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(54) Titre : FILM ORIENTE MULTICOUCHE A HAUT MODULE  
 (54) Title: MULTILAYER ORIENTED HIGH-MODULUS FILM

(57) **Abrégé/Abstract:**

The invention relates to a high modulus, bi-axially oriented film, heat-shrinkable or non heatshrinkable, comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene or propylene homo- or co-polymer, a core layer comprising an ethylene-vinyl alcohol copolymer, and no core polyamide or polyester layers. The film according to the present invention is prepared by orienting biaxially a flat extruded tape by means of a tenter frame, preferably simultaneously, and has a modulus higher than 6,000 kg/cm<sup>2</sup> in at least one direction. The film of the present invention is particularly useful, in the non heat-shrinkable version, for food and non food packaging applications.



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(54) Title: MULTILAYER ORIENTED HIGH-MODULUS FILM

(57) Abstract: The invention relates to a high modulus, bi-axially oriented film, heat-shrinkable or non heatshrinkable, comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene or propylene homo- or co-polymer, a core layer comprising an ethylene-vinyl alcohol copolymer, and no core polyamide or polyester layers. The film according to the present invention is prepared by orienting biaxially a flat extruded tape by means of a tenter frame, preferably simultaneously, and has a modulus higher than 6,000 kg/cm<sup>2</sup> in at least one direction. The film of the present invention is particularly useful, in the non heat-shrinkable version, for food and non food packaging applications.



**WO 2005/011978 A1**

## Description

### MULTILAYER ORIENTED HIGH-MODULUS FILM

#### Technical Field

[001] The present invention relates to a high modulus multilayer oriented film with a first outer layer comprising a polyester or co-polyester, a second outer layer comprising an ethylene- or propylene- homo- or co-polymer, a core layer comprising an ethylene-vinyl alcohol copolymer, and no polyamide or polyester core layers.

[002] The invention also relates to a process for the manufacture of the new film and to the use of the new film in packaging applications.

#### Background Art

[003] Oriented films with a first outer layer of a polyester or copolyester, a second outer layer of a polyolefin, and a gas-barrier layer of EVOH have been described in the patent literature, see for instance EP-A-476,836, WO 99/55528, WO 99/44824, WO 99/44823, EP-A-1,190,847, and WO 01/98081.

[004] In all those cases, the structures containing a first outer polyester layer, a second outer polyolefin layer, and a core EVOH layer also contain a core polyamide or polyester layer.

[005] In particular, EP-A-476,836 describes an oriented laminated film with a surface layer of a polyester, an EVOH core layer, an intermediate layer of certain polyamides and a heat-sealing layer of polyolefin. In the structures there claimed a given thickness ratio between the outer polyester layer and the core polyamide layer needs to be present, what improves orientability of the tape. The films described there are said to have excellent stretching processability, heat-sealing and packaging properties and good transparency after heat-sterilization.

[006] WO 99/44824 and WO 99/44823 describe EVOH-containing heat-shrinkable films with at least four layers, i.e. a first outer layer comprising i.a. a polyethylene, a second outer layer possibly comprising a polyester, a core EVOH layer and an additional core polyamide or polyester layer. The bags obtained therefrom can be stacked on top of one another and sealed simultaneously and the presence of the core polyamide or polyester layer is said to give i.a. enhanced impact strength and render the tape more easily orientable.

[007] WO 99/55528, EP-A-1,190,847, and WO 01/98081 relate to heat-shrinkable structures where in addition to the polyester and polyolefin outer layers, a core polyamide layer is always present and optionally also an EVOH core layer. These films are said to satisfy various properties required of a packaging material, through e.g. a control of the heat-shrinkage stress and of the heat-shrink.

[008] In all the above documents the process actually described for the manufacture of these films is the so-called trapped bubble process. According to this technique, the polymer feeds are extruded through an annular die to give a thick tubing, called "tape". Said tubing is quickly quenched at the exit of the extrusion die in order to control crystallization, then it is re-heated to the suitably selected orientation temperature and oriented transversely by inflating it with a gas to expand its diameter and longitudinally by running the nip rolls that hold the bubble at a differential speed.

[009] It has now been found that it is possible to obtain biaxially oriented films with a first outer layer of a polyester or copolyester, a second outer layer comprising an ethylene- or propylene- homo- or co-polymer, and a core layer comprising EVOH, without needing any polyamide or polyester core layer, by carrying out the biaxial orientation of the extruded tape by means of a tenter frame, preferably a simultaneous tenter frame.

[010] It has been found that the films which are thus obtained have a high modulus in at least one direction, and are therefore very useful for most of the currently used packaging systems as it is known that for a good machinability, as well as for a good printability, the packaging material needs to be stiff, i.e. it should have a high modulus.

[011] The films of the present invention are in particular characterized by a modulus which is higher than  $6,000 \text{ kg/cm}^2$  in at least one direction.

[012] Preferred films according to the present invention have a modulus which is higher than  $6,500 \text{ kg/cm}^2$  in at least one direction, and more preferred are those films which have a modulus higher than  $7,000 \text{ kg/cm}^2$  in at least one direction.

[013] It has also been found that when a heat-shrinkable structure is obtained, it is possible to conjugate a high free shrink with a low shrink force, particularly in the transverse direction. This would be an advantage in all the packaging applications where the product to be packaged is sensitive to a high shrink force and in particular can be crushed or distorted by films with a high shrink force when these films are shrunk around the product.

[014] Preferred heat-shrinkable films according to the present invention have in fact a free shrink of at least 10 % in each direction at  $120 \text{ }^\circ\text{C}$  and a maximum shrink tension in the transverse direction, in the temperature range of from  $20$  to  $180 \text{ }^\circ\text{C}$  of less than  $5 \text{ kg/cm}^2$ , more preferably less than  $3 \text{ kg/cm}^2$ , and even more preferably less than  $1 \text{ kg/cm}^2$ .

### **Disclosure of Invention**

[015] A first object of the present invention is therefore a multi-layer, bi-axially oriented, thermoplastic film comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene- or propylene- homo- or co-

77572-26

3

polymer, a core layer comprising an ethylene-vinyl alcohol copolymer, and no core polyamide or polyester layers, said film having a modulus (evaluated according to ASTM D882) higher than 6,000 kg/cm<sup>2</sup>, preferably higher than 6,500 kg/cm<sup>2</sup>, and more preferably higher than 7,000 kg/cm<sup>2</sup>, in at least one direction.

5 [016] In one embodiment the multi-layer, biaxially oriented, thermoplastic film of the present invention is heat-shrinkable and has a free shrink of at least 10 % in each direction at 120°C and a maximum shrink tension, in the transverse direction, in the temperature range of from 20 to 180°C of less than 5 kg/cm<sup>2</sup>, more preferably less than 3 kg/cm<sup>2</sup>, and even more preferably less than 1 kg/cm<sup>2</sup>.

10 [017] In another embodiment the multi-layer bi-axially oriented thermoplastic film of the present invention is a non-shrinkable, heat-set, film with a free shrink at 120°C which is  $\leq 10\%$ , preferably  $\leq 5\%$ , more preferably  $\leq 3\%$  in each direction.

[018] A second aspect is the process for the manufacture of a film of the first object by co-extrusion of a tape through a flat die followed by bi-axial orientation, with  
15 an orientation ratio generally comprised between about 2:1 and about 5:1 in each direction, by means of a tenter frame, said orientation step being optionally followed by a heat-setting step.

[019] In a preferred embodiment the biaxial orientation is carried out simultaneously in both directions, by a simultaneous tenter frame.

20 [020] A third aspect of the present invention is the use of a film according to the first object in packaging applications.

[020a] According to another aspect of the present invention, there is provided a multi-layer, bi-axially oriented, thermoplastic film comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an  
25 ethylene- or propylene-homo- or co-polymer, a core layer comprising an ethylene vinyl alcohol copolymer, first and second tie layers, directly adhered to both sides of

54699-3

3a

the core layer, and no core layer comprising more than 50% by weight of polyamide or polyester, said film having an elastic modulus, evaluated according to ASTM D882, higher than 6,000 kg(f)/cm<sup>2</sup> in at least one direction.

[020b] According to still another aspect of the present invention, there is  
5 provided a process for the manufacture of a bi-axially oriented, thermoplastic film comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene- or propylene-homo- or co-polymer, a core layer comprising an ethylene-vinyl alcohol copolymer, first and second tie layers, directly adhered to both sides of the core layer, and no core layer comprising more than 50%  
10 by weight of polyamide or polyester, said film having an elastic modulus, evaluated according to ASTM D882, higher than 6,000 kg(f)/cm<sup>2</sup> in at least one direction, which process comprises co-extruding the film resins through a flat die and bi-axial orientating the obtained cast sheet simultaneously in the two perpendicular directions at an orientation ratio in the longitudinal direction higher than 2:1, and at an  
15 orientation ratio in the cross-wise direction higher than 2:1, by means of a tenter frame.

