

METALLIZED UNIAXIALLY SHRINKABLE
BIAXIALLY ORIENTED POLYPROPYLENE FILM

The present invention relates to the field of polymer films and, more particularly to a
5 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, polyvinyl chlorides, polyesters, polystyrenes and polyvinylidene chlorides.

A shrink film's distinguishing characteristic is its ability upon exposure to some level of
10 heat to shrink or, if restrained, to create shrink tension within the film. 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 usual functions required of packaging materials such as protection of the product from loss of
15 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 household products, office supplies and forms, foods, phonograph records, and industrial parts.

The manufacture of shrink films requires relatively sophisticated equipment including
20 extrusion lines with "racking" capability, irradiation units when cross-linking 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 heated to their orientation temperature range which varies with different polymers but is usually above room temperature
25 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, unoriented dimension.

Certain applications, e.g., labeling, covering, or packaging of materials such as boxes,
30 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 desirable to effect shrinkage along a single axis without substantial shrinkage in the cross-direction. For example, in the process of labeling bottles by shrinking a tube of heat shrinkable material, if the film shrinks along its length, the label may not be placed in the right position but rather placed
35 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 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 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 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 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.

By utilizing a metallized label, containers of different construction can be given the same appearance as a standard aluminum can. For this look to be effective the label must
5 wrap completely around the container and conform to the shape of the container.

Therefore, it is an object of the present invention to provide a metallized uniaxially heat shrinkable, biaxially oriented multilayer film comprising a polypropylene core.

The present invention relates to a metallized uniaxially heat-shrinkable, biaxially oriented, multilayer film having a polypropylene-containing-core layer, said core layer
10 comprising isotactic polypropylene and a modifier which reduces the crystallinity of the propylene containing core layer. A layer of aluminum can be deposited on the multilayer film structure of the present invention. The coated film can then be wrapped around a container and shrunk to fit the contours of the container.

Core

15 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 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 atactic and
20 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 than isotactic polypropylene due to a higher degree of chain imperfections, lower isotacticity, blended or not, or a different tacticity such as
25 atactic or syndiotactic polypropylene. 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. The modifier can be selected from the group consisting of atactic polypropylene, syndiotactic polypropylene, ethylene-propylene copolymer, propylene-butene-1
30 copolymer, ethylene-propylene-butene-1 terpolymer, polybutene-1, polyethylene and linear low density polyethylene.

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
35 levels of greater than 30% or greater than 35%, 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 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 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., 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.%.

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.

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.

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 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.

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 to 1 wt.% ethylene, the balance being propylene. These fractional
5 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 isotactic polypropylene, mixed with propylene-butene-1 copolymer. The core layer can comprise 5 to 20 wt.% propylene-butene-1 copolymer,
10 preferably 10 to 20 wt.%. Suitable propylene-butene-1 copolymers include Cefor SRD4-105, and Cefor SRD4-104 available from Shell Chemical 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
15 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 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
20 Exact 2009, Exact 2010, and Exact 3016 available from Exxon Chemical Co.

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
25 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
30 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 $\sim n_r$ of the syndiotactic sequences is preferably greater than 20, more preferably greater than 25. The molar mass distribution corresponds to the relation

35
$$M_w = k \times M_n,$$

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
5 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.

10 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 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
15 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.% RPP, preferably up to 15 wt.% RPP.

20 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-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
25 orientation, resulting in a white opaque product.

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 used include iron oxides, carbon black, graphite, aluminum, TiO_2 ,
30 and talc.

A 30 micron polygauge, 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 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
35 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
5 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
10 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.

15 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-
20 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.%
25 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% 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 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 density poly-ethylenes may be derived from ethylene together with other higher comonomers such as butene-1, hexene-1 or
35 octene-1.

In another aspect of the invention skin layers of substantially high density polyethylene (HDPE) having a 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
5 a major proportion of 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 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
10 both on the outside of the structure, heat sealability is maintained. The net result of the lamination could be carried to a 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
15 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
20 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
25 (.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
30 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-melttable silicone resin, e.g., particulate cross-linked hydrocarbyl-substituted polysiloxanes.
35 Particularly preferred particulate cross-linked hydrocarbyl-substituted polysiloxanes include the polymonoalkylsiloxanes. Most particularly preferred are non-melttable

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.

A metallized coating may be applied to the corona treated or flame treated outer layer by any of known methods, for example electroplating, sputtering and vacuum metallizing. A preferred method of metallizing the corona treated outer layer is by vacuum deposition. However, when using the vacuum metallizing process, the use of chemical primers is not necessary to obtain enhanced adhesion of the metallized coating to the substrate.

