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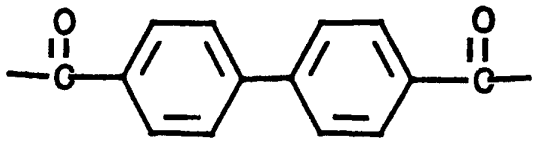
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(54) Title: BIAXIALLY ORIENTED COPOLYESTER FILM PRIMED WITH A FUNCTIONAL SILANE AND FILM LAMINATES THEREOF

(57) Abstract

The invention relates to a biaxially oriented self-supporting copolyester mono- or multilayer film having a continuous primer coating composition on one or both sides thereof, wherein the copolyester film is a PENBB film and wherein said coating composition comprises the dried residue of a hydrolyzed silane compound. PENBB is a copolyester containing units of formula (I).



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BIAXIALLY ORIENTED COPOLYESTER FILM PRIMED WITH A FUNCTIONAL SILANE AND FILM LAMINATES THEREOF

The present invention relates to biaxially oriented PENBB film coated on one or both sides with a primer coating composition comprising a hydrolyzed functional silane which renders the film more receptive to lamination with other polymeric film materials and which is excellent for the field of silicone release films and yields superior adhesion performance over known silicone release films, while exhibiting improved stiffness (tensile modulus), tensile strength, dimensional stability and especially UV resistance.

Background Of The Invention

Oriented polyester film, particularly biaxially oriented film composed of polyethylene terephthalate (PET), has been widely used as a packaging material or as a base film for microfilm, reprographic films, proofing films, and the like. It has good optical clarity, however its stiffness, tensile strength, dimensional stability, and especially UV stability still need to be improved.

PET films have recently found expanded applications as transparent and translucent layers applied to solid substrates and particularly to transparent substrates. Thus, such films may be applied to windows and viewing or lighting media to control the transparency thereof. Another more recent application for PET film involves its use as an antilacerative layer in the construction of automotive glazing products such as windshields, rear windows, sun roof panels and the like, and in architectural safety glass. One of the simpler automotive glazing products may comprise a flexible interlayer of polyvinylbutyral sandwiched between glass on one side and a moderately high modulus film on the opposite side. Polyvinylbutyral layers are used in sandwich automotive glass construction to prevent breaking of the glass in the case of impact (so called safety glass), whereas the role of the PET film positioned on the interior glass surfaces is to prevent skin lacerations caused by hard impact of the head or body with automotive glass causing the glass to shatter, as a consequence of an automobile accident. Constructions of

this type and techniques for applying the PET film to automotive glass surfaces are disclosed in U.S. Patent No. 4,973,364, the disclosure of which is incorporated herein by reference.

The above referenced patent teaches the use of a layer of plasticized polyvinylbutyral (PVB) as an adhesive layer to facilitate adhesion of the PET film to the glass. While PVB adheres very well to glass, the adhesion between it and PET film is not as great, particularly at subfreezing temperatures. Corona discharge treatment and flame treatment have been used to give adhesion between PVB sheet and PET film as disclosed in U.S. Patent No. 3,900,673. Coatings of gelatin and PVDC and acrylic latex coatings have also given adhesion between PET film and PVB. However, none of these methods of imparting adhesion give adhesion at the subfreezing temperatures to which windows in automobiles and buildings are commonly subjected. It is believed that any improvement of the adhesion of the film to the PVB improves the function of the film as an antilacerative shield.

Numerous primer coatings are known in the prior art for the application to the surface of PET film to improve the adhesion of the film to various materials. Examples of such coatings include compositions based on vinylidene chloride polymers (U.S. Patent No. 2,698,240), thermosetting acrylic or methacrylic polymers (U.S. Patent No. 3,819,773) and like materials. Certain water dispersible PETs have also been disclosed as adhesives for laminating sheets of PET film to one another or to sheets of nylon film as taught in U.S. Patent Nos. 3,563,942 and 3,779,993. Solvent based polyurethane adhesives have also been used to promote adhesion, but with attendant problems of solvent emissions and safety.

