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(54) PARCHMENT PAPER WITH HIGH OXYGEN BARRIER PROPERTIES

(57) This invention relates to a barrier paper comprising a parchment paper base material and a non-continuous coating formed on a surface thereof, wherein the non-continuous coating is made of at least one of a water-soluble polymer and a water-dispersible polymer.

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Description

Technical field

[0001] The present invention relates to a parchment paper that can be used as an oxygen barrier layer in packaging materials for oxygen sensitive items. Further aspects of the present invention include a method for producing the oxygen barrier parchment paper and a packaging material comprising the oxygen barrier parchment paper.

Background art

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[0002] Packaging materials cause a large amount of waste, which many countries presently try to reduce by exchanging fuel based plastic packaging materials with fully biodegradable, compostable and bio-sourced packaging materials. Such biodegradable packing materials must fulfil various conditions depending on the end use. For example, when being used as food packaging, they must be safe for food contact, when being used as packaging for life science and diagnostic devices, they must meet stringent safety requirements. In particular, when used as packaging material for oxygensensitive products, sufficient gas barrier properties of the packaging material are required. Genuine vegetable parchment (GVP) made of 100% cellulose is known as biodegradable packaging material having moisture vapor barrier properties and intrinsic grease barrier properties.

[0003] In order to achieve the desired oxygen barrier properties, the parchment paper is either produced so as to have a very high level of parchmentization or an additional oxygen barrier layer is laminated thereon.

[0004] EP 3 819 426 A1 describes parchment paper having a very high level of parchmentization.

[0005] However, when using a GVP having a very high parchmentization level, there are some limitations concerning the mechanical properties. Even though such very highly parchmentized GVP grades are extremely interesting due to the fact that they have an intrinsic oxygen barrier property and they are completely bio-sourced (made of 100% cellulose) and certified to be home compostable, very highly parchmentized GVP grades can be more brittle and fragile due to being very highly transformed, which makes them relatively sensitive to folds and tear. This can be a limit to the use of highly parchmentized GVP grades for some packaging applications, especially those applications where the sheet needs to be formed into the desired shape to contain the food. They can also be somewhat difficult to handle in converting equipment running at higher web load.

[0006] Furthermore, very highly parchmentized GVP grades require a very specific manufacturing process to offer an oxygen transmission rate (OTR) value of below 5 cm³/m²/day and can lead to high amount of waste in the production process and low production efficiencies. Consequently, there is a need to come up with an improved process and product for achieving a high OTR, simplifying the manufacturing process and reducing the amount of waste.

[0007] WO 2018/197676 A1 describes a multilayer article that comprises a vegetable parchment support and an oxygen barrier layer containing polyvinyl alcohol (PVOH).

[0008] When coating a GVP with an oxygen barrier coating such as PVOH, polyvinylidene chloride (PVdC) and others, the obtained OTR properties are not always satisfactory, either due to the sensitivity of the coating to the conditions of use (PVOH is sensitive to moisture), or because of environmental concerns (PVdC). When laminating a GVP with an oxygen barrier layer such as a polymeric layer (e.g. polyolefin extrusion coatings), barrier properties can be imparted but these methods involve an additional processing stage and have a negative impact on the life cycle of the products. In other words, the use of polyolefin lamination has a very detrimental effect on the sustainability of the packaging material (lower bio-sourced content and no positive end of its life scenario).

[0009] Moreover, vapor phase deposition can also be used to cover the GVP. Even though metallization or other vapor phase processes allow to impart excellent barrier properties with very little raw material, these processes are quite expensive and are usually done with specific vacuum conditions, which require external converting steps. Moreover, if a paper substrate is used, it requires an additional coating step to improve the surface roughness before metallization. Indeed, without such additional coating the paper substrate can swell with moisture and the metal coating can crack and lose barrier properties. In addition to having a strong impact on packaging costs, the life cycle of these processes is still subject to discussions.

[0010] In summary, to obtain the desired oxygen barrier properties, specialized process conditions or the use of non-biodegradable material were required.

[0011] Therefore, it is an object of the present invention to provide an improved biodegradable packaging material having very good oxygen barrier properties and excellent mechanical properties with respect to for example tear strength, wet burst strength and dry burst strength. A further object of the present invention is the provision of a biodegradable packaging material that is easy to manufacture in an energy and waste-efficient way and at low costs.

[0012] Compared to the prior art paper as taught in WO 2021/089778 A1, this invention has better mechanical properties and can be produced in a more efficient manner due to the parchment paper used as the base material having a lower parchmentization level and the thin non-continuous oxygen barrier coating formed thereon. Compared to the existing

multilayer products comprising a parchment base paper and an oxygen barrier coating, this invention offers a fully compostable material having better oxygen barrier properties due to the thin non-continuous coating made of a water-soluble polymer and/or a water-dispersible polymer.

5 Summary of the invention

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[0013] The present invention solves the problems of the prior art by the following means.

[0014] In a first aspect, the present invention relates to a barrier paper comprising a parchment paper as a base material and a non-continuous coating formed on a surface of the base material, wherein the non-continuous coating is made of at least one of a water-soluble polymer and a water-dispersible polymer.

[0015] It has been found that a non-continuous coating of a water-soluble polymer and/or a water-dispersible polymer applied to a parchment paper solves the problems of the prior art by providing a biodegradable barrier paper having excellent oxygen barrier properties and simultaneously exhibiting favourable mechanical properties.

[0016] In a second aspect, the present invention relates to a method for producing a barrier paper comprising applying at least one water-soluble polymer or water-dispersible polymer onto a surface of a parchment paper as a base material to form a non-continuous coating.

