

BARRIER FILM

TECHNICAL FIELD

- 5 The present invention relates to a multi-layer oxygen barrier film with good oxygen barrier properties that are maintained in the presence of moisture. The multi-layer oxygen barrier film is suitable for use as a packaging film even in high humidity environments.

10 BACKGROUND

- Films can be used to provide barrier properties against a variety of compounds. For example, US2019322429 discloses a mineral oil barrier film. However, a commonly required barrier film is an oxygen barrier film that can be used to reduce the oxygen
15 transmission rate through the film.

- Many materials are known to provide oxygen barrier properties to polymeric packaging films. For example, polyvinyl alcohol (PVOH) is widely used as an oxygen barrier layer in packaging films. However, PVOH layers suffer from a loss
20 in oxygen barrier performance in the presence of moisture, as PVOH is soluble in water and therefore susceptible to degradation when exposed to moisture. This means packaging films containing PVOH layers may be unsuitable for use in packaging environments that involve high humidity levels.

Various methods to circumvent the problem of PVOH moisture sensitivity are known in the prior art. One such method involves crosslinking the PVOH to reduce its sensitivity to moisture. To achieve this, a crosslinking agent is typically added to
5 the PVOH layer.

US6444750 describes a polymeric film structure having an enhanced oxygen barrier produced by the process comprising: coating at least one side of a polymeric substrate adapted for receipt of an oxygen barrier with a solution of polyvinyl
10 alcohol, formaldehyde-containing crosslinking agent and crosslinking-promoting acid catalyst, said solution having a pH of about 3.5 or less, and wherein said acid catalyst is selected from the group consisting of phosphoric acid, nitric acid and hydrochloric acid.

15 However, crosslinkers can cause packaging films to have a reduced shelf-life. In addition, some crosslinkers have health hazards associated therewith making them unsuitable for use in certain packaging applications, for example food packaging.

20 It is also known to include a component in the PVOH layer that reacts with the PVOH to make it more stable in the presence of moisture.

For example, EP1211295 describes a gas barrier coating composition comprising (a) polyvinyl alcohol resin and (b) at least one member selected from the group consisting of a metal alcoholate, a hydrolysate of the metal alcoholate, a condensate of the metal alcoholate, a chelate compound of the metal alcoholate, 5 a hydrolysate of the chelate compound and a metal acylate.

Another known method for addressing the issue of moisture sensitivity of PVOH layers is to include the PVOH layer as part of a laminate structure, for example the PVOH layer may be coated on a film substrate. However, PVOH and similar 10 compounds tend to exhibit poor adhesion to film substrates e.g., polyolefins.

To improve adhesion of a PVOH layer to a film substrate, it is commonplace to include an adhesion promoter in the PVOH layer.

15 For example, EP3842229 describes a water-resistant gas barrier film in which at least a gas barrier layer is disposed on a substrate film, wherein the gas barrier layer is formed from a coating liquid containing (a) at least one of carboxy group-modified polyvinyl alcohol and partially saponified polyvinyl alcohol, (b) completely saponified polyvinyl alcohol, and (c) polyethyleneimine. The polyethyleneimine acts 20 as an adhesion promoter to bond the coating film and the substrate.

EP3405536 describes a primer coating comprising: an aqueous mixture comprising amorphous polyvinyl alcohol, an adhesion promoter comprising one or more of polyethyleneimine and polyurethane, a crosslinker, and optionally a catalyst.

- 5 Films with PVOH layers including adhesion promoters are also described in EP0960159, JP2001/121658, EP2762539, EP2245092, EP2914670 and WO22/124171.

- However, as with crosslinkers, some adhesion promoters have health hazards
10 associated therewith making them unsuitable for use in certain packaging applications, for example food packaging.

- Primer layers are also referenced in the art as a way to improve adhesion between PVOH layers and film substrates. Primer layers prepare polymeric surfaces for the
15 addition of further layers. Typically, primer layers are used to level a polymeric surface and prepare it for receiving a functional coating.

- WO2022/084397 describes a multilayer system comprising at least the following layers: (a) a packing foil, (b) on the packing foil a primer layer containing at least
20 5% by weight of at least one polymer containing carboxylic groups, wherein the at least one polymer has a carboxyl number of 50 to 200, and (c) on the primer layer a barrier layer containing at least one polyvinyl alcohol and/or at least one copolymer containing polyvinyl alcohol.

EP0461772 describes a film combination which comprises a polymeric substrate susceptible of transmitting oxygen, at least one side thereof having been treated to a surface free energy of at least about 35 dynes/cm, that side having a primer
5 coating thereon; and, on the primer coating, an oxygen transmission inhibiting layer comprising a cross-linked polyvinyl alcohol.

Polyurethane primer layers are frequently referenced in the art in combination with PVOH layers.

