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(54) **STRETCHABLE HIGH-DENSITY PAPER**

(57) A paper having:
- a density measured according to ISO 534:2011 above 1000 kg/m³;
- a strain at break measured according to ISO 1924-3:2005 in the machine direction above 3%;

- a basis weight measured according to ISO 536:2012 below 100 g/m², such as below 70 g/m²; and
- a Bendtsen surface roughness on at least one side below 150 ml/min when measured according to ISO 8791-2:2013.

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Description**TECHNICAL FIELD**

5 **[0001]** The present disclosure relates to a paper substrate to be used in a multi-layered material for packing of oxygen-sensitive goods, such as foods.

BACKGROUND

10 **[0002]** Paperboard-based packaging laminates for liquid food packaging typically include an aluminum foil to render the packaging container gas-tight, in particular oxygen tight.

[0003] To facilitate recycling and reduce the carbon footprint, it would be beneficial to find an alternative to the aluminum foil.

15 **[0004]** WO 2011/003565 discloses a packaging laminate in which the aluminum foil is replaced with a paper or cellulose-based material (a "substrate") that is precoated and then covered by a metal vapor deposited layer (i.e. metalized). It is stated that the basis weight (grammage) of the substrate preferably is from 20 to 100 g/m².

[0005] A later patent application, WO 2017/089508, discloses further details about such a substrate, namely that it is a compact-surface barrier paper having a density of 800 kg/m³ or higher, a surface roughness value below 450 ml/min (Bendtsen, ISO 8791-2), a thickness of 60 μm or lower and a grammage of 60 g/m² or lower. A specific example of the
20 compact-surface barrier paper is "Super Perga WS" (Nordic Paper) having a grammage of 32 g/m² and a surface roughness value of about 200 ml/min.

SUMMARY

25 **[0006]** An objective of the present disclosure is to provide a new cellulose-based substrate that improves the barrier properties of non-aluminum foil packaging. Another objective is to provide a new cellulose-based substrate that facilitates recycling of a packaging material comprising the substrate. A final, general objective is to reduce the environmental impact of packaging materials.

[0007] Accordingly, there is provided paper having:

- 30
- a density measured according to ISO 534:2011 above 1000 kg/m³;
 - a strain at break measured according to ISO 1924-3:2005 in the machine direction above 3%;
 - a basis weight measured according to ISO 536:2012 below 100 g/m², such as below 70 g/m²; and
 - a Bendtsen surface roughness on at least one side below 150 ml/min when measured according to ISO 8791-2:2013.

35 **[0008]** As shown in table 1 below, such a paper exhibits a high degree of recyclability. Further, table 2 shows that the paper improves the barrier properties of non-aluminum foil packaging applications.

[0009] Further, there is provided a method of producing a high-density paper having a density above 1000 kg/m³, a strain at break in the machine direction above 3% and a basis weight below 100 g/m², such as below 70 g/m², said
40 method comprising the steps of:

- forming a paper web;
- drying the paper web in a drying section to obtain a paper, said drying section comprising an extensible unit that compacts the paper web in the machine direction; and
- 45 - supercalendering the paper to obtain the high-density paper.

DETAILED DESCRIPTION

[0010] As a first aspect of the present disclosure there is provided a paper having:

- 50
- a density above 1000 kg/m³;
 - a strain at break in the machine direction above 3%;
 - a basis weight below 100 g/m²; and
 - a Bendtsen surface roughness on at least one side below 150 ml/min.

55 **[0011]** The density is preferably obtained by supercalendering. Accordingly, the paper of the present disclosure is preferably supercalendered. In an embodiment, the density is at least 1050 kg/m³, such as at least 1070 kg/m³. A typical upper limit for the density may be 1300 kg/m³. In the present disclosure, density is measured according to ISO 534:2011.

[0012] The strain at break in the machine direction is preferably in the range of 3.5% - 9.0%, such as 4.0% - 8.0%. The strain at break in the cross direction is preferably above 5.0%, such as 5.5%-8.5%. In the present disclosure, strain at break is measured according to ISO 1924-3:2005.

[0013] The basis weight of the paper is preferably below 70 g/m², such as 66 g/m² or lower, such as 30-66 g/m², such as 35-66 g/m². If the basis weight is too high, the paper may become too stiff to be efficiently used as a barrier substrate in some packaging materials. However, the strength and toughness of the paper may be insufficient if the basis weight is too low. In the present disclosure, basis weight is measured according to ISO 536:2012.

[0014] Cellulose fibres preferably constitute at least 90% of the dry weight of the paper.

[0015] In one embodiment, the Bendtsen surface roughness on at least one side of the paper is below 100 ml/min, such as below 70 ml/min. If the surfaces of the paper are too rough, it may be difficult to form a continuous coating thereon. In the present disclosure, Bendtsen surface roughness is measured according to ISO 8791-2:2013.

[0016] In one embodiment, at least one side, such as both sides, of the paper is coated or impregnated with a polymer. The polymer is preferably selected from PVOH, EVOH, starch and carboxymethylated cellulose (CMC). Other examples are nanocrystalline cellulose (NCC) and carboxy methyl starch (CMS). More preferably, the polymer is PVOH or EVOH.