The metal coating may be any of typical metals such as aluminum, copper, silver and chromium. for example, a layer of aluminum can be deposited on the multilayer film structure

of the present invention. The coated film is then wrapped around the container and shrunk to fit the contours of the container. Surprisingly, it has been found that the film of the present invention appears to shrink without the development of any noticeable crazing of the metal.

Primary Orientation

5 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
10 temperature of 100° to 170°C, e.g., 155°C. Generally, biaxial orientation temperatures differ for MD orientation (115° to 130°C, e.g., 120°C) and TD orientation (130° to 170°C, e.g., 155°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.

15 Secondary Orientation

 The primarily oriented film is then reheated to 100° to 145°C, say 125° to 135°C, preferably by use of heated cylinders and stretched an additional 10 to 40%, preferably 25 to 30%, in the first direction of orientation only, e.g., machine direction (MD). In order to minimize compressive stress which can adversely affect second direction heat stability, e.g.,
20 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 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
25 mils).

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 biaxial orienting is effected by accelerating along a
30 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 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
35 opposed pairs of tenter clips along some portion 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 annealing and subsequent cooling before leaving the tenter frame such that the resulting film will have good machine direction
5 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 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 secondary orientation can range in
10 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 secondary orientation exhibits at temperatures of 100° to 145°C, say, 135°C, greater than 15%, preferably greater than 18%,
15 20%, or even greater than 25% shrinkage in the direction of secondary orientation, e.g., machine direction. Shrinkage is determined by measuring the 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 direction. Such
20 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 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
25 normal to the direction of secondary orientation, after heating to 135°C (275°F) shrinks or 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 secondary orientation in the direction of secondary orientation (% elongation)
30 under common processing conditions, e.g., print drying temperatures of 54° to 66°C (130° to 150°F), preferably 60°C (140°F) or less. 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 less than 134 g per linear cm (0.75 pli), and temperatures normally encountered by the film during processes prior to thermoshrinking, e.g., drying after
35 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

A multilayer film having the following structure is metallized with aluminum on the corona treated side in a bell jar:

Aluminum

Corona Treatment

100 wt.% ethylene-propylene-butene-1 (EPB) terpolymer (Chisso 7701)

96 wt.% isotactic polypropylene (iPP) (Fina 3371) + 4 wt.% syndiotactic polypropylene (sPP) (Fina 9630)

99.8 wt.% EPB terpolymer (Chisso 7701) + 0.2 wt.% Tospearl 145

The multilayer film is primarily oriented by stretching 4.6 times in the machine direction and 7.6 times in the transverse direction. The film is reheated and stretched an additional 1.27 times in the machine direction to give a machine direction shrinkage of 19%. Final film thickness is 30 microns.

The multilayer film is metallized by inserting a sheet of film into a metal frame and then placing in a lab scale Bell Jar metallizer with the corona treated surface toward the aluminum source. The bell jar is evacuated to 10^{-5} torr. The wire current is set to 25 amps for 10 seconds then increased to 50 amps for 2 seconds.

Following removal from the bell jar and metal frame, the film is tested for metal adhesion. To test the metal adhesion, strips of tape are applied to the metallized surface. The tape is pulled manually. The tape test shows good metal adhesion with minimal metal pick off.

The film is then cut to size and hand wrapped around a container and shrunk with a hot air gun. After shrinkage metal appearance appears unchanged.

Example 2

The film of Example 1 is metallized on the non-corona treated side. After putting the film in the metal frame it is installed with the non-corona treated surface toward the aluminum source.

The bell jar is evacuated to 10^{-5} torr. The wire current is set to 25 amps for 10 seconds then increased to 50 amps for 2 seconds.

Following removal from the bell jar and metal frame, the film is tested for metal adhesion. To test the metal adhesion, strips of tape are applied to the metallized surface.

- 5 The tape is pulled manually. The tape test shows good metal adhesion with minimal metal pick off.

The film is then cut to size and hand wrapped around a container and shrunk with a hot air gun. After shrinkage metal appearance appears unchanged.

Example 3

- 10 A multilayer film having the following structure is metallized with aluminum on the corona treated side in a bell jar:

Aluminum

Corona Treatment

EPB terpolymer (Chisso 7701)

- 15 92 wt.% iPP (Fina 3371) + 4 wt.% sPP (Fina 9630) + 4 wt.% TiO_2
86 wt.% iPP (Fina 3371) + 4 wt.% sPP (Fina 9630) + 10 wt.% PBT
92 wt.% iPP (Fina 3371) + 4 wt.% sPP (Fina 9630) + 4 wt.% TiO_2
99.8 wt.% EPB terpolymer (Chisso 7701) + 0.2 wt.% Tospearl 145

- 20 The multilayer film is primarily oriented by stretching 4.8 times in the machine direction and 8 times in the transverse direction. The film is reheated and stretched an additional 1.27 times in the machine direction to give a machine direction shrinkage of 20%. Final cavitated film thickness is 30 microns. Final film density is 0.6 gram/cm^3 .

