



(43) International Publication Date
3 August 2017 (03.08.2017)

(10) International Publication Number
WO 2017/131998 A1

- (51) **International Patent Classification:**
B32B 27/32 (2006.01) *C08L 23/06* (2006.01)
C08J 5/18 (2006.01)
- (21) **International Application Number:**
PCT/US2017/013708
- (22) **International Filing Date:**
17 January 2017 (17.01.2017)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
16382033.5 29 January 2016 (29.01.2016) EP
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- (81) **Designated States** (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN,
KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA,
MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG,
NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS,
RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY,
TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN,
ZA, ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

Published:

— *with international search report (Art. 21(3))*

— *with amended claims and statement (Art. 19(1))*

(54) **Title:** FILMS, AND RELATED COMPOSITIONS AND METHODS OF MAKING

(57) **Abstract:** Disclosed in embodiments herein are monolayer or multilayer films. The films include at least one layer including a) a polyethylene polymer component comprising linear low density polyethylene; and b) a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the film. Also disclosed in embodiments herein are related compositions and methods of making monolayer or multilayer films.



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FILMS, AND RELATED COMPOSITIONS AND METHODS OF MAKING

RELATED APPLICATION

[0001] The present Application claims priority to commonly owned European patent application having application number EP16382033.5, filed on January 29, 2016, which Application is incorporated herein by reference in its entirety.

FIELD

[0002] Embodiments of the present disclosure relate to monolayer and multilayer stretch wrap films that include polyethylene, and more particularly, to monolayer and multilayer stretch wrap films that include polyethylene that include a nonpolar, polyethylene wax, and related compositions and methods of making.

BACKGROUND

[0003] Stretch wrap films such as silage wrap films can be used to wrap silage so as to limit the exposure of the silage to air so that the silage can undergo anaerobic fermentation for a desirable amount of time. Because silage can be a rough material to handle, the baled silage can be stored outside in a wide variety of weather conditions, and the baled silage can be handled by heavy equipment, it can be desirable for silage wrap to have highly durable mechanical properties to withstand such conditions while at the same time providing desirable oxygen barrier properties. Unfortunately, material properties that can enhance oxygen barrier properties may degrade mechanical properties.

[0004] Accordingly, alternative stretch wrap films having improved oxygen barrier properties while at the same time having durable mechanical properties to contain silage in a wide variety of environmental conditions is desirable.

SUMMARY

[0005] Disclosed in embodiments herein are monolayer or multilayer films. The films include at least one layer, wherein the at least one layer includes: a) a polyethylene polymer component including linear low density polyethylene; and b) a wax component including nonpolar, polyethylene wax. The nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and is present in an amount of at least 3 percent by weight of the film.

[0006] Also disclosed in embodiments herein are compositions including: a) a polyethylene polymer component comprising linear low density polyethylene; and b) a wax component comprising nonpolar, polyethylene wax. The nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and is present in an amount of at least 3 percent by weight of the composition.

[0007] Also disclosed in embodiments herein are methods of making a film (a monolayer film or a multilayer film). The methods include a) providing a melted blend, wherein the melted blend includes a wax component including melted nonpolar, polyethylene wax and a first polyethylene polymer component including melted linear low density polyethylene. The nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and is present in an amount of at least 3 percent by weight of the film. The methods further include forming the melted blend into a film via cast film techniques or blown film techniques.

DETAILED DESCRIPTION

[0008] Reference will now be made in detail to films, compositions, and methods thereof according to the present disclosure. The films may be used as stretch wrap in wrapping silage to allow anaerobic fermentation to occur for a desirable amount of time. It is noted, however, that this is merely an illustrative implementation of the embodiments disclosed herein. The embodiments are applicable to other technologies that are susceptible to similar problems as those discussed herein. For example, the films described herein may be used in other flexible packaging applications, such as, heavy duty shipping sacks, liners, sacks, stand-up pouches, detergent pouches, sachets, etc., all of which are within the purview of the present embodiments.

[0009] General film structure and composition film can be monolayer film or multi-layer film.

[0010] A - Polyethylene Polymer Component

[0011] The polyethylene polymer component can be selected to help provide, e.g., desirable properties in the film so that the film can be used as a stretch wrap such as silage wrap (discussed in section "F" below).

[0012] The polyethylene polymer component may include one or more polyethylene polymers in an amount such that the film includes from greater than 50 wt.% to 95 wt.% of one or more polyethylene polymers based on the total weight of the film. All individual values and subranges are included and disclosed herein. For example, in some embodiments, a film can have from 55 wt.% to 95 wt.% of one or more polyethylene polymers based on the total weight of the film, from 60 wt.% to 95 wt.% of one or more polyethylene polymers based on the total weight of the film, or from 65 wt.% to 95 wt.% of one or more polyethylene polymers based on the total weight of the film. In other embodiments, a film can have from 55 wt.% to 90 wt.% of one or more polyethylene polymers based on the total weight of the film, from 60 wt.% to 85 wt.% of one or more polyethylene polymers based on the total weight of the film, or from 60 wt.% to 70 wt.% of one or more polyethylene polymers based on the total weight of the film.

[0013] In some embodiments, a film includes only the polyethylene polymer component and the nonpolar, polyethylene wax component (discussed below), where the polyethylene polymer component is present in an amount of 97 wt.% or less based on the total weight of the film and the nonpolar, polyethylene wax component is present in an amount of 3 wt.% or more based on the total weight of the film.

[0014] A.1 - Linear Low Density Polyethylene (LLDPE)

[0015] The polyethylene polymer component may include at least linear low density polyethylene. The linear low density polyethylene may include, in polymerized form, a majority weight percent of ethylene based on the total weight of the linear low density polyethylene. In an embodiment, the linear low density polyethylene is an interpolymer of ethylene and at least one ethylenically unsaturated comonomer. In one embodiment, the comonomer can be a C₃-C₂₀ α -olefin. In another embodiment, the comonomer is a C₃-C₈ α -olefin. In another embodiment, the C₃-C₈ α -olefin can be selected from propylene, 1-butene, 1-hexene, or 1-octene. In an embodiment, the linear low density polyethylene can be selected from the following copolymers: ethylene/propylene copolymer, ethylene/butene copolymer, ethylene/hexene copolymer, and ethylene/octene

copolymer. In a further embodiment, the linear low density polyethylene is an ethylene/octene copolymer.

[0016] The linear low density polyethylene may have a density of from 0.890 g/cc to 0.940 g/cc. All individual values and subranges are included and disclosed herein. For example, in some embodiments, the linear low density polyethylene may have a density of from 0.890 g/cc to 0.935 g/cc, 0.890 g/cc to 0.930 g/cc, or 0.900 g/cc to 0.930 g/cc. In other embodiments, the linear low density polyethylene may have a density of from 0.905 g/cc to 0.940 g/cc, 0.910 g/cc to 0.940 g/cc, or 0.915 g/cc to 0.940 g/cc.