### **Mode for the Invention**

#### [021] DEFINITIONS

[022] As used herein, the term "film" is used in a generic sense to include  
20 plastic web, regardless of whether it is film or sheet. Typically, films of and used in the present invention have a thickness of 150 µm or less, preferably they have a thickness of 120 µm or less, more preferably a thickness of 100 µm or less, still more preferably a thickness of 75 µm or less, and yet, still more preferably, a thickness of 60 µm or less.

25 [023] As used herein, the phrase "outer layer" refers to any layer of film having only one of its principal surfaces directly adhered to another layer of the film.

54699-3

3b

[024] As used herein, the phrases "inner layer" and "internal layer" refer to any layer having both of its principal surfaces directly adhered to another layer of the film.

[025] As used herein, the phrase "inside layer" when referred to a package  
5 made using the multi-layer film of the invention refers to the outer layer of the film which is closest to the packaged product, relative to the other layers thereof.

[026] As used herein, the phrase "outside layer" when referred to a package made using the multi-layer film of the invention refers to the outer layer of the film which is

furthest from the product relative to the other layers thereof.

- [027] As used herein, the term "core", and the phrase "core layer", refers to any internal layer that preferably has a function other than serving as an adhesive or compatibilizer for adhering two layers to one another.
- [028] As used herein, the phrases "seal layer", "sealing layer", "heat seal layer", and "sealant layer", refer to an outer layer involved in the sealing of the film to itself, to another layer of the same or another film, and/or to another article which is not a film. With respect to packages having only fin-type seals, as opposed to lap-type seals, the phrase "sealant layer" generally refers to the inside layer of a package.
- [029] As used herein, the phrase "tie layer" refers to any internal layer having the primary purpose of adhering two layers to one another. Preferred polymers for use in tie layers include, but are not restricted to, suitably modified polyolefins and blends thereof with polyolefins.
- [030] As used herein, the phrase "machine direction", herein abbreviated "MD", refers to a direction "along the length" of the film, i.e., in the direction of the film as the film is formed during extrusion and/or coating.
- [031] As used herein, the phrase "transverse direction", herein abbreviated "TD", refers to a direction across the film, perpendicular to the machine or longitudinal direction.
- [032] As used herein, the phrases "orientation ratio" and "stretching ratio" refer to the multiplication product of the extent to which the plastic film material is expanded in the two directions perpendicular to one another, i.e. the machine direction and the transverse direction.
- [033] As used herein, the phrases "heat-shrinkable," "heat-shrink," and the like, refer to the tendency of the film to shrink upon the application of heat, i.e., to contract upon being heated, such that the size of the film decreases while the film is in an unrestrained state. As used herein said term refer to films with a free shrink in at least one direction, as measured by ASTM D 2732, of at least 10 % at 120 °C.
- [034] As used herein, the term "polymer" refers to the product of a polymerization reaction, and is inclusive of homo-polymers, and co-polymers.
- [035] As used herein, the term "homo-polymer" is used with reference to a polymer resulting from the polymerization of a single monomer, i.e., a polymer consisting essentially of a single type of mer, i.e., repeating unit.
- [036] As used herein, the term "co-polymer" refers to polymers formed by the polymerization reaction of at least two different monomers. The term "co-polymer" is also inclusive of random co-polymers, block co-polymers, and graft co-polymers.
- [037] As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., typical polymers prepared, for example,



using conventional Ziegler-Natta catalysts. Although there are a few exceptions (such as TAFMER™ linear homogeneous ethylene- $\alpha$ -olefin copolymers produced by Mitsui, using Ziegler-Natta catalysts), heterogeneous polymers typically contain a relatively wide variety of chain lengths and co-monomer percentages.

[038] As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers are structurally different from heterogeneous polymers, in that homogeneous polymers exhibit a relatively even sequencing of co-monomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of length of all chains, i.e., a narrower molecular weight distribution. Furthermore, homogeneous polymers are typically prepared using metallocene, or other single-site type catalysts, rather than using Ziegler Natta catalysts.

[039] As used herein, the term "polyolefin" refers to the polymer or co-polymer resulting from the polymerisation or co-polymerisation of unsaturated aliphatic, linear or cyclic, straight or branched, hydrocarbon monomers that may be substituted or unsubstituted. More specifically, included in the term polyolefin are film-forming homo-polymers of olefin, co-polymers of olefin, co-polymers of an olefin and an non-olefinic co-monomer co-polymerizable with the olefin, such as vinyl monomers, and the like. Specific examples include polyethylene homo-polymer, polypropylene homo-polymer, polybutene homo-polymer, ethylene- $\alpha$ -olefin co-polymer, propylene- $\alpha$ -olefin co-polymer, butene- $\alpha$ -olefin co-polymer, ethylene-unsaturated ester co-polymer, ethylene-unsaturated acid co-polymer, (e.g., ethylene-(C<sub>1</sub>-C<sub>4</sub>)alkyl acrylate or methacrylate copolymers, such as for instance ethylene-ethyl acrylate co-polymer, ethylene-butyl acrylate co-polymer, ethylene-methyl acrylate co-polymer, ethylene-methyl methacrylate co-polymer, ethylene-acrylic acid co-polymer, and ethylene-methacrylic acid co-polymer), ionomer resin, polymethylpentene, etc.

[040] As used herein the term "modified polyolefin" is inclusive of modified polymers prepared by co-polymerizing the homo-polymer of the olefin or co-polymer thereof with an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like. It is also inclusive of modified polymers obtained by incorporating into the olefin homo-polymer or co-polymer, by blending or preferably by grafting, an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like.

[041] As used herein, the phrase "ethylene- $\alpha$ -olefin copolymer" refer to such heterogeneous materials as linear low density polyethylene (LLDPE, with a density usually in the range of from about 0.915 g/cm<sup>3</sup> to about 0.930 g/cm<sup>3</sup>), linear medium

density polyethylene (LMDPE, with a density usually in the range of from about 0.930 g/cm<sup>3</sup> to about 0.945 g/cm<sup>3</sup>) and very low and ultra low density polyethylene (VLDPE and ULDPE, with a density usually lower than about 0.915 g/cm<sup>3</sup>); and homogeneous polymers such as metallocene-catalyzed homogeneous ethylene- $\alpha$ -olefin copolymer resins and linear homogeneous ethylene- $\alpha$ -olefin copolymer resins obtainable under homogeneous catalysis conditions but using Ziegler-Natta catalysts (Tafmer® resins by Mitsui). All these materials generally include co-polymers of ethylene with one or more co-monomers selected from C<sub>4</sub> to C<sub>10</sub>  $\alpha$ -olefin such as butene-1, hexene-1, octene-1, etc. in which the molecules of the copolymers comprise long chains with relatively few side chain branches or cross-linked structures.

- [042] As used herein, the term "adhered", as applied to film layers, broadly refers to the adhesion of a first layer to a second layer either with or without an adhesive, a tie layer or any other layer therebetween, and the word "between", as applied to a layer expressed as being between two other specified layers, includes both direct adherence of the subject layer to the two other layers it is between, as well as a lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers the subject layer is between.
- [043] In contrast, as used herein, the phrase "directly adhered" is defined as adhesion of the subject layer to the object layer, without a tie layer, adhesive, or other layer therebetween.
- [044] As used herein, "EVOH" refers to ethylene/vinyl alcohol copolymer. EVOH includes saponified or hydrolyzed ethylene/vinyl acetate copolymers, and refers to a vinyl alcohol copolymer having an ethylene comonomer, and prepared by, for example, hydrolysis of vinyl acetate copolymers. The degree of hydrolysis is preferably at least 50%, and more preferably, at least 85%. Preferably, the EVOH comprises from about 28 to about 48 mole % ethylene, more preferably, from about 32 to about 44 mole % ethylene.
- [045] As used herein, the term "polyamide" refers to both polyamide homo-polymers and polyamide co-polymers, also called co-polyamides.
- [046] As used herein the term "co-polyamide" on the other hand identifies the polyamide product built from at least two different starting materials, i.e. lactams, aminocarboxylic acids, equimolar amounts of diamines and dicarboxylic acids, in any proportion; this term therefore also encompasses ter-polyamides and, in general, multi-polyamides.
- [047] As used herein the terms "major proportion" and "minor proportion" when referred to a resin as a component of a layer, refer to an amount respectively higher than 50 wt. % or lower than 50 wt. % of said resin calculated on the overall weight of the layer.

