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(54) Title: UNIAXIALLY SHRINKABLE BIAXIALLY ORIENTED POLYPROPYLENE FILM WITH HDPE SKIN (57) Abstract A uniaxially heat-shrinkable, biaxially oriented, multilayer film having a polypropylene-containing core layer comprising at least 70 wt.% of said multilayer film and at least one polyolefin-containing skin layer adjacent said core layer is prepared by biaxially orienting a coextrudate and thereafter orienting said coextrudate by stretching 10 to 40 % in the machine direction. The core layer contains isotactic polypropylene and a modifier which reduces the crystallinity of the polypropylene by increasing chain imperfections or reducing isotacticity of the polypropylene-containing core. Such modifiers can be selected from the group consisting of atactic polypropylene, syndiotactic polypropylene, ethylene-propylene copolymer, propylene-butene-1 copolymer, ethylene-propylene-butene-1 terpolymer, and linear low density polyethylene. The skin layer can be high density polyethylene on both sides or high density polyethylene on one side and isotactic polypropylene on the other side.		

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UNIAXIALLY SHRINKABLE BIAXIALLY ORIENTED
POLYPROPYLENE FILM WITH HDPE SKIN

The present invention relates to the field of polymer
5 films and, more particularly to a uniaxially heat
shrinkable biaxially oriented polypropylene film.

As noted in U.S. Patent No. 4,194,039, polyolefins can
be used to prepare shrink films for wrapping purposes.
Other suitable synthetic resins include various ionomers,
10 polyvinyl chlorides, polyesters, polystyrenes and
polyvinylidene chlorides.

A shrink film's distinguishing characteristic is its
ability upon exposure to some level of heat to shrink or,
if restrained, to create shrink tension within the film.
15 This ability is activated by the packager when the wrapped
product is passed through a hot air or hot water shrink
tunnel. The resulting shrinkage of the film results in an
aesthetically pleasing transparent or opaque wrapping which
conforms to the contour of the product while providing the
20 usual functions required of packaging materials such as
protection of the product from loss of components,
pilferage, or damage due to handling and shipment. Typical
items wrapped in polyolefin shrink films are toys, games,
sporting goods, stationery, greeting cards, hardware and
25 household products, office supplies and forms, foods,
phonograph records, and industrial parts.

The manufacture of shrink films requires relatively
sophisticated equipment including extrusion lines with
"racking" capability, irradiation units when cross-linking
30 is desired, tenter frames, mechanical centerfolders, and
slitters. "Racking" or "tenter framing" are conventional
orientation processes which cause the film to be stretched
in the cross or transverse direction and in the
longitudinal or machine direction. The films are usually
35 heated to their orientation temperature range which varies
with different polymers but is usually above room
temperature and below the polymer's melting temperature.

After being stretched, the film is rapidly cooled to quench it thus freezing the molecules of film in their oriented state. Upon heating, the orientation stresses are relaxed and the film will begin to shrink back to its original,
5 unoriented dimension.

Certain applications, e.g., labelling, covering, or packaging of materials such as boxes, plates, vessels, bottles, tubes, cylindrical material, e.g., pipes, and rods, etc. are especially susceptible to covering with heat shrinkable films. However, in certain situations it is
10 desirable to effect shrinkage along a single axis without substantial shrinkage in the cross-direction. For example, in the process of labelling bottles by shrinking a tube of heat shrinkable material, if the film shrinks along its
15 length, the label may not be placed in the right position but rather placed at above the desired position upon shrinkage. Moreover, printing and other conversion processes of such label surfaces require heat stability in substantially one direction to meet machinability
20 requirements. Uniaxially shrinkable materials can also be used in preparing tightly wrapped containers by lap heat sealing or lap hot melt adhesive sealing uniaxially shrinkable film resulting in shrink down of the wrapping.

In order to obtain uniaxially shrinkable materials it
25 is possible to employ uniaxially oriented materials, i.e., materials which are oriented in only one direction. However, uniaxially oriented film can lack the requisite strength and toughness necessary for use in such applications. Inasmuch as biaxially oriented films exhibit
30 desirable strength and tear resistance in both directions of orientation, it would be desirable to obtain a uniaxially heat shrinkable film which is biaxially oriented and thus substantially stable in the cross-direction.

For more detailed disclosures of heat shrinkable
35 films, reference may be had to aforesaid U.S. Patent No. 4,194,039, as well as U.S. Patent Nos. 3,808,304;

4,188,350; 4,377,616; 4,390,385; 4,448,792; 4,582,752 and 4,963,418.

U.S. Patent No. 5,292,561 (corresponding to EPA 0498249) discloses a process for producing polyolefin shrink films having high unidirectional shrinkage (at least 10% longitudinal shrinkage and less than 2% transverse shrinkage at 100°C) under conditions comprising an MD reorientation mechanical MD/TD draw ratio between 1.01 and 7.5. The base layer of the films contain propylene polymer and optionally, hydrogenated hydrocarbon resin.

EPA 0204843 discloses a low temperature shrinkable film comprising linear low-density polyethylene resin having film shrink properties of 30% or more MD and 5% or less TD at 90°C, which is prepared by drawing the film at a high draw ratio (3 to 6) in the machine direction.