[0017] Thus, a further advantage of the present invention resides in the fact that the barrier paper as described herein can be prepared in a sustainable and more efficient manner and waste and production costs can be reduced compared to prior art procedures.

[0018] In a third aspect, the present invention relates to a packaging material for oxygen sensitive products comprising the barrier paper described herein.

Brief description of the drawings

[0019] Fig. 1 shows a cross-sectional view of an uncoated parchment paper with scanning electron microscope (SEM).

Detailed description of the invention

[0020] The present invention relates to a barrier paper comprising a parchment paper as a base material and a non-continuous coating formed on a surface of the base material, wherein the non-continuous coating is made of at least one of a water-soluble polymer and a water-dispersible polymer.

[0021] In the context of the present invention, the following definitions and test methods apply.

[0022] The expression "biodegradable" is generally defined in line with the EN13432 standard. The expression "biodegradable" when applied to a material or a product means that the material, or the entire product, will both biodegrade and disintegrate. By "biodegrade" it is meant that the chemical structure or the material breaks down under the action of micro-organisms, while by "disintegrates" it is meant that the material, or the product made from it, will physically fall apart into fine visually indistinguishable fragments, at the end of a typical composting cycle.

[0023] The term "parchment paper" or "genuine vegetable parchment (GVP)" refers to a material comprised substantially of cellulose, which has been subjected to a parchmentizing process. Cellulose materials are derived from manmade sources such as regenerated cellulose fibers or films or from natural sources such as fibers or pulp from woody plants or non-woody plants. In the parchmentizing process, a cellulose paper sheet is treated with a gelatinizing agent comprising, for example, sulfuric acid under conditions where the reaction time between the gelatinizing agent and the cellulose is limited to control cellulose dissolution, hydrolysis and degradation. The treated paper is then washed thoroughly so as to remove the gelatinizing agent, after which it is dried. The bath chemical partially dissolves or gelatinizes the cellulose in the paper sheet. The dissolved cellulose is subsequently precipitated when the bath chemical is diluted by washing the treated paper. This process, called parchmenting or parchmentizing, forms a very tough, stiff, smooth paper with an appearance somewhat like that of a genuine parchment. Because paper treated in this manner has a tendency to become brittle and to wrinkle upon drying, it is sometimes treated with a plasticizing agent, for example glycerin, glucose or Sorbitol. Vulcanized fiber is a related product made by treating a cellulose paper sheet with a gelatinizing agent comprising, for example, zinc chloride. The surface of a parchment paper or a GVP typically has small cracks and recesses formed therein, which can result in a certain average surface roughness.

[0024] The term "non-continuous coating" refers to a coating formed on a surface of the base material, which provides a non-continuous coverage of said surface. That means, whilst the non-continuous coating is equally distributed over the entire surface of the base material, it may be applied in an amount that is not sufficient to form a continuous coating layer. In the present invention, the non-continuous coating does not necessarily cover the whole surface area of the base material but can represent a partial coating, as long as the non-continuous coating fills in the cracks and recesses of the surface of the base material. Some parts of the surface can remain exposed without being covered by the coating. The cracks and recesses that are filled with the non-continuous coating are distributed equally over the entire surface

area of the base material so that a more even surface (having a reduced surface roughness than the base material used) is formed.

[0025] The term "water-soluble polymer" refers to polymers that are substantially soluble in water, i.e. polymers that form a substantially homogeneous solution with water by being dissolved therein. The water-soluble polymers described herein are entirely solubilized before use. Examples of the water-soluble polymer are carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), hydroxypropyl methylcellulose (HPMC), polyvinyl alcohol and cationic starch.

[0026] The term "water-dispersible polymer" refers to polymers that are substantially not soluble in water but that can be mixed with water so as to form a heterogeneous mixture, which can be a dispersion or an emulsion. Examples of the water-dispersible polymer are acrylic latex, styrene-butadiene latex, styrene acrylic latex, starches and biopolyesters such as polylactic acid (PLA), polyhydroxybutyrate (PHB), polyhydroxyalkanoate (PHA) or mixtures thereof.

[0027] The "oxygen transmission rate (OTR)" of a material refers to the amount of oxygen (cm³) that is transmitted through a specified area of the material (m²) during one day at atmospheric pressure of 1.013 bar (1 atm), a temperature of 23 °C and a relative humidity of 50%. The oxygen transmission rate (OTR) (cm³/m²/day) is measured in accordance with ASTM D 3985 and ASTM F 1927. Unless described otherwise, the OTR described herein is measured on an OXTRAN 2/22 apparatus (supplier: MOCON), which complies with ASTM D3985. The OTR of a material is a measure for the oxygen barrier properties of the material and indicates the gas barrier level. In other words, the lower the OTR of a material, the smaller the amount of gas being transmitted through the material which results in the material offering a high barrier to gas, especially to oxygen.

[0028] As described above, the first aspect of the present invention relates to a barrier paper comprising a parchment paper as a base material having a non-continuous coating made of at least one of a water-soluble polymer and a water-dispersible polymer formed on a surface thereof. The inventors have surprisingly found that the barrier paper is provided with high oxygen barrier properties and simultaneously with excellent mechanical properties when coating a parchment paper with a water-soluble polymer and/or a water-dispersible polymer so as to obtain a non-continuous coating. The oxygen barrier properties are especially excellent when coating the parchment paper with 1.5 g/m² or less, preferably with 0.05 to 1.5 g/m², more preferably with 0.2 to 1.0 g/m² of a water-soluble polymer and/or a water-dispersible polymer. [0029] One important aspect of the present invention resides in the discovery that the formation of a non-continuous coating on a surface of a parchment paper is already sufficient to significantly improve the oxygen barrier properties thereof. As shown on Fig. 1, the surface of parchment paper typically contains certain unevenesses such as cracks and recesses, which reduce the oxygen barrier properties of the parchment paper. It is thought that the high oxygen barrier properties of the barrier paper according to the present invention result from the non-continuous coating filling in the unevennesses present in the surface of the parchment paper used as the base material.