[0017] The most preferred polymer in the group is PVOH. The degree of hydrolysis of the PVOH maybe 96%-100%, such as 97%-100%, such as 97%-99%. A PVOH having a high degree of hydrolysis is less sensitive to water and is preferred, both in production and in use. The weight average molecular weight (M_w) of the PVOH is preferably below 100,000 g/mol, such as 10,000-90,000 g/mol, such as 30,000-80,000 g/mol. Such a relatively low M_w is preferred during impregnation since it has a relatively low viscosity at a relatively high concentration. A PVOH of low M_w has a greater tendency to penetrate into the fiber web rather than staying on the surface of paper.

[0018] The viscosity of the PVOH when measured according to DIN 53015 is preferably below 20 mPa*s, such as 5-16 mPa*s, such as 6-13 mPa*s.

[0019] The degree of polymerization (DP) of the PVOH is preferably below 3000, such as 1000-2000. The DP can be determined from the viscosity-average degree of polymerization derived from the viscosity in water. In such case, viscosity is measured in a 4% aqueous solution at 20 °C and determined by Brookfield synchronized-motor rotary type viscometer.

[0020] An example of a suitable PVOH is Poval 10/98 from Kuraray, which has a viscosity of 10 mPa*s, a degree of hydrolysis of 98%, a DP of about 1400 and a M_w of about 61,000 g/mol. Another example is Poval 6/98 from Kuraray, which has a viscosity of 6 mPa*s and a degree of hydrolysis of 98%.

[0021] The PVOH or EVOH may comprise a cross-linker, such as glyoxal. The glyoxal to PVOH dry weight ratio may be between 3:100 and 12:100, preferably between 4:100 and 9:100, more preferably between 5:100 and 8:100.

[0022] In some applications it may be beneficial to select EVOH as the polymer. EVOH has high moisture resistance and excellent oxygen barrier properties. An example of an EVOH is Exceval® AQ-4104 from Kuraray, which provides for low viscosity.

[0023] As mentioned above, the polymer may also be NCC, which is a form of nano-cellulose, but not the same as microfibrillar cellulose ("MFC") or nanofibrillar cellulose ("NFC").

[0024] NCC may be defined in accordance with the draft TAPPI norm WI3021.

[0025] The term "NCC" is used for shorter particles and "rod-like" particles, having a width of 3-50 nm, and a length from 100 up towards 1000 nm, such as from 100 to 900 nm, such as from 100 to 500 nm, such as from 100 to 200 nm. The preferred dimensions of NCC for the purpose of impregnating and filling pores in a formed paper, meaning that the majority of the NCC particles in the composition should have this dimension, may be a length of 100-500 nm, such as 100-200 nm and a width of 3-50 nm.

[0026] In an embodiment, the paper is formed from at least 50% by dry weight chemical pulp, such as at least 75% by dry weight chemical pulp, such as at least 85% by dry weight chemical pulp, such as at least 95% by dry weight chemical pulp. The chemical pulp is preferably kraft pulp, but it may also be sulfite pulp (i.e. pulp obtained by the sulfite pulping process). Accordingly, the paper may be a kraft paper.

[0027] In an embodiment, 20-65 % by dry weight, such as 30-60 % by dry weight, of the pulp used to form the paper is hardwood pulp. In an alternative or complementary embodiment, 35-80 % by dry weight, such as 40-70 % by dry weight, of the pulp used to form the paper is softwood pulp. A benefit of including hardwood pulp is that it collapses relatively easy during refining, while it still allows for efficient dewatering in the wire section of the paper machine. A benefit of including softwood pulp is improved runnability in the paper machine and beneficial strength/toughness properties in the resulting paper. The latter properties may be improved by subjecting the softwood pulp to high consistency (HC) refining. HC refining may also increase strain at break values. HC refining means refining at a consistency of 20%-40%, preferably 25%-38%.

[0028] In an embodiment, the paper has a top ply and a bottom ply. In such a construction, the properties of the top ply may be tailored for receiving another barrier layer, while the bottom ply properties are tailored for strength/toughness. Alternatively, the top ply may be tailored for printing, while the bottom ply is coated with (a) further layer(s).

[0029] In an embodiment, the top ply is formed from at least 50% by dry weight hardwood pulp, such as at least 65% by dry weight hardwood pulp, such as at least 75% by dry weight hardwood pulp. Hardwood pulp may provide an

improved surface for printing or another barrier layer.

[0030] In an embodiment, the bottom ply is formed from at least 50% by dry weight softwood pulp, such as at least 65% by dry weight softwood pulp, such as at least 75% by dry weight softwood pulp. As mentioned above, softwood is associated with better runnability in the paper machine and provides beneficial strength/toughness properties in the resulting paper product.

[0031] In one embodiment, the bottom ply side is impregnated with a higher amount of polymer than the top ply.

[0032] Preferably, the beneficial barrier and recycling properties are obtained without sacrificing strength, such as tensile strength.

[0033] The tensile index measured in the MD of the paper according to ISO 1924-3:2005 is preferably above 90 Nm/g, such as 90-150 Nm/g. The tensile index measured in the CD according to ISO 1924-3:2005 is preferably above 50 Nm/g, such as 55-90 Nm/g, such as 60-90 Nm/g.

