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(57) Abstract: Multilaver "barrier" films which have excellent Water Vapor Transmission Rate (WVTR) performance are prepared using a core layer which comprises a blend of from 92 to 60 weight % of nucleated HDPE and from 8 to 40 weight% LDPE. The

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CURL RESISTANT BARRIER FILMS

TECHNICAL FIELD

This invention relates to new designs for multilayer plastic films having high barrier properties.

BACKGROUND ART

Plastic films having gas barrier properties are widely used in packaging for dry foods. The films should have a low Water Vapor Transmission Rate (WVTR) and a low Oxygen Transmission Rate (OTR). Aroma barrier is also desirable.

The paper packaging that was originally used in these applications was partially replaced by cellophane, but cellophane is expensive and difficult to process.

Barrier films prepared from high density polyethylene (HDPE) offer an alternative to paper or cellophane. HDPE films offer a good balance between cost and

15 performance. However, when additional barrier and/or toughness is required, it is known to prepare multilayer films which contain layers made of more expensive barrier resins (such as ethylene-vinyl alcohol (EVOH); polyamide (nylon); polyesters; ethylenevinyl acetate (EVA); or polyvinyldiene chloride (PVDC)) and/or layers of stronger/tougher resins such as ionomers or linear low density linear polyethylenes

20 ("LLDPE"). Sealant layers made from EVA, ionomer, "high pressure low density polyethylene" ("LDPE") or plastomers are also employed in multilayer structures.

The expensive barrier resins listed above (polyamide, EVOH, polyesters and PVDC) tend to be more polar than HDPE. This can cause adhesion problems between layers of polar and non-polar resins in multilayer film structures. Accordingly, "tie layers" or adhesives may be used between the layers to reduce the probability that the layers separate from one another.

Monolayer HDPE films are inexpensive, easy to prepare and offer moderate resistance to water vapor and oxygen transmission. Moreover, it is simple to provide increased barrier properties by just increasing the thickness of the film. However, the

mechanical properties (such as tear strength and impact strength) and sealing 30 properties of HDPE film are comparatively low so multilayer films are widely used.

Thus, the design of barrier films involves a cost/benefit analysis - with the low cost of HDPE resin being balanced against the better performance of the more expensive, polar resins. Another way to lower the cost of the film is to simply use less

material - by manufacturing a thinner or "down gauged" film. 35

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Examples of multilayer barrier films that use HDPE are disclosed in United States Patents 4,1 88,441 (Cook); 4,254,169 (Schroeder); and 6,045,882 (Sandford) and our previously published Canadian patent application CA 2,594,472 (Aubee et al.).

DISCLOSURE OF INVENTION

The present invention provides:

a barrier film comprising a core layer and two skin layers, wherein said core layer consists essentially of a blend of:

a) from 60 to 92 weight% of a nucleated high density polyethylene resin; and

b) 40 to 8 weight% of high pressure, low density polyethylene.

10 It will be appreciated by those skilled in the art of producing multilayer films that these films can roll up upon themselves or "curl." One generally accepted theory for the mechanism that causes curl is that "differential shrinkage" - i.e. the tendency for one layer to shrink at a different rate from the others - leads to curl. This theory has been discussed in the literature and is summarized in two papers that were presented at the annual conference of the Society of Plastics Engineers ("SPE") in 2002 (ref: Morris;

SPE (2002), 60th (Vol 1), 40-46 and Morris; SPE (2002), 60th (Vol 1), 32-39).

Two factors that may influence the degree of differential shrinkage are:

- 1) The materials of construction (for example, if a skin layer is made from a material that shrinks more than the material used for an inner layer; and
- 2) Process conditions: for example, if a freshly fabricated film is cooled on only one side of the film (such as the interior of a blown film), the rate of shrinkage on that side can be different from the rate of shrinkage on the "outside" of the blown film bubble.
- These problems can be increased when a nucleating agent is present in the 25 material used in one layer of a multilayer film because in general, the addition of a nucleating agent will cause a polymeric material to shrink more upon cooling (in comparison to the rate of shrinkage for the same polymer under the same cooling conditions in the absence of the nucleating agent). To some extent, this problem can be mitigated by using the same nucleated polymer in the core layer and at least one of the
- skin layers. An example of this type of film design is disclosed in Table 1 of CA
 2,594,472. We have now discovered another design alternative that utilizes a blend of
 HDPE and LDPE in the core layer of a multilayer film.