[0030] A further key aspect of the present invention is the discovery that a parchment paper having a high to moderate parchmentization level and having insufficient oxygen barrier properties prior to being coated with the non-continuous coating can be suitably used as the base material of the barrier paper. Specifically, when using a parchment paper having low oxygen barrier properties as the base material, improved oxygen barrier properties can be obtained by coating this parchment paper with the non-continuous coating made of a water-soluble polymer and/or a water-dispersible polymer.

[0031] The barrier paper described herein can therefore be advantageously used as barrier layer for the construction of highly gas and moisture impermeable packaging material, especially as packaging material for oxygen-sensitive items. Furthermore, as the barrier paper described herein has excellent mechanical properties with respect to tear strength, wet burst strength and dry burst strength, it can also be used as reinforcement layer for the construction of packaging material, particularly for packaging having a predetermined shape.

[0032] The present invention provides a fully biodegradable, compostable and bio-sourced product that substantially consists of cellulose and acts as an oxygen barrier layer as well as a reinforcing layer. Due to the fact that a parchment paper having a lower parchmentization level can be used as the base paper, whereby energy required during parchmentization in the production process can be saved and waste produced during the production can be reduced, rendering the production process more efficient and less expensive.

Base material

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[0033] The parchment paper used as the base material may be a genuine vegetable parchment (GVP). In a preferable embodiment, the parchment paper is substantially made of short fibres pulp.

[0034] The parchment paper used as the base material preferably comprises at least 50 percent and even more preferably at least 80 percent cellulose. In a preferable embodiment, the parchment paper is composed of 100% cellulose, rendering the parchment paper completely bio-sourced and fully biodegradable/compostable. The parchment paper therefore preferably contains no more than 5 wt.% of non-compostable material or material of undetermined compostability in order to meet the requirements of the EN 13432 standard. Most preferably, any additives added to the cellulose fiber base sheet are compostable.

[0035] The parchment paper to be used as the base material has preferably an OTR of less than 10,000 cm³/m²/day, more preferably less than 5000 cm³/m²/day, even more preferably less than 1000 cm³/m²/day, as measured at 23 °C and a relative humidity of 50%. When a parchment paper having an OTR of more than 10,000 cm³/m²/day is used as the base material, the resulting barrier paper may not have a sufficiently low OTR value suitable for packaging of oxygen sensitive items. The higher the OTR of the parchment paper, the lower its parchmentization level provided the basis weight is the same. For example, a parchment paper having an OTR of about 5000 - 150,000 cm³/m²/day has a low parchmentization level (e.g. Sulpack, manufactured by Ahlstrom Munksjö), a parchment paper having an OTR of about 150 - 3000 cm³/m²/day has a medium parchmentization level (e.g. Sulflex, manufactured by Ahlstrom Munksjö), and a parchment paper having an OTR of 10 cm³/m²/day or less has a very high parchmentization level (e.g. PureBarrier, manufactured by Ahlstrom Munksjö).

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[0036] A very highly parchmentized parchment paper (e.g. PureBarrier) can exhibit a favourable OTR value of less than 10 cm³/m²/day. However, when increasing the parchmentization level, the mechanical properties of the parchment paper are reduced, because a very high parchmentization level leads to the paper being more brittle and sensitive to cracking. By combining a parchment paper having a high to moderate parchmentization level with a non-continuous coating, the reduction of the mechanical properties can be avoided and a barrier paper having significantly better mechanical properties (e.g. in terms of tear resistance) as well as having excellent oxygen barrier properties can be obtained. [0037] The average Bekk smoothness of the parchment paper to be used as the base material is preferably between 4.0 and 20.0 s, more preferably between 5.0 and 16.0 s. When having an average Bekk smoothness in this range, the non-continuous coating can be formed on the surface of the parchment paper in such a way that the unevenesses (cracks and recesses) present in the surface of the parchment paper are filled in with the coating and a more homogeneous thickness profile can be obtained. As a consequence, the OTR of the resulting barrier paper can be advantageously reduced. The average Bekk smoothness of the parchment paper to be used as the base material can be measured according to the Bekk roughness determination method ISO 5627:1995. The average Bekk smoothness can be determined with a Buchel 131 ED apparatus.

[0038] The profile roughness parameters of the parchment paper to be used as the base material is preferably as follows. It is preferable that the parchment paper base material has

- a Ra value of less than 6 μm, preferably between 1 and 6 μm and more preferably between 1 and 4 μm;
- a Rq value of less than 15 μ m, preferably between 2 and 15 μ m and more preferably between 2 and 10 μ m; and
- a Rz value of less than 35 μ m, preferably between 5 and 35 and more preferably between 5 and 25.

[0039] The Ra value is the arithmetic average of profile height deviations from the mean line, the Rq value is the root mean square average of profile height deviations from the mean line, and the Rz value is the maximum peak to valley height of the profile within a single sampling length. The lower the Ra, Rq, Rz values, the more homogeneous the thickness profile of the substrate. Since the OTR is a function of the thickness, it is preferred to have a relatively constant thickness profile, to minimize the occurrence of weak points. The profile roughness parameters, Ra, Rq and Rz can be measured using a surface roughness tester according to the EN ISO 4287 standard.