[0017] The linear low density polyethylene may have a melt index, or I_2 , of from 0.1 g/10 min to 10 g/10 min. All individual values and subranges are included and disclosed herein. For example, in some embodiments, the linear low density polyethylene may have a melt index (I_2) from 0.1 to 6 g/10 min, 0.1 to 5 g/10 min, 0.1 to 4 g/10 min, 0.1 g/10 min to 3.5 g/10 min, 0.1 g/10 min to 2 g/10 min, 0.1 g/10 min to 1.5 g/10 min. In other embodiments, the linear low density polyethylene may have a melt index (I_2) from 0.1 g/10 min to 1.1 g/10 min. In further embodiments, the linear low density polyethylene may have a melt index (I_2) of 0.2-0.9 g/10 min.

[0018] The linear low density polyethylene can be made by a variety of techniques. For example, the linear low density polyethylene may be produced via a gas phase or a solution phase and using single-site catalysts techniques and/or Ziegler-Natta catalyst techniques. Methods for producing olefin polymers using single site catalysts can be U.S. Pat. No. 5,272,236 (Lai et al.), 5,324,800 (Welborn, Jr. et al.), and U.S. Pat. No. 6,486,284 (Karande et al.), the entirety of which patents are incorporated herein by reference. Single-site catalyst systems may include metallocene catalysts and post-metallocene catalysts. Ziegler-Natta catalysts are described in U.S. Publication Numbers 2008/0038571 (Klitzmiller et al.) and 2008/0176981 (Biscoglio et al.), the entirety of which patent documents are incorporated herein by reference.

[0019] In one embodiment, the linear low density polyethylene can be a Ziegler-Natta catalyzed ethylene and octene copolymer. The linear low density polyethylene can have crystallinity from about 40% to about 50%, or about 47%.

[0020] In another embodiment, the linear low density polyethylene can be a single-site catalyzed linear low density polyethylene ("sLLDPE").

[0021] As used herein, "sLLDPE" is a LLDPE polymerized using a single site catalyst such as a metallocene catalyst or a constrained geometry catalyst. A "metallocene catalyst" is a catalyst composition containing one or more substituted or unsubstituted cyclopentadienyl moiety in combination with a Group 4, 5, or 6 transition metal. A "constrained geometry catalyst" comprises a metal coordination complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table and a delocalized pi-bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted pi-bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar pi-bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted pi-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted pi-bonded moiety. The constrained geometry catalyst further comprises an activating co-catalyst. Nonlimiting examples of suitable constrained geometry catalysts are disclosed U.S. Pat. No. 5,132,380 (Mullins et al.), the entire content of which is incorporated by reference herein.

[0022] The sLLDPE, may be unimodal or multimodal (i.e., bimodal). A "unimodal sLLDPE" is a LLDPE polymer prepared from one single-site catalyst under one set of polymerization conditions. A "multimodal sLLDPE" is an LLDPE polymer prepared from two or more different catalysts and/or under two or more different polymerization conditions. A "multimodal sLLDPE" comprises at least a lower molecular weight component (LMW) and a higher molecular weight (HMW) component. Each component is prepared with a different catalyst and/or under different polymerization conditions. The prefix "multi" relates to the number of different polymer components present in the polymer. A nonlimiting example of multimodal sLLDPE is set forth in U.S. Patent No. 5,047,468 (Lee et al.), the entire content of which is incorporated by reference herein.

[0023] The LLDPE can be present in an amount of from greater than 50 wt.% to 95 wt.% based on the total weight of the film. All individual values and subranges are included and disclosed herein. For example, in some embodiments, a film can have from 55 wt.% to 95 wt.% of LLDPE based on the total weight of the film, from 60 wt.% to 95 wt.% of LLDPE based on the total weight of the film, or from 65 wt.% to 95 wt.% of LLDPE based on the total weight of the film. In other embodiments, a film can have from 55 wt.% to 90 wt.% of LLDPE based on the total weight of the film, from 60 wt.% to 85 wt.% of LLDPE based on the total weight of the film, or from 60 wt.% to 65 wt.% of LLDPE based on the total weight of the film.

[0024] Nonlimiting examples of suitable and commercially available linear low density polyethylene are LLDPE sold under the tradenames DOWLEX™ 2045 S, DOWLEX™ SL2103G, and ELITE™ AT 6301, available from The Dow Chemical Company, Midland, Michigan.

[0025] In some embodiments, the polyethylene component includes only LLDPE.

[0026] A.2 - Optional Polyethylene Polymers

[0027] Optionally, in some embodiments, the polyethylene component includes a blend of LLDPE with one or more additional polyethylene polymers chosen from the group of ultra-high-molecular-weight polyethylene (UHMWPE), high-density polyethylene (HDPE), medium-density polyethylene (MDPE), low-density polyethylene (LDPE), very low-density polyethylene (VLDPE), and ultra-low-density polyethylene (ULDPE). In some embodiments, the polyethylene component includes a blend of linear low density polyethylene and at least one polyethylene polymer chosen from low density polyethylene, medium density polyethylene, and high density polyethylene.

[0028] The one or more additional polyethylene polymers can be present in an amount of from greater than 0.5 wt.% to 50 wt.% based on the total weight of the film. All individual values and subranges are included and disclosed herein. For example, in some embodiments, a film can have from 5 wt.% to 40 wt.% of one or more additional polyethylene polymers based on the total weight of the film, or from

10 wt.% to 20 wt.% of one or more additional polyethylene polymers based on the total weight of the film. In other embodiments, a film can have from 0.5 wt.% to 15 wt.% of one or more additional polyethylene polymers based on the total weight of the film, or from 0.5 wt.% to 10 wt.% of one or more additional polyethylene polymers based on the total weight of the film.

[0029] A nonlimiting example a of suitable and commercially available ULDPE is ULDPE sold under the tradename ATTANE™, available from The Dow Chemical Company, Midland, Michigan.

[0030] B – Optional Polymer Component

[0031] The polyethylene polymer component can optionally be blended with one more polymers in addition to polyethylene polymers. Exemplary optional polymers include propylene-based polymers, ethylene-vinyl acetate (EVA) copolymers, ethylene vinyl alcohol (EVOH) copolymers, and other polymers useful in forming mechanically tough oxygen barriers such as silage wrap.

[0032] The one or more optional polymers can be present in an amount of from greater than 0.5 wt.% to 50 wt.% based on the total weight of the film. All individual values and subranges are included and disclosed herein. For example, in some embodiments, a film can have from 5 wt.% to 40 wt.% of one or more optional polymers based on the total weight of the film, or from 10 wt.% to 20 wt.% of one or more optional polymers based on the total weight of the film.

[0033] C - Wax Component

[0034] The wax component according to the present disclosure can include one or more waxes to help decrease oxygen transmission rate of the film while at the same time not negatively impacting the mechanical properties of the film to an undue degree (e.g., so that the film can be used to wrap silage without tearing and the like to an undue degree). It has been discovered that a film including at least one nonpolar, polyethylene wax having a density of 0.955 grams/cm³ or greater, and in an amount of at least 3 percent by weight of the film can unexpectedly provide a significant reduction in stretched oxygen transmission rate (e.g., stretched OTR) while at the same time providing film mechanical properties that are sufficient for the film to be used as a silage wrap. This finding is unexpected because, without

being bound by theory, it is believed that as the crystallinity of a polymer used in a film increases, the stretched oxygen transmission rate of the film tends to decrease, but the mechanical properties of the film tend to degrade to an undue degree, especially in the context of a silage wrap.

