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(54) FILM DE HDPE REVETU ET SON PROCEDE DE FABRICATION
(54) COATED HDPE FILM AND ITS METHOD OF MANUFACTURE

(57) L'invention porte sur une composition pour film revêtus comprenant: un film à base de polyéthylène à haute densité (HDPE) à orientation biaxiale composé d'au moins 50% en poids de HDPE et présentant une densité d'au moins 0,960; et un revêtement dérivé d'un groupe consistant en un polymère ou copolymère de chlorure de polyvinyle, en un polymère ou copolymère d'acide acrylique et en un polymère d'alcool polyvinylique (PVOH); ainsi que sur son procédé de fabrication.

(57) The invention relates to a coated film composition comprising: a) a biaxially oriented high density polyethylene (HDPE) film comprising at least 50 wt. % of HDPE having a density of 0.960 or greater; and b) a coating which is derived from the group consisting of polyvinylidene chloride polymer or copolymer, acrylic acid polymer or copolymer, and polyvinyl alcohol polymer (PVOH); and its method of manufacture.

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(54) Title: COATED HDPE FILM AND ITS METHOD OF MANUFACTURE

(57) Abstract

The invention relates to a coated film composition comprising: a) a biaxially oriented high density polyethylene (HDPE) film comprising at least 50 wt. % of HDPE having a density of 0.960 or greater; and b) a coating which is derived from the group consisting of polyvinylidene chloride polymer or copolymer, acrylic acid polymer or copolymer, and polyvinyl alcohol polymer (PVOH); and its method of manufacture.

COATED HDPE FILM AND ITS METHOD OF MANUFACTURE

This invention is concerned with coated oriented high density polyethylene film having the utility of a packaging film.

All polymeric films possess both good and bad characteristics. An organic polymer film that may be an excellent barrier film for excluding the transmission of oxygen and water vapor may be a poor film regarding flexibility, heat sealability, printability, appearance, etc. Polyethylene film, while excellent for structures such as grocery sacks or bread wrappers, is not an excellent packaging film for products such as, snack foods, etc. Polyethylene, in some applications lacks sufficient flavor/aroma barrier properties. Moreover, polyethylene lacks the ability to provide a peelable seal which is often required by food packagers.

It is an object of the present invention to present a coated oriented high density polyethylene coated for improved properties, especially relating to oxygen barrier, flavor/aroma barrier, and seal peelability.

The present invention is concerned with a coated film comprising:

a) a biaxially oriented high density polyethylene (HDPE) film comprising at least 50 wt. % of HDPE having a density of 0.960 or greater; and

b) a coating which is derived from the group consisting of polyvinylidene chloride polymer or copolymer, acrylic acid polymer or copolymer, ethylene acrylic acid polymer or copolymer, and polyvinyl alcohol polymer (PVOH).

As indicated above the film of the present invention comprises essentially a biaxially oriented high density polyethylene film and a coating which provides improved properties without significantly affecting water vapor transmission resistance. The film is preferably a biaxially oriented high density polyethylene film having a density of 0.960 or greater. Films of this type are disclosed in U.S. Patent No. 4,870,122. The HDPE film can be composed exclusively of a single HDPE resin, a mixture of HDPE resins, or of HDPE containing a minor proportion of up to about 10 wt. % microcrystalline wax. Films made with either a blend of HDPE resins or with microcrystalline wax reduce the splittiness of the film which manifests itself as a tendency of the film to break in the transverse direction (TD) during packaging on vertical, form, fill and seal (VFFS) machinery.

The blends of HDPE polymers can comprise two or more polymers all of which preferably have densities of 0.960 or greater. Blends of HDPE polymers advantageously comprise a major proportion of HDPE having a melt index of 0.6 to 1.2 and one or more polymers having a different melt index.

Terblends have been found particularly desirable. Suitable terblends generally comprise 50 to 98 weight percent, preferably 84 to 96 weight percent of HDPE having a density of 0.960 or higher and a melt index of greater than 0.5 to 2.0; 1 to 25 weight percent, preferably 3 to 8 weight percent of HDPE having a density of 0.960 or greater and a melt index of 0.1 to 0.5; and 1 to 25 weight percent, preferably 3 to 8 weight percent, of HDPE having a density of 0.960 or higher and a melt index of greater than 2 to 8. Preferably, the second and third HDPE polymers, which are minor components, are present in about equal amounts.

It is preferred that the HDPE films of this invention be biaxially oriented in an unbalanced manner. By this is meant that the HDPE is oriented to a degree of 1.25:1 to 2:1 in the machine direction (MD) and to a degree of about 6:1 to 12:1 in the transverse direction (TD). The HDPE can be coextruded with conventional heat-seal materials, e.g. Surlyn or EP copolymers.