- [048] As used herein with the terms "polyamide layer" or "polyester layer" it is intended to refer to layers comprising a major proportion of polyamide or of polyester respectively.
- [049] DETAILED DESCRIPTION OF THE INVENTION
- [050] In the film according to the present invention, the first outer layer, that in the use of the film in packaging applications will be the outside, abuse-resistant, optionally printed layer, comprises a film forming polyester or co-polyester. Suitable film forming polyesters and co-polyesters can be crystalline, semi-crystalline, or amorphous. If crystalline or semi-crystalline, their melting point is preferably comprised between about 100°C and about 260°C, and is higher, preferably at least 10°C higher, and even more preferably at least 20°C higher, than the melting point of the polyolefin resin of the second outer layer, in order to favor heat-sealability of the film through said second outer layer. The Tg of the film forming polyesters or co-polyesters used for the first outer layer needs to be below 130°C, in order to allow orientation of the extruded structure at conventional temperatures. Preferably said Tg will be below 110°C, more preferably below 100°C, and even more preferably below 90°C.
- [051] Preferred polyesters and co-polyesters are aromatic ring-containing polymers.
- [052] Suitable linear homopolymeric polyesters include poly(ethylene terephthalate), poly(1,2-propylene terephthalate), poly(ethylene 2,5-dimethyl-terephthalate), poly(butylene terephthalate), poly(ethylene isophthalate), poly(ethylene 5-t-butyl-isophthalate), poly(butylene 2,6-naphthalate), and the like homopolymers.
- [053] Suitable copolymers can be random copolymers, i.e. those copolymers where the various components are randomly incorporated into the copolymer chain; alternating or patterned copolymers, i.e. those copolymers whose constituent units stand in a regular pattern of succession along the molecular chains; or block or segmented copolymers.
- [054] Examples of dicarboxylic acids that can be included in the copolyester resin are terephthalic acid, isophthalic acid, 2,5-dimethyl-terephthalic acid, 5-t-butyl-isophthalic acid, naphthalene dicarboxylic acid, cyclohexane-dicarboxylic acid, diphenyl ether dicarboxylic acid, sebacic acid, adipic acid, azelaic acid, and the like acids. Examples of diols that can be included in the copolyester resins are ethylene glycol, 1,2-propane-diol, 1,3-propane-diol, 1,4-butanediol, 1,6-hexane-diol, 1,4-cyclohexane-dimethanol, 2,2-bis(4-hydroxyphenyl)propane, and the like.
- [055] In the copolyester at least one of the carboxylic acids or of the diols is used in combination of at least two species.
- [056] The first outer layer may also comprise a blend of at least two components independently selected from polyesters and copolyesters.
- [057] Said layer may also comprise minor proportions of other compatible polymers and/

or copolymers blended therein, such as polyamides and copolyamides, polyurethanes, and the like polymers.

- [058] Preferably however said first outer layer will comprise at least 70 wt. %, more preferably at least 80 wt. %, and even more preferably at least 90 wt. % calculated on the basis of the overall weight of the layer, of one or more polyesters and/or one or more copolyesters.
- [059] In a most preferred embodiment said first outer layer will be essentially made of one or more polyesters and/or one or more copolyesters.
- [060] Said first outer layer may also contain nucleating agents as known in the art (see for instance Table 1 of the Literature Review by H. Zhou available at the internet address [www.crd.ge.com](http://www.crd.ge.com) as 98CRD138). A class of particularly preferred nucleating agents are the inorganic compounds such as talc, silicate, clay, titanium dioxide, and the like. These compounds can be used in an amount of less than 5 % by weight, typically in an amount of 1-2 % by weight on the total weight of the layer. Other preferred nucleating agents are certain compatible polymers such as fluoropolymers (PTFE) and the faster crystallising polymers that can be blended with the polyester and/or copolyester of the first outer layer in an amount of up to e.g. 5-10 % by weight.
- [061] The thickness of said first outer layer will typically be up to about 45 % of the thickness of the overall structure, preferably up to about 40 %, more preferably up to about 35 % of the overall thickness.
- [062] Typically the thickness of said first outer layer will be comprised between about 8 and about 40 %, and preferably between about 10 and about 35 %, of the overall film thickness.
- [063] The second outer layer, that in the end package will be the inside, preferably heat-sealable, layer, will comprise one or more polymers selected from the group of ethylene homopolymers, ethylene co-polymers, propylene homopolymers and propylene co-polymers.
- [064] Ethylene homo- and co-polymers suitable for the second outer layer are selected from the group consisting of ethylene homo-polymers (polyethylene), heterogeneous or homogeneous ethylene- $\alpha$ -olefin copolymers, ethylene-vinyl acetate co-polymers, ethylene-(C<sub>1</sub>-C<sub>4</sub>) alkyl acrylate or methacrylate co-polymers, such as ethylene-ethyl acrylate co-polymers, ethylene-butyl acrylate co-polymers, ethylene-methyl acrylate co-polymers, and ethylene-methyl methacrylate co-polymers, ethylene-acrylic acid co-polymers, ethylene-methacrylic acid co-polymers, and blends thereof in any proportion.
- [065] Preferred ethylene homo- and co-polymers for said second outer layer are e.g. polyethylene having a density of from about 0.900 g/cm<sup>3</sup> to about 0.950 g/cm<sup>3</sup>, heterogeneous and homogeneous ethylene- $\alpha$ -olefin copolymers having a density of from

about 0.880 g/cm<sup>3</sup> to about 0.945 g/cm<sup>3</sup>, more preferably of from about 0.885 g/cm<sup>3</sup> to about 0.940 g/cm<sup>3</sup>, yet more preferably of from about 0.890 g/cm<sup>3</sup> to about 0.935 g/cm<sup>3</sup>, and ethylene-vinyl acetate copolymers comprising from about 3 to about 28 %, preferably, from about 4 to about 20 %, more preferably, from about 4.5 to about 18 % vinyl acetate comonomer, and blends thereof.

[066] Even more preferred ethylene homo- and co-polymers for said second outer layer are selected from the group consisting of heterogeneous ethylene- $\alpha$ -olefin copolymers having a density of from about 0.890 g/cm<sup>3</sup> to about 0.940 g/cm<sup>3</sup>, homogeneous ethylene- $\alpha$ -olefin copolymers having a density of from about 0.890 g/cm<sup>3</sup> to about 0.925 g/cm<sup>3</sup>, ethylene-vinyl acetate copolymers comprising from about about 4.5 to about 18 % vinyl acetate comonomer, and blends thereof.

[067] In one embodiment of the present invention the second outer layer comprises a blend of at least two different ethylene- $\alpha$ -olefin copolymers with a density of from about 0.890 g/cm<sup>3</sup> to about 0.935 g/cm<sup>3</sup>, more preferably a blend of a homogeneous and a heterogeneous ethylene- $\alpha$ -olefin copolymer, optionally blended with ethylene-vinyl acetate copolymer.

[068] Preferably, the ethylene homo- or co-polymers for said second outer layer have a melt index of from about 0.3 to about 10 g/10 min, more preferably from about 0.5 to about 8 g/10 min, still more preferably from about 0.8 to about 7 g/10 min, even more preferably from about 1 to about 6 g/10 min (as measured by ASTM D1238 – 190 °C, 2.16 kg).

[069] Propylene homo- and co-polymers suitable for the second outer layer are selected from the group consisting of propylene homo-polymers (polypropylene), crystalline or highly amorphous (i.e., a polypropylene with a crystalline fraction of not more than about 10 wt. %), and propylene copolymers with up to 50 wt.%, preferably up to 35 wt.%, of ethylene and/or a (C<sub>4</sub>-C<sub>10</sub>)- $\alpha$ -olefin, and blends thereof in any proportion.

[070] Preferred propylene homo- and co-polymers for said second outer layer are e.g. polypropylene, and propylene copolymers with up to 35 wt.%, of ethylene and/or butene-1, pentene-1, or hexene-1, and blends thereof in any proportion.

[071] Even more preferred propylene homo- and co-polymers for said second outer layer are selected from the group consisting of highly amorphous polypropylene, propylene-ethylene copolymers with an ethylene content lower than about 25 wt.%, more preferably lower than about 15 wt.% and even more preferably lower than about 12 wt.%, propylene-ethylene-butene co-polymers and propylene-butene-ethylene copolymers with a total ethylene and butene content lower than about 40 wt.%, preferably lower than about 30 wt.%, and even more preferably lower than about 20 wt.%.

[072] Preferably, the propylene homo- or co-polymers for said second outer layer have a

melt index of from about 0.5 to about 20 g/10 min, more preferably from about 0.8 to about 12 g/10 min, still more preferably from about 1 to about 10 g/10 min (as measured by ASTM D1238 – 230°C, 2.16 kg).

