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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. It is stated that the basis weight (grammage) of the substrate preferably is from 20 to 100 g/m<sup>2</sup>.
- [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/m<sup>3</sup> 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/m<sup>2</sup> or lower. A specific example of the
- 20    compact-surface barrier paper is "Super Perga WS" (Nordic Paper) having a grammage of 32 g/m<sup>2</sup> 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, the following itemized list of embodiments of the present disclosure is provided:

- 30     1. A high-density paper having a grammage measured according to ISO 536:2012 of 30-75 g/m<sup>2</sup> and a density measured according to ISO 534:2011 above 1000 kg/m<sup>3</sup> and wherein the high-density paper is impregnated on each side with 0.3-4.0 g/m<sup>2</sup>, such as 0.5-3.0 g/m<sup>2</sup>, of a polymer selected from the group consisting of polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH), carboxymethylated cellulose (CMC), nanocrystalline cellulose (NCC)
- 35     and carboxy methyl starch (CMS).
2. The high-density paper of item 1, which is formed from at least 50% by dry weight kraft pulp, such as at least 75% by dry weight kraft pulp, such as at least 85% by dry weight kraft pulp, such as at least 95% by dry weight kraft pulp.
- 40     3. The high-density paper of item 1 or 2, wherein 20-65 % by dry weight, such as 30-60 % by dry weight, of the pulp used to form the high-density paper is hardwood pulp.
4. The high-density paper of any one of the preceding items, wherein 35-80 % by dry weight, such as 40-70 % by dry weight, of the pulp used to form the high-density paper is softwood pulp, preferably softwood that has been
- 45     subjected to high consistency (HC) refining.
5. The high-density paper of any one of the preceding items having a top ply and a bottom ply.
6. The high-density paper of item 5, wherein 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.
- 50     7. The high-density paper of item 5 or 6, wherein 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.
- 55     8. The high-density paper of any one of the preceding items, wherein the grammage measured according to ISO 536:2012 is 35-65 g/m<sup>2</sup>.
9. The high-density paper of any one of the preceding items, wherein at least one side of the high-density paper

has a Bendtsen roughness measured according to SS-ISO 8791-2:2013 of 7-80 ml/min, such as 8-70 ml/min, such as 10-60 ml/min, such as 30-60 ml/min.

10. The high-density paper of any one of the preceding items having a tear index measured in the machine direction (MD) according to ISO 1924-3:2005 of at least 4.1 mNm<sup>2</sup>/g, such as at least 4.4 mNm<sup>2</sup>/g.

11. The high-density paper of any one of the preceding items having a tear index measured in the cross direction (CD) according to ISO 1924-3:2005 of at least 4.9 mNm<sup>2</sup>/g, such as at least 5.3 mNm<sup>2</sup>/g.

12. The high-density paper of any one of the preceding items having an ash content measured according to ISO 2144:2015 of the high-density paper is less than 5% by dry weight, such as less than 3% by dry weight, such as less than 1% by dry weight.

13. The high-density paper of any one of the preceding items, which has a Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of 33-50, such as 35-45, after repulping according to ISO 5263-1:2004.

14. The high-density paper of any one of the preceding items, which has a Canadian Standard Freeness (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.

15. The high-density paper of any one of the preceding items, which has a fines content measured with a L&W Fibretester+ (ABB, Lorentzen & Wettre, Sweden) of less than 40%, such as less than 34%, such as less than 32%, after repulping according to ISO 5263-1:2004, wherein fines are defined as fibrous particles shorter than 0.2 mm.

16. A high-density paper having a grammage measured according to ISO 536:2012 of 30-75 g/m<sup>2</sup> and a density measured according to ISO 534:2011 above 1000 kg/m<sup>3</sup> and wherein the high-density paper is impregnated on at least one side with a composition comprising polyvinyl alcohol (PVOH) and glyoxal.

17. The high-density paper of item 16, wherein the glyoxal to PVOH dry weight ratio in the composition is between 3:100 and 12:100, preferably between 4:100 and 9:100, more preferably between 5:100 and 8:100.

18. A method of forming a high-density paper having a grammage measured according to ISO 536:2012 of 30-75 g/m<sup>2</sup> and a density measured according to ISO 534:2011 of above 1000 kg/m<sup>3</sup>, said method comprising the steps of:

- impregnating each side of a paper substrate with 0.3-4.0 g/m<sup>2</sup>, such as 0.5-3.0 g/m<sup>2</sup>, of a polymer selected from the group consisting of polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH), carboxymethylated cellulose (CMC), nanocrystalline cellulose (NCC) and carboxy methyl starch (CMS) to obtain an impregnated substrate; and
- supercalendering the impregnated substrate to obtain the high-density paper.