EPA 0321964 describes a process for extruding a shrink film from a linear low density copolymer of ethylene and at least one alpha-olefin having 3 to 6 carbon atoms to provide a material which exhibits shrinkage at 135°C of at least 30% MD and at least 10% TD.

EPA 0477742 discloses a transparent polypropylene shrink film which exhibits shrinkage at 100°C of at least 10% MD and less than 2% TD. The polypropylene comprises a 15% or less, preferably 2 to 6% n-heptane soluble component.

EPA 0299750 discloses a mono- or biaxially stretched film having a heat shrinkage of 20% or more in one of the longitudinal and transverse directions and 60% or more in the other direction. The film comprises principally a linear polyethylene and optionally, a branched low-density polyethylene.

EPA 0595270 discloses a heat sealable laminate having high unidirectional shrinkage produced from biaxially oriented polymeric film such as biaxially oriented polypropylene or blends of polypropylene and copolymers of propylene with minor amounts of ethylene or an alpha-olefin. Uniaxial shrinkability is achieved by balancing

MD reorientation process variables such as temperature, draw ratio, line speed, and oriented polymer film properties. Heat sealability is imparted by the presence of a heat seal layer.

5 It is an object of the present invention to impart uniaxial heat shrinking properties to a biaxially oriented multilayer film comprising a polypropylene core.

It is a further object of the present invention to provide a biaxially oriented multilayer film comprising a
10 polypropylene core which is uniaxially heat shrinkable.

It is a further object of the present invention to provide a biaxially oriented polypropylene core which contains isotactic polypropylene and a modifier which reduces the crystallinity of the polypropylene by
15 increasing chain imperfections or reducing isotacticity of the polypropylene-containing core.

The present invention relates to a uniaxially heat-shrinkable, biaxially oriented, multilayer film having a polypropylene-containing core layer and at least one high
20 density polyethylene containing skin layer adjacent said core layer. The core layer contains isotactic polypropylene and a modifier which reduces the crystallization or crystallinity of the polypropylene by increasing chain imperfections or reducing isotacticity of
25 the polypropylene-containing core.

Core

The composition of the polypropylene-containing core layer of the multilayer film of the present invention must provide sufficient operability so that the film after
30 biaxial orientation exhibits crystallinity which is low enough to permit the secondary orientation of the film, which imparts the uniaxial shrinkability to the film, without tearing. The core layer material can be a single polypropylene homopolymer material which is sufficiently
35 atactic and which has a specific melting point, as determined by the DSC (Differential Scanning Calorimetry) method, e.g., at a heating rate of 2°C/minute.

Alternately, the core layer material can comprise a blend of a more isotactic polypropylene with modifiers which are polyolefin materials which are less crystallizable due to a higher degree of chain imperfections or lower isotacticity.

- 5 Suitable DSC melting points for the core layer, blended or not, can be less than 160°C, e.g., less than 150°C, or even less than 140°C.

Modifiers suited to use in the present invention include polyolefins other than isotactic polypropylene.

- 10 The modifier can be selected from the group consisting of atactic polypropylene, syndiotactic polypropylene, ethylene-propylene copolymer, propylene-butene-1 copolymer, ethylene-propylene-butene-1 terpolymer, polybutene-1, and linear low density polyethylene.

- 15 Several ways have been found to provide a polypropylene core having a higher degree of chain imperfections and the desired post primary orientation crystallinity. The desired crystallinity avoids tearing of the biaxially oriented film during secondary orientation at stretch levels of greater than 30% or greater than 35%,
20 e.g., up to 40% or even up to 45%. Isotactic polypropylene, i.e., polypropylene having less than 5% atacticity, say less than 3% atacticity, can be combined with a modifier, e.g., atactic polypropylene, to provide a
25 suitable core layer. Atactic content can be measured by a polymer's insolubility in boiling n-hexane with chain imperfections being observed via NMR tests.

- In one aspect of the present invention, the modifier, e.g., atactic polypropylene, is added to the core in
30 amounts sufficient to provide a core layer having an overall atacticity greater than 2%, preferably greater than 4%, greater than 5% or greater than 6%, say, e.g., 6 to 15%. For present purposes, atactic polypropylene has an atacticity of at least 10%, preferably at least 15%, e.g.,
35 15 to 20% or 15 to 25%. Atactic polypropylene can be used alone as the core or added to isotactic polypropylene in amounts such that the resulting mixture comprises 10 to 99

wt.% atactic polypropylene, e.g., 10 to 30 wt.%, preferably 15 to 20 wt.%. atactic polypropylene. Blends of 15 wt.% atactic polypropylene (15% atacticity) and 85 wt.% isotactic polypropylene (of 4 to 5% atacticity) are especially preferred.

