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PVOH-BASED COATING COMPOSITION

The present invention relates to a coating composition which is based on poly(vinyl alcohol) ("PVOH") and which provides enhanced oxygen and flavor/odor barrier characteristics to a hydrophobic polymeric substrate, such as a packaging film.

Attempts have been made in the past to produce waterborne adhesive coating compositions including PVOH for use on hydrophobic polymeric substrates. For example, one PVOH containing coating is obtained by reacting PVOH with isocyanate or blocked isocyanate to form a coating which is adherent to polyolefins, but also contains residual, unreacted toxic isocyanates. As a result, such coating cannot be used in food packaging applications.

Certain polymeric films employed for the packaging of foods inherently permit the transmission of oxygen from the atmosphere to the inside of the packaged food. Oxygen causes the spoilage of packaged food by oxidation.

PVOH coatings, have been applied to various substrates in the past, and are known to provide a barrier to the transmission of oxygen. In certain applications, such as condiments packaging, PVOH has been used to prevent the flavor of condiments from passing through the packaging. In other applications, PVOH containing polymeric films have been used to protect the packaged food contents against acquisition of odors or even other flavors from the outside the packaging.

Polyvinyl alcohols are polymers containing $(-CH_2-CHOH-)$ groups. They can be applied from water solution and are in many respects attractive materials for use as oxygen and flavor/odor barrier coatings for thermoplastic polymer substrates. However, PVOH is soluble in water and, as a result, susceptible to attack by moisture. The poor water resistance of PVOH restricts its use as a barrier coating to those few applications in which nearly anhydrous conditions prevail. Moisture may act to cause staining or wear due to friction, an unpleasant feel

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to the touch and a dull appearance. It is also known that oxygen and flavor/odor permeability of PVOH coatings increases in proportion to its moisture content.

5 A number of methods have been known for increasing the water resistance of PVOH, but none provides entirely satisfactory results. In spite of various heretofore practiced methods, PVOH still tends to soften, swell and lose adhering strength when exposed to water or even moisture vapor. When applied to hydrophobic surfaces, such
10 as polyolefins, coatings including PVOH do not adhere well and are not moisture resistant. As a result, the polymeric substrate surface must be coated with a primer coating first and then covered with the PVOH containing coating. Thus, there is not presently available a single coating
15 composition which acts as both a primer and a barrier. The coatings known to date which are used to increase or enforce barrier characteristics generally require a primer to improve adhesion or binding between the barrier coating and the film.

20 It has now been found that by drying a solution of PVOH and urea at temperatures which allow PVOH to react with urea, primer coating compositions for hydrophobic polymer substrates can be obtained which have heretofore unknown oxygen barrier characteristics. During the drying
25 of the PVOH/urea solution, the PVOH and urea become crosslinked, and urethane linkages are formed at least with the polymeric substrate. The resulting coating compositions are no longer water soluble, adhere tenaciously to hydrophobic polymeric surfaces, preferably
30 polyolefins and have excellent oxygen and flavor/odor barrier characteristics.

Accordingly, the present invention resides in one aspect in a hydrophobic polymer substrate comprising a moisture resistant coating having oxygen and flavor/odor
35 barrier characteristics, said coating comprising polyvinyl



alcohol crosslinked with urea such that urethane linkages are formed between the substrate and the coating.

In a further aspect, the invention resides in a method of forming a moisture resistant coating having oxygen and
5 flavor/odor barrier characteristics on a hydrophobic polymer substrate comprising the steps of:

- (i) providing a coating composition comprising a solution of polyvinyl alcohol and urea on a surface of said substrate;
- 10 (ii) drying said solution at a temperature sufficient to allow polyvinyl alcohol to cross-link with urea thereby forming said moisture resistant coating on said substrate.

The coating compositions of the present invention when
15 applied to a suitable substrate, such as oriented polypropylene, provide a combination of primer characteristics and improved barrier characteristics which have been hitherto unavailable in a single coating component. Consequently the adhesion, gloss and/or
20 durability of subsequently applied top coatings such as, for example, heat sealable acrylic is improved.

The coating compositions of the present invention are used mainly as primers. The term "primer" as used in the present invention means a coating applied to a substrate to
25 improve the adhesion, gloss and/or durability of a subsequently applied coating.

The coating compositions of the present invention are prepared by dissolving PVOH and urea in an ionic solvent, preferably water. The solution thus obtained is applied
30 onto a suitable substrate and then the coating is dried to drive off the solvent at temperatures sufficient to allow PVOH to react with urea thereby forming urethane linkages with the substrate. A useful temperature range is 90 to 150°C (200 to 300°F). The range of 120 to 135°C (250 to
35 275°F) is preferred.



The term "urethane linkages" as used herein refers to any functionality that has one nitrogen, carbon, hydrogen and two oxygens formed during crosslinking, wherein the elements are most likely linked through covalent bonding.