[0035] As used herein, “nonpolar” refers to a polyethylene wax that has an acid value of no more than 5 (mg KOH/g). In some embodiments, the nonpolar, polyethylene wax may have an acid value of from 0 to 5 (mg KOH/g). All individual values and subranges are included and disclosed herein. For example, in some embodiments, the nonpolar, polyethylene wax may have an acid value of from 0 to 4, 0 to 3, 0 to 2, or 0 to 1 (mg KOH/g). In some embodiments, a nonpolar, polyethylene wax does not include any polar functional groups.

[0036] The nonpolar, polyethylene wax may have a saponification value of no more than 5 (mg KOH/g). In some embodiments, the nonpolar, polyethylene wax may have a saponification value of from 0 to 5 (mg KOH/g). All individual values and subranges are included and disclosed herein. For example, in some embodiments, the nonpolar, polyethylene wax may have a saponification value of from 0 to 4, 0 to 3, 0 to 2, or 0 to 1 (mg KOH/g).

[0037] As used herein, “polyethylene wax” refers to both ethylene homopolymers and copolymers of ethylene with α -olefins having a chain length of C_3 – C_{18} . Nonpolar polyethylene waxes according to the present disclosure can be made by polymerizing ethylene to produce a relatively high density polyethylene wax having properties as described herein below. Nonpolar, polyethylene wax can be prepared by thermal degradation of branched or unbranched polyethylene polymers or by direct polymerization of ethylene. Examples of suitable polymerization processes include free-radical processes, in which ethylene is reacted under high pressures and temperatures to form a wax with a greater or lesser degree of branching, and also processes in which ethylene and/or higher 1-olefins are polymerized to branched or unbranched waxes using organometallic catalysts, such as Ziegler-Natta or metallocene catalysts, for example. Corresponding methods of preparing olefin homopolymer and copolymer waxes are described for example in U.S. Pat. No. 8,765,848 (Fell et al.), the entirety of which patent is incorporated herein by reference.

[0038] The nonpolar, polyethylene wax may have a density of 0.955 g/cc or greater, or even 0.965 g/cc or greater. In some embodiments, the nonpolar, polyethylene wax may have a density of from 0.955 g/cc to 0.995 g/cc. All individual values and subranges are included and disclosed herein. For example, in some embodiments, the nonpolar, polyethylene wax may have a density may have a density of from 0.955 g/cc to 0.990 g/cc, 0.955 g/cc to 0.980 g/cc, or 0.955 g/cc to 0.975 g/cc. In other embodiments, the linear low density polyethylene may have a density of from 0.960 g/cc to 0.995 g/cc, 0.965 g/cc to 0.990 g/cc, or 0.970 g/cc to 0.985 g/cc.

[0039] The nonpolar, polyethylene wax may have a viscosity of from 100 (mPa-s) to 30,000 (mPa-s). All individual values and subranges are included and disclosed herein. For example, in some embodiments, the nonpolar, polyethylene wax may have a viscosity of from 100 (mPa-s) to 600 (mPa-s), 100 (mPa-s) to 400 (mPa-s), or 300 (mPa-s) to 400 (mPa-s). In other embodiments, the nonpolar, polyethylene wax may have a viscosity of from 20,000 (mPa-s) to 30,000 (mPa-s), 20,000 (mPa-s) to 28,000 (mPa-s), or 22,000 (mPa-s) to 27,000 (mPa-s).

[0040] The nonpolar, polyethylene wax may have a drop point of from 125°C to 145°C. All individual values and subranges are included and disclosed herein. For example, in some embodiments, the nonpolar, polyethylene wax may have a drop point of from 125°C to 140°C, 125°C to 135°C, or 125°C to 130°C. In other embodiments, the nonpolar, polyethylene wax may have a drop point of from 130°C to 145°C, 135°C to 145°C, or 140°C to 145°C.

[0041] The wax component may include nonpolar, polyethylene wax in an amount such that the film includes from 3 wt.% to 30 wt.% of nonpolar, polyethylene wax based on the total weight of the film. All individual values and subranges are included and disclosed herein. For example, in some embodiments, a film can have from 3 wt.% to 25 wt.% of nonpolar, polyethylene wax based on the total weight of the film, from 3 wt.% to 20 wt.% of nonpolar, polyethylene wax based on the total weight of the film, from 3 wt.% to 15 wt.% of nonpolar, polyethylene wax based on the total weight of the film, or from 3 wt.% to 10 wt.% of nonpolar, polyethylene wax based on the total weight of the film. In other embodiments, a film can have from 5 wt.% to 30 wt.% of nonpolar, polyethylene

wax based on the total weight of the film, from 10 wt.% to 30 wt.% of nonpolar, polyethylene wax based on the total weight of the film, or from 15 wt.% to 30 wt.% of nonpolar, polyethylene wax based on the total weight of the film.

[0042] Nonlimiting examples of suitable and commercially available nonpolar, polyethylene waxes are nonpolar, polyethylene wax sold under the tradenames LICOWAX® 130 or LICOWAX® 190 from Clariant International Ltd., Muttenz, Switzerland.

[0043] D - Optional Additives

[0044] One or more layers of a film disclosed herein may further include one or more additives. Additives can be individually present in an amount of up to about 2% based on the total weight of the polyethylene-based film. Such additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, fillers, pigments, primary antioxidants, secondary antioxidants, processing aids, UV stabilizers, anti-blocks, slip agents, tackifiers, fire retardants, anti-microbial agents, odor reducer agents, anti-fungal agents, and combinations thereof. For example, one or more layers of a film disclosed herein may include additives that facilitate forming a stretch wrap such as silage wrap. Exemplary silage wrap additives include polyisobutylene (PIB). One or more layers of a film disclosed herein may include from about 0.01 to about 10 percent by the combined weight of such additives, based on the total weight of the polyethylene-based film.

[0045] E - Films

[0046] A film according to the present disclosure may be a monolayer film or a multilayer film that includes: a polyethylene polymer component comprising linear low density polyethylene; and a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the film. For multilayer films, one or more layers of the multilayer film can include: a polyethylene polymer component comprising linear low density polyethylene; and a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the film.

[0047] A multilayer film can include two more or more layers. For example, three layers, four layers, five layers, six layers, seven layers, etc. In some embodiments, a multilayer film can include at least a first layer, a second layer, and a third layer. The second layer is between the first layer and the third layer. The second layer can include a polyethylene polymer component comprising linear low density polyethylene; and a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the film. In some embodiments, the first layer can be referred to as the first outer layer, the second layer can be referred to as the core layer, and the third layer can be referred to as the second outer layer. In embodiments herein, the multilayer films may further include one or more intermediate layers positioned between the core layer and at least one outer layer. In some embodiments, the multilayer films may include one or more intermediate layers positioned between the core layer and the first outer layer. In other embodiments, the multilayer films may include one or more intermediate layers positioned between the core layer and the second outer layer. In further embodiments, the multilayer films may include one or more intermediate layers positioned between the core layer and the first outer layer, and between the core layer and the second outer layer. Any layer of a multilayer film may be compositionally the same as or different from the second (or core) layer. The one or more intermediate layers may include ethylene-based polymers, such as, LDPE, LLDPE, MDPE, HDPE, or blends thereof.

