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BIODEGRADABLE STARCH-BASED ARTICLES.

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Description

The present invention relates to biodegradable articles and particularly to thin-walled articles such as starch-based films (sheets) which are substantially insoluble in water and can constitute effective liquid-, gas- and vapour-barriers.

EP-A-0 032 802 describes the production of self-supporting, flexible and biodegradable films produced from formulations including starch, ethylene-acrylic acid copolymer and polyethylene.

EP-A-0 400 532 describes the production of films which have good mechanical characteristics and are produced from formulations based on starch and ethylene-vinyl alcohol copolymer.

The films produced according to the methods of the patent applications cited above have good tear strength and resistance to dissolving in water and can therefore be used to replace conventional, non-biodegradable synthetic, thermoplastic materials for a wide range of applications. In the presence of water, however, the films tend to swell, which adversely affects their properties as gas- and vapour-barriers.

EP-A-0 388 924 describes composite films including a layer of starch and a synthetic thermoplastic polymer and a layer of a barrier material which is deposited or laminated onto the starch layer and is constituted by a copolymer or terpolymer of vinylidene chloride, copolymers of vinyl chloride and methyl acrylate, copolymers or terpolymers of vinylidene chloride and vinylidene fluoride, copolymer of ethylene-vinyl alcohol and nylon with polyvinylidene chloride.

WO90/14938 describes a method of producing films which are derived from starch with a high amylose content and can be laminated with polymeric materials having barrier properties, such as polypropylene, polyethylene, polyvinyl chloride, polycarbonate, polyether, polyesters, ionomer resins, acrylates and nylon.

The object of the present invention is to provide a laminated film which has good mechanical and barrier properties whilst its biodegradability characteristics remain unchanged or are improved. For this purpose, the subject of the invention is a laminated film including at least one first layer of polymeric material including starch and at least one second layer of hydrophobic material, characterised in that the second layer includes a natural or synthetic wax.

In a first embodiment, the hydrophobic material is constituted essentially by natural or synthetic wax. The natural waxes include:

- petroleum waxes, such as paraffin waxes with n-alkane contents of from about 75% to about 100% by weight and molecular weights of from about 280 to about 560 (C₂₀-C₄₀),
- microcrystalline waxes composed mainly of isoparaffinic and naphthenic hydrocarbons saturated with n-alkanes and having molecular weights within the range of from 450 to 800 (C₉₅-C₂₅₀) with melting points within the range of from 50 to 95 °C,
- animal waxes such as beeswax and spermaceti wax, in particular,
- vegetable waxes such as candelilla waxes, carnauba waxes, Japan wax, ouricury wax, bayberry wax, jojoba wax and montan wax.

The synthetic waxes include, in particular, Fischer-Tropsch wax, polyethylene waxes, fatty acids and amides of fatty acids.

The waxy materials are used in solution, in aqueous emulsion, or in the fused state and are applied to the starchy layer in thicknesses which, according to the desired barrier properties, may vary within wide limits, typically from 0.2 microns to 20 microns, preferably from 0.5 microns to 10 microns.

Alternatively, the hydrophobic material used as the second layer is constituted by a mixture of two or more waxes or by a mixture of one or more waxes with a polymeric material selected from the materials mentioned below and mixtures thereof:

a) poly-ethylene-vinyl alcohol with an ethylene content of from about 15% to about 90% in moles, preferably from 30% to 50% in moles,
b) ethylene-acrylic acid or ethylene-acrylic acid-alkyl acrylate copolymers with ethylene contents of from 10 to 30% in moles, preferably about 20% in moles, with free carboxylic acid groups or carboxylic acid groups salified by a base, preferably ammonium hydroxide,
c) polyvinyl acetate,
d) copolymers of ethylene-vinyl acetate containing from 5 to 50% in moles, preferably from 10 to 40% in moles, of vinyl acetate,
e) rosin or rosin derivatives such as abietic acid, levopimaric acid and palustic acid and esters thereof, such as methyl, ethyl, hexadecyl, oxyxypentylmethyl, 2-hydroxyethyl, 3-hydroxyvinyl esters and esters of 1,2,3-propantriol, and addition products of the acids mentioned above formed with maleic anhydride and copolymers of those acids with glycols, particularly glycerol, and phthalic acids,
f) alkyd resins such as vegetable oils, for example, linseed oil, safflower oil, sunflower oil, soya oil, rape oil, castor oil, tung oil, oiticica oil and tall oil,
g) natural gum in emulsion or thermoplastic gum.

