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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B32B 33/00, D06N 7/04	A1	(11) International Publication Number: WO 94/13480 (43) International Publication Date: 23 June 1994 (23.06.94)
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(54) Title: COATED BIAXIALLY ORIENTED COPOLYESTER FILM (57) Abstract The invention deals with a coated biaxially oriented mono-or multilayered copolyester film, wherein at least one layer is composed of PENBB and wherein the coating contains a thermoplastic polymer.		

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COATED BIAXIALLY ORIENTED COPOLYESTER FILM

This invention relates to improved biaxially oriented copolyester films, especially PENBB films. In particular, this invention relates to improving the surface, tensile strength, modulus and dimensional stability of thermoplastic films.

The surfaces of polyester films do not readily retain printing ink impressions nor do they tend to form strong bonds to coatings for other films to be heat sealed to them. Polyester films also tend to acquire static charges.

Polyethylene terephthalate (PET) films are very useful for wrapping, especially when oriented. PET films are also used as a base for, e.g. photographic films, magnetic recording tapes or impact or thermal transfer printer ribbons. However, there is still a need for further improvement of the base films' tensile strength, modulus and dimensional stability, which then would allow the use of thinner film, which in turn would increase the capacity. In addition, PET films show poor adherence to printing inks, magnetic, photographic coatings and the like. It was therefore an object of the present invention to provide a thermoplastic base film with improved tensile strength, stiffness (tensile modulus), dimensional stability and strong adherence to coatings.

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.

According to the present invention one or both surfaces of an orientable PENBB film are covered with a thermoplastic polymer and the coated film is then stretched to produce a biaxially oriented coated PENBB film, the total

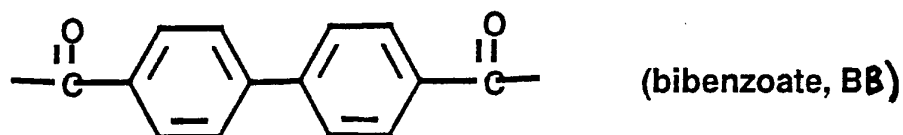
thickness of the coating layer being at least 50 times thinner than the thickness of the base layer.

The final covering of thermoplastic polymer of this invention may be very thin, i.e. down to molecular thicknesses. There may even be gaps in the coverings but, of course, it is a requirement that the coverings should provide a substantially uniform effect over the film. Very thin coverings are best applied to the PENBB films as solution or dispersion. Any suitable coating technique may be used; a convenient method of applying a thin liquid coat is by means of roller coating, spray coating, gravure coating, slot coating, or immersion coating. They are most easily applied at room temperature or at not unduly elevated temperature, so that the solvent or dispersion medium does not tend to evaporate during the application stage. Dispersions in water are the least expensive form of providing the thermoplastic polymer and these can give uniform coverings if the polymer is fluid at the drawing temperature and forms a film. Concentrated aqueous dispersions are preferred, i.e. those containing 30 percent dry weight of the polymer because the energy required to heat the film to its stretching temperature is then normally sufficient to evaporate the small amount of water in the covering. These dispersions do not usually contain more than 55 percent dried weight of polymer because of the practical difficulties of preparing stable, mobile dispersions with a higher dry weight content. In some cases it may, however, be necessary to decrease the solid content of the dispersions to obtain the desired thinness of covering. For practical reasons of the ease of obtaining uniform coverings and to obtain the most effective coverings, the coverings according to this invention on the drawn PENBB film are usually at least 3 nm thick. The total thickness of the coverings is preferably at least 200 times thinner than the PENBB base layer if both sides are covered, and 400 times thinner if only one side is covered.