[0040] The basis weight of the parchment paper to be used as the base material may be selected according to the fiber and/or filament constitution and the intended end use. In some embodiments, the basis weight of the parchment paper on a dry basis may be 200 gsm or less, preferably from 30 gsm to 130 gsm, more preferably from 45 to 115 gsm. When the basis weight of the parchment paper is within these ranges, the barrier paper obtained therewith has excellent mechanical properties and offers excellent barrier properties.

[0041] The parchment paper to be used as the base material typically has an average thickness of from 30 μ m to 200 μ m, preferably from 35 μ m to 140 μ m, even more preferably from 45 μ m to 120 μ m, from the viewpoint of achieving excellent mechanical reinforcement properties.

[0042] The parchment paper to be used as the base material preferably has a density of at least 800 kg/m³, more preferably from 800 kg/m³ to 1200 kg/m³, even more preferably from 850 kg/m³ to 1150 kg/m³, from the viewpoint of achieving excellent oxygen barrier properties. Indeed, the higher the density the lesser the pore volume. Consequently, one can achieve a satisfactory OTR value by applying a non-continuous coating.

[0043] Typically, the parchment paper will not include binders and other additives. However, additives may be used to achieve specific desired results. For example, a softener such as glycerol can be added to make the parchment paper less brittle, or a filler such as TiO₂ may be added to modify opacity of the parchment paper, or a pigment may be added to change the colour of the parchment paper. Preferably, the parchment paper contains no more than 5 wt.% of non-compostable material or material of undetermined compostability, in order to meet the requirements of the EN 13432 standard. Most preferably, any additives that are added are biodegradable and/or compostable.

Non-continuous coating

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[0044] The non-continuous coating is formed on a surface of the base material. It is preferable that the non-continuous coating is applied in an amount of 1.5 g/m² or less. Applying the non-continuous coating is such a light amount, i.e. in an amount of at most 1.5 g/m², is already sufficient to obtain excellent oxygen barrier properties. A small amount of the coating can be applied, because it is sufficient that the cracks and recesses present in the surface of the parchment paper are at least partly filled with the coating. In a further preferable embodiment, the non-continuous coating is applied in an amount of 0.1 to $1.5 \, \text{g/m}^2$, more preferably 0.1 to $1.0 \, \text{g/m}^2$, even more preferably 0.1 to $0.5 \, \text{g/m}^2$, and most preferably 0.2 to $0.3 \, \text{g/m}^2$, so that the unevenesses present in the surface of the parchment paper used as the base material are filled so that the resulting barrier paper has a smoother surface, i.e. a surface having reduced profile roughness parameters. The profile roughness parameters can be reduced by around 10 to 20%, further minimizing the occurrence of weak points. As a consequence, the barrier paper has a low OTR of less than $10 \, \text{cm}^3/\text{m}^2/\text{day}$.

[0046] The non-continuous coating is made of at least one of a water-soluble polymer and a water-dispersible polymer. [0046] The water-dispersible polymer is not particularly limited, as long as it is dispersible at conditions of use. The water-dispersible polymer is preferably at least one selected from acrylic latex, styrene-butadiene latex, styrene acrylic latex, starches and biopolyesters such as polylactic acid (PLA), polyhydroxybutyrate (PHB), polyhydroxyalkanoate (PHA) or mixtures thereof. In a preferable embodiment, the water-dispersible polymer is acrylic latex.

[0047] The water-soluble polymer is not particularly limited, as long as it is entirely soluble at conditions of use. The water-soluble polymer is preferably at least one selected from carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), hydroxypropyl methylcellulose (HPMC), polyvinyl alcohol (PVOH) and cationic starch. In a more preferable embodiment, the water-soluble polymer is CMC.

[0048] Whilst CMC is commonly known to be used as a thickener additive for coating compositions, the present inventors have surprisingly discovered CMC to be useful as a thin non-continuous coating for a GVP resulting in high OTR properties. The non-continuous coating preferably comprises 50% by weight or more of CMC, more preferably 80% by weight of CMC and even more preferably 100% by weight of CMC. When the non-continuous coating is made primarily or even entirely of CMC, very high OTR properties can be obtained.

[0049] The CMC preferably has a molecular weight (Mw) of between 100,000 and 750,000 g/mol, preferably between 100,000 and 400,000 g/mol. The Mw of CMC can be adjusted both by raw material selection and the conditions of its manufacturing process.

[0050] The Mw of CMC has a critical effect on the coating composition. When the Mw is lower than 100,000 g/mol, this results in a lower viscosity of the CMC, which makes the application thereof easier, but reduces the oxygen barrier properties of the resulting barrier paper. When the Mw is higher than 750,000 g/mol, this results in a higher viscosity of the CMC, which causes problems with the application thereof to the surface of the base material whilst there is no gain on OTR properties. Consequently, using CMC having a Mw falling within the above-mentioned ranges is preferable from the viewpoint of selecting the best compromise between rheology and OTR properties.

[0051] The OTR properties of the barrier paper can be further enhanced by adding a softener such as glycerol to the non-continuous coating composition. The softener helps to form a more homogeneous non-continuous coating, which evenly fills in the unevenesses in the surface of the base material and avoids the formation of additional cracks, thus leading to further enhanced oxygen barrier properties of the obtained barrier paper. In a preferable embodiment, the non-continuous coating composition includes less than 20% by weight of glycerol, relative to the total dry amount of the non-continuous coating composition.