[0034] Preferably, density of the paper is obtained without any substantial addition of inorganic filler to the furnish. Silica or bentonite used as retention agent, typically in an amount of less than 1 kg per tonne dry pulp, is not considered to be inorganic filler. Accordingly, the ash content measured according to ISO 2144:2015 of the paper is preferably less than 5% by dry weight, such as less than 3% by dry weight, such as less than 1% by dry weight.

[0035] The paper of the present disclosure may be obtained without extensive low consistency (LC) refining, which improves the speed of the paper-making process (and reduces its energy consumption) and facilitates recycling. Such a comparatively limited refining can be reflected by the drainability measured after repulping. In an embodiment, the paper exhibits a Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of 30-50, such as 33-45, after repulping according to ISO 5263-1:2004. Another drainability value is Canadian Standard Freeness (CSF). In an embodiment, the paper exhibits a CSF measured according to ISO 5267-2:2001 of at least 200 ml, such as 200-450 ml, such as 200-350 ml, after repulping according to the Valmet repulping method carried out in a Valmet repulper of the type HD400. The Valmet repulping method is described below in the Examples section.

[0036] As a second aspect of the present disclosure, there is provided a method of producing a high-density paper having a density above 1000 kg/m³, a strain at break in the machine direction above 3% and a basis weight below 100 g/m², such as below 70 g/m², said method comprising the steps of:

- forming a paper web;
- drying the paper web in a drying section to obtain a paper, said drying section comprising an extensible unit that compacts the paper web in the machine direction; and
- supercalendering the paper to obtain the high-density paper.

[0037] In an alternative configuration of the second aspect, no extensible unit is employed. Instead, the strain at break value is obtained by negative draws in the drying section.

[0038] Preferably, the paper web is subjected to drying in the drying section upstream and downstream the extensible unit. The moisture content of the web in the extensible unit is preferably in the range of 25%-40%, such as 30%-40%, such as 30%-38%.

[0039] The extensible unit is preferably an Expanda unit or a Clupak unit. Such units are known to the skilled person.

[0040] In one embodiment, the method further comprises the step of coating or impregnating at least one side, such as both sides, of the paper with a composition comprising a polymer, which coating or impregnating step is carried out between the drying step and the supercalendering step.

[0041] Suitable examples of the polymer are described above in connection with the first aspect.

[0042] In one embodiment, the impregnating step comprises adding an aqueous composition comprising the polymer to one or both sides of the paper. The viscosity measured at 60°C of the aqueous composition may be 55-90 mPa·s. Such a relatively low viscosity facilitates penetration of the polymer into the fiber web. The concentration of the polymer in the aqueous composition is preferably 7.0%-13.0% (w/v), such as 8.0%-12.0% (w/v).

[0043] The 60°C viscosity measurement is preferably carried out using a Brookfield rotational viscometer equipped with spindle no.3 at 100 rpm.

[0044] In one embodiment, the polymer is PVOH or EVOH. In such an embodiment, the aqueous composition may further comprise a crosslinker, such as a glyoxal crosslinker. The dry weight ratio of PVOH or EVOH to glyoxal crosslinker in the aqueous composition may be from 100:3 to 100:8, such as from 100:4 to 100:7.

[0045] The aqueous composition may further comprise inorganic particles, preferably in a low amount.

[0046] To facilitate the densification and possibly also the impregnation, the impregnated paper entering the supercalendering step preferably has a relatively high moisture content, such as 11.0%-20.0%. The moisture content may for example be 12.0%-19.0%, such as 13.5%-18.0%.

[0047] In one embodiment, the impregnated paper is dried after the impregnating step to a moisture content below 11%, such as below 10%, such as below 9%. Then, it is re-moisturized prior to the supercalendering step, e.g. to a moisture content in the range of 11.0%-20.0%, 12.0%-19.5% or 13.5%-18.0%.

[0048] The impregnating step is preferably carried out by means of a size press or a film press. A film press is the most preferred equipment. The film press may be an OptiSizer Film (Valmet) or a SpeedSizer (Voith).

[0049] The number of nips of the supercalendering step may be 7-19, preferably 11-17. The surface temperature of the thermo rolls of the supercalendering step may be 120-160 °C.

[0050] The total nip impulse of the supercalendering step may be at least 600 kPa*s.

[0051] In an embodiment of the second aspect, the head box consistency or, in case of a multiply paper, the head box consistencies is/are in the range of 0.06%-0.60%, such as 0.10%-0.40%, such as 0.10%-0.30%. Such relatively low consistencies facilitate the production of a paper of low porosity, which indirectly means a high density.

[0052] In one embodiment, the paper web of the second aspect is formed from at least 50% by dry weight chemical pulp, such as at least 75% by dry weight chemical pulp, such as at least 85% by dry weight chemical pulp, such as at least 95% by dry weight chemical pulp. The chemical pulp is preferably kraft pulp, but may also be sulfite pulp.

[0053] In one embodiment, the paper web of the second aspect is formed from 20-65 % by dry weight hardwood pulp, such as 30-60 % by dry weight hardwood pulp and/or 35-80 % by dry weight softwood pulp, such as 40-70 % by dry weight softwood pulp.