Additives such as fillers, antioxidants, pigments, antistatic agents, slip agents, antitack agents can be incorporated in the high density polyethylene film.

Coatings can be derived from any of the terpolymeric compositions disclosed in U.S. Pat. No. 3,753,769, and 4,865,908. These coating compositions contain as a film forming component a resin consisting essentially of an interpolymer of (a) from 2 to 15, and preferably from 2.5 to 6, parts by weight of an alpha-beta monoethylenically unsaturated carboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof, and (b) from 85 to 98, and preferably from 94 to 97.5, parts by weight of neutral monomer esters, said neutral monomer esters preferably comprising (1) methyl acrylate or ethyl acrylate and (2) methyl methacrylate. These interpolymer compositions are further characterized by preferably comprising from 30 percent to 55 percent by weight of methyl methacrylate when said alkyl acrylate is methyl acrylate, and from 52.5 percent to 69 percent by weight of methylmethacrylate when said alkyl acrylate is ethyl acrylate. As more fully described infra, such coating compositions can be applied to the films herein in a variety of ways including in the form of ammoniacal solutions.

Similarly useful are copolymeric coating compositions prepared from the foregoing neutral monomer esters. These coating compositions are advantageously applied to the film laminates in the form of emulsions.

The coating can also be based on any of the known and conventional polyvinylidene chloride (PVDC) compositions heretofore employed as coatings in film manufacturing operations, e.g., any of the PVDC materials described in U.S. Pat. Nos. 4,214,039 and 4,447,494 preferably with prior application of a primer layer to enhance adhesion of the PVDC coating layer to the film surface to which it is applied. Commercially available PVDC latexes having a vinylidene chloride content of at least 50% and preferably from 75% to 92% may be employed. The PVDC can also be provided as a copolymer of vinylidenechloride and one or more other ethylenically unsaturated comonomers including alpha, beta ethylenically unsaturated acids such as acrylic and methacrylic acids; alkyl esters containing 1-18 carbon atoms of said acids, such as methylmethacrylate, ethyl acrylate and butyl acrylate. In addition alpha, beta ethylenically unsaturated nitriles such as acrylonitrile and methacrylonitrile and monovinyl aromatic compounds such as styrene and vinyl chloride comonomers can be employed. Specific PVDC latexes contemplated comprise: 82% by weight vinylidene chloride, 14% by weight ethyl acrylate and 4% by weight acrylic acid. Alternatively a polymer latex comprising about 80% by weight vinylidene chloride, about 17% methyl acrylate and about 3% by weight methacrylic acid can likewise be employed.

The vinyl alcohol polymers which may be used as coatings can be any commercially available material. For example, Vinol 125, 99.3 +% super hydrolyzed polyvinyl alcohol, or Vinol 325, 98% hydrolyzed polyvinyl alcohol obtained from Air Products, Inc.

Before applying the coating composition to the appropriate substrate, the upper surface of the film is preferably treated to increase its surface energy and therefor insure that the coating layer will be strongly adherent thereto thereby reducing the possibility of the coating peeling or being stripped from the film. This treatment can be accomplished employing known techniques, such as, for example, film chlorination, i.e., exposure of the film surface to gaseous chlorine, treatment with oxidizing agents such as chromic acid, hot air or steam treatment and flame treatment. Although any of these techniques is effectively employed to pretreat the film surface, a particularly desirable method of treatment is the so-called electronic treatment method which comprises exposing the film surface to a high voltage corona discharge while passing the film between a pair of spaced electrodes. After electronic treatment of the film surface, the coating composition is then applied thereto.

In applications where even greater coating-to-film adherence is desired, i.e., greater than that resulting from treatment of the film surface by any of the aforediscussed methods, an intermediate primer coating can be employed to increase the adherence of the coating composition to the film. In this case, the film is advantageously first treated by one of the foregoing methods to provide increased active adhesive sites thereon (thereby promoting primer adhesion) and to the thus treated film surface there is subsequently applied a continuous coating of a primer material. Such primer materials are well known in the prior art and include, for example, epoxy and poly(ethylene imine) (PEI) materials. U.S. Patent Nos. 3,753,769 to Steiner, 4,0858,645 and 4,439,493 disclose the use and application of such primers. The primer provides an overall adhesively active surface for thorough and secure bonding with the subsequently applied coating composition and can be applied to the base film by conventional solution coating means, for example, by mating roller application.