Suitable thermoplastic polymers for the coverings according to this invention include polyethylene, polyvinylacetate, hydrolyzed and partially hydrolyzed polyvinylacetate, copolymers of butadiene with, for instance, acrylonitrile or methylmethacrylate, copolymers of styrene with, for instance,

butadiene, methacrylic acid, acrylic acid, or esters thereof and low molecular weight polyamides. Very suitable thermoplastic polymers according to this invention are the copolymers of vinylidene chloride, for instance those with one or more of acrylonitrile, vinyl chloride, alkyl acrylates, itaconic acid, methacrylic acid and acrylic acid. Further suitable thermoplastic polymers for use for these coverings are polyurethanes, polystyrenes and aliphatic acid salts such as alkali metal salts of unsaturated fatty acids having from 10 to 18 carbon atoms, or alkali earth metal salts of fatty acids having from 10 to 18 carbon atoms. Suitable polyurethanes are for instance those wherein the carboxyl groups are introduced by esterifying the terminal hydroxyl groups and amidizing any terminal amine groups of the polyurethane with a dicarboxylic acid anhydride. The most generally useful thermoplastic polymers as coverings are those having at least one carbon atom with a polar substituent per every 6 carbon atoms of the polymer chain. Polyethylene may be used though it normally requires an oxidation treatment, e.g. a corona treatment, before it is suitable for bonding printing inks or other coatings on the base film.

PENBB as mentioned hereinbefore is a copolyester containing as acid-derived unit at least 5 mole percent of a radical of the formula



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In the case that more than 10 mole percent of terephthalic acid derived radicals are present in the copolymer, the content of bibenzoate derived units is at least 25 mole percent. Films of these copolyesters are mentioned in the unpublished German Patent Application P 4224161.8, which is incorporated herein by reference. Preferably PENBB is a copolyester wherein at least 80 mole percent of the acid derived units (NBB) consist of bibenzoate (20 to 80 mole percent, preferably 40 to 60 mole percent) and naphthalate (80 to 20 mole percent, preferably 60 to 40 mole percent). The remaining 20 or less mole percent may consist of other acid derived units, which e.g. affect the

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melting point or the crystallization kinetics. Preferably at least 80 mole percent of the diol-derived units consist of $-O(CH_2)_2-O$ -units. The remaining 20 or less mole percent consist of other diol-derived units, which e.g. may also affect the melting point or the crystallization kinetics. It may also be desirable to replace minor amounts of the acid- and/or diol-derived units with hydroxycarboxylic-acid-derived units, e.g. such derived from p-hydroxybenzoic acid.

The inherent viscosity of the polymer is above 0.5 dl/g and preferably between 0.55 and 1.7 dl/g (measured at a concentration of 0.1 weight percent in a 1 : 1 mixture by weight of pentafluorophenol and hexafluoroisopropanol at 25°C).

The copolyester is obtained by polycondensation of the corresponding mixture of diacids or lower dialkyl diesters and the corresponding diol. Both components should preferably be employed in equimolar ratios. It may, however, be advantageous to employ one of the components -- especially the diol -- in excess, 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 or a corresponding mixture of two or more of these acids and/or esters 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 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 a stream of dry air or inert gas.

To produce the film, the polymer melt is extruded through a die onto a chill roll where it solidifies, is then biaxially oriented, heat set, optionally post treated and wound on a roll. For a multilayer film known methods for coextrusion, in-line or off-line coating can be used. 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 or vacuum, air knife or the like.

The biaxial orientation of the film is achieved by stretching the film at elevated temperature in the machine (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). The total stretch ratios (λ) in MD and TD 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 to 30 preferably between 5 to 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.

In order to optimize properties, relaxation steps can be included in the orientation and heat setting processes.

The heat setting takes place at a temperature between the cold crystallization temperature and the melt temperature of the copolymer composition.

Prior to coating the PENBB film surface with the thermoplastic coating composition, the film may be surface treated in a conventional manner by

exposure to, e.g., an electric corona discharge, plasma, or flame treatment.

It is preferred to apply the covering layer before the film is drawn transversely, i.e. after the longitudinal stretching step. This process is preferred to coating the PENBB film before drawing in either direction because
5 coating before any drawing involves drawing the film at an elevated temperature between tensioning rollers running at different speeds and when such a process is applied to coated film there is a tendency for the coating to stick to the drawing rolls. The coated PENBB films according to this invention have the advantage that, as the coverings are so thin, the PENBB films can
10 be recovered by the normal method of scrap recovery involving, for instance, compression and melting, without the thermoplastic polymer of the covering causing a significant contamination of the PENBB. This is an important advantage because, in the production of oriented films, scrap film is inevitably produced and the recovery of this scrap is necessary for economy in the production of oriented films. The process according to this invention has the
15 advantage of simplicity and, therefore, cheapness.