[0052] The OTR properties of the barrier paper can also be further enhanced by adding a processing aid such as salts to the non-continuous coating composition. Salts can reduce the viscosity of the composition and help spread the coating more homogeneously. This enhances oxygen barrier properties of the obtained barrier paper. In a preferable embodiment, the non-continuous coating composition includes less than 5% by weight of salt such as calcium chloride, relative to the total amount of the non-continuous coating composition.

Barrier paper

[0053] The barrier paper according to the present invention comprises the parchment paper as a base material and a non-continuous coating formed on a surface of the base material. Due to the non-continuous coating of a water-soluble polymer and/or a water-dispersible polymer applied to a surface of the parchment paper base material, a biodegradable barrier paper having excellent oxygen barrier properties and simultaneously exhibiting favourable mechanical properties is provided.

⁵⁵ **[0054]** Due to the non-continuous coating applied thereto, the barrier paper preferably has an OTR between 0.05 and 20.0 cm³/m²/day, more preferably between 0.05 and 5.0 cm³/m²/day.

[0055] According to the construction of the barrier paper of the present invention, it is possible to obtain sufficient oxygen barrier properties, even when using a parchment paper having a lower parchmentization level and concomitant

low gas barrier properties as the base material.

Method for producing barrier paper

[0056] In a second aspect, the present invention relates to a method for manufacturing a barrier paper comprising applying at least one water-soluble polymer or water-dispersible polymer onto a surface of a parchment paper as a base material to form a non-continuous coating.

[0057] The parchment paper that is used as the base material preferably has an OTR of less than 10,000 cm³/m²/day, more preferably less than 5000 cm³/m²/day, even more preferably less than 1000 cm³/m²/day. Furthermore, it is preferable that the parchment paper used as the base material has an OTR of not less than 150 cm³/m²/day. When using a parchment paper that exhibits an OTR of at least 150 cm³/m²/day as the base material (i.e. a parchment paper having a moderate to high parchmentization grade), the production of said base material is easier and more efficient because it is not required to conduct an excessive parchmentization treatment as would be required for obtaining a parchment paper having a very high parchmentization grade.

[0058] The water-soluble polymer and/or water-dispersible polymer and amount thereof as previously described herein can be used in the method for producing the barrier paper according to the present invention.

[0059] The step of applying the water-soluble polymer and/or water-dispersible polymer onto the surface of the parchment paper base material is preferably conducted using a pressure of 300 kPa or more, more preferably 500 kPa to 2000 kPa. This can be done for example by using a size press process, film press process or a pressure-impregnation process. A subsequent calendering step can also be optionally included. Calendering can help homogenize the thickness and increase the density of the barrier paper, thus improving the oxygen barrier properties. Optionally, a calendering step can also be carried out before the coating step to improve surface properties of the base material.

[0060] When applying the water-soluble polymer and/or water-dispersible polymer using a pressure of at least 300 kPa, the water-soluble polymer and/or water-dispersible polymer can penetrate better into the cracks and recesses present in the surface of the parchment paper base material leading to a better (more homogeneous) formation of the non-continuous coating. As a result, the obtained barrier paper has higher oxygen barrier properties.

Packaging material

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[0061] In a third aspect, the present invention relates to a packaging material for oxygen sensitive products comprising the barrier paper described herein.

[0062] The packaging material is not particularly limited and can be used for preserving oxygen sensitive items, for example, oxygen sensitive food or oxygen sensitive life science and diagnostic devices. The packaging material for oxygen sensitive food may for example be selected from the group consisting of butter wrapping, beverage container, coffee capsule, coffee pad, chocolate packaging and biscuit packaging. Preferably, the packaging material is used in the construction of a coffee capsule, more preferably a lid of a coffee capsule. The packaging material for oxygen sensitive life science and diagnostic devices may for example be selected from the group consisting of test kits packaging, biospecimen collection and preservation cards packaging, laboratory test filters packaging, test pads packaging and DNA/RNA extraction medias packaging.

40 [0063] The packaging material comprises the barrier paper and optionally additional layers. That is, the packaging material may be a multi-layer product comprising the barrier paper as a first material layer and at least one additional material layer, wherein the at least one additional material layer is laminated on a surface of the barrier paper. The additional layer is not particularly limited and may be appropriately selected dependent on the desired additional property, with which the packaging material should be supplemented. The additional layer is preferably selected from the group consisting of a water vapor barrier layer, an aroma barrier layer, a water-resistant layer, a thermo-sealable layer, a grease-resistant layer, finishing varnish layer and a printable layer.

Examples

[0064] The properties of the parchment papers used in the present examples and the barrier papers prepared in the present examples have been measured according to the following methods.

[0065] The oxygen transmission rate (OTR) has been measured in accordance with ASTM D 3985 on an OTR measurement apparatus "OX-TRAN 2/22" (produced by MOCON).

[0066] The wet burst strength has been measured according to ISO 3689 and the dry burst strength has been measured according to ISO 2758.

[0067] The average Bekk smoothness has been measured according to the Bekk roughness determination method ISO 5627:1995

[0068] The profile roughness parameters, Ra, Rq and Rz have been measured using a surface roughness tester

according to EN ISO 4287 standard on surface roughness tester Mitutoyo, Surftest SJ-210[mm], "R2 μ m; 0,75mN". **[0069]** The following raw materials have been used in the present examples.

Base material:

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[0070] The base materials used in the present examples and comparative examples are shown in Table 1.