Particularly when the hydrophobic layer is applied in emulsion, the compositions may include:
- additives which can improve the wettability of the films, such as alcohols, for example, methyl, ethyl, propyl, isopropyl, butyl and isobutyl alcohols and glycols such as, for example, 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, polyethylene glycol and polypropylene glycol;
- surfactants and stabilisers, such as alkyl sulphates, aryl sulphates, alkyl sulphonates, aryl sulphonates, derivatives of ethylene oxide, fatty acids, alkylamine salts, quaternary ammonium salts, starch, dextrin, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose (sodium salt), methyl cellulose and polyvinyl alcohol;
- thickeners such as, for example, starch, methyl cellulose, hydroxyethyl cellulose, alginate, casein and polyurethanes;
- plasticisers such as dibutyl phthalate, n-heptyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl maleate, 2-ethylhexyl fumarate, dibutyl sebacate, polyglycol adipate, tricresyl phosphate, dioctyl phthalate, tributoxyethyl phosphate;
- fillers and pigments such as titanium dioxide, talc, calcium carbonate, and silica.

Alternatively, if the hydrophobic coating material is applied by coextrusion or casting techniques or by a hot-melt technique, the waxy materials are preferably mixed with components selected from:
- ethylene-vinyl acetate copolymers containing from 5 to 50% in moles, preferably from 10 to 40% in moles, of vinyl acetate in the presence of rosin and rosin derivatives, particularly addition products formed with maleic anhydride,
- ethylene-acrylic acid or ethylene-acrylic acid-alkyl acrylate copolymers with free carboxylic acids, and
- ethylene-vinyl alcohol copolymers with ethylene contents of from about 50% to about 97% in moles, preferably from 60 to 90% in moles,
- polyhydroxyalkanoate copolymers, particularly PHB (polyhydroxybutyrate), or PHB/V (polyhydroxybutyrate/valerate),
- copolymers of (D-, L-) and (L-) lactic acid,
- poly-ε-caprolactone,
- lactic acids copolymerised with glycolic acids and/or with epsilon-caprolactone,
- conjugated or non-conjugated fatty acids, such as oleic, linoleic, linolenic, ricinoleic, eleostearic, licin and palmitic acids.

Plasticisers (phthalates, fatty acids, vegetable oils), pigments, fillers, UV stabilisers, antioxidants and antioxidising agents may be added to the products at the extrusion stage.

If the hydrophobic layer is constituted by a mixture of one or more waxes with a synthetic polymer such as those mentioned above, the composition preferably includes from 10 to 100% of wax and from 0 to 90% by weight of synthetic polymer, with reference to the sum of the wax and the synthetic polymer.

Laminated films including a first starchy layer, a second hydrophobic layer formed essentially by a wax or a mixture of waxes, and a third layer also having hydrophobic properties and formed by a mixture of one or more waxes with one or more of the substances a)-g) mentioned above fall within the scope of the invention.

Laminated films formed by a starchy layer treated on both sides with a wax-based coating or a coating including one or more waxes with one of more of the substances a)-g) also fall within the scope of the invention.

The starchy layer may be formed by starch, possibly including plasticiser or, preferably, by a polymeric composition including starch and a synthetic thermoplastic polymer.

Polymeric compositions including starch and a synthetic thermoplastic polymer suitable for producing the first starchy-based layer of the laminated film according to the invention are described in the patent applications W090/10671, W091/02025, W091/02024 and EP-A-0 400 532.

The preferred polymers used in the starchy mixture are polymers and copolymers which are derived from ethylenically unsaturated monomers and which have repeating units with at least one polar functional group such as a hydroxy, alkoxy, carboxy, carboxyalkyl, alkylcarboxy or acetal group. Preferred polymers include polyvinyl alcohol and copolymers of an olefin selected from ethylene, propylene, isobutene and styrene with acrylic acid, vinyl alcohol and/or vinyl acetate. These olefin copolymers include, in particular, ethylene copolymers such as ethylene-acrylic acid, ethylene-vinyl alcohol, ethylene-vinyl acetate and mixtures thereof. Particularly preferred are polyvinyl alcohol and copolymers of polyvinyl acetate and ethylene-vinyl alcohol with ethylene contents of from 10 to 50% by weight, produced by the hydrolysis of the corresponding polymers of ethylene-vinyl acetate, with degrees of hydrolysis generally of between 50
and 100.