[0048] For multilayer films having first and second outer layers, the first and second outer layers may be the same or different in composition and/or thickness. For example, a three-layer film may have an ABA film structure, where the A skin layers may be the same or different in thickness, but are symmetrical in the composition, or an ABC film structure, where the A and C may be the same or different in thickness, but the skin layers are unsymmetrical in composition. This type of characterization can be similarly applied to multilayer films having more than three layers (e.g., 5, 7, or more layers).

[0049] The thickness ratio of the at least one outer layer to the core layer can be any desirable ratio. In some embodiments, the thickness ratio of the at least one outer layer to the core layer can be any ratio suitable to maintain the oxygen barrier and mechanical properties of a silage wrap film. In some embodiments, the thickness ratio of the at least one outer layer to the core layer may be 1:5 to 1:1, 1:4 to 1:1, 1:3 to 1:1, 1:2 to 1:1, or 1:1.5 to 1:1. The thickness ratio of the at least one outer layer to the core layer can also be captured by percentages. For example, in some embodiments, the core layer comprises from about 50 wt.% to about 95 wt.% of the overall film thickness. In other embodiments, the core layer comprises from about 60 wt.% to about 90 wt.% of the overall film thickness. In further embodiments, the core layer comprises from about 65 wt.% to about 85 wt.% of the overall film thickness.

[0050] In further embodiments, where the multilayer film includes a core layer positioned between the first and second outer layers, the thickness ratio of the first and second outer layers to the core layer can be any ratio suitable to maintain the oxygen barrier and mechanical properties of the film. In some embodiments, the thickness ratio of the first and second outer layers to the core layer may be 1:10 to 1:1, 1:5 to 1:1, 1:4 to 1:1, 1:2 to 1:1, or 1:1.5 to 1:1. The thickness ratio of the first and second outer layers to the core layer can also be captured by percentages. For example, in some embodiments, the core layer is from about 50 wt.% to about 95 wt.% of the overall film thickness. In other embodiments, the core layer is from about 60 wt.% to about 90 wt.% of the overall film thickness. In further embodiments, the core layer is from about 65 wt.% to about 85 wt.% of the overall film thickness. These percentages may be similarly applied to multilayer films having more than three layers (e.g., 5, 7, or more layers). The first and second outer layers may have an equal thickness, or alternatively, may have an unequal thickness. The monolayer or multilayer films described herein may have a total film thickness of 100 microns or less. All individual values and subranges are included and disclosed herein. For example, in some embodiments, the monolayer or multilayer films described herein may have a total film thickness of from 10 to 75 microns, from 10 to 50 microns, or from 10 to 30 microns. While there is no minimum thickness contemplated for the monolayer or multilayer films of the present

disclosure, practical considerations of current manufacturing equipment suggests that the minimum thickness will be at least 10 microns.

[0051] In some embodiments, the monolayer or multilayer films described herein that include a nonpolar, polyethylene wax can have a 100% stretched, oxygen transmission rate (OTR) of at least 10 percent less than the 100% stretched, oxygen transmission rate of the same film without the nonpolar, polyethylene wax.

[0052] In some embodiments, the monolayer or multilayer films described herein can have a silage puncture resistance of from 45 (J/cm³) to 200 (J/cm³). All individual values and subranges are included and disclosed herein. For example, in some embodiments, the monolayer or multilayer films described herein may have a silage puncture resistance of from 45 (J/cm³) to 150 (J/cm³), or from 50 (J/cm³) to 100(J/cm³).

[0053] In some embodiments, the monolayer or multilayer films described herein can have an Elmendorf Tear Strength CD greater than 500 grams. In some embodiments, the monolayer or multilayer films described herein may have an Elmendorf Tear Strength CD of from greater than 500 grams to 2000 grams. All individual values and subranges are included and disclosed herein. For example, in some embodiments, the monolayer or multilayer films described herein may have an Elmendorf Tear Strength CD of from greater than 500 grams to 1500 grams or from greater than 500 grams to 1000 grams.

[0054] F - How to make films

[0055] Films described herein can be made using a variety of techniques including cast film techniques and/or blown film techniques. A method of making blown films is described in U.S. Patent No. 6,521,338 (Maka), the entirety of which patent is incorporated herein by reference. A method of making a cast film is described in U.S. Patent No. 7,847,029 (Butler et al.), the entirety of which patent is incorporated herein by reference. In some embodiments, the monolayer film and/or the multilayer film is a blown film. As used herein, a "blown film" is a film produced by extruding (or coextruding) a polymer melt(s) from an annular die into a tube which is simultaneously pulled away from the die, and over a bubble of air trapped between the die and a collapsing device, such as one or more nip rolls, while

the air is blown around the outer film tube surface to stabilize and quench the tube. In a blown film process, contact of the outer film tube surface and optionally also the inner film tube surface with room temperature or cooler air can cool the radially expanding tubular polymer melt as it leaves the die and travels over the trapped bubble thereby causing it to solidify. The point of transition from polymer melt to solid can be referred to as the frost line. Above the frost line, the blown or inflated tube is collapsed and fed through nip rolls which can trap air within the tube to maintain an expanded bubble of fluid (typically air). Optionally, this air bubble may be used to internally cool the expanded film tube by continuously delivering cool air (e.g., at about 45-55°F (7-13°C)) while simultaneously removing warm air from inside the bubble via the die. This exchange of air can be performed at a constant rate to produce a final blown film of uniform size. The internal bubble cooling can assist in quenching the film and may also produce a film having improved optical properties (i.e., lower haze and higher gloss). The blow up ratio is the ratio of the film circumference after radial expansion and cooling to the die opening circumference and may be determined from the known annular die opening dimensions and by measuring the transverse width of the flattened, expanded and cooled tubular film. Blow up ratios can range from 2:1 to 5:1. Dimensions and properties of the blown film may be adjusted by altering the blow up ratio and/or the haul off (or draw) speed of the film as it is pulled out of the die in the machine direction, for example, by driven nip rolls.

[0056] One or more layers of a film according to the present disclosure can be a melt blend. As used herein, a “melt blend” (which includes a “melted blend”) means two or more layer components (e.g., linear low density polyethylene a nonpolar, polyethylene wax) are melted and blended together via an apparatus such as a compounding apparatus. The melt blend can be directly extruded or cooled to form a solid composition (e.g., pellets) for subsequent use.

[0057] In some embodiments, a method of making a film includes providing a melted blend, extruding the melted blend in an extruder to form a tube; and cooling the tube to form a blown stretch film. The melted blend can include a wax component including a melted nonpolar, polyethylene wax as described above and a

first polyethylene polymer component including a melted linear low density polyethylene as also described above.