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For example, US4927689 describes a composite structure comprising a base synthetic thermoplastic polymeric layer having two coatings on one side of the base layer, the first coating being adjacent the base layer and being a solvent-based urethane primer, which when dry allows an aqueous dispersion or solution
15 of polyvinyl alcohol to "wet out" the primer, in an amount in the range of from 0.3 to 3.0 g/m² of the base layer, and the second coating being placed on the exposed surface of the first coating and comprising a polyvinyl alcohol gas barrier material in an amount in the range up to about 2.0 g/m² of said base layer, said second coating having been formed from a dispersion or solution.

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US6106950 describes a method of providing an improved oxygen and moisture resistance onto at least one surface of a substrate comprising: (a) coating at least one surface of a substrate with a primer layer composition; said primer composition

- comprising: (i) at least one aqueous polyurethane dispersion (A); and (ii) at least one crosslinking agent (B) selected from the group consisting of polyfunctional isocyanate and polyfunctional aziridine; (b) drying the primer coated substrate; (c) coating at least one surface of the primer layer with a barrier layer composition;
- 5 said barrier layer composition comprising: (i) at least one aqueous polyvinyl alcohol or its copolymers (C); and (ii) at least one crosslinking agent (D) selected from the group consisting of polyethyleneimine, melamine, melamine derivatives and mixtures thereof; and (d) drying the coated substrate.
- 10 EP3553115 describes a multilayer oxygen barrier film with improved hot water resistance, comprising: a substrate film layer formed from polyethylene terephthalate, nylon, polypropylene, or polyethylene; an oxygen barrier layer; and an adhesive layer formed between the substrate film layer and the oxygen barrier layer. The oxygen barrier layer includes polyvinyl alcohol in combination with a
- 15 silane and the adhesive layer is a polyurethane primer layer.

However, in some instances, primer layers and adhesion promoters appear to have a detrimental effect on oxygen barrier performance of the overall film. For example, a reduction in oxygen barrier performance is observed when polyurethane primer

20 layers are employed.

WO9946120 describes a composite film structure that is intended to have a very low oxygen transmission rate. This is achieved using two inorganic layers,

preferably formed from a metal, and a polymeric barrier, which may be PVOH. These barrier layers are applied to polyester films, which are known to have a much higher oxygen barrier than polyolefin films, thereby further contributing to the oxygen barrier properties of this film.

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Thus, there remains a need in the art for a multi-layer oxygen barrier film based on a polyolefin film that has good oxygen barrier properties that are maintained in the presence of moisture, and which addresses the problems associated with prior art barrier films.

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SUMMARY OF INVENTION

According to one aspect of the invention there is provided a multi-layer oxygen barrier film, comprising: a base film layer comprising a polyolefin; an oxygen barrier
15 layer comprising a vinyl alcohol-based polymer; and a primer layer comprising polyethyleneimine, wherein the primer layer has a coat weight of at least about 0.005 g/m².

The inventors of the present invention have surprisingly found that the use of a
20 primer layer having a coat weight of at least about 0.005 g/m² and comprising polyethyleneimine in combination with an oxygen barrier layer comprising a vinyl alcohol-based polymer e.g., PVOH, significantly improves the oxygen barrier performance of the overall film, even at higher relative humidities such as up to

50% RH. The inventors of the present invention have observed a synergistic oxygen barrier effect between the primer layer and the oxygen barrier layer and, without wishing to be bound by any such theory, believe this may be due to a degree of crosslinking occurring between the vinyl alcohol-based polymer e.g.,
5 PVOH, and the polyethyleneimine. The presence of the primer layer also provides a smoother surface on which the oxygen barrier layer may be applied, which is believed to improve the oxygen barrier performance of the layer.

This finding is surprising as primer layers are conventionally used to aid adhesion
10 between layers in a film. It has not previously been recognised in the art that a primer layer could impart or enhance a particular property of a film e.g., oxygen barrier performance. The finding is particularly unexpected as many of the primer layers in the art that have been used in combination with oxygen barrier layers e.g., PVOH layers, have either made no difference to the oxygen barrier properties of
15 the film, or have had a detrimental effect on them, particularly in the case of polyurethane primer layers.

This finding of improved oxygen barrier performance is further unexpected as the base film layer comprises a polyolefin. Polyolefin polymers are known to have
20 inherently high oxygen transmission rates (OTR), for example oriented polypropylene (OPP) has an OTR of approximately 1500-2500 cc/m²/24 hr, cast polypropylene (PP) has an OTR of approximately 2300-3100 cc/m²/24 hr and high density polyethylene (HDPE) has an OTR of approximately 2300-3100 cc/m²/24 hr

at 73°F (23°C) 0% RH. Thus, polyolefin films have low oxygen barrier capabilities compared to other polymeric films that have an inherently low OTR such as polyester films, with OPET having an OTR of approximately 31–93 cc/m²/24 hr at 73°F (23°C) 0% RH. The inventors of the present invention have surprisingly
5 observed a significant increase in the oxygen barrier capabilities of a multi-layer oxygen barrier film comprising a polyolefin base film when using the combination of a vinyl alcohol-based polymer and a primer layer comprising polyethyleneimine in accordance with the present invention. Thus, this synergistic combination of layers is surprisingly able to reduce the oxygen transmission rate through a
10 polyolefin film to an acceptable level, despite the higher oxygen transmission rate of the polyolefinic film itself.