19. The method of item 18, wherein the impregnating step comprises adding an aqueous composition comprising the polymer to each side of the paper substrate.

20. The method of item 19, wherein the viscosity measured at 60°C of the aqueous composition is 55-90 mPa\*s.

21. The method of item 19 or 20, wherein the concentration of the polymer in the aqueous composition is 7.0%-13.0% (w/v), such as 8.0%-12.0% (w/v).

22. The method of any one of items 19-21, wherein the polymer is PVOH and the aqueous composition further comprises a glyoxal crosslinker.

23. The method of any one of items 19-22, wherein the dry weight ratio of PVOH to glyoxal crosslinker in the aqueous composition is from 100:3 to 100:8, such as 100:4 to 100:7.

24. The method of any one of items 18-23, wherein the impregnated substrate entering the supercalendering step has a moisture content of 11.0%-20.0%, preferably 12.0%-19.0%, more preferably 13.5%-18.0%.

25. The method of item 24, wherein the impregnated substrate is dried after the impregnating step to a moisture

content below 11% and then re-moisturized prior to the supercalendering step to the moisture content of 11.0%-20.0%, preferably 12.0%-19.0%, more preferably 13.5%-18.0%.

26. The method of item 25, wherein the impregnated substrate is dried after the impregnating step to a moisture content below 10%.

27. The method of item 26, wherein the impregnated substrate is dried after the impregnating step to a moisture content below 9%.

28. The method of any one of items 18-27, wherein the impregnating step is carried out by means of a size press or a film press.

29. The method of any one of items 18-28, wherein the number of nips of the supercalendering step is 7-19, such as 11-17.

30. The method of any one of items 18-29, wherein the surface temperature of the thermo rolls of the supercalendering step is 120-160 °C.

31. The method of any one of items 18-30, wherein the total nip impulse of the supercalendering step is at least 600 kPa\*s.

32. The method of any one of items 18-31, wherein the paper substrate is formed from at least 50% by dry weight kraft pulp, such as at least 75% by dry weight kraft pulp, such as at least 85% by dry weight kraft pulp, such as at least 95% by dry weight kraft pulp.

33. The method of any one of items 18-32, wherein the paper substrate is formed from 20-65 % by dry weight hardwood pulp, such as 30-60 % by dry weight hardwood pulp.

34. The method of any one of items 18-33, wherein the paper substrate is formed from 35-80 % by dry weight softwood pulp, such as 40-70 % by dry weight softwood pulp.

35. The method of item 34, wherein the softwood pulp has been subjected to high consistency (HC) refining.

36. The method of any one of items 18-35, wherein the paper substrate has a first ply and a second ply.

37. The method of item 36, wherein a first wire is used to form a first web that becomes the top ply and a second wire is used to form a second web that becomes the second ply, which first and second web are couched together.

38. The method of item 37, wherein the first web is 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.

39. The method of item 38, wherein the Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of the first furnish is 33-45.

40. The method of any one of items 37-39, wherein the second web is 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, preferably softwood pulp that has been subjected to high consistency (HC) refining.

41. The method of item 40, wherein the Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of the second furnish is 25-35.

42. The method of any one of items 36-41, wherein the second ply is impregnated with a higher amount of polymer than the first ply.

43. The method of any one of items 18-42, wherein the density measured according to ISO 534:2011 of the high-density paper is above 1050 kg/m<sup>3</sup>.

44. A coated paper comprising a high-density paper according to any one of items 1-17, wherein a surface of the

high density paper is provided with a barrier coating 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.

45. The coated paper of item 44, wherein the barrier coating comprises PVOH in an amount of 1-3 g/m<sup>2</sup>.

46. 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 high-density paper according to any one of items 1-17, provided that the food product is not a liquid, semi-liquid or viscous food product.

47. The use of item 46, wherein the multi-layered material comprises a coated paper according to item 44 or 45.

48. The high-density paper of any one of items 1-17, which is not PECVD- or PVD-coated.

49. The method of any one of items 18-43, provided that the method is not comprising PECVD or PVD coating of the high-density paper.

50. The coated paper of item 44 or 45, which is not PECVD- or PVD-coated.

51. The use of item 46 or 47, wherein the multi-layered material is not comprising a PECVD or PVD coating.

## BRIEF DESCRIPTION OF THE DRAWINGS

### [0008]

Figure 1A is a SEM image of a surface portion of the paper substrate produced in Example 1A below.

Figure 1B is a SEM image of a surface portion of the PVOH-impregnated paper substrate produced in Example 1B below.

Figure 1C is a SEM image of a surface portion of the high-density paper produced in Example 1C below.

Figure 2 is SEM image of a cross section of the high-density paper produced in Example 1C below.