[0058] A melted blend as described herein can be provided in a variety of ways. For example, a composition including a dry mixture of a first and second plurality of particles can be melted and blended to form a melted blend, followed by directly extruding the melted blend. The first plurality of particles can include a polyethylene polymer component including linear low density polyethylene; and the second plurality of particles can include a wax component including nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater and is present in an amount of at least 3 percent by weight of the melted blend.

[0059] Alternatively, the first and second plurality of particles a dry mixture of a first and second plurality of particles can be melted and blended to form a melted blend, followed by forming the melted blend into a composition including a third plurality of particles. The third plurality of particles are a melt blend of the first and second plurality of particles and can be stored, transported, sold, and the like for subsequent extrusion. As used herein, “particles” refer to any kind of plurality of discrete units that are solid at 25°C such as pellets, powder, and the like. In some embodiments, a melt blend of the first and second plurality of particles can form a second layer (e.g., a “core” layer as described above) in a multilayer film where extruding the melted blend in an extruder to form a tube includes co-extruding the melted blend with a second polyethylene polymer component to form a tube including a first layer, a third layer, and the second layer between the first layer and the third layer. The first and third layers include the second polyethylene polymer component, which includes linear low density polyethylene. After extruding, the tube can be cooled to form a multilayer blown, stretch wrap film.

[0060] A monolayer film and/or the multilayer film can be subjected to one or more post processing techniques. Nonlimiting examples of post processing techniques include radiation treatment and/or corona treatment. Sealing techniques to which the mono-/multi-layer film can be exposed include heat sealing, adhesive sealing, heat bar sealing, impulse heating, side welding, and/or ultrasonic welding.

[0061] Embodiments of the present disclosure include monolayer and/or multilayer films that have not undergone any orientation processes (drawing or stretching) and, thus, are not oriented films (not monoaxially or biaxially oriented films).

[0062] G - How to use films

[0063] Monolayer and multilayer films according to the present disclosure can be used as stretch films, especially to contain items so as to limit or prevent their exposure to air (e.g., silage wrap or "silage bale wrap"). A film as described herein may also be useful in silo bags and silo bunker barriers.

[0064] Silage bale wrap can be described as a film designed to wrap silage so as to improve the nutritional value of silage (e.g., grass and other vegetable fodder) for cattle. Silage wrap helps baled silage to undergo anaerobic fermentation of the vegetable organic material inside the bale. The fermentation process can increase the amount of protein and make the silage more easily digestible. Silage wrap can facilitate anaerobic fermentation by keeping the oxygen content inside the bale as low as possible. For example, as the fodder is being wrapped with silage wrap, the silage wrap can facilitate pressing air out of the fodder. Further, the oxygen barrier properties of the silage wrap can facilitate keeping air out of the wrapped silage. To help facilitate this, silage wrap can have good mechanical properties, adhesion properties, and oxygen barrier properties. The mechanical properties of silage wrap are desirably good enough to prevent damage to the film from puncturing, stretching, tearing or other mechanical abuse, that could potentially break the film and allow air inside. The adhesion properties between successive layers of film in a bale are desirably good enough to provide a tight and hermetic closing of a bale. The oxygen barrier properties of the film (especially as the film is stretched to wrap silage) are desirably good enough to prevent oxygen in air from going through the layers of film into the bale.

[0065] An example of baling silage is described herein below. Silage can be baled by wrapping and stretching a silage wrap film around a bale of a forage crop and forming a barrier around the bale. It is noted that a silage wrap film may stretch up to 80-100% when it is being tightly wrapped around silage by a silage bale wrapping machine. As used herein, a "silage wrap film" is a monolayer film or any

multilayer film disclosed herein. The silage wrap film can be wrapped and stretched around the bale to produce a barrier that is composed of one, two, three, four, or more layers of the silage wrap film. Thus, the barrier can be a single layer of the silage wrap film or multiple layers of the silage wrap film. As used herein, a "barrier" is an airtight covering or an airtight encasement that can reduce the permeation of oxygen in air so that the OTR is as described herein.

[0066] As used herein, "bale silage" is one or more forage crops formed into a bale and covered with a silage wrap film to help exclude oxygen. A "forage crop" is any plant that is grown and fed to livestock. Nonlimiting examples of forage crops suitable for bale silage include beans, clover, corns, cornstalk, grasses, grains (barley, oats, rice, wheat, rye, millet), hay, legumes (alfalfa, red clover, white clover, alsike clover, birdsfoot trefoil, vetches, sweetclover), sorghums, soybeans, vegetables, and any combination of the foregoing.

[0067] A bale of silage can be wrapped using, e.g., a bale wrapping device that wraps and stretches the silage wrap film around the bale to form the barrier. A bale wrapping device can include a loading arm that lifts the bale and places it on a wrapping table. The wrapping table can include rollers and belts which rotate the bale while the table itself revolves. A dispensing device can provide one or more rolls of the silage wrap film. As the bale turns, the silage wrap film can be stretched as it is pulled through the dispensing device and wrapped tightly around the bale to help remove oxygen from the bale. When the table has revolved a predetermined number of times, a lift device can tilt the wrapping table to tip the wrapped bale off of the wrapping table. The dispensing device can cut the silage wrap film prior to the wrapped bale falling from the wrapping table. Operation of the bale wrapping device can be controlled automatically (by way of a computer or similar logic) or manually. In some embodiments, bale wrapping procedures can involve wrapping a bale with about four to about six layers of the silage wrap film to produce bale silage.

[0068] Once wrapped, the forage crop can undergo an ensiling process whereby anaerobic microorganisms ferment carbohydrates present in the forage crop to lactic acid forming silage.

[0069] An example of silage wrap is also disclosed in US 2011/0185683 (Domenech et al.).

[0070] **Test Methods**

[0071] **Density**

[0072] The density of the polymers in the polyethylene polymer component is measured according to ASTM D792, Method B.

[0073] The density of the nonpolar, polyethylene wax in the wax component is measured according to ISO 1183 at 23°C.

[0074] **Melt Index (I₂)**

[0075] The Melt Index (I₂) is measured according to ASTM D-1238 (condition 190°C/2.16kg).

[0076] **Percent Crystallinity**

[0077] Percent crystallinity for ethylene-based polymers (e.g., LLDPE) is determined by differential scanning calorimetry (DSC), using a TA Instruments Model Q1000 Differential Scanning Calorimeter. A sample of about 5-8 mg size is cut from the material to be tested, and placed directly in the DSC pan for analysis. For higher molecular weight materials, a thin film is normally pressed from the sample, but for some lower molecular weight samples, they may be either too sticky or flow too readily during pressing. Samples for testing may, however, be cut from plaques that are prepared, and used, for density testing. The sample is first heated at a rate of about 10°C/min to 180°C for ethylene-based polymers, and held isothermally for three minutes at that temperature to ensure complete melting (the first heat). Then the sample is cooled at a rate of 10°C per minute to -60°C for ethylene-based polymers, and held there isothermally for three minutes, after which, it is again heated (the second heat) at a rate of 10°C per minute until complete melting. The thermogram from this second heat is referred to as the "second heat curve." Thermograms are plotted as watts/gram versus temperature. The percent crystallinity in the ethylene-based polymers may be calculated using heat of fusion data, generated in the second heat curve (the heat of fusion is normally computed automatically by typical commercial DSC equipment, by integration of the relevant area under the heat curve). The equation for ethylene-based polymers is percent Cryst. = $(H_f \div 292 \text{ J/g}) \times 100$; and the equation for propylene-based polymers is:

percent Cryst. = $(H_f \div 165 \text{ J/g}) \times 100$. The "percent Cryst." represents the percent crystallinity and " H_f " represents the heat of fusion of the polymer in Joules per gram (J/g).