[0054] When softwood pulp is used, it may have been subjected to high consistency (HC) refining, i.e. refining at a consistency of 20%-40%, such as 25%-38%. The specific energy of the HC refining step maybe at least 100 kWh/tonne, such as at least 150 kWh/tonne, such as 150-300 kWh/tonne. The "tonne" of the unit means tonne of dry fiber.

[0055] Effects of the selection pulp(s) are described above in connection to the first aspect.

[0056] In one embodiment, the paper of the second aspect has a first ply and a second ply. A first wire may be used to form a first web that becomes the first ply (top ply) and a second wire may be used to form a second web that becomes the second ply (bottom ply), which first and second web are couched together.

[0057] The first web may be formed from a first furnish comprising at least 50% by dry weight hardwood pulp, such as at least 65% by dry weight hardwood pulp, such as at least 75% by dry weight hardwood pulp. The head box consistency of the first furnish maybe 0.12%-0.60%, such as 0.18%-0.35%.

[0058] The Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of the first furnish in the head box may be 33-50, such as 40-50. Such a SR number may facilitate a sufficiently high density without causing dewatering and/or recycling problems and may be obtained by adjusting the degree of low consistency (LC) refining.

[0059] The second web may be formed from a second furnish comprising at least 50% by dry weight softwood pulp, such as at least 65% by dry weight softwood pulp, such as at least 75% by dry weight softwood pulp. This softwood pulp preferably has been subjected to high consistency (HC) refining (suitable specific energies are discussed above). The head box consistency of the second furnish maybe 0.06%-0.40%, such as 0.10%-0.25%.

[0060] In one embodiment, the head box consistency of the second furnish is lower than the head box consistency of the first furnish.

[0061] The Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of the second furnish in the head box may be 23-35. Such a SR number may facilitate sufficiently high density without causing dewatering and/or recycling problems and may be obtained by adjusting the degree of low consistency (LC) refining.

[0062] Preferably, the furnishes comprises less than less than 2% by weight inorganic filler, such as less than 1% by dry weight inorganic filler, such as substantially no inorganic filler.

[0063] In one embodiment, the second ply side is impregnated with a higher amount of polymer than the first ply.

[0064] Otherwise, the embodiments of the first aspect discussed above apply to the second aspect *mutatis mutandis*.

[0065] As demonstrated in the Examples section below, the paper of the first aspect is an excellent substrate for coating, in particular an oxygen-barrier coating. As a third aspect of the present disclosure, there is thus provided a coated paper comprising a paper according to the first aspect, wherein a surface of the paper is provided with a barrier coating, e.g. comprising polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH), a starch or starch derivative, a nano or micro-fibrillar cellulose, polyvinylidene chloride (PVDC) or a polyamide. A preferred barrier coating comprises PVOH and/or EVOH, e.g. in an amount of 1-3 g/m².

[0066] In one embodiment, the coated paper of the third aspect comprises several barrier layers, e.g. including one water vapor barrier layer.

[0067] The coated paper of the third aspect may be used for packaging oxygen-sensitive products, such as dry and/or fatty foods. Examples of fatty foods are cheese, butter and spreads. Such packaging may be flow-wrap packaging or form, fill, seal (FFS) packaging, e.g. in bags. It may also be packaging in a jar, tray, lidded spread container, collapsible tube, clam-shell package, sleeve, envelope or wrapper. Another application is use as a packaging window. In these applications, the packaging material typically undergoes folding or a similar type of stress (e.g. creasing, stretching), which make the packaging material based on the paper of the present disclosure particularly suitable.

[0068] As a fourth aspect of the present disclosure, there is provided a use of a multi-layered material for packaging of a food product or another oxygen-sensitive product, wherein one layer of the multilayered material is a paper according to the first aspect, provided that the food product is not a liquid, semi-liquid or viscous food product. In the context of the present disclosure, "liquid food" includes water.

[0069] Applications of the fourth aspect are discussed above in connection with the third aspect.

[0070] The multi-layered material of the fourth aspect may comprise a coated paper according to the third aspect.

EXAMPLES

EXAMPLE 1 (Inventive)

1A: Paper substrate production

[0071] Two pulps were provided: i) an ECF-bleached kraft pulp from softwood (i.e. a mixture of pine and spruce); and ii) an ECF-bleached kraft pulp from hardwood (i.e. birch).

[0072] The softwood pulp was refined using high-consistency (HC) refiners at a specific energy of 200 kWh/tonne. The HC-refined pulp was then mixed in a mixing chest with a broke pulp comprising a blend of bleached softwood and hardwood pulps (the majority of the broke was obtained from the same paper production). The share of broke in this softwood-based mixture was 10%. The softwood-based mixture was then refined by low-consistency (LC) refining at a specific energy of 80-85 kWh/tonne. This LC refining resulted in a Schopper-Riegler ($^{\circ}\text{SR}$) according to ISO 5267-1:1999 of $\sim 26^{\circ}\text{SR}$.

[0073] The hardwood pulp was separately mixed with the same type of broke and then refined by low consistency refining using a specific energy of 90 kWh/tonne. The share of broke in hardwood-based mixture was 20%. The LC-refined hardwood-based mixture obtained a Schopper-Riegler ($^{\circ}\text{SR}$) value of $\sim 44^{\circ}\text{SR}$.