Figure 3 is a chart showing the oxygen transmission rate (ml/specimen) before and after the folding and unfolding of PVOH-coated papers described in Example 2 below.

## DETAILED DESCRIPTION

**[0009]** As a first aspect of the present disclosure, there is provided a high-density paper having a grammage measured according to ISO 536:2012 of 30-75 g/m<sup>2</sup> and a density measured according to ISO 534:2011 above 1000 kg/m<sup>3</sup>. Such a high density is preferably obtained by supercalendering. Accordingly, the high-density paper of the present disclosure is preferably supercalendered. In an embodiment, the density is at least 1050 kg/m<sup>3</sup>, such as at least 1070 kg/m<sup>3</sup>. A typical upper limit for the density may be 1300 kg/m<sup>3</sup>.

**[0010]** The high-density paper is impregnated on each side with 0.3-4.0 g/m<sup>2</sup>, such as 0.5-4.0 g/m<sup>2</sup>, such as 0.5-3.0 g/m<sup>2</sup>, of a polymer. "Impregnated" means that the polymer to a substantial degree has penetrated the fibre web. However, it does not necessarily mean that the fibre web, across its thickness direction, has been completely saturated with the polymer. Consequently, the high-density paper may comprise unfilled pores, especially in the middle. Here it is also referred to the discussion about figure 2 below. Hence, it may be determined by a SEM image of a cross section of the high-density paper that the polymer has penetrated the fiber web rather than formed a coating layer on the surface.

**[0011]** The polymer is selected from the group consisting of polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH), carboxymethylated cellulose (CMC), nanocrystalline cellulose (NCC) and carboxy methyl starch (CMS). PVOH, EVOH and CMC are preferred examples of the polymer. In one embodiment, the polymer is PVOH or EVOH.

**[0012]** To facilitate the application of the polymer, it is preferably water-soluble or water-dispersible.

**[0013]** 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.

**[0014]** 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.

**[0015]** 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.

**[0016]** 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%.

**[0017]** 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.

**[0018]** 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.

**[0019]** 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"). Whereas the term "MFC" may in general and incorrectly be used for all types of defibrillated cellulose, there more scientific view is that "MFC" should denote nano scale cellulose particle fibers or fibrils or fibril aggregates with at least one dimension of less than 100 nm. MFC may thus contain longer particles, so-called "fibrils" having a width of 10-100 nm, and a length of at least 1  $\mu$ m, such as up to 10  $\mu$ m, such as longer than 10  $\mu$ m.

**[0020]** Both MFC and NFC have an aspect ratio of 50 or above, while NCC may be defined to have an aspect ratio below 50, e.g. in accordance with the draft TAPPI norm WI3021.

**[0021]** 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.

**[0022]** In an embodiment, the high-density 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).

**[0023]** In an embodiment, 20-65 % by dry weight, such as 30-60 % by dry weight, of the pulp used to form the high-density 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 high-density 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.

**[0024]** In an embodiment, the high-density 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).

**[0025]** 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.

**[0026]** 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.

**[0027]** In one embodiment, the bottom ply side is impregnated with a higher amount of polymer than the top ply.

**[0028]** In an embodiment, the grammage measured according to ISO 536:2012 is 35-65 g/m<sup>2</sup>. A relatively low grammage may be beneficial since it may require less polymer in a packaging application, e.g. in order to make tight and durable seals when transforming the laminated material into filled and sealed, cuboid-shaped packages. In turn, the use of less polymer facilitates recycling streams of high fiber content. There are also indications that package integrity improves when the paper substrate grammage is lower. However, the strength and toughness of the paper may be insufficient if the grammage is too low.

**[0029]** In an embodiment, at least one side of the high-density paper has a Bendtsen roughness measured according

to SS-ISO 8791-2:2013 of 7-80 ml/min, such as 8-70 ml/min, such as 10-60 ml/min, such as 30-60 ml/min. Preferably, both sides of the high-density paper has a Bendtsen roughness measured according to SS-ISO 8791-2:2013 of 7-80 ml/min, such as 8-70 ml/min, such as 10-60 ml/min.

**[0030]** Preferably, the beneficial barrier and recycling properties are obtained without sacrificing strength, such as tensile strength and tear strength.

**[0031]** The tensile index measured in the MD according to ISO 1924-3:2005 is preferably above 100 Nm/g, such as 110-150 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 65-90 Nm/g.

**[0032]** In one embodiment, the tear index measured in the machine direction (MD) according to ISO 1924-3:2005 is at least 4.1 mNm<sup>2</sup>/g, such as at least 4.4 mNm<sup>2</sup>/g and/or the tear index measured in the cross direction (CD) according to ISO 1924-3:2005 of at least 4.9 mNm<sup>2</sup>/g, such as at least 5.3 mNm<sup>2</sup>/g. Typical upper limits in MD and CD may be 6.5 mNm<sup>2</sup>/g and 7.5 mNm<sup>2</sup>/g, respectively.