Table 1

10		Cristal 401 37gr	Cristalline MC 40g	Sulflex 70	PureBarrier 70	Highly parchmentized paper
	Parchmentization level	-	-	medium	Very high	high
15	Туре	Crystal paper	Crystalline paper	GVP, 100% cellulose	GVP, 100% cellulose	GVP, 100% cellulose
	OTR (cm ³ /m ² /day)	>5000	>5000	750	0.35	268
20	Bekk smoothness (s) side 1	4727.8 ± 54.9	330.8 ± 22.5	8.0 ± 0.0	9.5 ± 0.6	4.8 ± 0.5
	Bekk smoothness (s) side 2	9634.0 ± 619.0	940.5 ± 44.4	5.0 ± 0.0	8.3 ± 0.5	8.3 ± 0.5
25	Basis weight (g/m²)	37	40	70	70	70
	Thickness (μm)	28.3	38.8	82.4	76.3	82.2

Non-continuous coating:

30 (i) Water-soluble polymers:

[0071]

- "CMC FinnFix 300" (produced by Nouryon), which is an aqueous solution containing 2.3% by weight of carboxymethyl cellulose having a Mw of around 180,000 g/mol
 - "PVOH AQ 4104" (produced by Kuraray), which is an aqueous solution containing 3.2% by weight of polyvinylalcohol
- "PVOH Mowiol 28/99" (produced by Kuraray), which is an aqueous solution containing 2.6% by weight of polyviny-lalcohol
 - "Cationic Starch HiCat 5213A" (produced by Roquette), which is an aqueous solution containing 2.5% by weight of cationic starch
- "Cationic Starch Perfectafilm X115" (produced by Avebe), which is an aqueous solution containing 3.1% by weight
 of cationic starch
 - (ii) Water-dispersible polymers:

⁵⁰ [0072]

- "Acrylic latex Rhobarr 135" (produced by Dow), which is an aqueous acrylic emulsion containing 40% by weight of solids; the emulsion was diluted to have a solid content of 2.5% by weight so as to have a low coat weight
- Example 1: Evaluation of type of base paper

[0073] The oxygen barrier properties of different types of base papers, which are either uncoated or coated by applying

 0.3 g/m^2 of CMC FinnFix 300 to a surface thereof Examples 1.1 to 1.3 and Comparative Examples 1.1 and 1.2), have been evaluated as shown in Table 2.

Table 2

	Paper material	OTR (cm ³ /m ² /day)
Comparative Example 1.1	Cristal 401 37gr (uncoated) Cristal 401 37gr + CMC coating	>5000 >5000
Comparative Example 1.2	Cristalline MC 40g (uncoated) Cristalline MC 40g + CMC coating	>5000 >5000 >5000
Example 1.1	Sulflex 70 (uncoated) Sulflex 70 + CMC coating	750 0.34
Example 1.2	Highly parchmentized paper (uncoated) Highly parchmentized paper + CMC coating	268 0.3
Example 1.3	PureBarrier 70 (uncoated) PureBarrier 70 + CMC coating	0.35 0.2

[0074] The application of a CMC coating to Cristal[™] paper and Cristalline [™] paper did not significantly affect the oxygen barrier properties of these base material papers (cf. Comparative Examples 1.1 and 1.2). Such an effect could however be observed when applying a CMC coating to parchment paper. The OTR of the parchment papers having medium to high parchmentization level could be favourably reduced by applying a thin CMC coating thereto (cf. Examples 1.1 to 1.3). The reduction in OTR was especially prominent in the medium to highly parchmentized papers (cf. Examples 1.1 and 1.2). PureBarrier 70 having a very high parchmentization grade already has a low OTR from the outset so that the reduction in its OTR value is not as prominent (cf. Example 1.3).

Example 2: Evaluation of type of coating

[0075] The oxygen barrier properties of different types of non-continuous coating applied in an amount of 0.3 g/m² to a surface of Sulflex 70 used as parchment paper base material have been evaluated as shown in Table 3.

Table 3

	OTR (cm ³ /m ² /day)	
Example 2.1	CMC FinnFix 300	0.34
Example 2.2	PVOH Kuraray AQ 4104	4.3
Example 2.3	PVOH Kuraray Mowiol 28/99	0.4
Example 2.4	Cationic starch Roquette HiCat 5213A	2.3
Example 2.5	Cationic Starch Perfectafilm X115	3.1
Example 2.6	Acrylic latex Rhobarr 135	0.8

[0076] From the results of Examples 2.1 to 2.6, it can be seen that excellent oxygen barrier properties can be obtained when applying a thin layer of a water-soluble polymer or a water-dispersible polymer to a surface of the parchment paper base material, due to the non-continuous coating being formed.

Example 3: Evaluation of mechanical properties of barrier paper

[0077] The mechanical properties of different barrier papers have been evaluated as shown in Table 4.

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Table 4

5		Example 3.1	Reference Example 3.1	Reference Example 3.2
J	Base paper material	Highly parchmentized paper	Highly parchmentized paper	PureBarrier 70
	Parchmentization level	High	High	Very high
10	Coating	0.3 g/m ² CMC	-	-
	Basis weight (g/m²)	70	70	70
	OTR (cm³/m²/day)	0.3	268.0	0.35
15	Dry burst strength (kPa)	327.4	331.4	298.3
15	Wet burst strength (kPa)	165.2	164.7	137.5
	Tear strength, MD (mN)	309.0	317.0	247.2
	Tear strength, CD (mN)	311.0	312.0	258.0
20	Dry load at break, MD (N/15 mm)	119.4	118.1	108.7
	Dry load at break, CD (N/15 mm)	48.4	49.7	44.8
25	Wet load at break, MD (N/15 mm)	39.9	40.4	34.4
	Wet load at break, CD (N/15 mm)	28.1	27.9	27.6
30	MD = Machine direction CD = cross direction			

[0078] From the results shown in Table 4, it becomes clear that using a parchment paper having a high parchmentization level (cf. Reference Example 3.1) enables the barrier paper to have improved mechanical properties compared to using a parchment paper having a very high parchmentization grade (PureBarrier 70, cf. Reference Example 3.2), especially concerning dry burst strength, wet burst strength and tear strength. Thus, when seeking to achieve both, excellent mechanical properties as well as high oxygen barrier properties, it is advantageous to use a parchment paper not having been excessively parchmentized and applying a thin layer of the non-continuous coating thereto (cf. Example 3.1).