- [073] Said second outer layer may also contain a blend of one or more ethylene homo- and/or co-polymers with one or more propylene homo- and/or co-polymers, in any proportion.
- [074] Preferably however said second outer layer will comprise an ethylene homo- or co-polymer.
- [075] The second outer layer may also comprise a blend of a major proportion of one or more polymers of the group of ethylene homo- and copolymers and propylene homo- and copolymers, with a minor proportion of one or more other polyolefins or modified polyolefins, such as polybutene homo-polymers, butene-(C<sub>5</sub>-C<sub>10</sub>)- $\alpha$ -olefin copolymers, ionomers, anhydride grafted ethylene- $\alpha$ -olefin copolymers, anhydride grafted ethylene-vinyl acetate copolymers, anhydride grafted propylene homopolymer, anhydride grafted propylene copolymer, rubber modified ethylene-vinyl acetate copolymers, and the like.
- [076] Said additional polymers may be blended with the basic polymers of said second outer layer in an amount that is typically up to about 40 % by weight, preferably up to about 30 % by weight, more preferably up to about 20 % by weight, and still more preferably up to about 10 % by weight.
- [077] In a preferred embodiment however said second outer layer will essentially consist of one or more polymers selected from the group of ethylene homo- and co-polymers, and propylene homo- and co-polymers.
- [078] The thickness of said second outer layer may vary widely depending on the overall structure of the end film. More particularly it can range from about 1-2  $\mu$ m up to 60 % or more of the overall thickness of the film. Generally it is at least about 5 % of the overall thickness of the structure, being typically comprised between about 5 and about 60 % of the overall thickness of the film.
- [079] The film according to the present invention also contains a core layer, which acts as a gas-barrier layer, comprising an ethylene-vinyl alcohol copolymer.
- [080] The gas-barrier layer - as indicated - may comprise one or more EVOH optionally admixed with a minor amount of one or more polyamide components, as known in the art. In particular said core layer will comprise at least 70 %, still more preferably at least 80 %, and yet still more preferably at least 90 % by weight of a single EVOH or a blend of two or more EVOHs. Examples of EVOH that may well be employed in the production of films according to the present invention are EVAL<sup>TM</sup> EC F151A or EVAL<sup>TM</sup> EC F101A, marketed by Marubeni. The possible complement to 100 % in said core gas-barrier layer is typically made of one or more polyamides, either aliphatic

or aromatic, such as those commonly indicated as nylon 6, nylon 66, nylon 6/66, nylon 12, nylon 6,12, nylon 6I/6T, nylon MXD6/MXDI, and the like. In such a case a preferred polyamide is nylon 6/12, a copolymer of caprolactam with laurolactam, such as GRILON™ CF 6S or GRILON™ W8361 manufactured by EMS, MXD6/MXDI a copolyamide with units from metaxylylenediamine, adipic acid and isophthalic acid, such as GRILON™ FE458 manufactured by EMS or a multipolyamide with monomers from hexamethylenediamine, meta-xylylenediamine, adipic acid and sebacic acid, such as GRILON™ XE3569 manufactured by EMS. Other plasticisers and/or other resins compatible with EVOH, as known in the art, can however be present in addition to or alternatively to the polyamide.

- [081] Alternatively the possible complement to 100 % in said EVOH-containing core layer can be made of one or more low molecular weight plasticisers, such as for instance the low molecular weight diols or triols, e.g., 1,2-propanediol, butanediol, propanetriol or pentanediol which are known to increase the stretchability of the EVOH resins.
- [082] Still alternatively the possible complement to 100 % can be made by blends of polyamides with low molecular weight plasticisers.
- [083] In a most preferred embodiment however the core gas-barrier layer will essentially consist of EVOH as the gas barrier properties of 100 % EVOH are much higher than those of blended EVOH.
- [084] The thickness of said barrier layer will depend on the barrier properties desired for the end film. More particularly its thickness will be set in order to provide the overall multi-layer film with the desired Oxygen Transmission Rate (OTR) (evaluated by following the method described in ASTM D-3985 and using an OX-TRAN instrument by Mocon). For high gas barrier films an OTR lower than 100, preferably lower than 80, and even more preferably lower than  $50 \text{ cm}^3/\text{m}^2 \cdot \text{d} \cdot \text{atm}$ , when measured at 23 °C and 0 % of relative humidity is generally required. Typically, when EVOH is employed as the gas-barrier material, optionally blended with up to 20 % by weight of a polyamide, this is achieved with barrier layers 2 to 6  $\mu\text{m}$  thick. Thicker or thinner EVOH containing layers may however be employed depending on the barrier properties required and on the particular composition of said EVOH containing layer.
- [085] Unlike the films of the prior art, the films according to the present invention will not contain any polyamide or polyester core layer.
- [086] They may contain additional core layers, such as "bulk" layers or "structural" layers, i.e. layers that may be used to improve the abuse or puncture resistance of the film or just to provide the desired thickness, "shrink" layers, i.e. layers that may be added to improve the shrink properties of the end film, when a heat-shrinkable film is desired, and/or "seal-assist" layers, i.e., inner layers that are directly adhered to the

second outer layer and favour the heat-sealability of the film (as described for instance in US-A-6,682,825 or in US-A-6,063,462), which are polyolefin layers. Preferably these layers, if present, are positioned between the core EVOH-containing layer and the second outer layer. Polymers particularly suitable for any of these polyolefin layers are ethylene homo- and co-polymers, e.g. low density polyethylene, ethylene-vinyl acetate copolymers, linear low density polyethylenes and linear very low density polyethylenes, optionally blended with minor proportions of other polyolefins. The thickness of these additional layers, if any, will depend mainly on the overall thickness desired for the film.

- [087] Other layers that may be present in the multi-layer film of the invention are tie or adhesive layers that are employed to better adhere one layer to another in the overall structure.
- [088] In particular the films of the present invention will preferably have tie layers directly adhered (i.e., directly adjacent) to one or both sides of the core EVOH-containing gas-barrier layer. Tie layers may also be used, when additional core layers are present, to better adhere said layers to the adjacent ones, e.g. to the first outer layer or the second outer layer.
- [089] Tie layers may include polymers having grafted polar groups so that the polymer is capable of covalently bonding to polar polymers. Useful polymers for tie layers include ethylene-unsaturated acid copolymers, ethylene-unsaturated ester copolymers, anhydride-modified polyolefins, and mixtures thereof. Preferred polymers for tie layers include one or more of thermoplastic polymers such as ethylene-vinyl acetate copolymers with high vinyl acetate content (e.g. 18- 28 wt. % or even more), ethylene-(meth)acrylic acid copolymers, ethylene homo-polymers or co-polymers, such as LDPE, heterogeneous or homogeneous LLDPE and VLDPE, or EVA, modified with anhydride or carboxylic acid functionalities, blends of these resins or blends of any of the above resins with an ethylene homo- or co-polymer, and the like known resins.
- [090] The tie layers are of a sufficient thickness to provide the adherence function, as is known in the art. Their thickness however is generally kept as low as possible in view of the high cost of these resins. Typically they will be from about 1, preferably about 2, to about 10, preferably about 8  $\mu\text{m}$ . While layers thinner than 1  $\mu\text{m}$  are generally not sufficient to provide the desired adherence, tie layers thicker than 10  $\mu\text{m}$  may well be employed but without providing a further increase in the bond properties.
- [091] The tie layers present in the overall structure may be of a substantially similar or of a different composition and/or thickness.
- [092] In one embodiment of the present invention the film has five layers, with the first outer layer, the second outer layer, the EVOH-containing core gas-barrier layer, a first tie layer directly adhering said core gas-barrier layer to the first outer layer and a



second tie layer directly adhering said core gas-barrier layer to the second outer layer. Preferred polymers for use in said tie layers are anhydride grafted ethylene-vinyl acetate and anhydride grafted ethylene- $\alpha$ -olefin copolymers that may be blended with one or more polyolefins. Most preferred polymers are anhydride grafted ethylene- $\alpha$ -olefin copolymers possibly blended with one or more polyolefins. In a most preferred embodiment said tie layers have the same composition.

[093] In another embodiment the film has six to eight layers with the first outer layer, the second outer layer, the EVOH-containing core gas-barrier layer, a first tie layer directly adhering said core gas-barrier layer to the first outer layer, a second tie layer between said core gas-barrier layer and the second outer layer and one to three additional core polyolefin layers positioned between the second outer layer and the second tie layer.

[094] In still another embodiment the film has seven to ten layers with the first outer layer, the second outer layer, the EVOH-containing core gas-barrier layer, a first tie layer between said core gas-barrier layer and the first outer layer, a second tie layer between said core gas-barrier layer and the second outer layer, an additional core polyolefin layer positioned between the first tie layer and the first outer layer, a third tie layer directly adhering said additional core polyolefin layer to the first outer layer and optionally one to three additional core polyolefin layers positioned between the second outer layer and the second tie layer.

[095] In all the film layers, not only in the outer layers, the polymer components may contain appropriate amounts of additives normally included in such compositions. These include slip and anti-block agents such as talc, waxes, silica, and the like, antioxidants, fillers, pigments and dyes, cross-linking inhibitors, cross-linking enhancers, UV absorbers, antistatic agents, anti-fog agents or compositions, and the like additives known to those skilled in the art of packaging films.

