according to any one or more of Claims 1 to 10, wherein the film is a trilayer film consisting of a base layer B and a cover layer A on one surface of the base layer B and a cover layer C on the other surface of the base layer B.

20 13. The biaxially oriented copolyester film according to Claim 11 or 12, wherein the base layer B essentially consists of PENBB.

25 14. The biaxially oriented copolyester film according to any one or more of Claims 11 to 13, wherein the base layer B contains large particles with a diameter of 0.05 to 2 μm .

30 15. The biaxially oriented copolyester film according to any one or more of Claims 11 to 14, wherein the cover layer A and/or C contains small particles with a diameter of 0.01 to 0.1 μm .

16. The biaxially oriented copolyester film according to any one or more of Claims 1 to 15, wherein the film has a birefringence of < 0.2 and the IV-

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value of the PENBB IS > 0.5 dl/g.

17. The biaxially oriented copolyester film according to any one or more of Claims 1 to 16, wherein the film has a thickness of 2 to 15 μm .

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18. Use of a biaxially oriented copolyester film according to any one or more of Claims 1 to 17 as magnetic tape.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10706

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : B32B 3/10, 27/06

US CL : 428/480, 910, 141

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. : 428/480, 910, 141

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, 3,793,132 (BHAKUNI ET AL) 19 FEBRUARY 1974. Entire document.	1-3
A	US, A, 3,991,013 (PLETCHER) 09 NOVEMBER 1976. Entire document.	1-3
A	4,781,963 (UTSUMI ET AL) 01 NOVEMBER 1988. Entire document.	1-3
A	US, A, 3,714,772 (BHAKUNI ET AL) 06 FEBRUARY 1973. Entire document.	1-3
A	US, A, 5,069,942 (ANDERSON) 03 DECEMBER 1991. 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)	*Z*	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

08 MARCH 1993

Date of mailing of the international search report

16 APR 1993

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10706**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.: 18
because they relate to subject matter not required to be searched by this Authority, namely:

Claim 18 is directed to a "USE". Use claims not in method terminology are not required to be searched by this ISA.
PCT Article 17(2)(a)(i).
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.: 4-18
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.