[0074] To each of the two fiber streams, papermaking chemicals were added (4 kg/tonne of cationic starch, 0.2 kg/tonne of silica, 1.5 kg/tonne of rosin size and 2.2 kg/tonne of alum). The softwood-based mixture was pumped to a bottom ply head box of a two-ply fourdrinier machine, while the hardwood-based mixture was pumped to the top ply head box of the same fourdrinier machine. The dry mass flow through each of the head boxes was similar and adjusted to reach a total grammage (prior to coating) of $\sim 62 \text{ g/m}^2$ divided between the bottom ply ($\sim 32 \text{ g/m}^2$) and the top ply ($\sim 30 \text{ g/m}^2$). The vertical slice lip was 33 mm for the bottom ply head box and 18.5 mm for the top ply head box, which reflect relatively low head box consistencies (about 0.14% for the bottom ply and about 0.21% for the top ply). The wire speed was 608 m/min. In a paper machine specifically adapted for this product, the wire speed can be considerably higher.

[0075] The two plies formed on the fourdrinier machine were couched together at a dryness of $\sim 10\%$ and further dewatered using vacuum foils boxes to $\sim 20\%$ dryness before being subjected to wet pressing in a press section having two single felted press nips, wherein the first press had the felt on the top side and the second press had the felt on the bottom side.

[0076] After wet pressing, the web was dried in a pre-drying section to a dryness level of $\sim 65\%$ before entering an extensible unit. The extensible unit, which was a double-roll compactor type usually referred to as "Expanda" was operated in such a way that the ingoing web speed was $\sim 638 \text{ m/min}$ and the outgoing web speed $\sim 581 \text{ m/min}$. Consequently, the paper web was compacted in the machine direction (the paper web became about 9% "shorter"), which increased the strain at break value ("stretchability") of the final paper. The drive groups after the extensible unit were operated at a somewhat increasing speed resulting in a reduction of the MD strain at break value. Directly after the extensible unit the paper web was dried in an after-drying section with conventional steam-heated cylinders to form a paper substrate having a moisture content of $\sim 6\%$.

1B: Impregnation

[0077] The paper substrate from 1A was off-line impregnated with an aqueous polyvinyl alcohol (PVOH) composition from both sides in a conventional film press. The type of PVOH was Poval 10/98 (Kuraray) and its concentration in the composition was 10% (in another trial, the concentration was instead 8%, which also worked). The composition further comprised glyoxal (Cartabond TSI) in an amount of 6 wt.% compared to the amount of PVOH. The glyoxal acted as a cross-linker. The viscosity of the composition was $74 \text{ mPa}\cdot\text{s}$ (measured at 60°C). The applied amount of PVOH was 1 g/m^2 on the top side and 2 g/m^2 on the reverse/bottom side. The reason for using a higher amount of PVOH for the reverse/bottom side was that the pulp used for forming the bottom ply had a lower SR number (and hence that the reverse/bottom side had a less dense surface compared to the top side). The PVOH-impregnated paper substrate was dried using hot air to a moisture content of about 8%.

1C: Supercalendering

[0078] The impregnated paper substrate from 1B was re-moisturized to 15%. The re-moisturized paper was fed to a pilot off-line multi-nip calender also referred to as a supercalender (the number of nips was 12). Supercalendering was carried out using a surface temperature of 140°C on the thermo rolls, which could be obtained by means of outside

induction heaters, to obtain a high-density paper. The line load in each nip was 360 kN/m (simulating 400 kN/m in full-scale production) and the speed was 360 m/min (simulating 400 m/min in full-scale production). The total supercalendering nip impulse was $\sim 720 \text{ kPa}\cdot\text{s}$ [$\# \text{nips} \times \text{line load} / \text{web speed}$]. The heating from the thermo rolls dried the high-density paper. The moisture content at wind-up was $\sim 5.5\%$. Properties of the high-density paper are presented in table 1 below.

EXAMPLE 2 (Comparative)

[0079] This comparative example is not published prior art but forms part of a co-pending patent application.

2A: Paper substrate production

[0080] Two pulps were provided: i) an ECF-bleached kraft pulp from softwood (i.e. a mixture of pine and spruce); and ii) an ECF-bleached kraft pulp from hardwood (i.e. birch).

[0081] The softwood pulp was refined using high-consistency (HC) refiners at a specific energy of 225 kWh/tonne. The HC-refined pulp was then mixed in a mixing chest with a broke pulp comprising a blend of bleached softwood and hardwood pulps (the majority of the broke was obtained from the same paper production). The share of broke in this softwood-based mixture was 30%. The softwood-based mixture was then refined by low-consistency (LC) refining at a specific energy of 75 kWh/tonne. This LC refining resulted in a Schopper-Riegler ($^{\circ}\text{SR}$) according to ISO 5267-1:1999 of $\sim 30^{\circ}\text{SR}$.

[0082] The hardwood pulp was separately mixed with the same type of broke and then refined by low consistency refining using a specific energy of 85 kWh/tonne. The share of broke in hardwood-based mixture was 20%. The LC-refined hardwood-based mixture obtained a Schopper-Riegler ($^{\circ}\text{SR}$) value of $\sim 38^{\circ}\text{SR}$.