Example 4: Evaluation of pressure used when applying the non-continuous coating

[0079] When applying a CMC coating to a surface of Sulflex 70 with an initial OTR value of 750 cm³/m²/day, as parchment paper base material using a 2.3% by weight CMC coating solution in a pilot scale parchmentizing apparatus $(target coating weight = 0.3 g/m^2)$ without using any pressure (i.e. using only the roll weight of the pilot scale parchmentizing apparatus of approximately 20 kg), the OTR of the obtained barrier paper is in the range of 300 to 500 cm³/m²/day. When however using a pressure of 5 bars in a laboratory size press, an OTR in the range of 1 to 3 cm³/m²/day can be obtained and when using a pressure of above 10 bars in an industrial process, an OTR in the range of 0.2 to 0.6 cm³/m²/day can be obtained. Thus, when forming the non-continuous coating using a sufficient pressure of e.g. 300 kPa or more, a barrier paper having higher oxygen barrier properties can be obtained.

Example 5: Evaluation of profile roughness parameters

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[0080] The profile roughness parameters of uncoated and coated parchment paper from Example 1.3 were measured as reported in Table 5. The non-continuous coating reduced the profile roughness parameters by values between 10 to 20%, thus improving the thickness profile of the barrier paper.

Table 5

		Machine direction		Cross direction			
		Ra	Rq	Rz	Ra	Rq	Rz
Comparative	Highly						
Example 5.1	parchmentized	3.3	4.1	19.2	3.8	4.7	22.4
	paper	3.3	4.1	19.2	3.0	4.7	22.4
	(uncoated)						
Example 5.1	Highly						
	parchmentized						
	paper +	2.9	3.6	16.9	3.1	3.9	19.4
	0.3 g/m ² CMC						
	coating						
	Roughness						
	variation after	-13%	-13%	-12%	-18%	-16%	-14%
	coating						

Claims

1. A barrier paper comprising:

a parchment paper as a base material; and

a non-continuous coating formed on a surface of the base material,

wherein the non-continuous coating is made of at least one of a water-soluble polymer and a water-dispersible polymer.

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- 2. The barrier paper according to claim 1, wherein the non-continuous coating is formed on the surface of the base material in an amount of 1.5 g/m² or less, preferably 0.1 to 1.5 g/m², more preferably 0.1 to 1.0 g/m², and even more preferably 0.1 to 0.5 g/m².
- 3. The barrier paper according to claim 1 or 2, wherein the parchment paper to be used as the base material has an oxygen transmission rate of less than 10,000 cm³/m²/day, preferably less than 5000 cm³/m²/day, more preferably less than 1000 cm³/m²/day, as measured at 23 °C and a relative humidity of 50%.
- 4. The barrier paper according to any one of claims 1 to 3, wherein the water-soluble polymer is at least one selected from carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, polyvinyl alcohol and cationic starch and the water-dispersible polymer is at least one selected from acrylic latex, styrene-butadiene latex, styrene acrylic latex, starches and biopolyesters such as polylactic acid (PLA), polyhydroxybutyrate (PHB) or polyhydroxyalkanoate (PHA).
- 50 **5.** The barrier paper according to any one of claims 1 to 4, wherein the non-continuous coating comprises 50% by weight or more of carboxymethyl cellulose, preferably 80% by weight or more of carboxymethyl cellulose.
 - **6.** The barrier paper according to claim 5, wherein the carboxymethyl cellulose has a molecular weight of between 100,000 and 750,000 g/mol, preferably between 100,000 and 400,000 g/mol.

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7. The barrier paper according to any one of claims 1 to 6, wherein the parchment paper to be used as the base material has an average Bekk smoothness of between 4.0 and 20.0 s, as measured according to the Bekk roughness determination method ISO 5627:1995.

- 8. The barrier paper according to any one of claims 1 to 7, wherein the parchment paper to be used as the base material has
 - a Ra value of less than 6 μ m, preferably between 1 and 6 μ m and more preferably between 1 and 4 μ m, a Rq value of less than 15 μ m, preferably between 2 and 15 μ m and more preferably between 2 and 10 μ m, and a Rz value of less than 35 μ m, preferably between 5 and 35 μ m and more preferably between 5 and 25 μ m, wherein the Ra, Rq and Rz values are measured according to EN ISO 4287.
- **9.** The barrier paper according to any one of claims 1 to 8, wherein the barrier paper has an oxygen transmission rate of between 0.05 and 20.0 cm³/m²/day, preferably between 0.05 and 5.0 cm³/m²/day.