The use of silane coupling agents to improve the bonding properties of polyethylene sheets and PET sheets is known. For example, PET sheets and polyethylene sheets primed with either vinyl trimethoxysilane or chloropropyltrimethoxysilane have been successfully laminated using a hot melt adhesive such as an ethylene/vinylacetate terpolymer or an elastomeric polyester as disclosed by E. Plueddemann, "Bonding Through Coupling Agents", Plenum Press, N.Y., 1985. In addition, the use of N-2-aminoethyl-3-aminopropyl-

trimethoxy silane (sold under the trademark Z-6020 by Dow Corning) as a primer coating to enhance the adhesion of an ionomer resin (salt of a copolymer of ethylene and methacrylic acid) to glass and to polycarbonate sheets is disclosed in U.S. Patent No. 4,663,228. Related silanes such as N-3-aminopropyltrialkoxy silanes are known to enhance the adhesion between polyurethane films and glass substrates, as disclosed in European Patent Application No. 171,917.

Release films are well known and are generally employed to serve as a temporary support for an adhesive or tacky surface such as labels, pressure sensitive tape, decorative laminates, transfer tape, etc. Silicone compositions have long been used as the release coating for rendering the support surface (usually a paper support) relatively non-adherent to adhesive materials. Using various polymeric films as temporary supports is well known but most polymeric materials are virtually inert, and thus it is difficult to obtain adhesion between the silicone release coating and the polymeric film. Commercially available silicone release films initially have acceptable adhesion performance (adhesion between the support and the silicone release coating). However, with time the adhesion of the silicone release coating lessens which causes the release coating to rub off. This may cause silicone release material to be removed from the support when the label is peeled away, and thus the label may fail to properly stick. Also, the poor adhesion of the silicone release coating to the support may cause the label to stick to the support (where the silicone release coating has been removed) and not properly detach for placement.

Prior commercial practice for manufacturing silicone release film does not involve employing primer coatings on the support. Typically, manufacturers have relied on silicone producers to formulate release compositions capable of adhering to the manufacturer's support. Consequently, there are many different types of silicone release compositions for many different supports.

Primer coating compositions for polymeric film supports are well known for product applications other than silicone release films. Primer coatings

based upon polyolefins, polyesters, vinyls, alcohols, acids and acrylates are well known for film applications in the packaging industry, magnetic tape industry, and reprographic film industry.

One approach for applying a primer coating to a polymeric support for silicone release applications is Japanese Patent 64-5838. This patent discloses a release film comprising a PET film, a primer layer applied to the PET film which consists of a crosslinkable silane coupling agent, and the silicone release layer applied to the silane coupling agent. The silane coupling agent may consist of a vinyl, epoxy (glycidoxy), amino, or mercapto silane. Once the silane primer coating has been applied and crosslinked with the PET support film, it is then ready for uniform application of the silicone release coating.

U.S. Patents 4,898,786 and 5,077,353 also deal with silicone based coated PET films, the coatings of which showed improved results.

None of these prior art disclosures provides a solution to the problems of maintaining, of good adhesion between the carrier film and a polymeric coating thereon especially at subfreezing temperatures where many primer materials fail. There is still an ongoing need for primer coated films with improved mechanical strength, stiffness, dimensional stability and UV stability.

Accordingly, it is an object of this invention to provide a biaxially oriented, self-supporting film material having enhanced adhesion when laminated with other polymer films, while at the same time exhibiting improved mechanical strength, stiffness, dimensional stability and UV stability.

A further object is to provide a primer coating for carrier film which enhances adhesion between the carrier film and polyvinylbutyral film and in part resistance to de-lamination even at subfreezing temperatures.

It is a further object of the present invention to provide a primer coated film which maintains its original bonding characteristics to a silicone release coating for a sufficient period of time.

Summary Of The Invention

These objects of the present invention may now be achieved by the provision of biaxially oriented PENBB film which has been primer coated with a hydrolyzed functional silane.

Preferably the functional silane useful as a primer layer for the purpose of this invention is a silane corresponding in its unhydrolyzed state to the general formula:

$$X\ Si(R^2)_a(R^3)_b$$

wherein

X is a radical selected from the group consisting of $H_2N\text{-}R^1\text{-}NH\text{-}R^1\text{-}$, $H_2N\text{-}R^1\text{-}NH\text{-}R^1\text{-}NH\text{-}R^1\text{-}$ and glycidoxy-C_1-C_8 alkylene;

R^1s are the same or different groups selected from the group consisting of C_1-C_8 alkylen and phenylene;

R^2 is a hydrolyzable group selected from the group consisting of C_1 to C_8 alkoxy, acetoxy and halide;

R^3 is a nonreactive, nonhydrolyzable group, selected from the group consisting of C_1 - C_3 alkyl and phenyl;

(a) is an integer ranging from 1 to 3;

(b) is an integer ranging from 0 to 2;

with the sum of (a) and (b) being 3.