A suitable atactic polypropylene for use in the present invention has an atacticity of 15% which can be added to isotactic polypropylene to provide a core mixture containing 15 wt.% atactic polypropylene thereby increasing overall core atacticity by 2.25 wt.%.
10

Commercially available isotactic propylene suited to use in the present invention includes Fina 3371 from Fina Oil and Chemical Co., Chemical Div., Dallas, TX. Atactic polypropylenes which are commercially available include L1300 from Novolen of BASF Corp., Parsippany, NJ.
15

In another embodiment, the present invention employs a core layer which comprises polypropylene as described above, preferably isotactic polypropylene, mixed with polybutene-1 modifier to provide a core layer containing 2 to 15 wt.% polybutene-1, preferably 5 to 10 wt.% polybutene-1. Suitable polypropylene/polybutene-1 homogeneous blends are described in U.S. Patent No. 3,808,304. This disclosure teaches blends containing from 30 to 90 weight parts of polypropylene and correspondingly, from 70 to 10 weight parts of polybutene-1. Suitable polybutylenes include PB 8430, available from Shell Chemical Co. of Houston, TX.
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In yet another aspect of the invention, the core layer comprises polypropylene as described above, preferably isotactic polypropylene, mixed with ethylene-propylene copolymer modifier, e.g., 2 to 10 wt.% ethylene-propylene copolymer, preferably 3 to 10 wt.% E-P copolymer. Suitable E-P copolymer can contain from 2 to 7 wt.% ethylene, the balance being propylene. The copolymers can have a melt index at 230°C generally ranging from 2 to 15, preferably from 3 to 8. The crystalline melting point is usually from 125° to 150°C, and the number average molecular weight is
30
35

25,000-100,000. The density is preferably from 0.89 to 0.92 g/cm³. Suitable E-P copolymers include EP 8573, available from Fina Oil and Chemical Co., Chemical Div., Dallas, TX.

5 In still another aspect of the invention, the core layer is a blend of polypropylene as described above, preferably isotactic polypropylene, mixed with 0 to 10 wt.% ethylene-propylene copolymer, said copolymer preferably being 50 to 100 wt.% E-P copolymer which contains from 0.5
10 to 1 wt.% ethylene, the balance being propylene. These fractional copolymers are commercially available as ready-mix resin containing 0.6 wt.% ethylene (4173 from Fina).

In another aspect of the invention, the core layer is a blend of polypropylene as described above, preferably
15 isotactic polypropylene, mixed with propylene-butene-1 copolymer. The core layer can comprise 5 to 20 wt.% propylene-butene-1 copolymer, preferably 10 to 20 wt.%. Suitable propylene-butene-1 copolymers include Cefor SRD4-105, and Cefor SRD4-104 available from Shell Chemical
20 Co. The core layer can comprise 5 to 20 wt.% of said propylene-butene-1 copolymer as modifier.

In yet another aspect of the invention, the core layer is a blend of polypropylene as described above, preferably isotactic polypropylene, mixed with linear low density
25 polyethylene (LLDPE). These polymers typically have a melt index of 1 to 10. The linear low density polyethylenes should have a density in the range 0.88-0.94 g/cc, preferably, 0.89-0.92 g/cc. The linear low density polyethylenes may be derived from ethylene together with
30 other higher comonomers such as butene-1, hexene-1 or octene-1. The core layer can comprise 2 to 15 wt.% LLDPE, preferably 5 to 10 wt.% LLDPE. Commercially available LLDPEs include Exact 2009, Exact 2010, and Exact 3016 available from Exxon Chemical Co.

35 In a particularly preferred embodiment, the core layer is a blend of polypropylene as described above, preferably

isotactic polypropylene, mixed with syndiotactic polypropylene and, optionally, ethylene-propylene copolymer.

Syndiotactic polypropylene can be present in the core layer in amounts ranging from 2 to 60 wt.%, preferably 4 to 30 wt.%, with 0 to 40 wt.% ethylene-propylene copolymer, preferably 0 to 20 wt.% E-P copolymer. Suitable E-P copolymers are described above. The presence of E-P copolymer improves MD tensile strength in the secondary orientation step. However, E-P copolymer content must be carefully determined inasmuch as the presence of E-P copolymer can cause undesirable film elongation even at lower temperatures, e.g., 60°C (140°F) drying temperatures, which elongation can cause registration problems during converting processes such as printing.

The syndiotactic polypropylene used as a modifier in the present invention can possess an isotacticity of less than 15%, in particular less than 6%. The mean length of sequence $\bar{n}_r$ of the syndiotactic sequences is preferably greater than 20, more preferably greater than 25. The molar mass distribution corresponds to the relation

$$M_w = k \times M_n,$$

where

M_w stands for the weight average of the molar mass distribution,

M_n stands for the number average of the molar mass distribution, and

k is a factor which is between 1 and 5, preferably between 2 and 3.

The weight average is preferably between 60,000 and 250,000, in particular between 90,000 and 160,000. The mean molar masses can be determined according to customary methods; of these, the method of gel permeation chromatography has proven to be particularly suitable.

Commercially available syndiotactic polypropylene resins suited to use in the present invention include EOD 9306, EOD 9502 and EOD 9630 available from Fina.