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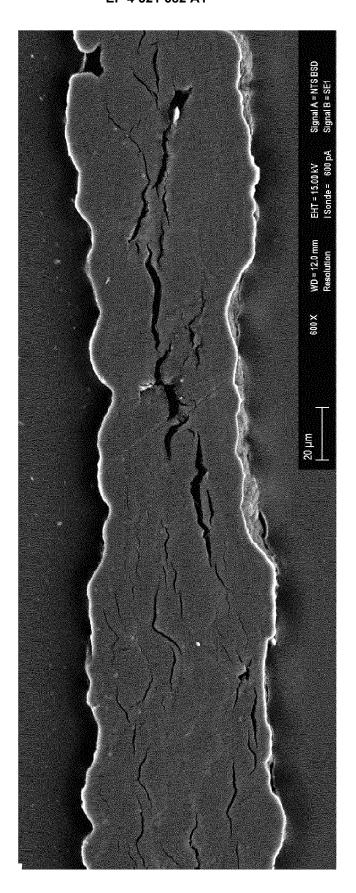
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- **10.** A method for producing a barrier paper, the method comprising: applying at least one water-soluble polymer or water-dispersible polymer onto a surface of a parchment paper as a base material to form a non-continuous coating.
- **11.** The method for producing a barrier paper according to claim 10, wherein the at least one water-soluble polymer or water-dispersible polymer is applied onto the surface of the parchment paper base material in an amount of 1.5 g/m² or less, preferably 0.1 to 1.5 g/m², more preferably 0.1 to 1.0 g/m², and even more preferably 0.1 to 0.5 g/m².
- 12. The method for producing a barrier paper according to claim 10 or 11, wherein the parchment paper that is used as the base material has an oxygen transmission rate of less than 10,000 cm³/m²/day, preferably less than 5000 cm³/m²/day, more preferably less than 1000 cm³/m²/day, as measured at 23 °C and a relative humidity of 50%.
 - **13.** The method for producing a barrier paper according to any one of claims 10 to 12, wherein the at least one water-soluble polymer or water-dispersible polymer is applied onto the surface of the parchment paper base material using a pressure of 300 kPa or more, preferably 500 kPa to 2000 kPa.
 - 14. The method for producing a barrier paper according to any one of claims 10 to 13, wherein the water-soluble polymer is at least one selected from carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, polyvinyl alcohol and cationic starch and the water-dispersible polymer is at least one selected from acrylic latex, styrene-butadiene latex, styrene acrylic latex, starches and biopolyesters such as polylactic acid (PLA), polyhydroxybutyrate (PHB) or polyhydroxyalkanoate (PHA), preferably wherein the non-continuous coating comprises 50% by weight or more of carboxymethyl cellulose, more preferably 100% by weight of carboxymethyl cellulose.
- 15. A packaging material for oxygen sensitive products comprising the barrier paper according to any one of claims 1 to 9.



FIG

DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document with indication, where appropriate, of relevant passages



Category

EUROPEAN SEARCH REPORT

Application Number

EP 22 30 6201

CLASSIFICATION OF THE APPLICATION (IPC)

Relevant

to claim

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3.82 (P04C01)	Place of Search
	Munich
	CATEGORY OF CITED DOCUMENT
EPO FORM 1503 03.82 (P04C01)	X : particularly relevant if taken alone Y : particularly relevant if combined with an document of the same category A : technological background O : non-written disclosure P : intermediate document

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x	WO 2016/081903 A1 (VAL: [US]; GEORGIA PACIFIC (26 May 2016 (2016-05-26 * paragraphs [0061], [0105], [0111]; figure	GYPSUM LLC [US]) 6) [0073], [0075],	1-15	INV. D21H19/20 A47J36/02 D21H27/06 A21B3/15	
x	EP 2 984 933 A1 (COFRES FRISCHHALTEPRODUKTE [DI 17 February 2016 (2016- * paragraph [0022]; cla example 1A *	E]) -02-17)	1-15		
x	WO 2020/209781 A1 (FERI 15 October 2020 (2020-: * page 4, line 4 - line * claims 1-20 *	10-15)	1-15		
				TECHNICAL FIELDS SEARCHED (IP	
				D21H	
				A47J F24C	
				A21B	
	The present search report has been o	drawn up for all claims Date of completion of the search		Examiner	
<u> </u>	Munich	23 January 2023	Pon	nsaud, Philipp	e
X:pa Y:pa do A:teo	CATEGORY OF CITED DOCUMENTS Inticularly relevant if taken alone riticularly relevant if combined with another cument of the same category chnological background	T : theory or princip E : earlier patent de after the filing de D : document cited L : document cited	le underlying the cument, but publi te in the application for other reasons	invention ished on, or	

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 22 30 6201

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-01-2023

								25 01 2025
10		atent document d in search report		Publication date		Patent family member(s)		Publication date
	WO :	2016081903	A1	26-05-2016	CA	2968517	A1	26-05-2016
					EP	3221140	A1	27-09-2017
					US	2017341337		30-11-2017
15					WO	2016081903		26-05-2016
	EP :	 2984933	A1	17-02-2016		102014111331		11-02-2016
					DK	2984933	т3	09-12-2019
					EP	2984933	A1	17-02-2016
20					ES	2760014	т3	12-05-2020
					${f PL}$	2984933	т3	31-03-2020
					PT	2984933	T	11-12-2019
	WO :	 2020209781	A1	15-10-2020	CA	3132460	A1	15-10-2020
25					CN	113661128	A	16-11-2021
25					EP	3953269	A1	16-02-2022
					JP	2022528565	A	14-06-2022
					SE	1930122	A1	13-10-2020
					US	2022185558	A1	16-06-2022
					WO	2020209781	A1	15-10-2020
35								
40								
45								
50								
55	FORM P0459							

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 3819426 A1 [0004]
- WO 2018197676 A1 [0007]

• WO 2021089778 A1 [0012]