Thus, according to another aspect of the present invention there is provided the use of a primer layer comprising polyethyleneimine to decrease the oxygen
15 transmission rate of a multi-layer oxygen barrier film.

Advantageously, the improvement in oxygen barrier performance of the film can be realised without the need for a crosslinker in the vinyl alcohol-based polymer layer e.g., PVOH layer. Due to the presence of the primer layer, it is also not
20 necessary to use an adhesion promoter to secure the oxygen barrier layer to the base film layer. As previously outlined, some crosslinkers and adhesion promoters have health hazards associated with them, so it is beneficial to have a multi-layer oxygen barrier film which can be formulated in their absence.

In addition, the improvement in oxygen barrier performance of the film, even at higher relative humidities such as up to 50% RH, provides the advantage of the multi-layer oxygen barrier film of the invention being suitable for use in a wide
5 variety of packaging applications including those where the packaging is exposed to moisture e.g., in food packaging.

Thus, according to another aspect of the invention there is provided use of the multi-layer oxygen barrier film as a packaging film.

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According to another aspect of the invention there is provided a package formed, at least in part, from the multi-layer oxygen barrier film. The package may be a sealed package and may comprise a seal between two regions of the film.

15 According to another aspect of the invention there is provided an article wrapped or packaged in a material comprising the multi-layer oxygen barrier film.

According to a further aspect of the invention there is provided a method for manufacturing a multi-layer oxygen barrier film, comprising: applying a primer
20 layer comprising polyethyleneimine onto at least one side of a base film layer comprising a polyolefin at a coat weight of at least about 0.005 g/m²; and coating the primer layer with an oxygen barrier layer comprising a vinyl alcohol-based polymer.

In the description that follows, it will be understood that all features relating to one aspect of the invention may also apply, where appropriate, to all other aspects of the invention and *vice versa*.

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DETAILED DESCRIPTION

The multi-layer oxygen barrier film of the present invention comprises a base film layer, an oxygen barrier layer and a primer layer.

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The oxygen barrier layer comprises a vinyl alcohol-based polymer.

The vinyl alcohol-based polymer may comprise polyvinyl alcohol (PVOH) and/or ethylene vinyl alcohol (EVOH). Preferably, the vinyl alcohol-based polymer

15 comprises polyvinyl alcohol.

The oxygen barrier layer may comprise at least 70% vinyl alcohol-based polymer by weight, preferably at least 80% vinyl alcohol-based polymer by weight, at least 90% vinyl alcohol-based polymer by weight, at least 95% vinyl alcohol-based

20 polymer by weight, or at least 98% vinyl alcohol-based polymer by weight.

The coat weight of the oxygen barrier layer may be selected with reference to the desired barrier properties of the film and will generally be in the range of from about 0.1 g/m² to about 10 g/m².

- 5 The oxygen barrier layer may have a coat weight of from about 0.2 g/m² to about 5 g/m², or from about 0.5 g/m² to about 2 g/m².

The term "coat weight" in this context and throughout the description refers to the dry coat weight unless otherwise specified.

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- The multi-layer oxygen barrier film may comprise a single oxygen barrier layer comprising a vinyl alcohol-based polymer. It has been found that a single oxygen barrier layer significantly improves the oxygen barrier properties of the multi-layer film without the need of any additional oxygen barrier layers. Therefore, the multi-layer oxygen barrier film of the invention provides a simpler overall multi-layer structure compared to multi-layer films in the art which require multiple oxygen barrier layers, whilst still maintaining effective oxygen barrier performance. The multi-layer oxygen barrier film may comprise a single oxygen barrier layer comprising a vinyl alcohol-based polymer on one side thereof. The multi-layer oxygen barrier film may comprise a single oxygen barrier layer on one side thereof. The multi-layer oxygen barrier film may comprise a single oxygen barrier layer.
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In some embodiments, the multi-layer oxygen barrier film may not comprise a second water-based coating layer (i.e., the oxygen barrier layer comprising a vinyl alcohol-based polymer is the first and only water-based coating layer present). The multi-layer oxygen barrier film may not comprise a second water-based coating layer on the side of the polyolefinic film that has the oxygen barrier layer. The multi-layer oxygen barrier film may not comprise a second water-based coating layer directly on the oxygen barrier layer. Coating a second water-based coating layer on the oxygen barrier layer can be difficult and the water in the second coating would be expected to destroy the crystal structure of the oxygen barrier layer. It has also been found to be unnecessary due to the improved barrier properties seen with the combination of the oxygen barrier layer and the PEI primer.