While it will be appreciated that no particular covering is ideal for all purposes, the coverings of this invention may be applied, for example, to improve the retention of printing ink impressions to the film or the covering
20 may form bonds of improved strength with further coatings embossed on the films. The covering may also serve to render the film heat sealable to itself and other thermoplastic polymer layers, this being of great importance if the film is used for packaging purposes. Suitable covered surfaces of the PENBB films according to this invention may be used as a base on which various top
25 coatings may be applied, e.g. coatings to render the film heat sealable, barrier coatings to form laminated films of low permeability to gases and vapors, e.g. coatings of vinylidene chloride copolymers, coatings containing ferromagnetic materials to form magnetic recording tapes, coatings to form photographic films, the photosensitive layer containing either, for instance, silver or
30 diazo compounds sensitive to light, coatings to form pressure sensitive adhesive films, coatings to form impact or thermal ribbon for printers.

These films show the desired combined features of tensile strength, stiffness (tensile modulus), dimensional stability and excellent adhesion toward other functional layers as mentioned above.

THAT WHICH IS CLAIMED IS:

1. Coated biaxially oriented mono- or multilayered copolyester film, wherein at least one layer is composed of PENBB and wherein the coating contains a thermoplastic polymer.
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2. Coated biaxially oriented copolyester film according to claim 1, wherein the coating contains one or more of the following compounds:
polyethylene, polyvinylacetate, polyurethane, polystyrene, alkali or earth alkali salts of fatty acids having 10 to 18 carbon atoms, copolymers of butadiene with acrylonitrile or methylmethacrylate, copolymers of styrene with butadiene, methacrylic acid, acrylic acid or esters thereof, polyamides, polyvinylidene chloride, copolymers of vinylidene chloride with one or more of acrylonitrile, vinyl chloride, alkyl acrylates, itaconic acid, methacrylic acid and acrylic acid.
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3. Coated biaxially oriented copolyester film according to claim 1 or 2, wherein the coating is applied to one or both surfaces.
4. Coated biaxially oriented copolyester film according to claims 1, 2 or 3, wherein the coating is applied before a first stretching procedure or after a first stretching procedure.
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5. Coated biaxially oriented copolyester film according to any one or more of the preceeding claims wherein the coating is at least 50 times thinner than the thickness of the copolyester film.
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6. Coated biaxially oriented copolyester film according to any one or more of the preceding claims wherein the film is a monolayered film.
7. Coated biaxially oriented copolyester film according to any one or more of the preceeding claims wherein the coating is applied as an aqueous dispersion.
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8. Coated biaxially oriented copolyester film according to claim 7, wherein the aqueous dispersion contains at least 30 percent by weight solid material.
9. Coated biaxially oriented copolyester film according to any one or more of the preceeding claims, wherein the coating has a thickness of at least 3 nm.
10. Coated biaxially oriented copolyester film according to any one or more of the preceeding claims, wherein the birefringence of the PENBB film is < 0.2.
11. Coated biaxially oriented copolyester film according to any one or more of the preceeding claims, wherein the IV-value of the PENBB polymer is > 0.5 dl/g.
12. Use of a coated biaxially oriented copolyester film according to claim 1 as packaging material.
13. Use of a coated biaxially oriented copolyester film according to claim 1 as a of magnetic tape base film.
14. Use of a coated biaxially oriented copolyester film according to claim 1 as photographic film.
15. Use of a coated biaxially oriented copolyester film according to claim 1 as adhesive tape.
16. Use of a coated biaxially oriented copolyester film according to claim 1 as a base layer for impact or thermal transfer printed ribbons.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10683**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :B32B 33/00; D06N 7/04

US CL :428/141, 143, 145, 147, 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, 147, 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, 096,773 (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
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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)	*G* 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 30 MAR 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 <i>Elizabeth Evans</i> ELIZABETH EVANS Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10683**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.: 12-16
because they relate to subject matter not required to be searched by this Authority, namely:

Claims 12-16 are directed to a "USE" PCT Article 17(2)(a)(i). "Use" claims not in method terminology is not searched 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. ☒ Claims Nos.: 4-11
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.