These coatings are disclosed for PET film in U.S. Patent No. 4,898,786. 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.

Examples of suitable silanes include N-(2-aminoethyl)-3-aminopropylmethyl-dimethoxysilane, N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, N-2-

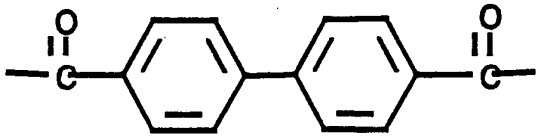
aminoethyl-3-aminopropyltris (2-ethylhexoxy) silane, (6-aminohexylaminopropyl)trimethoxysilane, (aminoethylaminomethyl)phenethyltrimethoxysilane and N-2-aminoethyl-2-aminoethyl-3-aminopropyltrimethoxysilane, glycidoxypropyl trimethoxysilane and glycidoxypropylmethyldiethoxysilane.

The hydrolyzed silane is applied to the film as an aqueous solution at any suitable stage during manufacture of the film, i.e. before or during the stretching operation, or it may also be applied to the finished film. For some applications it may also be useful to add a binder to the silane compound. Suitable binders are copolyesters such as those made of two different dicarboxylic acids, one of which is an aromatic dicarboxylic acid such as terephthalic or isophthalic acid, and the other one is aliphatic dicarboxylic acid preferably selected from the group consisting of malonic, adipic, azelaic, glutaric, sebacic, suberic, succinic, brassylic acid and mixtures thereof. Suitable glycols for the copolyester are those having from about 2 to 11 carbon atoms, especially ethylene glycol, butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, 1,10-decanediol, cyclohexane dimethanol, and diethylene glycol. In some cases it may also be desirable to add to this copolyester primer a sulfomonomer, preferably a sulfomonomer selected from the group consisting of ammoniumsulfoterephthalic acid, alkylsulfoterephthalic acid, ammonium 5-sulfoisophthalic acid, alkyl metal 5-sulfoisophthalic acid, ammonium sulfophthalic acid, alkyl metal sulfophthalic acid, 5-(p-ammoniumsulfophenoxy)-isophthalic acid and 5-(sulfopropoxy)-isophthalic acid. Such primer compositions are described, e.g. in U.S. Patent No. 5,077,353 which is incorporated herein by reference.

The resultant primed biaxially oriented PENBB film is found to exhibit excellent adhesion to other polymeric materials and can be readily laminated to other polymeric films. Adhesive qualities are maintained even at subfreezing temperatures. Moreover, the primed biaxially oriented PENBB film shows excellent mechanical stability, dimensional stability, and UV stability.

Detailed Description Of The Invention

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



(bibenzoate, BB)

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 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.

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 is obtained by polycondensation of the corresponding diacid or lower dialkyl diester and the corresponding diol. Both components should preferably be employed in equimolar ratios. It may, however, be ad-

vantageous 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 a 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 birefringeance is < 0.2, preferably < 0.1 to ensure adequately isotropic properties. Birefringeance as mentioned herein is the absolute value of the difference between the maximum and minimum refractive indices in the plane of the film, as measured on common instruments such as Abbé refractometer, optical bench or compensators.

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.

The primer formulation of this invention is prepared by mixing the silane and optionally the copolyester together with water at a level within the range of about 0.2 to about 6 percent by weight. Optionally, a weak acid such as acetic acid may be added to facilitate hydrolysis. At least one of the hydrolyzable groups of the silane is hydrolyzed into a silanol group (SiOH). It is believed that the hydrolysis product of the silane has a partially hydrolyzed, cyclized structure. Thus, the term hydrolyzed as used herein also may refer to such partially hydrolyzed structures.

The hydrolyzed silane primer coating of this invention in the form of an aqueous solution may be applied in-line at one of three stages during the film manufacture; the pre-draw stage at the point between the casting of the amorphous sheet and the first stretch such as disclosed for PET film, for example, in British Patent No. 1,411,564, the inter-draw stage subsequent to the uniaxial drawing but prior to biaxial drawing such as disclosed, for example, in the U.S. Patent No. 4,214,035 or the post draw stage subsequent to biaxial stretching, but prior to winding the film. Normally, the heat applied

to the film during the stretching or final conditioning stages is sufficient to evaporate off the water and other volatiles and dry the primer coating, although a separate drying step would be required if the coating were applied subsequent to such heating steps. The coating may also be applied off-line to finished film such as by first subjecting the film surface to a corona discharge treatment prior to the coating operation. The film surface is then dried to remove the water.