In some embodiments, the multi-layer oxygen barrier film may comprise an additional solvent-based coating layer.

The oxygen barrier layer may be absent of any crosslinker and/or adhesion promoter. In some instances, the oxygen barrier layer may be absent of any crosslinker and absent of any adhesion promoter. The oxygen barrier layer may also be absent a crosslinking-promoting acid catalyst. Crosslinkers or adhesion promoters may comprise any suitable compound known in the art, for example polyamideamine-epichlorohydrin (PAE) or polyethyleneimine (PEI).

The term "absent of" in this context preferably means that the amount of component (i.e., crosslinker or adhesion promoter) in the oxygen barrier layer is less than about 1% by weight of the layer, less than about 0.5% by weight of the layer, less than about 0.1% by weight of the layer, substantially 0% by weight of the layer, or completely absent i.e., 0% by weight of the layer. For the avoidance of doubt, these values relate to the dry content of the layer. It is thought that the adhesion promoter may disrupt the crystal structure of the barrier layer, thereby reducing the barrier properties of the layer.

- 10 Alternatively, the oxygen barrier layer may comprise a crosslinker and/or adhesion promoter.

The crosslinker and/or adhesion promoter may be present in the oxygen barrier layer in a small amount, preferably in an amount of less than 5% by weight of the layer. The crosslinker and/or adhesion promoter may be present in the oxygen barrier layer in an amount of less than 4%, less than 3%, or less than 2% by weight of the layer. For the avoidance of doubt, these values relate to the dry content of the layer.

- 20 It has been found that the inclusion of a crosslinker or adhesion promoter in the oxygen barrier layer in higher amounts can have a detrimental effect on the oxygen transmission rate, particularly at higher humidity, such as up to 50% RH.

The primer layer comprises polyethyleneimine. The primer layer may consist of polyethyleneimine.

The polyethyleneimine may comprise branched and/or linear polyethyleneimine components.

The primer layer has a coat weight of at least about 0.005 g/m². It has been found that this minimum coat weight may be required for effective improvement in the oxygen barrier properties of the film. The primer layer may have a coat weight of

10 from about 0.005 g/m² to about 5 g/m², from about 0.005 g/m² to about 2 g/m², from about 0.005 g/m² to about 1 g/m², from about 0.005 g/m² to about 0.5 g/m², from about 0.005 g/m² to about 0.1 g/m², or from about 0.005 g/m² to about 0.05 g/m².

15 The primer layer may have a coat weight of at least about 0.01 g/m². The primer layer may have a coat weight of from about 0.01 g/m² to about 5 g/m², from about 0.01 g/m² to about 2 g/m², from about 0.01 g/m² to about 1 g/m², from about 0.01 g/m² to about 0.5 g/m², from about 0.01 g/m² to about 0.1 g/m², or from about 0.01 g/m² to about 0.05 g/m².

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The primer layer may be located between the base film layer and the oxygen barrier layer. Preferably, the primer layer is adjacent to the oxygen barrier layer i.e., without any intervening layers. The primer layer is able to both aid adhesion of the

oxygen barrier layer to the base film layer and improve the oxygen barrier performance of the overall film.

The base film layer comprises a polyolefin. At least one layer of the base film may
5 consist of one or more polyolefins and other additives. The base film layer may be at least 50% polyolefin, preferably at least 75% polyolefin.

The base film layer may comprise polyethylene, polypropylene, mixtures thereof, and/or other known polyolefins.

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The base film layer may comprise polypropylene, optionally biaxially oriented polypropylene. The biaxially oriented polypropylene base film layer may be prepared as a balanced film using substantially equal machine direction and transverse direction stretch ratios, or can be unbalanced, where the film is
15 significantly more oriented in one direction (MD or TD). Sequential stretching or simultaneous stretching may be used to form the base film layer. Simultaneous stretching may be achieved using the so-called bubble process, or simultaneous draw stenter stretching.

20 The base film layer may further comprise a polyester, a polyamide, a polystyrene, a polyurethane, a polyvinyl halide, an acetate, or a biopolymer.

The base film layer may be of a monolayer or multi-layer construction. For example, the base film layer may comprise a core layer e.g., of polypropylene, and one or more coextruded skin layers. The skin layer(s) may be sealing and/or laminating layers, for example. The skin layers may comprise a copolymer of ethylene and propylene or a terpolymer of propylene, ethylene and butylene, for example.

As a specific example, the base film layer may comprise a core layer e.g., of polypropylene, with a coextruded skin layer on either side thereof. The film may be heat set to reduce or remove shrinkage.

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The multi-layer oxygen barrier film may comprise one or more additional layers selected from: sealable layers e.g., heat sealable layers; printable layers; metallised layers; metal layers (such as laminated foil layers); and/or functional and/or aesthetic coatings.