The synthetic polymeric component may also include epsilon-polycaprolactone or copolymers thereof, polyhydroxybutyrate/valerate or polymers or copolymers of lactic acid with glycolic acid or caprolactone.

The starch used in these polymeric compositions is preferably a native starch, particularly maize starch or potato starch. The term "native" includes starches with high amylose contents and "waxy" starches. However, starches which have been modified physically or chemically, such as starch ethoxylates, starch acetates, cationic starches, oxidised starches and cross-linked starches may also be used. The native starch is normally used in the preparation of the formulations without being dried beforehand and has an intrinsic water content of about 9-15% by weight.

The method of preparing the starchy films does not differ substantially from the known methods already described in the patent literature cited above. In fact, the compositions are prepared by the mixing of the components in an extruder heated to a temperature high enough to produce a thermoplastic melt.

The composition supplied by the extruder includes starch, synthetic thermoplastic polymer, water and/or a high-boiling plasticiser in concentrations of between 1 and 50% by weight, preferably between 5% and 25% by weight, with reference to the weight of the total composition.

Suitable plasticisers include, in particular, glycerine, ethylene or propylene glycol, ethylene or propylene diglycol, ethylene or propylene triglycol, polyethylene glycol, polypropylene glycol, 1,2-propandiol, 1,3 propanediol, 1,2-, 1,3-, 1,4-butanediol, 1,5-pentanediol, 1,6-, 1,5-hexanediol, 1,2,6-, 1,3,5-hexantriol, neopentylglycol, trimethylol propane, pentaerythritol, sorbitol and the acetate, ethoxylate and propoxylate derivatives thereof, particularly sorbitol ethoxyrate, pentaerythritol ethoxylate, sorbitol acetate, pentaerythritol acetate, or a mixture of the plasticisers mentioned above.

The material supplied to the extruder may also include agents which can destroy hydrogen bonds, such as urea, and of which quantities of from 0.5 to 20% by weight, preferably between 2 and 7% by weight, with reference to the total composition, may be added to the starch and polymer mixture.

The polymeric material may also include cross-linking agents, such as aldehydes, ketones and glyoxals, process coadjuvants, release agents and lubricants, such as fatty acids, esters of fatty acids, higher alcohols, polyethylene waxes, antioxidants, opacifiers and stabilisers which are normally incorporated in compositions for moulding and extrusion. The formulation of the starchy layer may also include small quantities of hydrophobic polymers such as polyethylene, polypropylene, polystyrene, polystyrene/butadiene, in quantities generally no greater than 5% by weight with reference to the weight of the total composition.

Example 1: Preparation of the starchy film

37 parts of GLOBE 3401 starch (11% by weight of water), 37 parts of ethylene-vinyl alcohol polymer with an ethylene content of 42% in moles and a degree of hydrolysis of the acetate groups of 99.5%, 3 parts of ethylene-acrylic acid copolymer with 20% of acrylic acid, with a melt flow index of 2 (at 125°C and 0.325 Kg load) 5 parts of urea, 15 parts of sorbitol ethoxylate and 2.7 parts of water were mixed in a single-screw OMC extruder with a screw diameter d of 20 mm and an L/d of 30, having an intermediate degassing section and operating with the following heating profile:

90-180-150-140 °C (heating profile set).

The extruded material was transformed into pellets and processed by extrusion and blowing at about 160 °C to produce films having an average thickness of 20 and 30 microns, respectively.

Example 2

An aqueous dispersion including 30% by weight of a microcrystalline wax (C10, molecular weight 420, melting point 72°C) was supplemented with ethyl alcohol and a polyurethane thickener to produce a dispersion with a viscosity of 138 kPa.s at 20 °C.