In one preferred embodiment, the primer coating is applied after the film is uniaxially stretched, that is, after the film is stretched in one direction, but before the film is stretched in the orthogonal direction. In another preferred embodiment, the PENBB film is first stretched in the longitudinal direction prior to coating. In this preferred embodiment, after longitudinal stretching, the film is coated by any of the well known techniques employed in the art. For example, coating may be effected by roller coating, spray coating, slot coating or immersion coating. In a preferred embodiment, the PENBB film is coated by means of a gravure cylinder. Also, the uniaxially drawn film is preferably subjected to a corona discharge, plasma or flame treatment prior to coating as is known in the art. This surface treatment decreases the hydrophobic character of the PENBB film surface, which permits the water based coating to more easily wet the surface and thus improve the adhesion of the coating to the surface.

The hydrolyzed silane of the present invention is applied to the base film as an aqueous solution at a concentration of from about 0.2 to about 6 percent by weight of the hydrolyzed silane. A weak acid such as acetic, phosphoric or the like is then added at a level of from about 0.1 to about 0.5 percent by weight to facilitate hydrolysis. The preferred level of addition of the acid is about 0.2 percent by weight. The preferred concentration is such to yield a final dry primer coating weight of from about 0.5 to about 100 mg/m^2 of film. Preferably the range is from about 1.0 to about 7.5 mg/m^2, with about 4 mg/m^2 being the target weight for coatings applied in-line. Where the coating is applied off-line to finished film, the target dry coating weight is about 50 mg/m^2.

The coating of this invention may be applied to one or both sides of the film, or it may be applied to one side and a different coating such as a thermosetting acrylic or methacrylic polymer applied to the opposite side, such as taught in U.S. Patent No. 4,214,035. The coating may also in some cases be applied over a different primer coating to which it will adhere and which is already present on the surface of the film, such as a thermosetting acrylic coating as described in U.S. Patent No. 3,819,773.

An especially significant application in the glass field is the utilization of a biaxially oriented PENBB film coated on one side with the primer coating of this invention and on the opposite side with an abrasion resistant coating such as a radiation curable hydrolyzed vinyl-functional silane composition also containing a multifunctional crosslinking agent and an optional photoinitiator, such as disclosed for PET film in U.S. Patent No. 4,822,826, the disclosure of which is incorporated herein by reference. Such materials have shown improved abrasion resistance of the surfaces of a variety of plastic films, including PET film, making the films more useful in applications where the surface is likely to be subjected to abrasion. Examples of suitable vinyl-functional silanes disclosed in the referenced patent include vinyl alkoxy silanes such as vinyltriethoxysilane, vinyltrimethoxysilane and vinyl-tris(2-methoxyethoxy) silane. Preferred crosslinkers are multifunctional acrylate or methacrylate monomers such as ethoxylated trimethylolpropane triacrylate.

Other suitable abrasion resistant coatings may also be used, such as are disclosed for example in U.S. Patent Nos. 4,177,315, 4,239,798, 4,310,600 and 4,348,462.

The coating composition may also contain other ingredients so long as such ingredients do not detract from the adhesion promoting action of the hydrolyzed silane. Such would include minor amounts of colloidal silica, dyes, pH regulating agents, wetting agents and the like. The primer coating is present on the film surface as a continuous coating, which term is also intended to include cases where the primer may form a plurality of islands or segregated regions of coating.

Scrap film made during production that is coated with the primer coatings can be ground and mixed with fresh PENBB, re-melted, re-extruded and re-drawn to produce biaxially oriented PENBB film. Such film produced containing significant quantities of primed scrap reclaim exhibits very little degradation of physical properties due to the presence of the coating impurity, and color generation is also low. Thus, the primed film of this invention offers commercial advantage to the film manufacturers over many other primed films, such as films primed with vinylidene chloride containing copolymers as disclosed in U.S. Patent Nos. 2,627,088 and 2,698,240, which tend to degrade and discolor when reclaimed as set forth above.

As indicated above, the primer coated biaxially oriented PENBB film of this invention forms excellent adhesive bonds with other polymers and plastic films to which it is laminated. Examples of such polymers and films include polyvinylbutyral, polycarbonate, polyurethane, polyolefins such as polyethylene or polypropylene, polystyrene, and similar films and silicone release coatings. Laminates may be made by forming a sandwich of the films and heating the structure to a temperature below the melting point of the PENBB film but above the melting point of the other film, preferably while simultaneously applying moderate pressure to the sandwich structures. Preferred heating temperatures generally range from about 125°C to 230°C. The other plastic films used to form the laminates may themselves be primer coated if desired.