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Accordingly, in some embodiments, the multi-layer oxygen barrier film may comprise a metallised or a metal layer.

Alternatively, in some embodiments, the multi-layer oxygen barrier film may not comprise a metallised or a metal layer. The inventors have found that improved oxygen barrier properties and a low oxygen transmission rate can be achieved without the requirement of a metallised layer, particularly for RH of between 0 and 50%.

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The multi-layer oxygen barrier film or any of its layers may comprise additional materials such as anti-block additives, opacifiers, fillers, UV absorbers, colourants, anti-static agents, antioxidants, cavitating agents, slip additives and the like.

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The multi-layer oxygen barrier film in accordance with the present invention can be a variety of thicknesses according to the application requirements. For example, the thickness of the multi-layer barrier film may be from about 10 μm to about 240 μm .

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The multi-layer oxygen barrier film preferably exhibits an oxygen transmission rate when measured in accordance with ASTM D3985 of below about $5 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $3 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $1 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $0.5 \text{ cm}^3/\text{m}^2/24 \text{ hr}$ at a relative humidity of 0%.

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The multi-layer oxygen barrier film preferably exhibits an oxygen transmission rate when measured in accordance with ASTM F1927-14 of below about $20 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $10 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $5 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $3 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, at a relative humidity of 50%.

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The multi-layer oxygen barrier film of the present invention preferably has an OTR at 0% relative humidity at least 10%, preferably at least 20% and more preferably

at least 30% lower than a corresponding film of the same structure but without the primer layer.

The multi-layer oxygen barrier films of the invention may be used as a packaging
5 film, for example in food packaging.

Also provided in accordance with the invention is a package formed, at least in part, from the multi-layer oxygen barrier film. The package may be a sealed package and may comprise a seal between two regions of the multi-layer barrier
10 film.

Also provided in accordance with the invention is an article wrapped or packaged in a material comprising the multi-layer oxygen barrier film.

15 Also provided in accordance with the invention is a method for manufacturing a multi-layer oxygen barrier film, comprising: a. applying a primer layer comprising polyethyleneimine onto at least one side of a base film layer at a coat weight of at least about 0.005 g/m²; and b. coating the primer layer with an oxygen barrier layer comprising a vinyl alcohol-based polymer.

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The composition of the present invention does not require a multi-step or multi-pass process such as deposition of an inorganic metal oxide layer, thereby allowing a simple and cheap coating method to be used.

The vinyl alcohol-based polymer may comprise polyvinyl alcohol.

The method may further comprise the step of corona treating the side of the base
5 film layer to which the primer layer is applied, prior to step a.

The primer layer and/or the oxygen barrier layer may be applied using a standard
coating technique, for example a roller coating method such as gravure or reverse
gravure, a slot die coating method, a semi-flexo coating method, a slide coating
10 method, or a curtain coating method.

Both the vinyl alcohol-based polymer and the polyethyleneimine may be provided
as a solution which is coated onto the base film layer and subsequently dried.

15 The vinyl alcohol-based polymer solution may have a solids content of from about
1% to about 50% by weight of the solution, or from about 5% to about 20% by
weight of the solution. The polyethylene imine solution may have a solids content
of from about 1% to about 20%, or from about 2% to about 10% by weight of the
solution.

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The vinyl alcohol-based polymer solution may have a pH of about 11 or less, about
10 or less, about 9 or less, about 8 or less, about 7 or less, about 6 or less, about 5

or less, about 4 or less, or about 3 or less. The vinyl alcohol-based polymer solution may have a pH of about 4 or more, or about 5 or more, or about 6 or more.

Also provided in accordance with the invention is the use of a primer layer
5 comprising polyethyleneimine to decrease the oxygen transmission rate of a multi-layer oxygen barrier film.

It has surprisingly been found that a primer layer of polyethyleneimine can be used to improve the oxygen barrier properties of a film, in addition to enhancing
10 adhesion of the layer. The barrier effects are particularly advantageous at coat weights of at least about 0.005 g/m².

EXAMPLES

15 The invention will now be more particularly described with reference to the following, non-limiting examples.

EXAMPLE 1 (COMPARATIVE)

20 A 25 µm polypropylene base film was boost (corona) treated on the corona treated side of the film with a power density of 15.4 W/min/m², a running speed of 20 m/min and a drying temperature of 100°C in a 1.8 m oven.

A pilot RK coater was used to apply a PVOH coating (Mica™ EL-1421 HS) directly onto the boosted surface of the base film. The PVOH coating was applied at 10% solids using a 120 Trihelical gravure using the reverse gravure coating technique at a coat weight of 1 g/m² of dry coating.

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EXAMPLE 2

A 25 µm polypropylene base film was boost (corona) treated on the corona treated side of the film with a power density of 15.4 W/min/m², a running speed of 20 m/min and a drying temperature of 100°C in a 1.8 m oven.