The composition of the dispersion, expressed in parts by weight, comprised:

| Microcrystalline wax (30% by weight aqueous dispersion) | 80 parts |
| Ethyl alcohol | 20 parts |
| Polyurethane thickener | 3.5 parts |

The aqueous dispersion was spread onto a sample of the film produced in Example 1 with dimensions of 30cm x 60 cm x 30 microns, by means of a chromium-plated steel roller.
The treated film was dried at 100 °C for 15 seconds. The thickness of wax obtained was 0.6 microns. The permeability of the film to water vapour at 38 °C and 90% relative humidity was 402 g x 30 microns/m² x 24 h compared with 888 g x 30 microns/m² x 24 h for the untreated film.

The same film treated with a second layer of wax enabled a coating 1.3 microns thick to be obtained, with a permeability to water vapour of 215 g x 30 microns/m² x 24 h.

Example 3

A sample of film produced as described in Example 1, with dimensions of 30 cm x 60 cm x 30 microns, was treated as described in Example 2 and then covered with a layer of polyethylene-acrylic acid.

The poly-ethylene-acrylic acid-based coating was deposited by a chromium-plated steel roller with the use of an aqueous dispersion of the following composition, expressed in parts by weight:

| polyethylene-acrylic acid (ammonium salt) | 80 parts |
| isobutyl alcohol | 20 parts |

The thickness of the acrylic layer was 0.6 microns.

The permeability of this film to water vapour at 38 °C and 90% relative humidity was 210 g x 30 microns/m² x 24 h, compared with 880 g x 30 microns/m² x 24 h for the untreated film.

Example 4

A sample of film produced as described in Example 1, with dimensions of 30 cm x 60 cm x 30 microns, was treated as described in Example 2 and then covered with a hydrophobic layer constituted by a derivative of abietic acid (abietic acid with glycerine and phthalic acid, in which the abietic acid constituted 90% of the product by weight, was supplied).

The rosins derivative was used in a solution containing 70% by weight in acetone and was deposited with a chromium-plated steel roller.

Drying was carried out at 80 °C for 30 seconds. The thickness of the layer was 1.0 micron.

The permeability of the film to water vapour at 38 °C and 90% relative humidity was 111 g x 30 microns/m² per 24 h compared with 880 g x 30 microns/m² per 24 h for the untreated film.

Example 5

A sample of film produced as described in Example 1, with dimensions of 30 cm x 60 cm x 30 microns, was treated as described in Example 2 and then covered with a layer of polyvinyl acetate in an aqueous dispersion containing 35% by weight.

The coating was deposited with a chromium-plated steel roller. Drying was carried out at 100 °C for 30 seconds.

The permeability of the film to water vapour at 38 °C and 90% relative humidity was 470 g x 30 microns/m² x 24 h.

Example 6

The surface of a sample of film 30 microns thick, produced as described in Example 1, was treated, with the use of a wax-lamination system, with a product constituted by 80 parts by weight of paraffin wax and 20 parts by weight of polyethylene-vinyl acetate (vinyl acetate content 28%, melt index 150), in the fused state.

The surface treatment of the film was carried by a “hot melt” surface-treatment machine. The thickness of the coating was 7 microns.

The permeability of the film to water vapour at 38 °C and 90% relative humidity was 20 g x 30 microns/m² x 24h.

Example 7

Two samples of film 20 microns thick, produced as described in Example 1, were joined together with the use of the mixture described in Example 6.
The resulting film was constituted by two layers 20 microns thick of the film described in Example 1, and an intermediate hydrophobic layer 7 microns thick as described in Example 6.

The permeability of the film to water vapour at 38°C and 90% relative humidity was 30 g x 30 microns/m² x 24 h.

Example 8

Two samples of film 20 microns thick produced as described in Example 1, were joined together with the use of a mixture constituted by 80 parts by weight of carnauba wax and 20 parts by weight of poly-epsilon-caprolactone. The resulting film was constituted by two layers of film 20 microns thick as described in Example 1, and by an intermediate hydrophobic layer 7 microns thick.

The permeability of the film to water vapour at 38°C and 90% relative humidity was 52 g x 30 microns/m² x 24 h.

The term "film" as used in the present description is intended also to include sheets for thermoforming, the surfaces of which have been treated with the waxy coatings described above.