In yet another aspect of the invention, the core layer is a blend of polypropylene as described above, preferably isotactic polypropylene, mixed with ethylene-propylene-butene-1 terpolymer as modifier. The core layer can
5 comprise 5 to 20 wt.% of the terpolymer. Suitable terpolymers include those containing 3 to 5 wt.% ethylene and 3 to 6 wt.% butene-1. Such terpolymers are available from Chisso, under the tradename Chisso 7700 Series. Other
10 suitable ethylene-propylene-butene-1 terpolymers include those containing 0.5 to 3 wt.% ethylene, and 13 to 20 wt.% butene-1. Such terpolymers are available from Chisso, under the tradename Chisso 7800 Series.

Suitable core layers of the present invention can comprise recycled polypropylene (RPP), e.g., up to 25 wt.%
15 RPP, preferably up to 15 wt.% RPP.

The core layer of the present invention may also comprise a plurality of voids formed by cavitation a solid cavitation agent. Polybutene-1 terephthalate (PBT), e.g.,
in amounts comprising 4 to 10 wt.% of the core layer, well-
20 dispersed as fine spherical particles, e.g., 0.2 to 2 microns in diameter, as described in U.S. Patent Nos. 5,288,548, 5,267,277 and 4,632,869, is a suitable cavitation agent. The spherical particles form microvoids on orientation, resulting in a white opaque product.

25 The opacity and low light transmission of the film may be enhanced by the addition to the core layer itself of from 1% by weight and up to 10% by weight of opacifying compounds, which are added to the melt mixture of the core layer before extrusion. Opacifying compounds which may be
30 used include iron oxides, carbon black, graphite, aluminum, TiO₂, and talc.

A 30 micron polygag, clear film equivalent, white opaque film described above will have a density of 0.6 to 0.75 g/cc, an optical-cavitated thickness gauge of 36 to 45
35 microns and light transmission of 15 to 25% depending on percentage of PBT dispersed and the orientation conditions,

including the extent of stretching as well as MD and TD orientation temperatures.

Such a core layer can further comprise a supporting layer of polypropylene, preferably isotactic polypropylene, on one or both sides of the core. One of said supporting layers may contain 2 to 18 wt.% TiO_2 . Further description of such use of TiO_2 -containing layers is found in U.S. Patent No. 5,091,236. The supporting layer may also contain 2 to 60 wt.%, preferably 4 to 30 wt.%, syndiotactic polypropylene. Incorporation of skin layers over the supporting layers serves to encapsulate the abrasive TiO_2 and provides a highly opaque, five layer structure. The multilayer film has improved functionality for printing, metallizing, adhesives, coatings, and heat sealability.

Alternatively, clear five layer structures can be prepared by substituting a supporting layer of polypropylene on both sides of the core, which layer does not contain opacifying materials such as TiO_2 or PBT.

The aforementioned blends of propylene and other constituents noted above may be admixed by any suitable means to form a homogeneous blend, such as dry mixing, solution mixing, or mixing the two polymers together while in a molten state or combinations thereof.

Skin Layer

The skin layer of the present invention may be any of the coextrudable, biaxially orientable heat shrinkable film-forming resins known in the prior art. Such materials include those discussed above which are suited to use in the core layer, including isotactic polypropylene, atactic polypropylene, polypropylene blended with polybutene-1, propylene-butene-1 copolymer, and ethylene-propylene copolymer, including fractional E-P copolymer. In addition, polyethylene or ethylene-propylene-butene-1 terpolymer may be employed as the skin layer.

Ethylene-propylene-butene-1 random terpolymers suited to use in the skin layers of the present invention include those containing 1 to 5 wt.% random ethylene, 10 to 25 wt.%

random butene-1. The amounts of the random ethylene and butene-1 components in these copolymers are typically in the range of 10 to 25% total (ethylene plus butene-1). Typical terpolymers of this type include those with 1 to 5%
5 ethylene and 10 to 25% butene-1.

These copolymers typically have a melt flow rate in the range of 5 to 10 with a density of 0.9 and a melting point in the range of 115° to 130°C.

In one aspect of the invention the skin layer is
10 derived from a linear low density polyethylene (LLDPE). These polymers typically have a melt index of 1 to 10. The linear low density polyethylenes may have a density as high as 0.94, usually in the range 0.90 - 0.91, e.g., 0.92 or 0.91, with a melt index from 1 to 10. The linear low
15 density poly-ethylenes may be derived from ethylene together with other higher comonomers such as butene-1, hexene-1 or octene-1.

In another aspect of the invention skin layers of substantially high density polyethylene (HDPE) having a
20 density of 0.94 or greater, with no other olefinic polymeric materials, may be employed. Alternatively, a skin of substantially HDPE with no other olefinic polymeric materials may be employed as the skin layer on one side of the core layer and a skin containing a major proportion of
25 propylene homopolymer, preferably isotactic polypropylene, may be employed as the skin layer on the other side of the core layer.

Using HDPE on both sides or HDPE on one side and isotactic polypropylene on the other side results in
30 improved machinability over the use of terpolymers in the skin layer. When laminated to a second film of similar structure in such a way that the HDPE skins are both on the outside of the structure, heat sealability is maintained. The net result of the lamination could be carried to a
35 single web by using HDPE as the skins on both sides with at least one of the HDPE skins containing some anti-block.

HDPE on both outside surfaces produce acceptable heat seals on the side seams as well.