[096] In one particularly advantageous embodiment of the present invention, the film will comprise at least six layers, with the first outer layer, the second outer layer, the EVOH-containing core gas-barrier layer, a first tie layer between said core gas-barrier layer and the first outer layer, a second tie layer between said core gas-barrier layer and the second outer layer, and a bulk polyolefin layer positioned between the second outer layer and the second tie layer, characterised in that the second outer layer is very thin (few  $\mu\text{m}$ , e.g., about 1 to 3  $\mu\text{m}$ ) and comprises slip and anti-blocking agents and the bulk layer which is directly adhered thereto, is a thicker layer containing the anti-fog additives. In a preferred embodiment said bulk layer comprises the same polymer or polymer composition of the adjacent second outer layer. By the time the film is used in packaging applications these additives, which are known to migrate within the polyolefin layers, will be present on the outer surface of the second outer layer.

- [097] Preferably, the film of the present invention has an overall thickness of from about 10 to about 80  $\mu\text{m}$ , more preferably, from about 12 to about 70  $\mu\text{m}$ , and, still more preferably, from about 14 to about 60  $\mu\text{m}$ .
- [098] The film according to the present invention can be obtained by melt extruding the polymers or polymer blends used for each layer through a flat die, cooling quickly the multi-layer sheet exiting from the extrusion die by means of a chill roll, optionally irradiating the cast sheet thus obtained to get cross-linking, reheating this flat tape to the suitably selected orientation temperature, and biaxially stretching the heated tape at a stretching ratio of at least 2:1 in each direction, by a tenter apparatus, optionally stabilizing the obtained bi-axially oriented film by an annealing or a heat-setting step and finally cooling the thus obtained bi-axially oriented, multi-layer film.
- [099] Preferably the biaxial stretching will be carried out simultaneously as it has been found that it is possible in this way to reach much higher stretching ratios, even when the core EVOH-containing layer does not comprise plasticizers, and obtain films with a higher modulus.
- [100] In particular it has been found that using the simultaneous flat orientation technique in connection with a multi-layer tape with a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene- or propylene- homo- or copolymer, a core layer comprising an ethylene-vinyl alcohol copolymer, and no core polyamide or polyester layers, it is possible to easily reach stretching ratios of 5:1 in each direction even when the core gas-barrier layer is 100 % EVOH and it is expected that also higher stretching ratios, such as for instance 5.5:1, 6:1, or 6.5:1, could be applied, at least in one direction, possibly by suitably adjusting the stretching conditions and/or the composition of the core EVOH-containing layer.
- [101] The oriented films thus obtained, whether heat-shrinkable or heat-set, are characterized by a modulus higher than 6,000  $\text{kg}/\text{cm}^2$  in at least one direction.
- [102] Preferred films of the present invention have a modulus higher than 6,500  $\text{kg}/\text{cm}^2$  in at least one direction, and more preferably higher than 7,000  $\text{kg}/\text{cm}^2$  in at least one direction. Even more preferred films of the present invention have a modulus higher than 6,000  $\text{kg}/\text{cm}^2$  in both directions.
- [103] Using the simultaneous tenter frame stretching technique it is also possible to obtain a bi-axially oriented heat-shrinkable film with a maximum shrink tension in the transverse direction, in the temperature range of from 20 to 180°C, of less than 5  $\text{kg}/\text{cm}^2$ . Such a low shrink tension value in the transverse direction can be obtained also with heat-shrinkable films showing a high free shrink at 120°C, e.g., films with a total free shrink at 120 °C of 40 %, 50 %, 60 %, or even more.
- [104] A second object of the present invention is therefore a process for the manufacture of a bi-axially oriented, thermoplastic, multi-layer film comprising a first outer layer

comprising a polyester or a copolyester, a second outer layer comprising an ethylene- or propylene homo- or co-polymer, a core layer comprising an ethylene-vinyl alcohol copolymer, and no polyamide or polyester core layers, which process comprises co-extrusion of the film resins through a flat die and bi-axial orientation of the obtained cast sheet, by means of a tenter frame, simultaneously in the two perpendicular directions at an orientation ratio in the longitudinal direction higher than 2:1, preferably higher than 3:1 and at an orientation ratio in the cross-wise direction higher than 2:1, preferably higher than 3:1.

[105] The process according to the present invention involves feeding the extruders with the solid polymer or polymer blend beads for the various layers, melting the polymer beads in the extruders and then forward the molten resins of the layers into a flat extrusion die where they are combined to give the desired sequence. The obtained tape, that is preferably from about 0.1 mm to about 2 mm thick, is then cooled, either by means of a chill roll, typically with the aid of an air knife or an electrostatic pinning system to keep the sheet in contact with the chill roll, or by using a liquid-knife as described in WO-A-95/26867 where a continuous and substantially uniform layer of water or of any other cooling liquid flows onto the surface of the sheet that does not contact the chill roll. Any other known means for cooling the cast web can however be employed.

[106] The cooled sheet is then optionally fed through an irradiation unit, typically comprising an irradiation vault surrounded by a shielding. The flat sheet may in fact be irradiated with high energy electrons (i.e., ionizing radiation) from an iron core transformer accelerator. Irradiation is carried out to induce cross-linking. The flat sheet is preferably guided through the irradiation vault on rolls. It is thus possible by suitably combining the number of rolls and the path of the traveling web within the irradiation unit to get more than one exposure of the sheet to the ionizing radiation. In one embodiment, the sheet is irradiated to a level of from about 10 to about 200 kGy, preferably of from about 15 to about 150 kGy, and more preferably of from about 20 to about 120 kGy, wherein the most preferred amount of radiation is dependent upon the polymers employed and the film end use. While irradiation is preferably carried out on the extruded cast sheet just before orientation, as described above, it could also be carried out, alternatively or additionally, during or after orientation.

[107] The optionally irradiated tape is then fed to the pre-heating zone of a simultaneous tenter apparatus, with or without a prior passage through an IR heated oven. The temperature of the oven in said pre-heating zone, the length thereof and the time spent by the traveling web in said zone (i.e. the web speed) can suitably be varied in order to bring the sheet up to the desired temperature for bi-axial orientation. In a preferred embodiment the orientation temperature is comprised between about 90°C and about

140°C and the temperature of the pre-heating zone is kept between about 90°C and about 150°C. In said pre-heating zone the sheet is clipped but it is not yet stretched. Thereafter, the resulting hot, optionally irradiated, and clipped sheet is directed to the stretching zone of the simultaneous tenter. Any simultaneous stretching means can be used in said zone. Preferably however the clips are propelled throughout the opposed loops of the tenter frame by means of a linear synchronous motor. A suitable line for simultaneous stretching with linear motor technology has been designed by Brückner GmbH and advertised as LISIM® line. An alternative line for simultaneous stretching of the extruded flat tape is the DMT line, based on a pantograph, equipped with two separated monorails on each side of the orientation unit. The configuration of the tenter can be varied depending on the stretching ratios desired. The stretching ratios that are applied in the process according to the present invention are generally comprised between about 2:1 and about 5:1 for MD stretching and between about 2:1 and about 5:1 for TD stretching. Preferably however stretching ratios higher than 2.5:1 in both directions are applied, wherein stretching ratios higher than 3:1 in both directions are more preferred. The temperature in the stretching zone is kept close to the selected orientation temperature. The stretched film is then transferred in a zone that, depending on whether a heat-shrinkable or non heat-shrinkable film is desired, may be a relaxation/annealing or heat-setting zone, heated to a temperature of about 70-100 °C, or 130-170°C respectively. Following said annealing or heat-setting step the film is transferred to a cooling zone where generally air, either cooled or kept at the ambient temperature, is employed to cool down the film. The temperature of said cooling zone is therefore typically comprised between about 20 and about 40 °C. At the end of the line, the edges of the film, that were grasped by the clips and have not been oriented, are trimmed off and the obtained bi-axially oriented, heat-shrinkable or heat-set film is then wound up, with or without prior slitting of the film web to the suitable width.

[108] To allow recycling of the trimmed edges, or at least of part thereof, a multi-manifold die may preferably be employed in the co-extrusion so that the edges of the extruded tape that will be grasped by the clips are of a single polymer or polymer composition, typically, in the present process, the polymer(s) of the first outer layer.

[109] The bi-axially oriented film of the present invention, when heat-shrinkable, may have a total % free shrink (% shrink in MD + % shrink in TD), at 120 °C, of from about 20 to about 140 %, preferably from about 30 to about 130 %, more preferably from about 40 to about 120 %, and still more preferably from about 50 to about 110 %.

[110] As indicated above the bi-axially oriented heat-shrinkable films obtained by the process according to the present invention, are also characterised by a maximum shrink tension in at least the transverse direction, in the temperature range of from 20 to 180 °C, of less than 5 kg/cm<sup>2</sup>, preferably less than 3 kg/cm<sup>2</sup>, and more preferably less than

1 kg/cm<sup>2</sup>.