The invention also includes articles with fairly thin walls, such as articles produced by injection and co-injection and co-blown bottles, the walls of which have a composite structure formed by at least one starchy layer and one or more layers of wax or a mixture of waxes, alone or in combination with a thermoplastic polymer.

The uses of the products according to the invention include, in particular, the production of refuse sacks or bags, films for hygiene/sanitary articles such as nappies, sanitary towels and colostomy bags, containers, for example, for cosmetic products and for food and cutlery.

Claims

1. A laminated film including at least one first layer of polymeric material including starch and at least one second layer of hydrophobic material, characterised in that the second layer includes a natural or synthetic wax or a mixture of waxes.

2. A laminated film according to Claim 1, in which the wax is a petroleum wax selected from paraffin waxes with n-alkane contents of from 75% to 100% and molecular weights of from 280 to 560 and microcrystalline wax composed of isoparaffinic and naphthenic hydrocarbons saturated with n-alkanes and having molecular weights of from 450 to 800 and melting points of from 50 to 90°C.

3. A laminated film according to Claim 1, in which the wax is an animal wax selected from beeswax and spermaceti wax.

4. A laminated film according to Claim 1, characterised in that the wax is a vegetable wax selected from candelilla wax, carnauba wax, Japan wax, ouricury wax, bayberry wax, jojoba wax and mixtures thereof.

5. A laminated film according to Claim 1, characterised in that the wax is a mineral wax.

6. A laminated film according to Claim 1, characterised in that the wax is a synthetic wax selected from Fischer-Tropsch wax, polyethylene wax, fatty acids and amides of fatty acids.

7. A laminated film according to any one of Claims 1 to 6, in which the layer of hydrophobic material includes one or more waxes in combination with a material selected from the group consisting of polyethylene-vinyl alcohol, polyethylene-acrylic acid, polyethylene-acrylic acid-alkyl acrylate, polyvinyl acetate, ethylene-vinyl acetate copolymers, rosin and derivatives thereof, alkyl resins, natural gum and thermoplastic gum.

8. A laminated film according to Claim 7, in which the hydrophobic layer includes one or more waxes and a derivative of rosin selected from abietic acid, levopimaric acid and palustic acid, esters thereof selected from methyl, ethyl, hexadecyl, oxypropylmethyl, 2-hydroxyethyl and 3-hydroxyphenyl esters, and esters of 1,2,3-propantriol.

9. A laminated film according to Claim 7, in which the hydrophobic layer includes one or more waxes and a derivative of rosin selected from the addition products of abietic acid, levopimaric acid or palustic
acid formed with maleic anhydride and polymers of those acids with glycols and phthalic acids.

10. A laminated film according to any one of Claims 1 to 9, in which the layer of hydrophobic material is formed by an emulsion including surfactants and stabilisers selected from alkyl sulphates, aryl sulphates, alkyl sulphonates, aryl sulphonates, derivatives of ethylene oxide, fatty acids, alkyamine salts, quaternary ammonium salts, starch, dextrin, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose (sodium salt), methyl cellulose and polyvinyl alcohol.

11. A laminated film according to Claim 10, in which the hydrophobic layer includes an alcohol selected from methyl, ethyl, propyl, isopropyl, butyl and isobutyl alcohols.

12. A laminated film according to Claim 10, in which the hydrophobic layer includes a glycol selected from 2-methoxyethanol, 2-butoxyethanol, 2-ethoxyethanol, polyethylene glycol and polypropylene glycol.

13. A laminated film according to Claim 10, in which the hydrophobic layer is formed by an emulsion including a thickener selected from starch, methyl cellulose, hydroxyethyl cellulose, alginates, casein and polyurethanes.

14. A laminated film according to any one of the preceding claims, in which the layer of hydrophobic material is formed by an emulsion including a plasticiser selected from dibutyl phthalate, n-heptyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl maleate, 2-ethylhexyl fumarate, dibutyl sebacate, polyglycol adipate, tricresyl phosphate, dioctyl phthalate and tributoxyethyl phosphate.

15. A laminated film according to any one of the preceding claims, in which the hydrophobic layer includes fillers and pigments selected from titanium dioxide, talc, calcium carbonate and silica.