[0078] Acid Value

[0079] The acid value (mg KOH/g) of the nonpolar, polyethylene wax in the wax component is measured according to ISO 2114.

[0080] Saponification Value

[0081] The saponification value (mg KOH/g) of the nonpolar, polyethylene wax in the wax component is measured according to ISO 3681.

[0082] Viscosity

[0083] The viscosity (mPa-s) of the nonpolar, polyethylene wax in the wax component is measured according to DIN53019 at 140°C.

[0084] Drop Point

[0085] The drop point (°C) of the nonpolar, polyethylene wax in the wax component is measured according to ASTM D 3954.

[0086] Oxygen Transmission Rate (OTR)

[0087] Oxygen transmission rate is reported as (cubic centimeters (cc) of oxygen / (m²*day)) and is measured at 23°C, 75% Relative Humidity, 1 atm using a MOCON Ox-Tran Model 2/21 analyzer in accordance with ASTM D 3985-05. The test specimen is held such that it separates two sides of a test chamber. One side is exposed to a nitrogen atmosphere while the other side is exposed to an oxygen atmosphere. A coulometric sensor monitoring the exit port of the nitrogen side measures the amount of oxygen present. Testing is complete when the concentration of oxygen in the nitrogen side atmosphere is constant. For a 100% stretched sample, the film is first stretched using an Instron tensile machine by stretching the film at 2 inches/minute until the film length is two times its original length. The stretched film is then held on a metallic frame to avoid film relaxation, the film-on-frame subsequently placed in the chamber to measure the oxygen transmission.

[0088] Puncture Resistance

[0089] Puncture Resistance is measured in accordance with ASTM D5748-95 using an Instron® testing machine.

[0090] Silage Puncture Resistance

[0091] Silage Puncture Resistance as measured in accordance with UNE-EN 14932 using an Instron® testing machine as modified according to UNE-EN 14932.

[0092] Elmendorf Tear Strength Cross Direction (CD)

[0093] Elmendorf Tear Strength, CD is measured according to ASTM D 1922-09 using an FX3750 Elmendorf Tester from TEXTTEST Instruments. Elmendorf Tear Strength, CD measures the tear strength of a plastic film in the cross (or transversal) direction. Elmendorf Tear Strength, CD can be reported in grams (g).

[0094] Elmendorf Tear Strength MD

[0095] Elmendorf Tear Strength, MD measures the tear strength of a plastic film in the machine direction. Elmendorf Tear Strength, MD can be reported in grams (g) and can be measured according to ASTM D1922.

[0096] Examples**[0097] Example 1**

[0098] Both monolayer films and three-layer films were made in Example 1 using small scale blown film lines.

[0099] Table 1: Process conditions:

Pre-compounding	The melt-blending of polyethylene and wax was done using a BUSS kneader compounder (MDK/E46)
Monolayer films	25µm-thick films were produced using the COLLIN monolayer laboratory blown film line. This is a 30mm diameter extruder with a 25 L/D screw and a die gap used was 1.2 mm. Output was 5 kg/h with a screw speed of 50rpm. BUR=2.5. melt temperature was 239-240°C in all cases.
Three-layer films	The three-layer films have been made using the COLLIN co-extrusion Blown Film Line. This line allows for different configuration of layers when running three layer formulations (i.e. 25%/50%/25% or 45%/10%/45% or 20%/60%/20%). The extruders used were 1, 2, and 3. Screw 1 is a 25 mm diameter with a 25 LxD length; screws 2& 3 are 30 mm diameter screws with a 25 LxD length. In all cases the BUR was 2.5, die gap was 1.8 mm and the line output was 8 kg/h. All films

	are 25µm thick. Melt temperature ranged from 214-228°C. Screw 1 corresponds to a first outer layer, screw 2 corresponds to the core layer, and screw 3 corresponds to the second outer layer.
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[0100] Table 2: film compositions:

Sample number	Structure	Layer Ratio	Layer composition
ICE1	Monolayer	100	100% DOWLEX 2045S
ICE2	Monolayer	100	99% DOWLEX 2045S + 1% Licowax 130
ICE3	Monolayer	100	90% DOWLEX 2045S + 10% Licowax 520
ICE4	Monolayer	100	90% DOWLEX 2045S + 10% Licowax 521
ICE5	Three layer	20/60/20	All three layers were 100% DOWLEX 2045S
ICE6	Three layer	20/60/20	(ABA) First and second outer layers were DOWLEX 2045S and the core layer was 90% DOWLEX 2045S +10% SASOLWAX H1
ICE7	Three layer	20/60/20	(ABA) First and second outer layers were DOWLEX 2045S and the core layer was 90% DOWLEX 2045S +10% SASOLWAX 4608
1Ex1	Monolayer	100	90% DOWLEX 2045S + 10% Licowax 130
1Ex2	Monolayer	100	95% DOWLEX 2045S + 5% Licowax 130
1Ex3	Three layer	20/60/20	(ABA) First and second outer layers were DOWLEX 2045S and the core layer was 90% DOWLEX 2045S +10% Licowax 130

[0101] Table 3: relevant properties and variations with respect to the reference film; all monolayer films

Monolayer Films	OTR	OTR (100% stretched)	% Δ OTR (unstretched)	% Δ OTR (100% stretched)	Silage puncture resistance	Puncture resistance	Elmendorf Tear Strength CD	Overall 1% Wax
Unit	cc/(m ² ·day)	cc/(m ² ·day)			J/cm ³	J/cm ³	g	%
ICE1	8988	7872	0	0	51.7	12.6	530	0
ICE2	8789	7818	-2	-1	51.5	11.8	551	1
ICE3	9285	8058	3	2	46.7	7.5	551	10
ICE4	10402	Not measured	16	NM	55.3	10.7	588	10
1Ex1	6148	5935	-32	-25	46.1	7.7	580	10
1Ex2	7418	6956	-17	-12	46.4	9.2	534	5

[0102] In the three-layer films (table 4), we see that the film with 10% Licowax 130 in the core layer, which means 6% wax in the total structure, also meets the OTR decrease and the mechanical properties are maintained or improved. In the comparative examples, other PE waxes and paraffin waxes are included but they do not show the desired balance of properties.