- [111] The biaxially oriented films of the present invention, when heat-set, will have a free shrink, at 120 °C, lower than 10 %, preferably lower than 5 %, more preferably lower than 3 %, and even more preferably lower than 2 %, in each direction.
- [112] The films thus obtained have a thickness variation of less than 10 percent, preferably less than 8 percent, and more preferably less than 5 percent.
- [113] The thus obtained films may then be subjected to a corona discharge treatment to improve the print receptivity characteristics of the film surface. As used herein, the phrases "corona treatment" and "corona discharge treatment" refer to subjecting the outer surfaces of the film to a corona discharge treatment, i.e., the ionization of a gas such as air in close proximity to a film surface, the ionization initiated by a high voltage passed through a nearby electrode, and causing oxidation and other changes to the film surface, such as surface roughness. Corona treatment of polymeric materials is disclosed in e.g. US-A-4,120,716.
- [114] The thus obtained films may also be coated on the surface of the second outer layer with e.g. an antifog composition, with or without a binder to incorporate the antifog additive into the film; a liquid smoke; an aroma transfer composition; an antibacterial or anti-mould composition; etc. as known in the field.
- [115] The present invention is further illustrated by the following examples, which are provided for the purpose of representation, and are not to be construed as limiting the scope of the invention.
- [116] Example 1
- [117] A five-layer, heat-shrinkable film with the following layer arrangement (B)/(D)/(A)/(D)/(C), a total thickness of 25 µm, and a thickness ratio of 4/1/1/1/1.3 is produced by the general process described above. In particular, the temperature of the chill roll is kept at 15-25 °C and the extruded sheet is pinned to the chill roll by means of an air knife. The thickness of the cast extruded sheet before orientation is about 0.4 mm and the linear speed of the quenched sheet is about 8 m/min. The sheet is not irradiated. The temperature in the pre-heating zone is kept between about 120 and about 130 °C. The stretching ratios applied are 4:1 in MD and 4:1 in TD and the temperature in the stretching zone is maintained between about 110 and about 120 °C. The annealing step is carried out at about 80-85 °C and the cooling step at about 30-35 °C. After cooling, the film edges are trimmed off and the film is wound onto a roll at a speed of about 36 m/min.
- [118] The resins employed for the various layers were as follows:
- [119] (A) EVOH-1 (= ethylene-vinyl alcohol copolymer containing 44 mole % of ethylene (EVAL™ E151B from Marubeni));
- [120] (B) EAO-1 (= a blend of 50 wt. % of a heterogeneous ethylene-octene copolymer

with a density of  $0.920 \text{ g/cm}^3$  and a melt index of  $1.0 \text{ g/10 min}$  (Dowlex™ 2045 by Dow); 25 wt. % of a heterogeneous ethylene-octene copolymer with a density of  $0.935 \text{ g/cm}^3$  and a melt index of  $2.6 \text{ g/10 min}$  (Dowlex™ SC 2108 by Dow); 15 wt. % of a homogeneous ethylene-octene copolymer with a density of  $0.902 \text{ g/cm}^3$  and a melt index of  $1.0 \text{ g/10 min}$  (Affinity™ PL1850 by Dow); and 10 wt. % of a master-batch based on ethylene-vinyl acetate copolymer (3.5 % of vinyl acetate content) containing slip (3 wt. %) and anti-block (0.9 wt. %) agents);

[121] (C) PET-1 (= PETG with Tg  $81 \text{ }^\circ\text{C}$  (Estar 6763 by Voridian));

[122] (D) Tie- 1 (= homogeneous ethylene- $\alpha$ -olefin copolymer (Tafmer™ like) with  $d = 0.906 \text{ g/cm}^3$  and MFI =  $1.5 \text{ g/10'}$ , modified with maleic anhydride (m.p.  $116^\circ\text{C}$ ) (ADMER™ AT1094E by Mitsui)).

[123] The modulus of the obtained film was  $6,400 \text{ kg/cm}^2$  in LD and  $7,000 \text{ kg/cm}^2$  in TD.

[124] The free shrink at  $120 \text{ }^\circ\text{C}$  was 43 % in LD and 50 % in TD.

[125] The shrink force was evaluated by the method described hereinbelow in the temperature range of from  $20$  to  $180 \text{ }^\circ\text{C}$  and the maximum shrink tension thus determined was  $0.14 \text{ kg/cm}^2$  in TD (at  $113 \text{ }^\circ\text{C}$ ) and  $0.21 \text{ kg/cm}^2$  in LD (at  $110 \text{ }^\circ\text{C}$ ): specimens of the films ( $2.54 \text{ cm} \times 14.0 \text{ cm}$ ) were cut in the longitudinal and transverse directions and clamped between two jaws, one of which was connected to a load cell. The two jaws kept the specimen in the center of a channel into which an impeller blowed heated air and three thermocouples measured the temperature. The signal supplied by the thermocouples was amplified and sent to an output connected to the "X" axis of an X/Y recorder. The signal supplied by the load cell was also amplified and sent to the "Y" axis of the X/Y recorder. The impeller started blowing hot air and the force released by the sample was recorded in grams. As the temperature increased, the measured profile of the shrink force versus the temperature was drawn on the X/Y recorder. When the temperature of  $180 \text{ }^\circ\text{C}$  was reached, the heater was turned off, the specimen temperature gradually reduced and the profile of the shrink force under negative temperature gradients (cooling) was recorded.

[126] The instrument produced a curve of the shrink force (g) versus temperature ( $^\circ\text{C}$ ); dividing the value by the specimen width, shrink force in  $\text{kg/cm}$  was obtained and further dividing by the specimen thickness the shrink tension, in  $\text{kg/cm}^2$ , was obtained.

[127] Example 2

[128] A five-layer, heat-shrinkable film with essentially the same layer arrangement as in Example 1 but with PET-2 (= PET 18696 with I.V. 0.71 by Voridian) replacing the PET-1 in layer (C), and with a thickness ratio of 5/1/1/1/1.5 is produced by the same process described in Example 1 with the only difference that the stretching ratio was 3:1 in the longitudinal direction and 3.5:1 in the transverse direction.

[129] A film with a thickness of  $25 \text{ }\mu\text{m}$  was obtained characterized by a modulus of 7,000

kg/cm<sup>2</sup> in LD and 9,000 kg/cm<sup>2</sup> in TD.

[130] The film had a free shrink of 15 % in LD and 55 % in TD at 120 °C and a shrink tension of 0 kg/cm<sup>2</sup> in TD and 1.20 kg/cm<sup>2</sup> in LD (at 105 °C)

[131] Example 3

[132] A five-layer, heat-shrinkable film with the same layer arrangement and thickness ratio as in Example 1 is produced by the same process there described with the only difference that the cast sheet is irradiated before orientation to 45 kGray by means of a scan beam unit operated at 500 kVolt and the sheet is passed twice under the irradiation window to provide for a uniform cross-linking.

[133] Example 4

[134] The process of Example 1 has been repeated with the only difference that instead of annealing at a temperature of 85-90°C, the bi-axially oriented film is heat-set at a temperature of 110-120 °C by reducing the line speed by 20 % and allowing the stretching clips to converge by 20 %.

[135] The obtained film showed a total % free shrink (% free shrink in MD + % free shrink in TD) at 120 °C lower than 5.

[136] Example 5

[137] The process of Example 2 has been repeated with the only difference that instead of annealing at a temperature of 85-90°C, the bi-axially oriented film was heat-set at a temperature of 110-120 °C by reducing the line speed by 20 % and allowing the stretching clips to converge by 20 %.

[138] The obtained film showed a total % free shrink at 120 °C lower than 5.

[139] Examples 6-10

[140] The five layer heat-shrinkable films of Examples 6 to 10, having the following layer arrangement (B)/(D)/(A)/(D)/(C), have been prepared by substantially the same general process described in Example 1, with the following modifications : for melt casting an electrostatic pinning system (tension 12 kVolt and current 2 mA) was used instead of the air knife; the temperatures used in the pre-heating/stretching /annealing zones were 100-110/95-100/95-100 °C respectively; and 5 % relaxation in MD was applied in the annealing zone.