16. A laminated film according to any one of the preceding claims, in which the layer of hydrophobic material includes a layer of waxy material covered by a layer of a material selected from the group consisting of ethylene-vinyl alcohol copolymers, ethylene-acrylic acid copolymers, ethylene-acrylic acid-alkyl acrylate copolymers, polyvinyl acetate, ethylene-vinyl acetate copolymers, rosin and derivates of rosin, alkyd resins and natural gum.

17. A laminated film according to Claim 1, in which the layer of hydrophobic material includes one or more waxy materials together with a material selected from the group consisting of ethylene-vinyl acetate copolymers and ethylene-acrylic acid, ethylene-acrylic acid-alkyl acrylate, polyethylene-vinyl alcohol copolymers, polyhydroxyalkanoate, homopolymers of lactic acid, poly-epsilon-caprolactone, lactic acid copolymerised with glycolic acids and/or epsilon-caprolactone and fatty acids, the hydrophobic coating being deposited on the starchy layer by coextrusion, casting, or a hot-melt technique.

18. A laminated film according to any one of the preceding claims, in which the starchy layer includes starch and one or more synthetic thermoplastic polymers selected from the group consisting of polyvinyl alcohols, poly-ethylene-vinyl alcohol copolymers, ethylene-acrylic acid copolymers, and ethylene-vinyl acetate copolymers.

19. Thin-walled articles which can be produced by co-injection or co-blowing and which have walls with a composite structure including a starchy layer and at least one layer including one or more natural or synthetic waxes.

**Patentansprüche**


2. Laminierte Folie nach Anspruch 1, wobei das Wachs ein Erdölwachs ist, ausgewählt aus Paraffinwachsen mit n-Alkan-Anteilen von 75 % bis 100 % und Molekulargewichten von 280 bis 560 und mikrokristallinem Wachs, zusammengesetzt aus isoparaffinischem und naphthenischem Kohlenwasser-
stoffen, gesättigt mit n-Alkanen und mit Molekulargewichten von 450 bis 800 und Schmelzpunkten von 50 bis 90 °C.

3. Laminierte Folie nach Anspruch 1, wobei das Wachs ein Tierwachs ist, ausgewählt aus Bienenwachs und Walrat.

4. Laminierte Folie nach Anspruch 1, dadurch gekennzeichnet, daß das Wachs ein Pflanzenwachs ist, ausgewählt aus Candellila wachs, Carnaubawachs, Japanwachs, Ouricurywachs, Myriakawachs, Jojobawachs und Gemischen davon.

5. Laminierte Folie nach Anspruch 1, dadurch gekennzeichnet, daß das Wachs ein Mineralwachs ist.


8. Laminierte Folie nach Anspruch 7, wobei die hydrophobe Schicht ein oder mehrere Wachse und ein Derivat von Kolophonium, ausgewählt aus Abietinsäure, Levopimarinsäure und Palustrinsäure, Estern davon, ausgewählt aus Methyl-, Ethyl-, Hexadecyl-, Oxypyrylimethyl-, 2-Hydroxyethyl- und 3-Hydroxyphenylestern und Estern von 1,2,3-Propandiol einschließt.


10. Laminierte Folie nach einem der Ansprüche 1 bis 9, wobei die Schicht des hydrophoben Materials durch eine Emulsion gebildet wird, die Tenside und Stabilisatoren einschließt, ausgewählt aus Alkylsulfaten, Arilsulfaten, Alkylsulfonaten, Arylsulfonaten, Derivaten von Ethylhexanol, Fettsäuren, Alkylaminsalzen, quaternären Ammoniumsalzen, Stärke, Dextrin, Hydroxyethylcellulose, Hydroxypropylcellulose, Carboxymethylcellulose (Natriumsalz), Methylcellulose und Polyvinylalkohol.

11. Laminierte Folie nach Anspruch 10, wobei die hydrophobe Schicht einen Alkohol einschließt, ausgewählt aus Methyl-, Ethyl-, Propyl-, Isopropyl-, Butyl- und Isobutylalkoholen.

12. Laminierte Folie nach Anspruch 10, wobei die hydrophobe Schicht ein Glycol, ausgewählt aus 2-Methoxyethanol, 2-Butoxyethanol, 2-Ethoxyethanol, Polyethylenglykol und Polypropyenglykol, einschließt.