An especially significant application in the glass field is the utilization of biaxially oriented PENBB film coated on one side with the above described primer coating. The primed side of the biaxially oriented PENBB film is laminated to a sheet of polyvinylbutyral that is also laminated to a sheet of glass. For this application the preferred silane is N-(2-aminoethyl)-3-aminopropyl trimethoxysilane (AE-APTMS). Biaxially oriented PENBB film primed with AE-APTMS has high adhesion to polyvinylbutyral at normal temperatures and also has good adhesion to polyvinylbutyral at subfreezing temperatures where adhesion fails with other primers and treatments.

The biaxially oriented PENBB film of this invention can be sandwiched between two layers of PVB and two layers of glass with at least one side of the film primed with the silane and the other side either being primed with the silane or having a metal or metal oxide coating for solar control and IR reflection. In another configuration the biaxially oriented PENBB film is laminated to the interior or inboard surface of the glass as an anti-lacerative layer with a layer of PVB between the film and the glass; the side of the film primed with the silane is laminated to the glass and the other side of the film is protected by an abrasion resistant coating.

The thickness of biaxially oriented PENBB film suitable for use in this invention may generally range from about 5 to 250 μm or more. In multilayer automotive windshield applications the preferred thickness is of the order of 75 to 100 μm.

In the following examples which are illustrative of the invention, the following methods are emoployed:

The mechanical properties are measured in a tensile testing machine made by Zwick (Ulm, Germany) on 15 mm wide strips of film. The initial distance between the chucks is 100 mm and the crosshead speed is 100 mm/min for the determination of strength and elongation and 10 mm/min for the tensile modulus determination.

The UV resistance is tested by measuring the retention of tensile elongation after exposure to UV light in a "Suntest" apparatus manufactured by Heraeus (Hanau, Germany) for 14 days.

To test the peel strength, a laminated sample, PENBB/PVB/glass is placed in an Instron tester with the glass/PVB clamped in the lower jaws of the Instron and the nonadhered leader hanging free and pointing down toward the jaws. A length of #610 "Scotch" tape (a 3M trademark) is doubled over and attached to the nonadhered leader. The length of Scotch tape is then clamped in the upper jaws of the tensile tester. The angle between the leader and PVB/glass was 180°. The peel is done at a rate of 2.54 cm/min for a length of 2.54 cm. The peak force needed to peel the PENBB from the PVB is read from the strip chart. Three laminated samples are made for each

example. For each 15x20 cm laminated sample three pulls are done at room temperature (23 °C), and three pulls are done at -10 °C.

EXAMPLE 1

N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AE-APTMS) is dispersed in ordinary tap water to form a concentration of 1.0 percent by weight of AE-APTMS. Acetic acid is then added at a concentration of 0.2 percent by weight to facilitate hydrolysis.

A biaxially oriented PENBB film which is made of 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. Granules of the polymer, having a melting point of 281°C are melted in a single screw extruder at temperatures of 280 to 320°C and extruded through a sheet die onto a cooling roll, temperature controlled at 30°C. A 120 μm thick film is obtained which is clear and transparent. Its density is 1.31 g/cm^3. This sheet is longitudinally stretched and then corona treated by a corona discharge apparatus and thereafter coated by reverse gravure with the solution of hydrolyzed silane prepared above. The corona treated, longitudinally drawn, coated film is dried at a temperature of about 100°C. Thereafter, the film is stretched in the transverse direction to produce a biaxially drawn film. The biaxially drawn film is then heat set. This film exhibits a marked improvement in peel resistance in both the room temperature test and also when tested after conditioning at - 10°C for 24 hours.

EXAMPLE 2

The same PENBB film as in Example 1 is in-line coated with a glycidoxysilane-copolyester dispersion. The coating is applied during the manufacturing of the PENBB film between the drawing steps (interdraw). The weight ratio of glycidoxysilane to copolyester is 1 to 2. The coating is applied as a 3 percent by weight aqueous dispersion. The so coated biaxially oriented PENBB film is then in-line coated with a silicone release coating. The silicone

used is a PCL No. 188 water based coating system with the following formulation:

silicone type 188 -- 40 g;

distilled water -- 156 g;

catalyst PC-95 -- 4 g;

(A No. 6 Meyer rod is used to apply this silicone to the pre-coated biaxially oriented PENBB film. The coated film is cured at 120°C for 45 seconds). This film shows good results in a rub off test wherein a finger is rubbed back and forth over the silicone release coated film and the area is then observed and rated. No silicone was removed even under strong pressure (highest rating in the rub off test).