[141] The resins used for the different layers, the thickness of each layer, as well as the stretching ratios (SR) applied and the shrink values at 120°C for some representative structures, are reported in following Table 1

[142]

**Table 1**

Ex. No.	(B) (µm)	(D) (µm)	(A) (µm)	(C) (µm)	SR	MD/TD % shrink at
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						120°C
6	EAO-2 (18)	Tie-1 (3)*	EVOH-1 (3)	PET-3 (8)	4x4.5	25/36
7	EAO-2 (18)	Tie-1 (3)*	EVOH-1 (3)	PET-4 (8)	4x4	22/14
8	EAO-3 (7)	Tie-1 (3)*	EVOH-1 (3)	PET-5 (12)	3.3x3.5	
9	EAO-3 (7)	Tie-1 (3)*	EVOH-1 (3)	PET-5 (12)	3.3x3.8	
10	EAO-4 (9)	Tie-2 (3)*	EVOH-1 (3)	PET-5 (10)	3.3x3.8	

[143] \*Both tie layers had the same thickness

[144] EAO-2 = blend of 90 wt. % of a homogeneous ethylene-octene copolymer with density of 0.910 g/cm<sup>3</sup> and melt index of 3.5 g/10 min (Affinity™ PL1845 by Dow) and 10 wt. % of a master-batch based on ethylene-vinyl acetate copolymer (3.5 % of vinyl acetate content) containing slip (3 wt. %) and anti-block (0.9 wt. %) agents;

[145] EAO-3 = blend of 90 wt. % of a homogeneous ethylene-octene copolymer with density of 0.910 g/cm<sup>3</sup> and melt index of 3.5 g/10 min (Affinity™ PL1845 by Dow) and 10 wt. % of a master-batch based on ethylene-vinyl acetate copolymer (3.5 % of vinyl acetate content) containing slip (3 wt. %) and anti-block (1.5 wt. %) agents;

[146] EAO-4 = blend of 50 wt. % of a homogeneous ethylene-octene copolymer with density of 0.910 g/cm<sup>3</sup> and melt index of 3.5 g/10 min (Affinity™ PL1845 by Dow) and 50 wt. % of a master-batch based on heterogeneous ethylene-octene copolymer with a density of 0.920 g/cm<sup>3</sup> and a melt index of 1.0 g/10 min (Dowlex™ 2045 by Dow) containing antiblock (0.7 wt. %) agents, 4 wt. % of polyethoxylated (C<sub>12</sub>-C<sub>14</sub>) alcohols, and 2 wt. % glycerol mono- and di-oleate;

[147] Tie 2 = ethylene- $\alpha$ -olefin copolymer with  $d = 0.915$  g/cm<sup>3</sup> and MFI = 4.5 g/10', modified with maleic anhydride (ADMER™ NF911 by Mitsui);

[148] PET-3 = a blend of 97 wt. % PETG with Tg 81 °C (Estar 6763 by Voridian) and 3 wt. % of a master-batch based on PET containing slip and antiblock agents (Sukano GDC S503);

[149] PET-4 = a blend of 97 wt. % PET with I.V. 0.71 (PET 18696 by Voridian) and 3 wt. % of a master-batch based on PET containing slip and antiblock agents (Sukano GDC S503);

[150] PET-5 = a blend of 95 wt. % PET with I.V. 0.71 (PET 18696 by Voridian) and 5 wt. % of a master-batch based on PET containing slip and antiblock agents (Sukano GDC S503);

[151] Example 11

[152] A five-layer, heat-shrinkable film with the same layer arrangement as in Example 7 but with EPC-1 (a blend of 90 wt. % of a propylene-ethylene copolymer with 3.4 % of ethylene units, and m.p. 134 °C (Eltex PKS 400 by Solvay) and 10 wt. % of a



masterbatch based on polypropylene containing slip (3 wt. %) and anti-blocking (0.5 wt. %) agents) to replace EAO-2 in layer (B), has been prepared by following essentially the same process of examples 6-10 but using stretching ratios of 3.8 X 4.2. The film showed a % free shrink at 120 °C of 30 (MD) and 23 (TD).

[153] Examples 12-14

[154] The processes of Examples 6, 7, and 11 have been repeated with the only difference that instead of being annealed, the bi-axially oriented films have been heat-set at a temperature of 130-140 °C by reducing the line speed by 20 % and allowing the stretching clips to converge by 20 %.

[155] The obtained films showed a free shrink at 120 °C  $\leq$  2 % in each direction.

[156] Example 15

[157] A heat-set, biaxially oriented, five-layer film with the following structure

[158] EAO-3 (13  $\mu$ m) /Tie-1 (3  $\mu$ m) /EVOH-1 (3  $\mu$ m) /Tie-1 (3  $\mu$ m) /PET-5 (13  $\mu$ m)

[159] has been prepared by the general process of example 9 but replacing the annealing step with a heat-setting step carried out at an average temperature of about 160°C.

[160] Examples 16 and 17

[161] The films of these examples have been prepared as described in Example 15 but replacing PET-5 with PET-6 (example 16) and PET-7 (example 17), respectively, wherein

[162] PET-6 = a blend of 92 wt. % PET with I.V. 0.71 (PET 18696 by Voridian), 5 wt. % of a master-batch based on PET containing slip and antiblock agents (Sukano GDC S503), and 3 wt. % of a PETG-based masterbatch containing talc as the nucleating agent;

[163] and

[164] PET-7 = a blend of 92 wt. % PET with I.V. 0.71 (PET 18696 by Voridian), 5 wt. % of a master-batch based on PET containing slip and antiblock agents (Sukano GDC S503), and 3 wt. % of a terpolymer propylene-butylene-ethylene with m.p. 135 °C (Adsyl 5C37F by Basell) as the nucleating agent.

[165] Examples 18-23

[166] Five-layer, heat-set films, having the following layer arrangement

[167] (B) (11  $\mu$ m) / (D) (3  $\mu$ m) / (A) (3  $\mu$ m) / (D) (3  $\mu$ m) / (C) (15  $\mu$ m)

[168] wherein the resins employed for each layer are reported in Table 2 below, have been prepared by the process of Example 15 but applying stretching ratios of 3.3 x 3.5.

[169]

**Table 2**

Ex. No.	(B)	(D)	(A)	(C)
18	EAO-3	Tie-1	EVOH-1	PET-4

19	EAO-3	Tie-2	EVOH-1	PET-4
20	EAO-3	Tie-1	EVOH-1	PET-6
21	EAO-3	Tie-1	EVOH-1	PET-8
22	EAO-3	Tie-1	EVOH-1	PET-9
23	EAO-3	Tie-1	EVOH-1	PET-10

- [170] PET-8 = a blend of 95 wt. % PET with I.V. 0.80 (PET 9921W by Voridian) and 5 wt. % of a master-batch based on PET containing slip and antiblock agents (Sukano GDC S503);
- [171] PET-9 = a blend of 92 wt. % PET with I.V. 0.80 (PET 9921W by Voridian), 5 wt. % of a master-batch based on PET containing slip and antiblock agents (Sukano GDC S503), and 3 wt. % of a PETG-based masterbatch containing talc as the nucleating agent;
- [172] PET-10 = a blend of 92 wt. % of PET with I.V. 0.9 (PET 12822 by Voridian), 5 wt. % of a master-batch based on PET containing slip and antiblock agents (Sukano GDC S503), and 3 wt. % of a PETG-based masterbatch containing talc as the nucleating agent.
- [173] Examples 24-25
- [174] The following heat-set structures have been prepared by the same general process of Example 15 but applying stretching ratios of 3.5 x 4.2 :
- [175] Ex. 24 EAO-2 (16  $\mu\text{m}$ ) /Tie-1 (3.5  $\mu\text{m}$ ) /EVOH-1 (3  $\mu\text{m}$ ) /Tie-1 (3.5  $\mu\text{m}$ ) /PET-4 (14  $\mu\text{m}$ )
- [176] Ex. 25 EAO-2 (13  $\mu\text{m}$ ) /Tie-1 (3.5  $\mu\text{m}$ ) /EVOH-2 (3  $\mu\text{m}$ ) /Tie-1 (3.5  $\mu\text{m}$ ) /PET-4 (14  $\mu\text{m}$ )
- [177] wherein
- [178] EVOH-2 = ethylene-vinyl alcohol copolymer containing 32 mole % of ethylene (EVAL<sup>TM</sup> F101B from Marubeni));
- [179] The heat-set films of examples 15 to 25 have a % free shrink at 120 °C which is  $\leq 1$  in each direction.
- [180] Example 26
- [181] The following heat-set film has been prepared by the same general process of Example 15 but applying stretching ratios of 3.3 x 4.0
- [182] EAO-2 (24  $\mu\text{m}$ ) /Tie-1 (5  $\mu\text{m}$ ) /EVOH-1 (5  $\mu\text{m}$ ) /Tie-1 (5  $\mu\text{m}$ ) /PET-4 (21  $\mu\text{m}$ )
- [183] Example 27
- [184] By following substantially the same process described in Example 15 it is possible to prepare a film differing from that of Example 15 for the second outer layer (B) where a blend of 40 wt. % of a propylene-butylene-ethylene terpolymer with m.p. 135

°C (Adsyl 5C37F by Basell) and 60 wt. % of a masterbatch based on an ethylene- $\alpha$ -olefin plastomer with density of 0.902 g/cm<sup>3</sup> and m.p. 99 °C (Affinity PL1880 by Dow) containing 4 wt. % of polyethoxylated (C<sub>12</sub>-C<sub>14</sub>) alcohols and 2 wt. % glycerol mono- and di-oleate (EAO-5) replaces EAO-3.