13. Laminierte Folie nach Anspruch 10, wobei die hydrophobe Schicht durch eine Emulsion gebildet wird, die ein Verdickungsmittel einschließt, ausgewählt aus Stärke, Methylcellulose, Hydroxyethylcellulose, Alginaten, Casein und Polyurethanen.


15. Laminierte Folie nach einem der vorangehenden Ansprüche, wobei die hydrophobe Schicht Füllstoffe und Pigmente einschließt, ausgewählt aus Titanoxid, Talkum, Calciumcarbonat und Siliciumdioxid.

16. Laminierte Folie nach einem der vorangehenden Ansprüche, wobei die Schicht des hydrophoben Materials eine Schicht aus wachsartigem Material einschließt, bedeckt mit einer Schicht eines Materials,

17. Laminierte Folie nach Anspruch 1, wobei die Schicht des hydrophoben Materials ein oder mehrere wachsartige Materialien einschließt, zusammen mit einem Material, ausgewählt aus der Gruppe, bestehend aus Ethylen-Vinylacetat-Copolymeren und Ethylen-Acrylsäure-, Ethylen-Acrylsäure-Alkylacrylat-, Polyethylvinylalkohol-Copolymeren, Polyhydroxyalkanoat, Homopolymeren von Milchsäure, Polyäthersulfon-Caprolacton, Milchsäure, copolymerisiert mit Glycolsäuren und/oder epsilon-Caprolacton und Fettsäuren, wobei die hydrophobe Beschichtung auf der stärkehaltigen Schicht durch Coextrusion, Gießen oder ein Heißschmelzverfahren abgeschieden wurde.


**Revendications**

1. Un film stratifié comprenant au moins une première couche d’un matériau polymère incluant de l’amidon et au moins une seconde couche d’un matériau hydrophobe, caractérisé en ce que la seconde couche comprend une couche naturelle ou synthétique ou un mélange de cires.

2. Un film stratifié selon la revendication 1, dans lequel la couche est une couche de pétrole sélectionnée parmi les cires de paraffine à teneur en n-alcanes de l’ordre de 75 à 100% et de poids moléculaire compris entre 280 et 560 et cire microcrystalline composée d’hérocarbures isoparaffiniques et naphthéniques saturés avec des n-alcanes et dont les poids moléculaires sont de 450 à 800 et les points de fusion compris entre 50 et 90 °C.

3. Un film stratifié selon la revendication 1, dans lequel la couche est une couche animale sélectionnée parmi les cires d’abeille et cires de spermaceti.

4. Un film stratifié selon la revendication 1, caractérisé en ce que la couche est une couche végétale sélectionnée parmi les cires de candelilla, cire de carnauba, cire du Japon, cire Ouricury, cire de cirier ou arbre à cire, cire de jojoba et leurs mélanges.

5. Un film stratifié selon la revendication 1, caractérisé en ce que la couche est une couche minérale.

6. Un film stratifié selon la revendication 1, caractérisé en ce que la couche est une couche synthétique sélectionnée parmi les cires Fischer-Tropsch, cire de polyéthylène, acides gras et amides d’acides gras.

7. Un film stratifié selon l’une quelconque des revendications 1 à 6, dans lequel la couche de matériau hydrophobe inclut une ou plusieurs cires en combinaison avec un matériau sélectionné dans le groupe consistant en: poly-éthylène-acéol vinyle, poly-éthylène-acide acrylique, poly-éthylène-acide acrylique-alkyl acrylate, poly-vinyl acétate, copolymère éthylène-vinyl acétate, collophane et ses dérivés, résines alkyde, gomme naturelle et gomme thermoplastique.

8. Un film stratifié selon la revendication 7, dans lequel la couche hydrophobe inclut une ou plusieurs cires et un dérivé de collophane sélectionné parmi acide abiotique, acide lévopimarique et acide palustrique, leurs esters sélectionnés parmi les esters de méthyle, d’éthyle, d’hexadécyle, d’oxypranyleméthyle, de 2-hydroxyéthyle et 3-hydroxyphényle et les esters de 1,2,3-propantriol.
9. Un film stratifié selon la revendication 7, dans lequel la couche hydrophobe inclut une ou plusieurs cires et un dérivé de collophane sélectionné parmi les produits d'addition de l'acide abiotique, de l'acide lévopomarine ou de l'acide palustrique formés avec l'anhydride mélèique et polymères de ces acides avec des glycols et des acides phthaliques.