[0083] To each of the two fiber streams, papermaking chemicals were added (4 kg/tonne of cationic starch, 0.2 kg/tonne of silica and 0.4 kg/tonne of AKD). The softwood-based mixture was pumped to a bottom ply head box of a two-ply fourdrinier machine, while the hardwood-based mixture was pumped to the top ply head box of the same fourdrinier machine. The dry mass flow through each of the head boxes was the same and adjusted to reach a total grammage of 60 g/m² prior coating (i.e. 30 g/m² per ply). The vertical slice lip was 34 mm for the bottom ply head box and 16 mm for the top ply head box, which reflect relatively low head box consistencies (about 0.12% for the bottom ply and about 0.25% for the top ply). The wire speed was 600 m/min. In a paper machine specifically adapted for this product, the wire speed can be considerably higher.

[0084] The two plies formed on the fourdrinier machine were couched together at a dryness of $\sim 10\%$ and further dewatered using vacuum foils boxes to $\sim 20\%$ dryness before being subjected to wet pressing in a press section having two single felted press nips, wherein the first press had the felt on the top side and the second press had the felt on the bottom side.

[0085] After wet pressing, the web was dried in a conventional multi-cylinder dryer to form a paper substrate having a moisture content of $\sim 5\%$. Prior winding up, the paper substrate was calendered in a soft nip at a line load of 20 kN/m.

2B: Impregnation

[0086] The paper substrate from 2A was off-line impregnated with an aqueous polyvinyl alcohol (PVOH) composition from both sides in a conventional film press. The type of PVOH was Poval 10/98 (Kuraray) and its concentration in the composition was 10% (in another trial, the concentration was instead 8%, which also worked). The composition further comprised glyoxal (Cartabond TSI) in an amount of 6 wt.% compared to the amount of PVOH. The glyoxal acted as a cross-linker. The viscosity of the composition was 74 mPa $\cdot$ s (measured at 60 $^{\circ}\text{C}$). The applied amount of PVOH was 1 g/m² on the top side and 2 g/m² on the reverse/bottom side. The reason for using a higher amount of PVOH for the reverse/bottom side was that the pulp used for forming the bottom ply had a lower SR number (and hence that the reverse/bottom side had a less dense surface compared to the top side). The PVOH-impregnated paper substrate was dried using hot air to a moisture content of about 8%.

2C: Supercalendering

[0087] The impregnated paper substrate from 2B was re-moisturized to 15%. The re-moisturized paper was fed to an off-line multi-nip calender also referred to as a supercalender (the number of nips was 12). Supercalendering was carried using a surface temperature of 140 $^{\circ}\text{C}$ on the thermo rolls, which could be obtained by means of outside induction heaters, to obtain a high-density paper. The line load in each nip was 405 kN/m (simulating 450 m/min in full-scale production). The total supercalendering nip impulse was $\sim 800 \text{ kPa}\cdot\text{s}$ [$\# \text{nips} \times \text{line load} / \text{web speed}$]. The heating from the thermo rolls dried the high-density paper. The moisture content at wind-up was 8%. Properties of the high-density paper are presented in table 1 below.

EXAMPLE 3 (Comparative)

[0088] This comparative example is not published prior art, but it is disclosed in a co-pending patent application.

[0089] A single-ply paper made for a different purpose, but having similar properties to the papers of examples 1 and 2 was provided. The single-ply paper was made from a mixture of pulps from Kraft softwood pulp and Kraft hardwood pulp and a small amount of CTMP pulp, to a mixture ratio of 45:45:10. The single-ply paper was impregnated with polyvinyl alcohol from the top side and subsequently calendered to a density of about 1050 kg/m³ with a resulting grammage of 45 g/m². The top-side surface had a surface roughness of about 25 ml/min Bendtsen.

RESULTS

[0090] Paper properties of the materials produced in examples 1-3 are presented in table 1 below. Table 1 also includes paper properties of Super Perga WS, which is a commercial greaseproof paper from Nordic Paper. Super Perga WS was used as a paper substrate in WO 2017/089508.

[0091] For table 1, the following applies:

Grammage (i.e. basis weight) was measured according to ISO 536:2012 and has the unit g/m². Density was measured according to ISO 534:2011 and has the unit kg/m³. Roughness means Bendtsen roughness and was measured according to ISO 8791-2:2013 and has the unit ml/min. Tensile index was measured in the MD and the CD according to ISO 1924-3:2005 and has the unit Nm/g. °SR was measured according to ISO 5267-1:1999 after repulping according to ISO 5263-1:2004. Canadian Standard Freeness ("CSF") has the unit ml and was measured according to ISO 5267-2:2001 after repulping according to a Valmet repulping method using a Valmet repulper of type HD400. The Valmet repulping method is described in further detail below. Recyclability was measured according to PTS Method PTS-RH 021/97. Oxygen Transmission Rate ("OTR") has the unit cm³/m²/24h, 0.2 atm (21%) oxygen. It was measured according to ASTM F1927-14 after lamination with 20 g/m² LDPE on the top side of the paper.

Table 1.