[185] Examples 28 and 29

[186] By following substantially the same process described in Example 15 it is possible to prepare six layer films with the following arrangement of layers (B)/(E)/(D)/(A)/(D)/(C) and thickness ratio of 1/6/1.5/1.5/1.5/6 wherein the composition of layers (A), (D), and (C) is as in Example 15, and

[187] in Example 28 layer (B) is a propylene-butylene-ethylene terpolymer with m.p. 135 °C (Adsyl 5C37F by Basell) containing 3 wt. % slip and 1 wt. % antiblocking agents and layer (E) is EAO-5 and,

[188] in Example 29 layer (B) is EAO-2 and layer (E) is a blend of 50 wt. % of a homogeneous ethylene-octene copolymer with density of 0.910 g/cm<sup>3</sup> and melt index of 3.5 g/10 min (Affinity™ PL1845 by Dow) and 50 wt. % of a master-batch based on heterogeneous ethylene-octene copolymer with a density of 0.920 g/cm<sup>3</sup> and melt index of 1.0 g/10 min (Dowlex™ 2045 by Dow) containing 4 wt. % of polyethoxylated (C<sub>12</sub>-C<sub>14</sub>) alcohols, and 2 wt. % glycerol mono- and di-oleate (EAO-6).

[189] The films obtained according to the present invention can be used in the packaging of food and non food, oxygen-sensible, products as known in the art. To this purpose they can be used as such in the form of a film or laminate and either wrapped up around the product or employed as a lid for any suitable container such as a tray, or they may be first converted into flexible containers, such as bags or pouches, by conventional techniques well known to the person skilled in the art. They can also be coupled or laminated to other films or sheets to obtain a packaging material of improved performance.

[190] In a most preferred embodiment the biaxially oriented non heat-shrinkable films of the present invention can conveniently be employed in all those processes that actually use sheets of biaxially oriented polyester (BO-PET) glue-laminated to a heat-sealable barrier film. While the performance of the films of the present invention in these packaging processes is at least comparable to that obtained with the conventional laminates because of the remarkable stiffness of the films of the present invention, the process for the manufacture thereof is much easier and much more convenient as any lamination step may be avoided, as well as the use of any glue and solvent involved therein.

[191] Although the present invention has been described in connection with the preferred embodiments, it is to be understood that modifications and variations may be utilized without departing from the principles and scope of the invention, as those skilled in the

art will readily understand. Accordingly, such modifications may be practiced within the scope of the following claims.

54699-3

25

CLAIMS:

1. A multi-layer, bi-axially oriented, thermoplastic film comprising  
a first outer layer comprising a polyester or a copolyester,  
a second outer layer comprising an ethylene- or propylene-homo- or co-  
5 polymer,  
a core layer comprising an ethylene-vinyl alcohol copolymer,  
first and second tie layers, directly adhered to both sides of the core  
layer, and  
no core layer comprising more than 50% by weight of polyamide or  
10 polyester,  
said film having an elastic modulus, evaluated according to ASTM  
D882, higher than 6,000 kg(f)/cm<sup>2</sup> in at least one direction.
2. The multi-layer, bi-axially oriented, thermoplastic film of claim 1 wherein  
the second outer layer comprises an ethylene homo- or co-polymer.
- 15 3. The multi-layer, bi-axially oriented, thermoplastic film of claims 1 or 2  
which is characterised by an elastic modulus higher than 6,500 kg(f)/cm<sup>2</sup> in at least one  
direction.
4. The multi-layer, bi-axially oriented, thermoplastic film of claims 1 or 2  
which is characterised by an elastic modulus higher than 7,000 kg(f)/cm<sup>2</sup> in at least one  
20 direction.
5. The multi-layer, bi-axially oriented, thermoplastic film of any one of  
claims 1 to 4 which is heat-shrinkable and has a total free shrink, at 120 °C, of from  
about 20 to about 140 percent, wherein the shrink in each direction is evaluated  
according to ASTM D2732.

54699-3

26

6. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 4 which is heat-shrinkable and has a total free shrink, at 120 °C, of from about 30 to about 130 percent, wherein the shrink in each direction is evaluated according to ASTM D2732.
- 5 7. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 4 which is heat-shrinkable and has a total free shrink, at 120 °C, of from about 40 to about 120 percent, wherein the shrink in each direction is evaluated according to ASTM D2732.
8. The multi-layer, bi-axially oriented, thermoplastic film of any one of  
10 claims 1 to 3 which is heat-shrinkable and has a total free shrink, at 120 °C, of from about 50 to about 110 percent, wherein the shrink in each direction is evaluated according to ASTM D2732.
9. The multi-layer, bi-axially oriented, thermoplastic film of any one of  
15 claims 5 to 8, which is characterized by a maximum shrink tension in the transverse direction, in the temperature range of from 20 to 180 °C, of less than 5 kg/cm<sup>2</sup>.
10. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 5 to 8, which is characterized by a maximum shrink tension in the transverse direction, in the temperature range of from 20 to 180 °C, of less than 3 kg/cm<sup>2</sup>.
11. The multi-layer, bi-axially oriented, thermoplastic film of any one of  
20 claims 5 to 8, which is characterized by a maximum shrink tension in the transverse direction, in the temperature range of from 20 to 180 °C, of less than 1 kg/cm<sup>2</sup>.
12. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 4 which is non heat-shrinkable and heat-set and is characterized by a free shrink at 120 °C which is  $\leq 10\%$ , in each direction, wherein the shrink is evaluated  
25 according to ASTM D2732.

54699-3

27

13. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 4 which is non heat-shrinkable and heat-set and is characterized by a free shrink at 120 °C which is  $\leq 5\%$ , in each direction, wherein the shrink is evaluated according to ASTM D2732.
- 5 14. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 4 which is non heat-shrinkable and heat-set and is characterized by a free shrink at 120 °C which is  $\leq 3\%$ , in each direction, wherein the shrink is evaluated according to ASTM D2732.
- 10 15. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 14, wherein the polyester or copolyester of the first outer layer is an aromatic ring-containing polymer.
- 15 16. The multi-layer, bi-axially oriented thermoplastic film of claim 2 wherein the ethylene homo- and co-polymers of the second outer layer are selected from the group consisting of polyethylene homo-polymers, heterogeneous or homogeneous ethylene- $\alpha$ -olefin copolymers, ethylene-vinyl acetate co-polymers, ethylene-(C<sub>1</sub>-C<sub>4</sub>)alkyl acrylate or methacrylate co-polymers, ethylene-acrylic acid co-polymers, ethylene-methacrylic acid co-polymers, and blends thereof in any proportion.
- 20 17. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 16, which has five layers, wherein the first tie layer directly adheres the core layer to the first outer layer and the second tie layer directly adheres the core layer to the second outer layer.
- 25 18. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 16, which has six to eight layers, wherein the first tie layer directly adheres the core layer and the first outer layer, and one to three additional core polyolefin layers are positioned between the second outer layer and the second tie layer.

54699-3

28

19. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 16, which has seven to ten layers, wherein an additional core polyolefin layer is positioned between the first tie layer and the first outer layer, and a third tie layer directly adheres said additional core polyolefin layer to the first outer layer.
- 5 20. The multi-layer, bi-axially oriented, thermoplastic film of claim 19, wherein one to three additional core polyolefin layers are positioned between the second outer layer and the second tie layer.
21. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 20, which comprises anti-fog agents in the second outer layer or/and in  
10 any polyolefin core layer possibly positioned between said second outer layer and the core layer.
22. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 21, which is irradiated to a level of from about 10 to about 200 kGy.
23. The multi-layer, bi-axially oriented, thermoplastic film of any one of  
15 claims 1 to 21, which is irradiated to a level of from about 15 to about 150 kGy.
24. The multi-layer, bi-axially oriented, thermoplastic film of any one of claims 1 to 21, which is irradiated to a level of from about 20 to about 120 kGy.
25. A process for the manufacture of a bi-axially oriented, thermoplastic film comprising a first outer layer comprising a polyester or a copolyester, a second outer  
20 layer comprising an ethylene- or propylene-homo- or co-polymer, a core layer comprising an ethylene-vinyl alcohol copolymer, first and second tie layers directly adhered to both sides of the core layer, and no core layer comprising more than 50% by weight of polyamide or polyester, said film having an elastic modulus, evaluated according to ASTM D882, higher than  $6,000 \text{ kg(f)/cm}^2$  in at least one direction, which  
25 process comprises co-extruding the film resins through a flat die and bi-axial orientating the obtained cast sheet simultaneously in the two perpendicular directions at an orientation ratio in the longitudinal direction higher than 2:1, and at an



54699-3

29

orientation ratio in the cross-wise direction higher than 2:1, by means of a tenter frame.

26. The process of claim 25, wherein the orientation ratio in the longitudinal direction is higher than 3:1.

5 27. The process of claim 25 or 26, wherein the orientation ratio in the cross-wise direction is higher than 3:1.

28. The process of any one of claims 25 to 27, which is followed by an annealing or heat-setting step.

10 29. A multi-layer, bi-axially oriented, thermoplastic film as defined in claim 1, manufactured according to the process as defined in claim 25.