Labels using terpolymer skins on both sides of the web suffer from knife stick and squealing on some labeling machines when used without mobility overlaquers. Knife stick leads to machine jamming while squealing is perceived by the machine suppliers as a condition with a high probability of having label length problems.

The use of HDPE on both sides or HDPE on one side and isotactic polypropylene on the other side eliminates knife stick and squealing in non overlaquer applications. The use of HDPE as skins on both sides of the core results in adequate heat seals. Alternatively, multilayer films with HDPE on one side of the core and propylene homopolymer on the other side of the core may be laminated together in such a manner that the HDPE is the outside layer for both sides of the lamination, resulting in adequate heat sealability.

Each skin layer adjacent to the core layer can range in thickness from 0.5 to 3 microns (.02 to .12 mil), preferably 0.5 to 1.0 micron (.02 to .04 mil), e.g., 0.5 to 0.75 micron (.02 to .03 mil).

Prior to incorporation in the film, e.g., before extrusion, at least one of the skin layers can be compounded with an anti-blocking effective amount of anti-blocking agent, e.g., silica, clays, talc, glass and the like which are preferably provided in the form of approximately spheroidal particles. The major proportion of these particles, for example, anywhere from more than half to as high as 90 wt.% or more, will be of such a size that significant portion of their surface area, for example, from 10 to 70% thereof, will extend beyond the exposed surface of the skin layer. In a preferred embodiment, the anti-blocking agent comprises non-meltable silicone resin, e.g., particulate cross-linked hydrocarbyl-substituted polysiloxanes. Particularly preferred particulate cross-linked hydrocarbyl-substituted

polysiloxanes include the polymonoalkylsiloxanes. Most particularly preferred are non-meltable polymonoalkylsiloxanes characterized as having a mean particle size of 0.5 to 20.0 microns and a three dimensional structure of siloxane linkages. Such materials are available from Toshiba Silicone Co., Ltd., worldwide, and in the United States from General Electric Co., and are marketed under the tradename Tospearl. Other commercial sources of similar suitable materials are also known to exist. Such materials are further described as non-meltable crosslinked organosiloxane resin powders in U.S. Patent No. 4,769,418. Effective amounts of the particulate cross-linked hydrocarbyl-substituted polysiloxane anti-blocking agent can range from 100 to 5000 ppm, preferably 1000 to 3000 ppm, say, from 1500 to 2500 ppm, based on loading of the resin from which the upper layer (c) is prepared.

The amount of anti-blocking agent in the skin layer is in the range of from 0.25 to 0.75 wt.% anti-block. More than one anti-blocking agent may be used. For example, 0.24 wt.% Sipernat 44, commercially available from Degussa Corporation of Akron, Ohio, and 0.3 wt.% Kaopolite 1152, produced by Kaopolite, Inc. of Union, New Jersey, may be used. When using HDPE as the skin layer on both sides of the core, it is preferred to use anti-block in at least one side. Likewise, when using HDPE as one skin layer and a propylene homopolymer as the other skin layer, it is preferred to use anti-block only in the propylene homopolymer side.

Reduced coefficient of friction and reduced antistatic characteristics at the surface of the skin layer or layers can be achieved in accordance with the disclosure set out in U.S. Patent No. 5,264,277, which discloses the use of migratory slip agents and antistatic agents in multilayer films. Reduced COF may also be obtained by treating one or both skins with 2000 to 15000 ppm silicone oil.

If desired, the exposed surface of the skin layer or skin layers can be treated in a known and conventional manner, e.g., by corona discharge to improve its receptivity to printing inks, coatings, adhesive anchorage, and/or its suitability for such subsequent manufacturing operations as lamination.

It is preferred that all layers of the multilayer film structures of the present invention be coextruded, after which the film can be biaxially oriented (primary orientation) and thereafter secondarily oriented in the direction in which shrinkability is desired. Coextrusion can be carried out in a multilayer melt form through a flat die.

Primary Orientation

The multilayer coextrudate film can be primarily oriented biaxially. Biaxially oriented film can be stretched 3 to 6 times, preferably 4 to 5 times in a first direction, preferably the machine direction (MD), and 5 to 10 times, preferably 7 to 8 times in a second direction which is substantially normal to the first direction, preferably the transverse direction (TD). Biaxial orienting can be carried out using a conventional tenter or stenter machine at a drawing temperature of 100° to 140°C, e.g., 130°C. Generally, biaxial orientation temperatures differ for MD orientation (115° to 130°C, e.g., 120°C) and TD orientation (130° to 160°C, e.g., 150°C). Film thickness at this stage can range from 25 to 75 microns (1.0 to 3.0 mils), preferably 25 to 66 microns (1.0 to 2.6 mils). Cooling of the film to temperatures below 100°C occurs prior to secondary orientation.

Secondary Orientation

The primarily oriented film is then reheated to 100° to 125°C, say 110° to 115°C, preferably by use of heated cylinders and stretched an additional 10 to 40%, preferably 25 to 30%, in the first direction of orientation, e.g., machine direction (MD). In order to minimize compressive stress which can adversely affect second direction heat

stability, e.g., TD heat stability, it is desirable to maintain a minimal distance between the reheating roll(s) and the cooling/stretching roll(s) used in secondary orientation. Such distances can be less than 30 cm, e.g.,
5 5 to 10 cm.