	Ref. Super Perga WS	Ref. Ex. 2C	Ref. Ex. 3	Inventive Ex. 1C
Grammage	32§	63	45	65
Density	865§	1100	1050	1082
Strain at brake (MD)	1.4%	2.3%	1.5%	5.2%
Strain at brake (CD)	2.1%	6.4%	4.7%	6.9%
Roughness	290	50	25	25
Tensile index (MD/CD)	94/41	133/70	112/44	103/68
°SR	74***			
CSF	53*	277		
PTS recyclability (%)			84.5	99.4
OTR 23°C, 50%RH, 0.2 atm O ₂	42*	6.1 (4.5 ^a)	9.2	10.5
OTR 23°C, 80%RH, 0.2 atm O ₂		13.9 (15.3 ^a)	12.6	20
§ According to the supplier's data sheet ^a Tested on a high-density paper that had been impregnated with 1.5 g/m ² PVOH on each side * The grammage was 38 g/m ² instead of 32 g/m ² ** After supercalendering according to example 1C (no PVOH-impregnation) *** The grammage was 45 g/m ² instead of 32 g/m ²				

[0092] Valmet repulping method: Repulping was carried out in a Valmet repulper that is designed for stock preparation, i.e. fiber disintegration, of the type HD400. Agitation was done with an impeller with three radial and serrated blades with the dimensions 30 by 40 mm rotating at a speed of 3000 rpm. The material to be repulped was cut in 90 by 90 mm pieces. 0.5 kg of air-dried pieces was mixed with 10 liters of water, i.e. to a consistency of 5%, and repulped at 2.5 minutes at a temperature of 57 °C. Then 5 liters of water was added, providing a consistency of 3.3 %, and further repulping at another 17.5 minutes at a temperature of 57 °C was performed. Total repulping time was thus 20 minutes.

EXAMPLE 4

[0093] High-density papers prepared according to Examples 1-3 were dispersion-coated twice with intermediate and subsequent drying operations to provide a 3 g/m² PVOH coating on the high-density papers. The PVOH-coated high-density papers were then metalized to an optical density of about 2. A laminated packaging material was then produced according to the following layer structure:

/ LDPE 12 g/m² / paperboard 80 mN / LDPE 15 or 20 g/m² / paper substrate +PVOH+met / Adhesive EAA copolymer 6 g/m² + 19 or 29 g/m² blend LDPE + mLLDPE /.

[0094] Packages were produced in a Tetra Pak® E3/CompactFlex filling machine. This type of filling machine has the capacity to fill portion packages at a speed of 9000 packages/hour and a flexibility that allows for quick change between different package formats. Packages were in the format of Tetra Brik® with a volume of 200 ml.

[0095] No major problems regarding packaging integrity (i.e. package tightness vs the surrounding environment) and sealing performance were identified during the trials, which therefore were considered successful.

[0096] Oxygen transmission rate of flat packaging material was measured using a coulometric detector according to the standard ASTM F1927-14. The moisture level was either 50% or 80% relative humidity. The unit is cm³/m²/24h, with the option of using 0.2 atm or 1 atm of oxygen pressure. To be able to compare OTR values measured at 1 atm with OTR values measured at 0.2 atm, the former values can be multiplied with 0.2.

[0097] The Oxygen transmission rate of packages (filled, emptied and dried) was measured according to ASTM F1307-14, at 0.2 atm (surrounding air containing 21 % oxygen). The unit is cm³/package/24h.

[0098] The package is mounted on a special holder; inside the package nitrogen is purged; the outside of the package is exposed to the environment surrounding the instrument. When oxygen permeates through the package into the nitrogen carrier gas, it is transported to the coulometric sensor. The sensor reads how much oxygen that leaks into the nitrogen gas inside the package.

[0099] The 32 g/m² greaseproof paper from Nordic Paper (Super Perga WS), was used to prepare further comparative examples (in the form of laminated packaging materials). Further details of these laminates are provided in table 2 below.

[0100] Properties of the laminated packaging materials are presented in table 2 below.

Table 2. The OTR values are measured at 23 °C and 50% RH.

Paper substrate (MD strain-at-break)	Super Perga WS (ref.) (1.4%)	Super Perga WS (ref.) (1.4%)	Ex. 2C (ref.) (2.3%)	Ex. 3 (ref.) (1.8%)	Ex. 1C (inventive) (5.7%)
Principal laminate structure: /LDPE/ paperboard /LDPE/ paper substrate +PVOH+met/ inside PE polymers/	260 mN paperboard; 1 g/m ² PVOH on the paper substrate; Met. to OD 2.5 *	80 mN paperboard; 1.5 g/m ² PVOH on the paper substrate; Met. to OD ~2.3 **	80 mN paperboard; 3 g/m ² PVOH on the paper substrate; Met. to OD ~2 **	80 mN paperboard; 3 g/m ² PVOH on the paper substrate; Met. to OD ~2 ***	80 mN paperboard; 3 g/m ² PVOH on the paper substrate; Met. to OD ~2.2 ****
Package format	Tetra Brik® Aseptic1000B	Tetra Brik® Aseptic200S	Tetra Brik® Aseptic200S	Tetra Brik® Aseptic200S	Tetra Brik® Aseptic200S
Package volume	1000 ml	200 ml	200 ml	200 ml	200 ml
Laminate area per package	0.077	0.030	0.030	0.030	0.030
Flat laminate OTR 1 atm	0.4 measured	1.3 measured			
Flat laminate OTR 0.2 atm	0.080 calculated	0.26 calculated	0.165 measured	0.240 measured	0.28 measured
Calculation of loss:					
Calculated, theoretical OTR per package, 0.2 atm	0.0062	0.0078	0.0050	0.0072	0.008
Measured OTR per package 0.2 atm	0.06	0.075	0.029	0.030	0.018