A polyethyleneimine primer layer (Mica™ WBA-131-X) was applied to the corona treated side of the film using a pilot RK coater. The polyethyleneimine primer layer was applied using a reverse gravure process and a 250Q gravure, giving a target coat weight of 0.02 g/m². The running speed was 40 m/min with a drying temperature of 75°C in a 1.8 m oven.

The pilot RK coater was then used to apply a PVOH coating (Mica™ EL-1421 HS) onto the primer layer. The PVOH coating was applied at 10% solids using a 120 Trihelical gravure using the reverse gravure coating technique at a coat weight of 1 g/m² of dry coating.

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EXAMPLE 3 (COMPARATIVE)

A 25 μm polypropylene base film was boost (corona) treated on the corona treated side of the film with a power density of 15.4 W/min/m², a running speed of 20 m/min and a drying temperature of 100°C in a 1.8 m oven.

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A polyurethane primer layer (Covestro™ NeoRez™ R-610) was applied to the corona treated side of the film using a pilot RK coater. The polyurethane primer layer was applied using a reverse gravure process and a 250Q gravure, giving a target coat weight of 0.02 g/m². The running speed was 40 m/min with a drying temperature of 75°C in a 1.8 m oven.

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The pilot RK coater was then used to apply a PVOH coating (Mica™ EL-1421 HS) onto the primer layer. The PVOH coating was applied at 10% solids using a 120 Trihelical gravure using the reverse gravure coating technique at a coat weight of 1 g/m² of dry coating.

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EXAMPLE 4 - OXYGEN TRANSMISSION RATE AT DIFFERENT RELATIVE HUMIDITIES

The film samples prepared in Examples 1 – 3 were assessed for oxygen transmission rate at a relative humidity of 0% and 50%, in accordance with standard test method ASTM D3985 and standard test method ASTM F1927-14

20

respectively. The data shown in Table 1 is an average of two replicate tests for each sample.

TABLE 1

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Example	Oxygen Transmission Rate (cm ³ /m ² /24 hr)	
	0% RH	50% RH
1 (Comp)	2.2	3.0
2	0.4	2.1
3 (Comp)	4.3	7.8

From the results it can be seen that the use of a polyethyleneimine primer significantly decreases the oxygen transmission rate of the film at 0% and 50% RH. Conversely, the use of a polyurethane primer appears to have a detrimental effect on the oxygen barrier properties of the film. These observations support the inventive concept of a synergy between the polyethyleneimine primer and PVOH functionality that improves the oxygen barrier performance.

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EXAMPLE 5 - EFFECT OF ADHESION PROMOTER VS PRIMER LAYER

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Various film samples were prepared with the compositions shown in Table 2, using either the general method outlined in Example 1 (no primer), Example 2 (with PEI primer) or Example 3 (with polyurethane primer).

The film samples A - H were assessed for oxygen transmission rate at a relative humidity of 0% and 50%, in accordance with standard test method ASTM D3985 and standard test method ASTM F1927-14 respectively. The data shown in Table 2 is an average of two replicate tests for each sample.

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TABLE 2

Sample	Base Film	Primer	PVOH Coating	Adhesion Promoter	Oxygen Transmission Rate (cm ³ /m ² /24 hr)	
					0% RH	50% RH
A (Comp)	PP	None	Henkel	None	0.3	1.8
B	PP	PEI	Henkel	None	<0.2	1
C (Comp)	PP	PU	Henkel	None	0.3	1.4
D (Comp)	PP	None	Henkel	PEI	0.3	2.3
E	PP	PEI	Henkel	PEI	0.2	1.7
F (Comp)	PP	PU	Henkel	PEI	3.3	2.7
G (Comp)	PP	None	Mica	None	2.2	3
H	PP	PEI	Mica	None	0.4	2.1
I (Comp)	PP	None	Mica	PAE	0.9	4
J	PP	PEI	Mica	PAE	0.3	4.2

- 10
- The PEI primer was Mica™ WBA-131-X
 - The PU (polyurethane) primer was Covestro™ NeoRez™ R-610
 - The PVOH coating was either Henkel™ Liofol™ BC 1580 or Mica™ EL-1421 HS
 - The PEI adhesion promoter was Henkel™ PR 1890, used at 2% by weight of the layer based on dry content

- The PAE (polyamideamine-epichlorohydrin) adhesion promoter was Solenis™ Polycup™ 9200 EU, used at 13.72% by weight of the layer based on dry content

- 5 Looking at the results for Samples A – F, it can be seen that using a PEI primer layer with a PVOH coating increases the oxygen barrier of the film at both 0% RH and 50% RH (Sample B).