[0103] Table 4: three-layer films with structure 20/60/20

Three-layer films 20/60/20	OTR	OTR (100% stretched)	% Δ OTR (unstretched)	% Δ OTR (100% stretched)	Silage puncture resistance	Puncture resistance	Elmendorf Tear Strength CD	% thickness of layer w wax	Overall 1% Wax	% wax in the layer that contains wax
Unit	cc/(m ² ·day)	cc/(m ² ·day)			J/cm ³	J/cm ³	g	%	%	%
ICE5	9733	7896	0	0	49.1	15.7	538	0	0	0
ICE6	8306	8632	-15	9	60.7	12.1	623	60	6	10
ICE7	8805	8663	-10	10	60.1	10.9	713	60	6	10
1Ex3	8081	7053	-17	-11	57.6	13.1	593	60	6	10

[0104] Example 2

[0105] Example 2 was carried out using a semi-industrial scale blown extrusion, three-layer line. In this experiment we have used Resin XZ, which is a blend of 90% ELITE AT 6301 and 10% LICOWAX 130. This blend has been melt compounded (total of 2000 kg).

[0106] The films are three layer with A/B/C structure, relative thickness of each layer 15%/70%/15% and total thickness of 23 microns. They were fabricated with an ALPINE blown film line, with the following characteristics in Table 5:

Table 5:

Main components	ALPINE inner bubble control MACRO dual lip cooling ring DOTEKO Profix thickness profile control KUNDIG capacitive thickness sensor Tandem winder(contact/surface mode)
Monolayer film screw diameter	65 mm
Monolayer screw length	30 x D
Maximum output (monolayer)	80 kg/h
Coex screw diameter (A & C)	50 mm
Coex screw length (A & C)	30 x D
Coex screw diameter (B)	65 mm
Coex screw diameter (B)	30 x D
Maximum output (coex)	220 kg/h (Thin Skin layers preferably around 10-25%)
Die size	200 mm

[0107] Specific details of processing conditions are given in Table 6:

Table 6. Processing conditions of 3-layer films made in the ALPINE blown film line

	<i>2CEI</i>	<i>2ExI</i>
	A:ELITE AT 6301 + 15%ATTANE 4100 + 9% PIB / B:ELITE AT 6301 + 9% PIB / C:ELITE AT 6301 + 10% LDPE 150	A: Resin XZ + 15%ATTANE 4100 + 9% PIB / B:Resin XZ + 9% PIB / C: Resin XZ + 10% LDPE 150
B.U.R.	2.8:1	2.8:1
Die gap (mm)	2.5	2.5
Layer percetaje Extr. A (%)	15	15
Layer percetaje Extr. B (%)	70	70
Layer percetaje Extr. C (%)	15	15
Melt Pressure Extr. A (bar)	121	145
Melt Pressure Extr. B (bar)	191	245
Melt Pressure Extr. C (bar)	124	160
Melt Temperature Extr. A (DegC)	219	218
Melt Temperature Extr. B (DegC)	219	212
Melt Temperature Extr. C (DegC)	210	210
Motor Current Extr. A (A)	19	24
Motor Current Extr. B (A)	49	52
Motor Current Extr. C (A)	31	33
Output Rate (Kg/h)	80	80
Screw Speed Extr. A (rpm)	23.1	23.1
Screw Speed Extr. B (rpm)	31.9	36.7
Screw Speed Extr. C (rpm)	18.0	22.0
Take-off Speed (m/min)	32.8	33.7

[0108] The composition of each ABC layer and film properties are shown in Table 7 below.

[0109] Table 7. Layer composition and properties of films produced in the ALPINE blown film line.

Table 7

		2CE1	2Ex1
		A:ELITE AT 6301 + 15%ATTANE 4100 + 9% PIB / B:ELITE AT 6301 + 9% PIB / C:ELITE AT 6301 + 10% LDPE 150	A: Resin XZ + 15%ATTANE 4100 + 9% PIB / B:Resin XZ + 9% PIB / C: Resin XZ + 10% LDPE 150
Elmendorf Tear Strength CD	g	480	684
Elmendorf Tear Strength MD	g	227	302
Silage Puncture Force	N	4.0	4.2
Un-stretched OTR	cm ³ /m ² .day	11119	8329
Stretched @ 100% OTR	cm ³ /m ² .day	9101	5562

[0110] These structures reflect the ones actually used in the industry, including a tackifier additive (poly-isobutylene, PIB), a cling layer that includes ATTANE® SL4100G ultra-low density polyethylene, ethylene/1-octene copolymer, made in the solution process with Ziegler-Natta catalyst, with I2=1.0 dg/min, density=0.912. LDPE 150 is made with the high pressure process in a tubular reactor and has I2=0.25 dg/min and density = 0.9210 g/cm³.

[0111] E1 example shows a lower oxygen transmission rate, for both the un-stretched and stretched film, while mechanical properties are maintained at good levels.

WHAT IS CLAIMED IS:

- 1) A film comprising at least one layer, wherein the at least one layer comprises:
 - a) a polyethylene polymer component comprising linear low density polyethylene; and
 - b) a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the film.
- 2) The film of claim 1, wherein the polymer component comprises a blend of linear low density polyethylene and at least one polyethylene polymer chosen from low density polyethylene, medium density polyethylene, and high density polyethylene.
- 3) The film of any preceding claim, wherein the nonpolar, polyethylene wax is present in an amount in the range from 5 to 30 percent by weight of the film.
- 4) The film of any preceding claim, wherein the nonpolar, polyethylene wax has an acid value of 5 (mg KOH/g) or less as measured in accordance with ISO 2114, and/or wherein the nonpolar, polyethylene wax has a saponification value of 5 (mg KOH/g) or less as measured in accordance with ISO 3681.
- 5) The film of any preceding claim, wherein the nonpolar, polyethylene wax has a viscosity in the range from 100 to 30,000 (mPa-s) as measured in accordance with DIN53019 at 140°C.
- 6) The film of any preceding claim, wherein the nonpolar, polyethylene wax has a drop point in the range from 125°C to 145°C as measured in accordance with ASTM D 3954.

7) The film of any preceding claim, wherein the film has a 100% stretched, oxygen transmission rate of at least 10 percent less than the 100% stretched, oxygen transmission rate of the same film without the nonpolar, polyethylene wax as measured in accordance with ASTM D 3985-05.

8) The film of any preceding claim, wherein the film has a silage puncture resistance of 45 (J/cm³) or greater as measured in accordance with UNE-EN 14932.

9) The film of any preceding claim, wherein the film has an Elmendorf Tear Strength Cross Direction greater than 500 grams as measured in accordance with ASTM D 1922-09.

10) The film of any preceding claim, wherein the film is a monolayer film.

11) The film of claim 1, wherein the film is a multilayer film comprising:

- a) a first layer;
- b) a second layer, wherein the second layer comprises the polyethylene polymer component and the wax component; and
- c) a third layer, wherein the second layer is between the first layer and third layer.

12) A composition comprising:

- a) a polyethylene polymer component comprising linear low density polyethylene; and
- b) a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the composition.

13) The composition of claim 12, wherein the composition is a plurality of particles.

14) A method of making a film, wherein the method comprises:

a) providing a melted blend, wherein the melted blend comprises a wax component comprising melted nonpolar, polyethylene wax and a first polyethylene polymer component comprising melted linear low density polyethylene, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the film; and

b) forming the melted blend into a film.