The resulting uniaxially shrinkable film after secondary orientation can range in thickness from 10 to 60 microns (0.4 to 2.4 mils), preferably 20 to 50 microns (0.8 to 2.0 mils).

10 Simultaneous Orientation

The films of the present invention can also be prepared by orienting on a line which utilizes linear motors to directly propel opposed pairs of tenter clips synchronously whereby primary orienting by simultaneous
15 biaxial orienting is effected by accelerating along a diverging path directly opposed pairs of tenter clips holding the film. In other words, the film can be primarily oriented by synchronously accelerating along a diverging path, directly opposed pairs of tenter clips
20 holding the film.

Secondary machine direction orientation on the same line can be effected along a parallel path subsequent to the diverging path by simultaneously accelerating the directly opposed pairs of tenter clips along some portion
25 of the parallel path. In other words, the film is secondarily oriented by synchronously accelerating along a straight path, directly opposed pairs of tenter clips holding the film.

The film can be further stabilized by heat setting and
30 annealing and subsequent cooling before leaving the tenter frame such that the resulting film will have good machine direction stability at temperatures less than 100°C and shrinkage at 25% or more at 135°C or greater in the machine direction and good TD direction stability at 135°C or
35 below, e.g., less than 5%.

The use of linear motors to directly propel tenter clips to effect simultaneous biaxial stretching is further disclosed in U.S. Patent No. 4,853,602 to Hommes, et al.

The resulting uniaxially shrinkable film after
5 secondary orientation can range in thickness from 10 to 60 microns, (0.4 to 2.4 mils), preferably 20 to 50 microns (0.8 to 2.0 mils).

Dimensional Stability

The resulting uniaxially shrinkable film after
10 secondary orientation exhibits at temperatures of 100° to 145°C, say, 135°C, greater than 15%, preferably greater than 18%, 20%, or even greater than 25% shrinkage in the direction of secondary orientation, e.g., machine direction. Shrinkage is determined by measuring the
15 difference of sample length before and after placing the sample, unrestrained, in a 135°C oven for 7 minutes.

Shrinkage in the direction of secondary orientation preferably occurs with minimal variation in the direction normal to said secondary orientation, e.g., transverse
20 direction. Such variation or stability can be described in terms of the change in length of the multilayer film in the direction normal to the secondary orientation and can include both expansion and shrinkage as a percentage of the dimension prior to heat exposure. The present invention's
25 films can exhibit $\pm 5\%$ stability, preferably $\pm 3\%$ stability, or even $\pm 1\%$ stability in the direction normal to that of secondary orientation. Stability of $\pm 5\%$ means that the dimension of the film normal to the direction of secondary orientation, after heating to 135°C (275°F) shrinks or
30 expands no greater than 5% of the original dimension of the film at room temperature.

Elongation at Lower Temperatures

Another parameter of interest is the resistance to stretching or dimensional stability of the film after
35 secondary orientation in the direction of secondary orientation (% elongation) under common processing conditions, e.g., print drying temperatures of 54° to 66°C

(130° to 150°F), preferably 60°C (140°F). It is desirable to provide a uniaxially shrinkable film which is resistant to elongation under the tensions 17.8 to 178 g per cm (0.10 to 1.0 pli [pounds per linear inch]), preferably 134 g per linear cm (0.75 pli), and temperatures normally encountered by the film during processes prior to thermoshrinking, e.g., drying after printing. To avoid registration problems during printing, MD elongation at 134 g per linear cm (0.75 pli) should be less than 0.6% at 60°C (140°F), preferably less than 0.4%. MD elongation is generally reduced and is thus less of a problem as secondary stretching (MD orientation) is increased.

Especially preferred films of the present invention show minimal MD elongation and TD shrinkage at processing temperatures of 60°C and 134 g/cm (0.75 pli), and maximum MD shrinkage at temperatures used to effect shrinkage, e.g., heat tunnel temperatures of 127° to 141°C (260° to 285°F), preferably 135°C (275°F) or higher, depending on residence time.

The invention is illustrated by the following non-limiting examples in which all parts are by weight unless otherwise specified.

EXAMPLE 1

This example shows a multilayer film having the following structure:

	Terpolymer (Chisso 7701) (3.0 gauge)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
30	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
	99.8 wt.% Terpolymer (Chisso 7701) + 0.2 wt.% ppm Tospearl (3.0 gauge)

The film structure of this example was produced by coextruding a multilayer cast sheet, with a thickness of 34 mil (864 microns). The cast sheet was reheated to 110°C

then stretched 4.4 times in the machine (MD) direction. Following MD orientation, the web was heated to 160°C then stretched approximately 7.5 times in the transverse direction (TD) by use of the tentering process. After
 5 cooling to 54°C the web was reheated to 121°C and stretched 1.3 times more in the MD direction. After the third stretching, the film was cooled to 27°C then corona treated on the terpolymer only skin side. Following corona
 10 treatment, the film was annealed at a temperature of 66°C by means of a heated roll. After annealing the web was cooled back to 27°C and wound into a roll. The resulting film had a thickness of 0.80 mil (20 microns). In the structure of Example 1, a thickness of 3 gauge = 0.03 mil (0.76 microns).