Compared to similarly coated biaxially oriented PET film, the films according to Examples 1 and 2 show improved tensile strength, stiffness (tensile modulus), dimensional stability and UV stability (c.f. Table 1)

TABLE 1

Property	Units	PENBB	PET
Tensile Strength MD TD	(MPa)	240 180	100-200
Elongation At Break MD TD	(%)	25 20	50
Tensile Modulus MD TD	(GPa)	9.2 8.0	4-6
Shrinkage (at 150°C for 15 minutes) MD TD	(%)	0.3 0.3	>1.0 >1.0
UV resistance	% retained tensile strength	77	0

THAT WHICH IS CLAIMED IS:

1. Biaxially oriented self-supporting copolyester mono- or multilayer film having a continuous primer coating composition on one or both sides thereof, wherein the copolyester film is a PENBB film and wherein said coating composition comprises the dried residue of a hydrolyzed silane compound.

2. Biaxially oriented copolyester film according to claim 1 wherein the hydrolyzed silane is a silane corresponding to the following general formula in its unhydrolyzed state

$$X\ Si(R^2)_a(R^3)_b$$

wherein

X is a radical selected from the group consisting of $H_2N\text{-}R^1\text{-}NH\text{-}R^1\text{-}$, $H_2N\text{-}R^1\text{-}NH\text{-}R^1\text{-}NH\text{-}R^1\text{-}$ and glycidoxy - $C_1\text{-}C_8$ alkylene;

R^1s are the same or different groups selected from the group consisting of $C_1\text{-}C_8$ alkylene and phenylene;

R^2 is a hydrolyzable group selected from the group consisting of $C_1\text{-}C_8$ alkoxy, acetoxy and halide;

R^3 is a nonreactive, nonhydrolyzable group, selected from the group consisting of C_1 - C_3 alkyl and phenyl;

(a) is an integer ranging from 1 to 3;

(b) is an integer ranging from 0 to 2;

with the sum of (a) and (b) being 3.

3. A biaxially oriented copolyester film according to claim 1 or 2, wherein the unhydrolyzed silane is selected from the group consisting of N-(2-aminoethyl)-3-aminopropylmethyl-dimethoxysilaneN-(2-aminoethyl-3-aminopropyl) trimethoxysilane, N-2-aminoethyl-3-aminopropyltris (2-ethylhexoxy) silane, (6-aminohexylaminopropyl) trimethoxysilane, (N-(2-aminoethyl)aminomethyl)-phenethyltrimethoxysilaneN-2-aminoethyl-2-aminoethyl-3-aminopropyltrimethoxysilane and glycidoxypropylmethyldiethoxysilane.

4. A biaxially oriented copolyester film according to any one or more of the preceeding claims, wherein the silane is applied to the film before, during or after the stretching operation.

5. A biaxially oriented copolyester film according to any one or more of the preceeding claims, wherein a binder is at added to the silane compound.

6. A biaxially oriented copolyester film according to claim 5, wherein a sulfomonomer is added to the silane and the binder.

7. A biaxially oriented copolyester film according to any one or more of the preceeding claims, wherein the primer coating composition is applied as aqueous dispersion.

8. A biaxially oriented copolyester film according to claim 7, wherein the solid content of the dispersion is between 0.2 to 6 percent by weight.

9. A biaxially oriented copolyester film according to any one or more of the preceeding claims, wherein the PENBB film is corona discharge treated.

10. A biaxially oriented copolyester film according to any one or more of the preceeding claims, wherein the film is a monolayer film.

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

12. Use of a biaxially oriented copolyester film according to claim 1 in glazing applications.

13. Use of a biaxially oriented copolyester film according to claim 1 as release film.

INTERNATIONAL SEARCH REPORT

Int. ational application No.
PCT/US92/10702

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 5/16, 9/04, 3/10
US CL :428/447, 451, 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. : 428/447, 451, 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	US, 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)	"&"	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	Date of mailing of the international search report
08 MARCH 1993	26 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 ROBERT FOLLETT Telephone No. (703) 308-2351

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

INTERNATIONAL SEARCH REPORT

Int. .ational application No.
PCT/US92/10702

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.: 12, 13
because they relate to subject matter not required to be searched by this Authority, namely:

Claims 12, 13 are directed to a "use". Use claims not drafted 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. [X] 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.