5 In the present invention crosslinking occurs while the PVOH/urea solution is dried, urethane linkages are formed not only between PVOH and urea, but also with molecules of the substrate and/or the top coating. As a result, the primer of the present invention is no longer moisture
10 sensitive and is also tacky.

"Polyvinyl alcohol" as used herein means a normally solid polymeric material, soluble in water, but insoluble in most organic solvents and characterized by the presence of $(-CH_2-CHOH-)$ units in the polymer chain. These polymers
15 are ordinarily prepared by the replacement of the acetate groups of polyvinyl acetate with hydroxyl groups as by hydrolysis or alcoholysis. The percent of acetate groups replaced by hydroxyl groups is the degree of hydrolysis of the PVOH thus formed and indicates the percent of hydroxyl
20 groups present in PVOH out of the total possible hydroxyl groups. The crosslinking reaction by which the superior barrier coatings of this invention are obtained proceeds through the hydroxyl groups of PVOH. Therefore, the PVOH useful in the present invention should have a degree of
25 hydrolysis from 80% to 99.6% hydrolyzed. A PVOH blend of 40% to 80% by weight PVOH which is 99.6% hydrolyzed and 20% to 60% by weight PVOH which is 86% hydrolyzed, respectively, is particularly preferred because such blend provides superior resistance, clarity, flexibility and
30 adhering strength. Most preferred is a PVOH blend of 99.6% hydrolyzed and 86% hydrolyzed in a ratio of 60:40, respectively.

The PVOH employed herein can be any commercially available material. For example, ELVANOL 71-30 or ELVANOL
35 90-30 are E.I. duPont products.

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The amount of urea useful in the present invention is from 1 to 20 dry wt. %, with 5 to 15 dry wt. % being preferred and about 7 dry wt. % being most preferred.

The polymeric materials contemplated as the substrate of the multilayer structure of the present invention include any oriented or unoriented polymeric film which inherently permits the transmission of oxygen and flavor/odors and wherein the utility of such film would call for decreasing the transmission of oxygen and flavor/odors. In most cases, the source of the oxygen referred to herein is atmospheric oxygen. A particularly preferred class of films are the polyolefins. Within the polyolefin class, homopolymers and copolymers of propylene, low density polyethylene ("LDPE"), linear low density polyethylene ("LLDPE") and high density polyethylene ("HDPE") are preferred. Particularly preferred are isotactic polypropylenes containing at least 80% by weight of isotactic polypropylene.

The preferred substrate layer can also be coextruded with a thin skin layer, amounting to from 2 to 12% of the total thickness of the substrate. The skin may be made of a propylene homopolymer, a copolymer of propylene with another olefin, e.g., ethylene or butene-1, and a terpolymer of polyethylene-polybutene-polypropylene. The other olefin which can be present in the copolymer is in an amount of from 1 to 15 wt %.

The polymeric substrate can be of any desired thickness, although thicknesses will typically range from 0.5 to 2 mils to ensure good machinability on high-speed packaging equipment. The oriented polypropylene ("OPP") film should preferably have a thickness of 1.0 mil.

It has been found advantageous to treat the substrate or base layer prior to receiving the oxygen and moisture barrier layers. Such treatment enhances the adhesion of other coatings, including that of a primer.



A preferred treatment involves treating the surface to a surface tension level of at least 35 and preferably from 38 to 45 dynes/cm in accordance with ASTM Standard D2578-84. The treatment can be flame treatment, plasma treatment, chemical treatment or corona discharge treatment. Flame treatment and corona discharge treatment are preferred with corona discharge treatment being particularly preferred. These treatments are believed to increase the oxygen species at the surface of the polyolefin substrate available for the formation of urethane linkages.

After this treatment, the coating compositions of the present invention may be applied in-line after the polymeric substrate has been stretched in the machine direction (MD) but prior to orientation in the transverse direction (TD). Thereafter, the coating composition is dried by passing the film through tenter ovens.

The coating compositions of the present invention may also be applied to the polymeric substrate by using an off-line process. Off-line application includes coating in any convenient and known manner, such as dipping, spraying, brushing, roll coating, gravure coating, and the like.

It has been found that the coating compositions of the present invention are heat sealable when applied to a hydrophobic polymeric substrate in excess of 190 grams/inch. A film structure with enhanced heat seal characteristics may be used for the inside surface of packaging films.

Other materials may be added directly to the aqueous solution of PVOH and urea in order to realize special advantages in addition to excellent oxygen barrier characteristics. To improve the hot slip characteristics of the coating, additional crosslinkers can be added directly to the aqueous solution of urea and PVOH. For example, melamine formaldehyde, urea formaldehyde resin, methylated melamine formaldehyde may be added to the



coating composition of the invention in the presence of sulfuric acid as the crosslinker catalyst. By adding additional crosslinkers the moisture sensitivity of FVOH is further reduced.

5 Ethylene acrylic acid copolymer ("EAA") may be added in an amount from 1 to 20 wt.%, preferably 5 or 15 wt.%, of the coating composition to improve the coefficient of friction of the coating. The resulting film has excellent slip characteristics and it can be wound up efficiently on
10 packaging machinery.