The coating composition can be applied to the high density polyethylene film as a solution, e.g., one prepared with an organic solvent such as an alcohol and ketone, ester. However, since the coating composition can contain insoluble, finely divided inorganic materials which are difficult to keep well dispersed in organic solvents, it is preferable that the coating composition be applied to the treated surface in any convenient and known manner, such as by gravure coating, roll coating, dipping, spraying, etc. The excess aqueous solution can be removed by squeeze rolls and doctor knives.

The polyethylene film can be stretched in the machine direction, coated with the coating composition and then stretched perpendicularly in the transverse direction. In yet another embodiment, the coating can be carried out after biaxial orientation is completed.

The coating composition should be applied in such amount that there will be deposited upon drying a smooth, evenly distributed layer, generally on the order of from 0.01 to 0.2 mil thickness (equivalent to about 0.2 to 3.5 g per 1000 sq. in. of film). In general, the thickness of the applied coating is such that it is sufficient to impart the desired seal peelability, oxygen and water vapor barrier characteristics to the resulting film. Generally, the coating comprises 1 to 25 (for example, 20 wt%) wt%, preferably 7 to 15 wt% of the entire coated film composition. The coating on the film is subsequently dried by hot air, radiant heat or by any other convenient means.

The total thickness of the polymer film of this invention is not critical and will be selected to meet particular service requirements. So, for example, when used in packaging, the total thickness of the oriented high density polyethylene as coated can be on the order of from about 0.3 to about 3 mils, with the polyethylene film representing about 95% of the total and the coating comprising the balance.

The following Examples illustrate the invention.

EXAMPLE 1

High density polyethylene film (M6211) having a melt index of 1 and a density of 0.96, and a thickness of 1.15 mil was obtained from Oxychem of Houston, TX. The film was oriented 1.2 times MD and 9 times TD. The crimp seal strength, water vapor transmission resistance, oxygen and flavor/aroma barrier were measured and are set out below in the Table.

EXAMPLE 2

The high density polyethylene film of Example 1 was coated after orientation with an ultra high barrier PVdC (Daran*8500 available from Hampshire Chemical of Lexington, MA). Coating was carried out by first corona treating, then priming with epoxy primer at approximately 0.15g/mil. 100 parts (by weight) top coat (PVdC) was formulated with 3 parts M-21520* wax (Michelman carnauba wax) and 0.25 parts talc. Coating was carried out using a reverse direct gravure coater and was applied at about 2.8 g/mil. Both primer and top coat were dried by forced air, gas fired ovens. The crimp seal strength, water vapor transmission resistance, and oxygen barrier were measured and are set out below in the Table.

The resulting PVdC-coated product exhibited reduced WVTR and had extremely low oxygen transmission properties.

EXAMPLE 3

The high density polyethylene film of Example 1 was coated after orientation with acrylic coating available from Valspar Corp. of Pittsburgh, PA. Coating was carried out by first corona treating, then priming with poly(ethylene imine) (PEI) primer. Acrylic top coat (PVdC) was formulated with 100 parts acrylic, 5 parts carnauba wax, 0.25 parts talc, 40 parts

* Trade-mark

colloidal silica, and 4 parts Resinall* 807, a rosin ester obtained from Resinall Corp., Stamford, CT.

Coating was carried out using a reverse direct gravure coater and was applied at about 0.7 g/mil. Both primer and top coat were dried by forced air, gas fired ovens. The crimp seal strength, water vapor transmission resistance, and oxygen barrier were measured and are set out below in the Table.

The resulting acrylic-coated product exhibited a relatively high crimp seal strength and flavor/aroma barrier.

EXAMPLE 4

The high density polyethylene film of Example 1 was coated after orientation with ethylene acrylic acid coating (Michemprime 4983) available from Michelman, Inc. of Cincinnati, OH. Coating was applied in line between machine direction orientation and transverse direction orientation.

The aqueous coating, ethylene acrylic acid, was placed in a reverse direct gravure coater which had been installed between the MD orienter and the TD orienter of a semi-works scale orienter. High density core resin (OXYCHEM*M 6211) was extruded through a three layer sheet die at 480°F, cast onto a cooling drum and quenched at 110°F. The core layer had co-extruded with it two skins, one on each side. The A layer consisted of 0.7 mil HDPE (OXYCHEM*M6211), the C layer consisted of 0.7 mil thick terpolymer (Chisso* 7820, available from Chisso of Japan. The total cast structure A/B/C was 12 mil thick. The cast co-extrusion was reheated to 220°F in the machine direction orienter (MDO) and stretched 1.2 times in the machine direction, then corona treated on the A layer for improved surface wettability. The resulting 10 mil film web was then passed through the gravure coater and coated with the aqueous coating. The coated web was dried in the pre-heat zones of the transverse direction orienter (TDO) at 300°F, then stretched eightfold in the transverse direction at 250°F and annealed at 235°F. The resulting biaxially stretched film was 1.15 mil thick and the coated film had properties reported in the Table below. Notably, the coated to coated seal strength was peelable and

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* Trade-mark

measured 400 g/in when crimped at 240°F.