15) The method of claim 14, wherein forming the melted blend into a film comprises:

a) extruding the melted blend in an extruder to form a tube; and

b) cooling the tube to form a blown stretch film, wherein, optionally, the melted blend forms a second layer in a multilayer film, and wherein extruding the melted blend in an extruder to form a tube comprises co-extruding the melted blend with a second polyethylene polymer component to form a tube comprising a first layer, a second layer and a third layer, wherein the second layer is between the first layer and the third layer, and wherein the second polyethylene polymer component comprises linear low density polyethylene.

AMENDED CLAIMS

received by the International Bureau on 26 May 2017 (26.05.2017)

- 1) A film comprising at least one layer, wherein the at least one layer comprises:
 - a) a polyethylene polymer component comprising linear low density polyethylene; and
 - b) a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount from 10 to 30 percent by weight of the film.
- 2) The film of claim 1, wherein the polymer component comprises a blend of linear low density polyethylene and at least one polyethylene polymer chosen from low density polyethylene, medium density polyethylene, and high density polyethylene.
- 4) The film of any preceding claim, wherein the nonpolar, polyethylene wax has an acid value of 5 (mg KOH/g) or less as measured in accordance with ISO 2114, and/or wherein the nonpolar, polyethylene wax has a saponification value of 5 (mg KOH/g) or less as measured in accordance with ISO 3681.
- 5) The film of any preceding claim, wherein the nonpolar, polyethylene wax has a viscosity in the range from 100 to 30,000 (mPa-s) as measured in accordance with DIN53019 at 140°C.
- 6) The film of any preceding claim, wherein the nonpolar, polyethylene wax has a drop point in the range from 125°C to 145°C as measured in accordance with ASTM D 3954.
- 7) The film of any preceding claim, wherein the film has a 100% stretched, oxygen transmission rate of at least 10 percent less than the 100% stretched, oxygen transmission rate of the same film without the nonpolar, polyethylene wax as measured in accordance with ASTM D 3985-05.
- 8) The film of any preceding claim, wherein the film has a silage puncture resistance of 45 (J/cm³) or greater as measured in accordance with UNE-EN 14932.

9) The film of any preceding claim, wherein the film has an Elmendorf Tear Strength Cross Direction greater than 500 grams as measured in accordance with ASTM D 1922-09.

10) The film of any preceding claim, wherein the film is a monolayer film.

11) A multilayer film comprising:

- a) a first layer;
- b) a second layer, wherein the second layer comprises:
 - i) a polyethylene polymer component comprising linear low density polyethylene; and
 - ii) a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the film; and
- c) a third layer, wherein the second layer is between the first layer and third layer.

12) A composition comprising:

- a) a polyethylene polymer component comprising linear low density polyethylene; and
- b) a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount from 10 to 30 percent by weight of the composition.

13) The composition of claim 12, wherein the composition is a plurality of particles.

14) A method of making a film, wherein the method comprises:

- a) providing a melted blend, wherein the melted blend comprises a wax component comprising melted nonpolar, polyethylene wax and a first polyethylene polymer component comprising melted linear low density polyethylene, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount from 10 to 30 percent by weight of the film; and

b) forming the melted blend into a film.

15) The method of claim 14, wherein forming the melted blend into a film comprises:

- a) extruding the melted blend in an extruder to form a tube; and
- b) cooling the tube to form a blown stretch film, wherein, optionally, the melted blend forms a second layer in a multilayer film, and wherein extruding the melted blend in an extruder to form a tube comprises co-extruding the melted blend with a second polyethylene polymer component to form a tube comprising a first layer, a second layer and a third layer, wherein the second layer is between the first layer and the third layer, and wherein the second polyethylene polymer component comprises linear low density polyethylene.

STATEMENT UNDER ARTICLE 19 (1)

According to the Written Opinion, independent claims 1, 12, and 14 lack novelty over each of D1 (EP 2216366 (Kawabe et al.)) and D2 (EP 2002963 (Uosaki et al.)).

D1 does not teach a film comprising at least one layer that includes “a) a polyethylene polymer component comprising linear low density polyethylene; and b) a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount from 10 to 30 percent by weight of the film,” as recited in claim 1 (underlining added for emphasis). D1 is not novelty destroying for independent claims 12 and 14 for similar reasons. Further D2 is not novelty destroying for independent claims 1, 12, and 14 for similar reasons.

D1 does not teach a multilayer film that includes “a) a first layer; b) a second layer, wherein the second layer comprises: i) a polyethylene polymer component comprising linear low density polyethylene; and ii) a wax component comprising nonpolar, polyethylene wax, wherein the nonpolar, polyethylene wax has a density of 0.955 grams/cm³ or greater, and wherein the nonpolar, polyethylene wax is present in an amount of at least 3 percent by weight of the film; and c) a third layer, wherein the second layer is between the first layer and third layer,” as recited in claim 11. D2 is not novelty destroying for independent claim 11 for similar reasons.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/013708

A. CLASSIFICATION OF SUBJECT MATTER
INV. B32B27/32 C08J5/18 C08L23/06
ADD.

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)
B32B C08J C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 216 366 A1 (MITSUI CHEMICALS INC [JP]) 11 August 2010 (2010-08-11) paragraphs [0001] - [0152]; claims 1-9 -----	1-15
X	EP 2 002 963 A2 (MITSUI CHEMICALS INC [JP]) 17 December 2008 (2008-12-17) paragraphs [0001] - [0280]; claims 1-6 -----	1-15
A	EP 2 554 377 A2 (DOW GLOBAL TECHNOLOGIES LLC [US]) 6 February 2013 (2013-02-06) abstract -----	1-15
A	EP 1 152 025 A1 (TOKUYAMA CORP [JP]) 7 November 2001 (2001-11-07) abstract -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

21 March 2017

Date of mailing of the international search report

29/03/2017

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/013708

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 2216366	A1	11-08-2010	CN	101874069 A		27-10-2010
			EP	2216366 A1		11-08-2010
			JP	5328670 B2		30-10-2013
			US	2010286326 A1		11-11-2010
			WO	2009069595 A1		04-06-2009

EP 2002963	A2	17-12-2008	EP	2002963 A2		17-12-2008
			TW	200808523 A		16-02-2008
			US	2009137729 A1		28-05-2009
			WO	2007114102 A1		11-10-2007

EP 2554377	A2	06-02-2013	CN	102227466 A		26-10-2011
			EP	2172510 A1		07-04-2010
			EP	2346930 A1		27-07-2011
			EP	2554377 A2		06-02-2013
			JP	5852884 B2		03-02-2016
			JP	2012504685 A		23-02-2012
			RU	2011116767 A		10-11-2012
			US	2011185683 A1		04-08-2011
			WO	2010039687 A1		08-04-2010

EP 1152025	A1	07-11-2001	EP	1152025 A1		07-11-2001
			JP	2001233982 A		28-08-2001
			US	2003100650 A1		29-05-2003
			WO	0144353 A1		21-06-2001