 The addition of EAA in excess of 20 wt. % results in a reduction of the heat sealable characteristics of the film. To render the film structure of the present invention heat sealable a coating of acrylic acid, commonly
15 called acrylic, amorphous PVdC, or EAA/acrylic blends, extrusion applied terpolymers, cast polypropylene or cast polyethylene may be applied over the adhesive coating composition of the present invention.

 In another embodiment of the present invention, the
20 polymeric substrate includes a skin on both surfaces. In yet another embodiment the coating composition of the present invention is applied onto both surfaces of the substrate. A layer of acrylic may also be applied on both surfaces of the primer coated polymeric substrate.

25 The invention will now be more particularly described with reference to the Examples.

EXAMPLE 1

 A homopolymer polypropylene core layer was coextruded with skin layers of an ethylene-propylene random copolymer.
30 The random copolymer contained approximately 3-5% by weight of ethylene. The extruded film was biaxially oriented to 4-5 times machine direction and 7-10 times transverse direction to yield a film having a thickness of approximately 1 mil. The thickness of the skin layers was
15 approximately 12% of the film. The skin layers were



approximately of equal thickness. This film combination was corona discharge treated in accordance with commonly employed prior art techniques to produce a surface with a wetting tension of about 42 dynes/cm. The treated film was coated on both sides with a primer composition composed of a 0.1% aqueous solution of PVOH and urea. The solution contained 91 wt. % of a blend of 99.6% hydrolyzed PVOH and 86% hydrolyzed PVOH in a ratio of 60:40, respectively, and 7 wt. % urea. The resulting coated film was then dried at temperatures between 90°C and 150°C.

The dried film were then tested in an oxygen-permeability device in which a stream of dry oxygen is passed through an aqueous salt solution-permeated pad to control the gas moisture content and then through the films, disposed at right angles to the stream with the crosslinked PVOH coating upstream. The oxygen transmitted was determined and the amount of oxygen passed per unit area of film per time period was calculated.

Similar tests were conducted on a similar film with an acrylic top coat provided on the PVOH/urea primer and on a film with a polyethyleneimine (PEI) primer and an acrylic top coat. The results are given in Table 1, which shows that the film with the PEI primer and acrylic top coat showed a high oxygen transmission rate due to poor oxygen barrier properties. The oxygen transmission rate was significantly decreased by the use of a coating of PVOH crosslinked with urea.



TABLE 1

	FILM STRUCTURE	FILM ¹ THICKNESS	COATING COMPOSITION	THICKNESS OF ¹ BARRIER LAYER	TO ₂ ²	TO ₂ ³	HEAT SEAL ⁴
5	Coated	1.00	Primer: PEI Top Coat: Acrylic	0.04	150	150	600
	Coated Substrate	1.00	Primer: PVOH/urea Top Coat: None	0.04	0.86	2.1	300
10	Coated Substrate	1.00	Primer: PVOH/urea Top Coat: Acrylic	0.08	0.86	2.1	450

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1. The thickness is measured in mil.
 2. Average oxygen transmission rate measured in cc/100 in²/24 hr. at 75°F, 0% RH.
 - 15 3. Average oxygen transmission rate measured in cc/100 in²/24 hr. at 75°F, 75% RH.
 4. Heat seal is measured in grams/in.

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CLAIMS

1. A hydrophobic polymer substrate comprising a moisture resistant coating having oxygen and flavor/odor barrier characteristics, said coating comprising polyvinyl alcohol crosslinked with urea such that urethane linkages are formed between the substrate and the coating.
2. A polymer substrate as claimed in Claim 1, wherein the substrate is a polyolefin film.
3. A polymer substrate as claimed in Claim 2, wherein said polyolefin is selected from polypropylene, low density polyethylene, linear low density polyethylene, and high density polyethylene.
4. A polymer substrate as claimed in Claim 2 or Claim 3, wherein said film includes a coextruded skin on at least one side thereof.
5. A polymer substrate as claimed in Claim 4, wherein said coextruded skin is selected from a $C_2 - C_4$ homopolymer, propylene-ethylene copolymer, and polyethylene-polybutene-polypropylene terpolymer.
6. A method of forming a moisture resistant coating having oxygen and flavor/odor barrier characteristics on a hydrophobic polymer substrate comprising the steps of:
 - (i) providing a coating composition comprising a solution of polyvinyl alcohol and urea on a surface of said substrate;
 - (ii) drying said solution at a temperature sufficient to allow polyvinyl alcohol to cross-link with urea thereby forming said moisture resistant coating on said substrate.

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7. A method as claimed in Claim 6, wherein said solution is aqueous.
8. A method as claimed in Claim 6 or Claim 7, wherein said substrate is a polyolefin film
- 5 9. A method as claimed in Claim 8, wherein said surface of the substrate is subjected to flame or corona treatment prior to step (i).
- 10 10. A method as claimed in any one of Claims 6 to 9, wherein said solution further comprises ethylene acrylic acid copolymer.

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