The resulting coated product exhibited a relatively high crimp seal strength which is suitable for a peelable seal while maintaining water vapor transmission resistance and oxygen barrier properties similar to uncoated oriented high density polyethylene.

EXAMPLE 5

The high density polyethylene film of Example 1 was coated with high barrier polyvinylidene chloride coating. The coating was applied in line between machine direction orientation and transverse direction orientation.

An aqueous coating, polyvinylidene chloride emulsion (DARAN 8540 TM obtained from W.R. Grace, Lexington, MA) was placed in a reverse direct gravure coater which had been installed between the MD orienter and the TD orienter of a semi-works scale orienter. High density core resin (OXYCHEM* M 6211) was extruded through a three layer sheet die at 480°F, cast onto a cooling drum and quenched at 110°F. The core layer had co-extruded with it two skins, one on each side. The A layer consisted of 0.7 mil HDPE (Oxychem* M-6211), the C layer consisted of 0.7 mil thick polypropylene terpolymer (Chisso* 7510). The total cast structure, A/B/C was 12 mil thick. The cast coextrusion was reheated to 220°F in the machine direction orienter (MDO) and stretched 1.2 times in the machine direction, then corona treated on the A layer for improved surface wettability. The resulting 10 mil thick film web was then passed through the gravure coater and coated on the A layer with the aqueous coating. The coated web was dried in the preheat zones of the transverse direction orienter (TDO) at 300°F, then stretched eight times in the TD at 250°F and annealed at 235°F. The biaxially stretched film measured 1.15 mil. The resultant coated film had properties reported below in the Table, notably improved resistance to oxygen transmission (TO_2) reduced from .129 to 6 cc/100in^2/day) and improved resistance to water vapor transmission (WVTR reduced from 0.22 to 0.19 g/100in^2/day). Improved flavor and aroma barrier is results from the improved

* Trade-mark

TO_2, PVdC being a good flavor and aroma barrier. Coated to coated film seals at 240°F of 160 g/in represent a capability to provide peelable or "easy to open" seals.

TABLE

EXAMPLE #	1	2	3	4	5
WVTR, g/100in2/24hr 100°F, 90%RH (ASTM F 1249-89)	.18-.24	.13	0.20	0.20	0.16- 0.22
TO2 cc/100in2/24hr strength, g/in (ASTM D 3985-81)	>129	0.7	>129	>129	6
Crimp seal strength g/in, 20psi, 3/4 sec. at 240°F	1170	305	830	400	160
Flavor/Aroma barrier	poor	excel.	good	___	good

CLAIMS:

1. A coated film composition comprising:

a) a biaxially oriented high density polyethylene (HDPE) film comprising at least 50 wt. % of HDPE having a density of 0.960 or greater; and

b) a coating which is derived from a homo- or co-polymer of vinylidene chloride; a homo- or co-polymer of acrylic acid; or from polyvinyl alcohol polymer (PVOH).

2. A composition according to claim 1 wherein the acrylic acid copolymer comprises a copolymer of ethylene and acrylic acid.

3. A composition according to claim 1 or 2 wherein the coating is derived from polyvinylidene chloride polymer.

4. A composition according to claim 1 or 2 wherein the coating comprises 1 to 25 wt% of the composition.

5. A method of preparing a coated film which comprises coating a biaxially oriented high density polyethylene (HDPE) film comprising at least 50 wt. % of HDPE having a density of 0.960 or greater with a coating which is derived from a homo- or co-polymer of vinylidene chloride; a homo- or co-polymer of acrylic acid or from polyvinyl alcohol polymer (PVOH).

6. A method of preparing a coated film which comprises
a) coating a machine direction uniaxially oriented high density polyethylene (HDPE) film comprising at least 50 wt. % of HDPE having a density of 0.960 or greater with a coating which is derived from a homo- or co-polymer of vinylidene chloride; a homo- or co-polymer of vinylidene chloride a homo- or co-polymer of acrylic acid; or from polyvinyl alcohol polymer (PVOH); and
b) orienting the resulting coated film in the transverse direction.

7. A method according to claim 5 or 6 wherein the acrylic acid copolymer comprises a copolymer of ethylene and acrylic acid.

8 A method according to claim 5 or 6 wherein the coating is derived from polyvinylidene chloride polymer.

9. A method according to claim 5 or 6 wherein the coating comprises 1 to 25 wt. % of the coated film composition.