- Comparing Samples A and D demonstrates that the addition of a PEI adhesion
- 10 promoter at a higher amount i.e., 10% by weight of the layer, appears to have little added benefit to the oxygen barrier of the film and is potentially damaging at 50% RH. In fact, Sample E demonstrates a slightly worse oxygen transmission rate than Sample B at 0% RH, with these samples demonstrating a larger detrimental effect on the addition of a PEI adhesion promoter at 50% RH, even when a PEI primer
- 15 layer is present.

- Comparing the results for Samples C and F further demonstrates the potentially negative impact of using a PEI adhesion promoter at a higher amount i.e., 10% by weight of the layer. For these samples, the detrimental effect on oxygen
- 20 transmission rate is observed at both 0% and 50% RH. Comparing the results for Samples C and F with those for Samples B and E respectively also highlights the benefit of using a PEI primer compared to a polyurethane primer with respect to the oxygen transmission rate at both 0% and 50% RH.

Looking at the results for Samples G – J, it is again observed that using a PEI primer layer with a PVOH coating increases the oxygen barrier of the film at both 0% RH and 50% RH (Sample H). The addition of a PAE adhesion promoter appears to
5 give an increase in oxygen barrier of the film at 0% RH. However, there appears to be a detrimental effect to the oxygen barrier at 50% RH. Additionally, the oxygen transmission rate with Sample J is worse than Sample H at 50% RH, demonstrating the detrimental effect of adhesion promoters on oxygen barrier properties when used in higher amounts.

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EXAMPLE 6 – EFFECT OF PVOH COAT WEIGHT, PRIMER, ADHESION PROMOTOR AND METALLISATION

Various film samples were prepared with the compositions shown in Table 3, using
15 the general method outlined in Example 2 (with one of two different PEI primers).

Where an adhesion promotor was used, this was blended with the PVOH coating at 1.95% by weight of the layer based on dry content.

20 The samples were metallised on a Bobst K5 metalliser at 300m/min under standard metallization conditions.

The film samples K – P were assessed for oxygen transmission rate at a relative humidity of 50%, in accordance with standard test method ASTM F1927-14. The data shown in Table 3 is an average of two replicate tests for each sample. The water vapour transmission rate was assessed in accordance with standard test
5 method ASTM F1249 - 13.

TABLE 3

Sample	Base Film	PVOH coat weight (g/m ²)	Primer	Adhesion Promoter	Metallisation	OTR (cm ³ /m ² /24 hr)	WVTR (g/m ² /24 hr)
K	PP	1.0	PR1883	None	Al	0.32	1.00
L	PP	1.0	Mica	PEI	Al	1.00	0.55
M	PP	1.0	PR1883	PEI	Al	0.96	0.46
N	PP	0.5	PR1883	PEI	Al	8.40	0.74
O	PP	1.0	PR1883	None	AlOx	0.73	5.20
P	PP	0.5	PR1883	PEI	AlOx	5.30	2.30

- The PEI primer was Mica™ WBA-131-X or Henkel™ PR1883
- 10 - The PEI adhesion promoter was Henkel™ PR 1890
- The PVOH coating was either Henkel™ Liofol™ BC 1580

Looking at the results for Samples K and M, it can be seen that the presence of an adhesion promoter has a potentially negative impact on the oxygen barrier
15 capabilities of the resulting multi-layer film.

Comparing results between L and M, it appears that there is no significant difference in the oxygen transmission rate between the two PEI primers.

Comparing results for M and N, it can be seen that there is a significant difference between the oxygen transmission rate and water vapor transmission rate between the higher and lower coat weight of PVOH. The higher coat weight
5 of 1.0 g/m² of PVOH demonstrates significantly increased oxygen barrier of the film compared to 0.5 g/m² of PVOH.

Comparing results K and O, it appears that metallisation with Al compared to AlOx provides improved oxygen barrier capabilities and a decreased oxygen
10 transmission rate. However, the metallised films in Table 3 provide a better oxygen barrier than the non-metallised films in Table 2.

CLAIMS

1. A multi-layer oxygen barrier film, comprising:
 - a base film layer comprising a polyolefin;
 - an oxygen barrier layer comprising a vinyl alcohol-based polymer;
 - and
 - a primer layer comprising polyethyleneimine,wherein the primer layer has a coat weight of at least about 0.005 g/m².
2. The multi-layer oxygen barrier film according to claim 1, comprising a single oxygen barrier layer comprising a vinyl alcohol-based polymer.
3. The multi-layer oxygen film according to any one of claims 1 to 2 wherein the multi-layer film does not comprise a second water-based coating layer.
4. The multi-layer oxygen barrier film according any one of claims 1 to 3, wherein the vinyl alcohol-based polymer comprises polyvinyl alcohol and/or ethylene vinyl alcohol.
5. The multi-layer oxygen barrier film according to any one of claims 1 to 4, wherein the vinyl alcohol-based polymer comprises polyvinyl alcohol.