- 25 The multilayer film is metallized by inserting a sheet of film into a metal frame and then placing in a lab scale Bell Jar metallizer with the corona treated surface toward the aluminum source. The bell jar is evacuated to 10^{-5} torr. The wire current is set to 25 amps for 10 seconds then increased to 50 amps for 2 seconds.

- 30 Following removal from the bell jar and metal frame, the film is tested for metal adhesion. To test the metal adhesion, strips of tape are applied to the metallized surface. The tape is pulled manually. The tape test shows good metal adhesion with minimal metal pick off.

The film is then cut to size and hand wrapped around a container and shrunk with a hot air gun. After shrinkage metal appearance appears unchanged.

Example 4

The film of Example 3 is metallized on the non-corona treated side. After putting the film in the metal frame it is installed with the non-corona treated surface toward the aluminum source.

- 5 The bell jar is evacuated to 10^{-5} torr. The wire current is set to 25 amps for 10 seconds then increased to 50 amps for 2 seconds.

Following removal from the bell jar and metal frame, the film is tested for metal adhesion. To test the metal adhesion, strips of tape are applied to the metallized surface. The tape is pulled manually. The tape test shows good metal adhesion with minimal metal
10 pick off.

The film is then cut to size and hand wrapped around a container and shrunk with a hot air gun. After shrinkage metal appearance appears unchanged.

Example 5

- 15 A multilayer film having the following structure is metallized with aluminum on the corona treated side in a commercial vacuum deposition metallizer:

Aluminum

Corona Treatment

100 wt.% ethylene-propylene-butene-1 (EPB) terpolymer (Chisso 7701)

- 96 wt.% isotactic polypropylene (iPP) (Fina 3371) + 4 wt.% syndiotactic polypropylene (sPP)
20 (Fina 9630)

99.8 wt.% EPB terpolymer (Chisso 7701) + 0.2 wt.% Tospearl 145

- The multilayer film is primarily oriented by stretching 4.6 times in the machine direction and 7.6 times in the transverse direction. The film is reheated and stretched an additional 1.27 times in the machine direction to give a machine direction shrinkage of 19%.
25 Final film thickness is 30 microns.

Metallization is conducted on a commercial vacuum deposition metallizer utilizing the following conditions: winder chamber pressure 7.5×10^{-3} torr, metal chamber pressure 30×10^{-5} torr, line speed 1600 feet per min., wire feed rate 32 inches per min., chill roll temperature -32°F (-36°C).

- 30 Following removal from the metallizer, the film is tested for metal adhesion. To test the metal adhesion, strips of tape are applied to the metallized surface. The tape is pulled manually. The tape test shows good metal adhesion with minimal metal pick off.

The film is then cut to size and hand wrapped around a container and shrunk with a hot air gun. After shrinkage metal appearance appears unchanged.

Example 6

35 The film of Example 5 is metallized on the non-corona treated side.

Metallization is conducted on a commercial vacuum deposition metallizer utilizing the following conditions: winder chamber pressure 7.5×10^{-3} torr, metal chamber pressure 30×10^{-5} torr, line speed 1600 feet per min., wire feed rate 32 inches per min., chill roll temperature -32°F (-36°C).

5 Following removal from the metallizer, the film is tested for metal adhesion. To test the metal adhesion, strips of tape are applied to the metallized surface. The tape is pulled manually. The tape test shows good metal adhesion with minimal metal pick off.

The film is then cut to size and hand wrapped around a container and shrunk with a hot air gun. After shrinkage metal appearance appears unchanged.

10 **Example 7**

A multilayer film having the following structure is metallized with aluminum on the corona treated side in a commercial vacuum deposition metallizer:

Aluminum

Corona Treatment

15 100 wt.% ethylene-propylene-butene-1 (EPB) terpolymer (Chisso 7701)

96 wt.% isotactic polypropylene (iPP) (Fina 3371) + 4 wt.% syndiotactic polypropylene (sPP) (Fina 9630)

99.8 wt.% EPB terpolymer (Chisso 7701) + 0.2 wt.% Tospearl 145

20 The multilayer film is primarily oriented by stretching 4.6 times in the machine direction and 7.6 times in the transverse direction. The film is reheated and stretched an additional 1.43 times in the machine direction to give a machine direction shrinkage of 24%. Final film thickness is 30 microns.