15 For machinability testing on the labeling lines, two webs of the film were adhesively laminated together in such a manner to give a structure with the anti-block-containing skins on both outside surfaces with a thickness of 40 microns. The results are shown in Table 1.

20 EXAMPLE 2

This example shows a multilayer film having the following structure:

25	99.46 wt.% iPP + 0.24 wt.% anti-block (Sipernat 44) + 0.3 wt.% anti-block (Kaopolite) (3.0 gauge)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
30	99.5 wt.% HDPE (Lyondell M6030) + 0.5 wt.% fluoropolymer processing aid (3.0 gauge)

The film structure of this example was produced by coextruding a multilayer cast sheet, with a thickness of 34 mil (864 microns). The cast sheet was reheated to 127°C
 35 then stretched 4.4 times in the machine (MD) direction. Following MD orientation, the web was heated to 160°C then

stretched 7.5 times in the transverse direction (TD) by use of the tentering process. After cooling to 54°C the web was reheated to 121°C and stretched 1.3 times more in the MD direction. After the third stretching, the film was

5 cooled to 27°C then corona treated on both sides. Following corona treatment, the film was annealed at a temperature of 66°C by means of a heated roll. After annealing the web was cooled back to 27°C and wound into a roll. The resulting film had a thickness of 0.80 mil (20

10 microns). In the structure of Example 2, a thickness of 3 gauge = 0.03 mil (0.76 microns).

For machinability testing on the labeling lines, adhesive lamination of two webs of the film were made in such a manner as to have one iPP + anti-block skin and one

15 HDPE skin on the outside with a thickness of 40 microns. The results are shown in Table 1 below.

EXAMPLE 3

This example shows a multilayer film having the following structure:

20

	99.46 wt.% iPP + 0.24 wt.% anti-block (Sipernat 44) + 0.3 wt.% anti-block (Kaopolite) (3.0 gauge)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
25	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
	99.5 wt.% HDPE (Lyondell M6030) + 0.5 wt.% fluoropolymer processing aid (3.0 gauge)

The film structure of this example was produced by

30 coextruding a multilayer cast sheet, with a thickness of 34 mil (864 microns). The cast sheet was reheated to 127°C then stretched 4.4 times in the machine (MD) direction. Following MD orientation, the web was heated to 160° then stretched 7.5 times in the transverse direction (TD) by use

35 of the tentering process. After cooling to 54°C the web was reheated to 121°C and stretched 1.3 times more in the

MD direction. After the third stretching, the film was cooled to 27°C then corona treated on both sides.

Following corona treatment, the film was annealed at a temperature of 66°C by means of a heated roll. After

5 annealing the web was cooled back to 27°C and wound into a roll. The resulting film had a thickness of 0.80 mil (20 microns). In the structure of Example 3, a thickness of 3 gauge = 0.03 mil (0.76 microns).

For machinability testing on the labeling lines,
10 adhesive lamination of two webs of the film were made in such a manner as to have iPP + anti-block skins on the outside with a thickness of 40 microns. The results are shown in Table 1.

EXAMPLE 4

15 This example shows a multilayer film having the following structure:

20	99.425 wt.% HDPE (Lyondell M6030) + 0.075 wt.% anti-block (Siloblock 45) + 0.5 wt.% fluoropolymer processing aid (3.0 gauge)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
	4 wt.% sPP (Fina 9502) + 92 wt. %iPP (Fina 3371)
25	99.5 wt.% HDPE (Lyondell M6030) + 0.5 wt.% processing aid (3.0 gauge)

The film structure of this example was produced by coextruding a multilayer cast sheet, with a thickness of 34 mil (864 microns). The cast sheet was reheated to 127°C
30 then stretched 4.4 times in the machine (MD) direction. Following MD orientation, the web was heated to 160°C then stretched 7.5 times in the transverse direction (TD) by use of the tentering process. After cooling to 54°C the web was reheated to 121°C and stretched 1.3 times more in the
35 MD direction. After the third stretching, the film was cooled to 27°C then corona treated on both sides.

Following corona treatment, the film was annealed at a temperature of 66°C by means of a heated roll. After annealing the web was cooled back to 27°C and wound into a roll. The resulting film had a thickness of 0.80 mil (20
5 microns).

For machinability testing on the labeling lines, adhesive lamination of two webs of the film were made in such a manner as to have HDPE + anti-block skins on the outside with a thickness of 40 microns. The results are
10 shown in Table 1.

Table 1

<u>Example</u> <u>No.</u>	<u>Skin Type</u>	<u>Label</u> <u>Speed</u>	<u>Film</u> <u>Temp.</u>	<u>Air</u> <u>Assist</u>	<u>Squeal</u>
1	Ter+Ab/Core/Ter/Adn/Ter/Core/Ter+Ab	75	65	4	3
		500	65	4	1
		75	20	4	5
		500	120	4	1
2	iPP+Ab/Core/HDPE/Adn/iPP+Ab/Core/HDPE	75	65	1	1
		500	65	1	1
		75	120	1	1
		500	120	1	1
3	iPP+Ab/Core/HDPE/Adh/HDPE/Core/iPP+Ab	75	65	1	3
		500	65	1	1
		75	120	1	3
		500	120	1	1
4	HDPE+Ab/Core/HDPE/Adh/HDPE/Core/HDPE+ Ab	75	65	1	1
		500	65	1	1
		75	120	1	1
		500	120	1	1

Ter = terpolymer

Ab = anti-block

Core = sPP+iPP blend. The core is the same for Examples 1-

5 4.