(continued)

5	Paper substrate (MD strain-at-break)	SuperPerga WS (ref.) (1.4%)	Super Perga WS (ref.) (1.4%)	Ex. 2C (ref.) (2.3%)	Ex. 3 (ref.) (1.8%)	Ex. 1C (inventive) (5.7%)
	Loss factor measured/ theoretical	9.7	9.6	5.8	4.2	2.2
10	* / LDPE 12 g/m ² / paperboard 260 mN / LDPE 20 g/m ² / paper substrate+ PVOH+met / LDPE 20 g/m ² / LDPE+mLLDPE 20 g/m ² /					
	** / LDPE 12 g/m ² / paperboard 80 mN / LDPE 20 g/m ² / paper substrate+ PVOH+met / LDPE 40 g/m ² /					
15	*** / LDPE 12 g/m ² / paperboard 80 mN / LDPE 20 g/m ² / paper substrate+ PVOH+met / Adhesive EAA copolymer 6 g/m ² + 29 g/m ² blend LDPE + mLLDPE /					
	**** / LDPE 12 g/m ² / paperboard 80 mN / LDPE 15 g/m ² / paper substrate+ PVOH+met / Adhesive EAA copolymer 6 g/m ² + 19 g/m ² blend LDPE + mLLDPE /					

[0101] Although there is a difference between laminates in table 2 in the amount of thermoplastic polyethylene-based polymers of the layers facing the inside of the package, this has no or very little practical influence on the comparison of OTR values. This is because polyethylene is a poor oxygen barrier in relation to the coated and metalized high-density papers. Typical oxygen transmission rates for LDPE of 40 μ m thickness is 600-900 cm³/m²/24h/0.2 atm at 23 °C.

[0102] As shown in table 2, the inventive high-density paper (Ex. 1C) not only provides the laminate material of the lowest measured OTR after forming packages, but it also provides the laminate of the lowest loss factor, which demonstrates a superior robustness in packaging applications. A low OTR value for a flat material is of almost no value in packaging application unless the OTR value remains low after folding to form three-dimensional packages.

Claims

1. A paper having:

- a density measured according to ISO 534:2011 above 1000 kg/m³;
- a strain at break measured according to ISO 1924-3:2005 in the machine direction above 3%;
- a basis weight measured according to ISO 536:2012 below 100 g/m², such as below 70 g/m²; and
- a Bendtsen surface roughness on at least one side below 150 ml/min when measured according to ISO 8791-2:2013.

2. The paper of claim 1, wherein the strain at break in the machine direction is in the range of 3.5% - 9.0%, such as 4.0% - 8.0%.

3. The paper of claim 1 or 2, wherein the strain at break measured according to ISO 1924-3:2005 in the cross direction is above 5.0%.

4. The paper of any one of the preceding claims, wherein the basis weight of the paper is 66 g/m² or lower, such as 30-66 g/m², such as 35-66 g/m².

5. The paper of any one of the preceding claims, wherein cellulose fibres constitute at least 90% of the dry weight of the paper.

6. The paper of any one of the preceding claims, wherein the Bendtsen surface roughness on at least one side is below 100 ml/min, such as below 70 ml/min.

7. The paper of any one of the preceding claims, wherein at least one side of the paper is coated or impregnated with a polymer, such as PVOH, EVOH, starch and/or CMC.

8. The paper of any one of the preceding claims, wherein both sides of the paper is coated or impregnated with a polymer, such as PVOH, EVOH, starch and/or CMC.

9. The paper of any one of the preceding claims, which is a kraft paper.

10. A method of producing a high-density paper having a density above 1000 kg/m^3 , a strain at break in the machine direction above 3% and a basis weight below 100 g/m^2 , such as below 70 g/m^2 , said method comprising the steps of:

- forming a paper web;
- drying the paper web in a drying section to obtain a paper, said drying section comprising an extensible unit that compacts the paper web in the machine direction; and
- supercalendering the paper to obtain the high-density paper.

11. The method of claim 10, wherein the method further comprises the step coating or impregnating at least one side of the paper with a composition comprising PVOH, EVOH, starch and/or CMC, which coating or impregnating step is carried out between the drying step and the supercalendering step.

12. The method of claim 11, wherein both sides of the paper is coated or impregnated with the composition comprising PVOH, EVOH, starch and/or CMC.

13. The method of claim 10 or 11, wherein the extensible unit is an Expanda unit or a Clupak unit.

14. A coated paper comprising a paper according to any one of claims 1-9, wherein a surface of the paper is provided with a barrier coating, e.g. comprising polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH), a starch or starch derivative, a nano or micro-fibrillar cellulose, polyvinylidene chloride (PVDC) or a polyamide.

15. A use of a multi-layered material for packaging of a food product or another oxygen-sensitive product, wherein one layer of the multilayered material is a paper according to any one of claims 1-9, provided that the food product is not a liquid, semi-liquid or viscous food product.



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