6. The multi-layer oxygen barrier film according to any one of claims 1 to 5, wherein the oxygen barrier layer has a coat weight of from about 0.1 g/m² to about 10 g/m², from about 0.2 g/m² to about 5 g/m², or from about 0.5 g/m² to about 2 g/m².
7. The multi-layer oxygen barrier film according to any one of claims 1 to 6, wherein the oxygen barrier layer is absent of any crosslinker and/or adhesion promoter, optionally wherein the oxygen barrier layer is absent of both crosslinker and adhesion promoter.
8. The multi-layer oxygen barrier film according to any one of claims 1 to 7, wherein the primer layer has a coat weight of at least about 0.01 g/m².
9. The multi-layer oxygen barrier film according to any one of claims 1 to 8, wherein the primer layer has a coat weight of from about 0.01 g/m² to about 5 g/m², from about 0.01 g/m² to about 2 g/m², from about 0.01 g/m² to about 1 g/m², from about 0.01 g/m² to about 0.5 g/m², from about 0.01 g/m² to about 0.1 g/m², or from about 0.01 g/m² to about 0.05 g/m².
10. The multi-layer oxygen barrier film according to any one of claims 1 to 9, wherein the primer layer is adjacent to the oxygen barrier layer.

11. The multi-layer oxygen barrier film according to any one of claims 1 to 10, wherein the primer layer is located between the base film layer and the oxygen barrier layer.
12. The multi-layer oxygen barrier film according to any one of claims 1 to 11, wherein the base film layer comprises polypropylene.
13. The multi-layer oxygen barrier film according to any one of claims 1 to 12, wherein the base film layer comprises biaxially oriented polypropylene.
14. The multi-layer oxygen barrier film according to any one of claims 1 to 13, wherein the film comprises one or more additional layers selected from:
- a sealable layer;
 - a printable layer;
 - a metallised layer; and/or
 - a functional and/or aesthetic coating.
15. The multi-layer oxygen barrier film according to any one of claims 1 to 14 wherein the film does not comprise a metallised layer.
16. The multi-layer oxygen barrier film according to any one of claims 1 to 15, wherein the thickness of the multi-layer barrier film is from about 10 μm to about 240 μm .

17. The multi-layer oxygen barrier film according to any one of claims 1 to 16, wherein the film exhibits an oxygen transmission rate when measured in accordance with ASTM D3985 of below about $5 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $3 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $1 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $0.5 \text{ cm}^3/\text{m}^2/24 \text{ hr}$ at a relative humidity of 0%.
18. The multi-layer oxygen barrier film according to any one of claims 1 to 17, wherein the film exhibits an oxygen transmission rate when measured in accordance with ASTM F1927-14 of below about $20 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $10 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $5 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, or below about $3 \text{ cm}^3/\text{m}^2/24 \text{ hr}$, at a relative humidity of 50%.
19. Use of the multi-layer oxygen barrier film according to any one of claims 1 to 18 as a packaging film.
20. A package formed, at least in part, from a multi-layer barrier film according to any one of claims 1 to 18.
21. An article wrapped or packaged in a material comprising a multi-layer oxygen barrier film according to any one of claims 1 to 18.
22. A method for manufacturing a multi-layer oxygen barrier film, comprising:

- a. applying a primer layer comprising polyethyleneimine onto at least one side of a base film layer comprising a polyolefin at a coat weight of at least about 0.005 g/m²; and
- b. coating the primer layer with an oxygen barrier layer comprising a vinyl alcohol-based polymer.

23. The method according to Claim 22, wherein the vinyl alcohol-based polymer comprises polyvinyl alcohol.

24. The method according to Claim 22 or Claim 23, further comprising the step of corona treating the side of the base film to which the primer layer is applied, prior to step a.

25. The method according to any one of claims 22 to 24, wherein step a. and/or step b. are carried out using a standard coating technique, optionally reverse gravure.

26. The method according to any one of claims 22 to 25, wherein step b. involves coating a vinyl alcohol-based polymer solution onto the primer layer and subsequently drying the layer.

27. The method according to Claim 26, wherein the vinyl alcohol-based polymer solution has a pH of about 11 or less, about 10 or less, about 9 or less, about

8 or less, about 7 or less, about 6 or less, about 5 or less, about 4 or less, or about 3 or less.

28. Use of a primer layer comprising polyethyleneimine to decrease the oxygen transmission rate of a multi-layer oxygen barrier film.

29. The use according to Claim 28, wherein the primer layer has a coat weight of at least about 0.005 g/m².

30. The use according to Claim 28 or Claim 29, wherein the multi-layer oxygen barrier film additionally comprises an oxygen barrier layer comprising a vinyl alcohol-based polymer, optionally polyvinyl alcohol.

31. The use according to any one of claims 28 to 30, wherein the multi-layer oxygen barrier film additionally comprises a base film layer, optionally comprising biaxially oriented polypropylene.