25 Metallization is conducted on a commercial vacuum deposition metallizer utilizing the following conditions: winder chamber pressure 7.5×10^{-3} torr, metal chamber pressure 30×10^{-5} torr, line speed 1600 feet per min., wire feed rate 32 inches per min., chill roll temperature -32°F (-36°C).

Following removal from the metallizer, the film is tested for metal adhesion. To test the metal adhesion, strips of tape are applied to the metallized surface. The tape is pulled manually. The tape test shows good metal adhesion with minimal metal pick off.

30 The film is then cut to size and hand wrapped around a container and shrunk with a hot air gun. After shrinkage metal appearance appears unchanged.

Example 8

A multilayer film having the following structure is metallized with aluminum on the corona treated side in a commercial vacuum deposition metallizer:

35 Aluminum

Corona Treatment

99.5 wt.% HDPE (Lyondell M6030) + 0.5 wt.% fluoropolymer processing aid
96 wt.% iPP (Fina 3371) + 4 wt.% sPP (Fina 9630)
99.46 wt.% iPP (Fina 3371) + .24 wt.% antiblock (Sipernat 44) + .3 wt.% antiblock
(Kaopolite)

5 The multilayer film is primarily oriented by stretching 4.6 times in the machine direction and 7.5 times in the transverse direction. The film is reheated and stretched an additional 1.27 times in the machine direction to give a machine direction shrinkage of 19%. Final film thickness is 30 microns.

10 Metallization is conducted on a commercial vacuum deposition metallizer utilizing the following conditions: winder chamber pressure 7.5×10^{-3} torr, metal chamber pressure 30×10^{-5} torr, line speed 1600 feet per min., wire feed rate 32 inches per min., chill roll temperature -32°F (-36°C). After metallization, the optical density is 2.2.

15 Following removal from the metallizer, the film is tested for metal adhesion. To test the metal adhesion, strips of tape are applied to the metallized surface. The tape is pulled manually. The tape test shows good metal adhesion with 10% metal pick off.

 The film is then cut to size and hand wrapped around a container and shrunk with a hot air gun. After shrinkage metal appearance appears unchanged

20 Table 1, below, shows dimensional stability after storage for the film of Examples 5, 6, 7 and 8 prior to metallization and after metallization. Dimensional stability is measured in terms of % dimensional change with a minus sign (-) indicating shrinkage and a plus sign (+) indicating growth. The results show that the films of the present invention can be metallized without significantly effecting the dimensional stability.

25 Table 2 below shows Brugger Heat Seal Test Data for the film of Example 5 before and after metallization. The test 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. The test results show acceptable heat seals on the non-metal/non-metal seal.

TABLE 1
 DIMENSIONAL STABILITY
 @ 275°F, 7 minutes

Example Number	MD	TD
5 Prior to metallization	-17.5	+0.3
5 After metallization	-16.85	+0.15
6 Prior to metallization	-17.0	+0.15
6 After metallization	-16.45	0.0
7 Prior to metallization	-22.3	-0.7
7 After metallization	-22.7	-0.45
8 Prior to metallization	-17.4	-0.84
8 After metallization	-17.2	-0.79

5

TABLE 2
 BRUGGER SEAL DATA FOR EXAMPLE 5

Seal	115°C	120°C	125°C	135°C	145°C
Surface/ Surface					
NT/NT	220	450	420	430	480
NM/NM	180	240	320	440	650
M/NM	0	0	0	0	0

NT = prior to metallization, no corona treatment

NM = after metallization, non-metal side

M = after metallization, metal side

10

It will be apparent to those skilled in the art that the specific embodiments discussed above can be successfully repeated with ingredients equivalent to those generically or specifically set forth above and under variable process conditions. From the foregoing specification, one skilled in the art can readily ascertain the essential features of this invention and without departing from the spirit and scope thereof can adapt it to various diverse applications.

15

CLAIMS:

1. A metallized uniaxially heat-shrinkable, biaxially oriented, multilayer film having a polypropylene-containing core layer and at least one metallized polyolefin-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 and wherein said skin layer.
2. The multilayer film of claim 1 wherein said skin layer is metallized with aluminum.
3. The multilayer film of claim 1 wherein said skin layer is corona treated or flame treated prior to metallization.
4. The multilayer film of claim 3 wherein said skin layer is selected from the group consisting of polypropylene, ethylene-propylene copolymer, polyethylene, propylene-butene-1 copolymer, ethylene-propylene-butene-1 terpolymer, and high density polyethylene, said skin layer having a thickness of 0.5 to 1.0 micron.
5. The multilayer film of claim 1 wherein said skin layer further comprises anti-block.
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.

This Sheet Has Been Replaced

THIS SHEET HAS BEEN
REPLACED