10. Un film stratifié selon l'une quelconque des revendications 1 à 9, dans lequel la couche de matériau hydrophobe est formée par une émulsion comprenant des agents tensioactifs et des agents stabilisants sélectionnés parmi les alkyl sulfates, aryl sulfates, alkyl sulfonates, aryl sulfonates, dérivés d'oxyde d'éthylène, acides gras, sels d'alkylamine, sels d'ammonium quaternaire, amidon, dextrine, hydroxyéthyl cellulose, hydroxypropyl cellulose, carboxyméthyl cellulose (sel de sodium), méthyl cellulose et alcool polyvinylique.

11. Un film stratifié selon la revendication 10, dans lequel la couche hydrophobe comprend un alcool sélectionné parmi les alcools méthylique, éthylène, propylique, isopropylique, butyléthyle et isobutylique.

12. Un film stratifié selon la revendication 10, dans lequel la couche hydrophobe comprend un glycol sélectionné parmi 2-méthoxyéthanol, 2-butoxyéthanol, 2-éthoxyéthanol, poly-éthylène glycol et polypropylène glycol.

13. Un film stratifié selon la revendication 10, dans lequel la couche hydrophobe est formée par une émulsion incluant un épaississant sélectionné parmi l'amidon, le méthyl cellulose, l'hydroxyéthyl cellulose, alginites, caséine et polyuréthanes.

14. Un film stratifié selon l'une quelconque des revendications précédentes, dans lequel la couche de matériau hydrophobe est formée par une émulsion comprenant un agent plastifiant sélectionné parmi le dibutyldiphosphate, le n-heptyl acrylate, le 2-éthyhexyl acrylate, le 2-éthyhexyl maléate, le 2-éthyhexyl fumurate, le dibutyl sébactate, le polyglycol adipate, le tricrésyl phosphate, le dioctyl diphosphate et le tributoxyéthyl phosphate.

15. Un film stratifié selon l'une quelconque des revendications précédentes, dans lequel la couche hydrophobe comprend des agents de charge et des pigments sélectionnés parmi le dioxyde de titane, le talc, le carbonate de calcium et la silice.

16. Un film stratifié selon l'une quelconque des revendications précédentes, dans lequel la couche de matériau hydrophobe comprend une couche de matériau cireux couverte par une couche de matériau sélectionné dans le groupe consistant en copolymères éthylène-alcool vinylique, copolymères éthylène-acide acrylique, éthylène-acide acrylique-alkyl acrylate, polyvinyl acélate, copolymères éthylène-acétate de vinylic, collophane et les dérivés de collophane, résines alkyde et gomme naturelle.

17. Un film stratifié selon la revendication 1, dans lequel la couche de matériau hydrophobe inclut un ou plusieurs matériaux cireux, associés à un matériau sélectionné parmi le groupe consistant en copolymères éthylène-acétate de vinylic et copolymères éthylène-acide acrylique, éthylène-acide acrylique-alkyl acrylate, polyéthylène-alcool vinylique, polyhydroxyalkanoate, homopolymères de l'acide lactique, poly-épsitone-caprolactone, acide lactique copolymérisé avec des acides glycoliques et/ou épsitone-caprolactone et acides gras, le revêtement hydrophobe étant déposé sur la couche amylacée par coextrusion, moulage, ou une technique de fusion à chaud.

18. Un film stratifié selon l'une quelconque des revendications précédentes, dans lequel la couche amylacée inclut de l'amidon et un ou plusieurs polymères thermoplastiques sélectionnés parmi le groupe consistant en alcools polyvinylque, copolymères poly-éthylène-alcool vinylique, copolymères éthylène-acide acrylique et copolymères éthylène-acétate de vinylic.

19. Articles à parois minces pouvant être fabriqués par co-injection ou co-soufflage et dont les parois présentent une structure composite comprenant une couche amylacée et au moins une couche incluant une ou plusieurs cires naturelles ou synthétiques.