Adh = laminating adhesive

iPP = isotactic polypropylene

HDPE = high density polypropylene

Film Temperature = °F

10 Speed = rate of label application in labels per minute

Air Assist is an indicator of the position of the air flow control valve necessary to prevent label jams caused by sticking to the knife. 1 = air turned off which is considered the best. 5 = air at the highest flow setting

15 which is considered the worst.

Squeal is a rating from 1-5 of the loudness of squealing noise generated as the labels slide over the rotary knife and vacuum transfer drum of a labeling machine. 1 = no sound and is considered the best. 5 = the
20 loudest sound and is considered the worst.

From Examples 1 to 4 as shown in Table 1 above, it can be seen that the multilayer film structure using the HDPE skin with anti-block on both sides (Example 4) and the HDPE skin on one side and isotactic polypropylene with anti-
25 block on the other side (Example 2) exhibit no squeal with no air assist as compared to both the terpolymer skins (Example 1) and isotactic polypropylene skins (Example 3) which exhibit squeal at 120°F. From this data, it can be seen that the film structures of the present invention
30 exhibit improved machinability over the use of terpolymer skins.

Example 5

The film structure of Example 4 was also tested for heat sealability using the Brugger Seal Test. The test
35 conditions include a dwell time of 0.2 seconds, a pressure of 0.5 Psi and temperatures of 115°C, 120°C, 125°C, 135°C and 145°C. Seal strength is measured in grams/inch.

Adequate seal strength is typically 200 grams/inch or greater.

Brugger Seal Data

5		115°C	120°C	125°C	135°C	145°C
	Example 4	0	30	90	390	450

It was found that the HDPE skins of Example 4 give acceptable heat seals on Krones Controll machines with
10 heat seal capability at production line speeds on both filled and unfilled cans.

CLAIMS:

1. A uniaxially heat-shrinkable, biaxially oriented, multilayer film having a polypropylene-containing core layer and at least one high density polyethylene-containing skin layer adjacent said core layer, said core layer comprising isotactic polypropylene and a modifier which reduces the crystallinity of the polypropylene by increasing chain imperfections or reducing isotacticity of the polypropylene-containing core.

2. The multilayer film of claim 1 wherein said high density polyethylene-containing skin layer comprises an anti-blocking agent.

3. The multilayer film of claim 1 having an isotactic polypropylene-containing skin layer adjacent said core layer.

4. The multilayer film of claim 3 wherein said isotactic polypropylene-containing skin layer comprises an anti-blocking agent.

5. The multilayer film of claim 1 having a high density polyethylene-containing skin layer on both sides of said core layer.

6. The multilayer film of claim 1 wherein said modifier is syndiotactic polypropylene.

7. The multilayer film of claim 1 wherein said core layer comprises polybutene-1 terephthalate (PBT) dispersed as particles of 0.2 to 2.0 microns diameter.

8. The multilayer film of claim 1 wherein said core layer comprises a plurality of voids formed by cavitation a solid cavitating agent.

9. The multilayer film of claim 1 wherein said core layer comprises an polypropylene supporting layer comprising 2 to 18 wt.% titanium dioxide.

10. The multilayer film of claim 1 wherein said film is capable of greater than 15% shrinkage at 100° to 145°C in a first direction with +/- 5% stability in a second direction substantially perpendicular to said first direction.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03576

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B32B 27/32; B65B 53/00

US CL : 428/34.9, 308.4, 516

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. : 428/34.9, 308.4, 516

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: isotac? polypropylene and (high density polyethylene# or hdpe#) and (stretch? or orient?) and (shrink); sleeve? and shrink? and polypropylene?; (polyester and polypropylene)ab

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- A	US 5,489,454 A (PEIFFER ET AL) 06 February 1996 (06-02-96), see the entire document, especially the examples and column 9, lines 56+.	1-6 --- 7-10
A	US 5,212,009 A (PEIFFER ET AL) 18 May 1993 (18-05-93), see the entire document, especially column 8, lines 1+.	1-10
A	US 5,234,733 A (SCHLOEGL ET AL) 10 August 1993 (10-08-93), see the entire document.	1-10
A	US 5,443,895 A (PEIFFER ET AL) 22 August 1995 (22-08-95), see the entire document.	1-10
A	US 4,542,886 A (YOSHIMURA ET AL) 24 September 1985 (24-09-85), see the entire document.	1-10

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

Date of the actual completion of the international search 27 APRIL 1998	Date of mailing of the international search report 18 MAY 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer D. LAWRENCE TARZANO Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03576

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,341,690 A (MARSH) 27 July 1982 (27-07-82), see the abstract.	7