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BEST MODE FOR CARRYING OUT THE INVENTION

<u>A._-_HDP</u>E

Preferred HDPE for use in the films of this invention has a density of from 0.950 grams per cubic centimeter (g/cc) to about 0.970 g/cc as determined by ASTM D1505.
5 Preferred HDPE also has a density of greater than 0.955 g/cc and the most preferred HDPE is a homopolymer of ethylene having a density of greater than 0.958 g/cc. Preferred HDPE is further characterized by having a melt index, l₂, of from 0.3 to 20 grams per 10 minutes, especially from 0.5 to 10 grams per 10 minutes (as measured by ASTM D1238 at 190° C with a 2.16 kg load and commonly referred to as "l₂")

10 The molecular weight distribution of the HDPE [which is determined by dividing the weight average molecular weight (Mw) by number average molecular weight (Mn), where Mw and Mn are determined by gel permeation chromatography, according to ASTM D 6474-99] is preferably from 2 to 20, especially from 2 to 10.

A highly preferred HDPE is prepared by a solution polymerization process using two reactors that operate under different polymerization conditions. This provides a uniform, in situ blend of two HDPE blend components. An example of this process is described in U.S. patent 7,737,220 (Swabey et al.), the disclosure of which is incorporated herein by reference. The use of the "dual reactor" process also facilitates the preparation of blends which have very different melt index values. It is highly

20 preferred to use a blend (prepared by the dual reactor process) in which the first HDPE blend component has a melt index (I_2) value of less than 0.5 g/10 minutes and the second HDPE blend component has an I_2 value of greater than 100 g/10 minutes. The amount of the first HDPE blend component of these blends is preferably from 40 to 60 weight % (with the second blend component making the balance to 100 weight %). The

25 overall HDPE blend composition preferably has a MWD (Mw/Mn) of from 3 to 20.

B. Nucleating Agents

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The term nucleating agent, as used herein, is meant to convey its conventional meaning to those skilled in the art of preparing nucleated polyolefin compositions, namely an additive that changes the crystallization behavior of a polymer as the polymer melt is cooled.

Nucleating agents are widely used to prepare polypropylene molding compositions and to improve the molding characteristics of polyethylene terephthalate (PET).

A review of nucleating agents is provided in USP 5,981,636; 6,466,551 and 6,559,971, the disclosures of which are incorporated herein by reference.

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The multilayer films of this invention comprise a core layer which must contain "nucleated HDPE". As used here, the term "nucleated HDPE" is meant to convey its plain meaning, namely HDPE (as described in Part A above) which contains a nucleating agent (as described in Part B).

5 The nucleating agent is preferably well dispersed in the HDPE. The amount of nucleating agent used is preferably guite small - from 100 to 3000 parts per million by weight (based on the weight of the polyethylene) so it will be appreciated by those skilled in the art that some care must be taken to ensure that the nucleating agent is well dispersed. It is preferred to add the nucleating agent in finely divided form (less 10 than 50 microns, especially less than 10 microns) to the polyethylene to facilitate mixing. An alternative to a "physical blend" (i.e. a mixture of the nucleating agent and the resin in solid form) is the use of a "masterbatch" of the nucleator (where the term "masterbatch" refers to the practice of first melt mixing the additive - the nucleator, in this case - with a small amount of HDPE resin - then melt mixing the "masterbatch" 15 with the remaining bulk of the HDPE resin).

It is especially preferred to include a metal stearate (such as zinc or calcium

stearate) in a 1/2 to 2/1 weight ratio with respect to the nucleating agent. While not wishing to be by theory, it is believed that the stearate may improve the dispersion of the nucleating agent.

20 Examples of nucleating agents which may be suitable for use in the present invention include the cyclic organic structures disclosed in USP 5,981,636 (and salts thereof, such as disodium bicycio [2.2.1] heptene dicarboxylate); the saturated versions of the structures disclosed in USP 5,981 ,636 (as disclosed in USP 6,465,551 ; Zhao et al., to Milliken); zinc glycerolate; the salts of certain cyclic dicarboxylic acids having a 25 hexahydrophtalic acid structure (or "HHPA" structure) as disclosed in USP 6,559,971 (Dotson et al., to Milliken); and phosphate esters, such as those disclosed in USP 5,342,868 and those sold under the trade names NA-1 1 and NA-21 by Asahi Denka Kogyo. Preferred barrier nucleating agents are cylic dicarboxylates and the salts thereof, especially the divalent metal or metalloid salts, (particularly, calcium salts) of

30 the HHPA structures disclosed in USP 6,559,971. For clarity, the HHPA structure generally comprises a ring structure with six carbon atoms in the ring and two carboxylic acid groups which are substituents on adjacent atoms of the ring structure. The other four carbon atoms in the ring may be substituted, as disclosed in USP 6.559.971. A preferred example is 1.2 - cyclohexanedicarboxylic acid, calcium salt

(CAS registry number 491589-22-1). 35



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