**[0033]** Preferably, the high density 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 high-density 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.

**[0034]** The high-density paper of the present disclosure may be obtained without extensive low consistency (LC) refining, which improves the speed of the papermaking 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 high-density paper exhibits a Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of 33-50, such as 35-45, after repulping according to ISO 5263-1:2004. Another drainability value is Canadian Standard Freeness (CSF). In an embodiment, the high-density 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.

**[0035]** A moderate degree of refining may also be reflected by a relatively low fines content. In an embodiment, the high-density paper has a fines content measured with a L&W Fibretester+ (ABB, Lorentzen & Wettre, Sweden) of less than 40%, such as less than 34%, such as less than 32%, after repulping according to ISO 5263-1:2004. "Fines" are defined as fibrous particles shorter than 0.2 mm. The L&W Fibretester+ operates according to ISO 16065-2:2014. A typical lower limit for the fines content is 15% or 20%.

**[0036]** As a configuration of the first aspect, there is provided a high-density paper having a grammage measured according to ISO 536:2012 of 30-75 g/m<sup>2</sup> and a density measured according to ISO 534:2011 above 1000 kg/m<sup>3</sup> and wherein the high-density paper is impregnated on at least one side with a composition comprising polyvinyl alcohol (PVOH) and glyoxal.

**[0037]** The embodiments of the first aspect discussed above apply to the configuration *mutatis mutandis*.

**[0038]** Accordingly, the glyoxal to PVOH dry weight ratio in the composition of the configuration may be between 3:100 and 12:100, preferably between 4:100 and 9:100, more preferably between 5:100 and 8:100.

**[0039]** In one embodiment, the high-density paper of the first aspect (and its configuration) is not PECVD- or PVD-coated. However, the high-density paper of this embodiment may be intended for PECVD or PVD coating. PECVD means plasma-enhanced chemical vapor deposition. PVD means plasma vapor deposition.

**[0040]** As a second aspect of the present disclosure, there is provided a method of forming a high-density paper having a grammage measured according to ISO 536:2012 of 30-75 g/m<sup>2</sup> and a density measured according to ISO 534:2011 of above 1000 kg/m<sup>3</sup>, said method comprising the steps of:

- impregnating each side of a paper substrate with 0.3-4.0 g/m<sup>2</sup>, such as 0.5-4.0 g/m<sup>2</sup>, such as 0.5-3.0 g/m<sup>2</sup>, of a polymer selected from the group consisting of polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH), carboxymethylated cellulose (CMC), nanocrystalline cellulose (NCC) and carboxy methyl starch (CMS) to obtain an impregnated substrate; and
- supercalendering the impregnated substrate to obtain the high-density paper.

**[0041]** In one embodiment, the impregnating step comprises adding an aqueous composition comprising the polymer to each side of the paper substrate. 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).

**[0042]** The 60°C viscosity measurement is preferably carried out using a Brookfield rotational viscometer equipped with spindle no.3 at 100 rpm.

**[0043]** In one embodiment, the polymer is PVOH or EVOH and the aqueous composition further comprises 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.

**[0044]** The aqueous composition may further comprise inorganic particles, preferably in a low amount.

**[0045]** To facilitate the densification and the impregnation, the impregnated substrate entering the supercalendering step preferably has a relatively high moisture content, such as 11.0%-20.0%. More preferably, the moisture content is 12.0%-19.0%, such as 13.5%-18.0%.

**[0046]** In one embodiment, the impregnated substrate 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%.

**[0047]** 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).

**[0048]** 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.

**[0049]** The total nip impulse of the supercalendering step may be at least 600 kPa\*s.

**[0050]** In an embodiment of the second aspect, the head box consistency or the head box consistencies in case of a multiply paper 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 means a high density.

**[0051]** In one embodiment, the paper substrate 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.

**[0052]** In one embodiment, the paper substrate 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.

**[0053]** 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 may be 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.

**[0054]** Effects of the selection pulp(s) are described above in connection to the first aspect.

**[0055]** In one embodiment, the paper substrate 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 top ply and a second wire may be used to form a second web that becomes the second ply, which first and second web are couched together.

**[0056]** 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%.

**[0057]** The Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of the first furnish in the head box may be 33-45. 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.

**[0058]** 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%.

**[0059]** In one embodiment, the head box consistency of the second furnish is lower than the head box consistency of the first furnish.

**[0060]** The Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of the second furnish in the head box may be 25-35. 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.

**[0061]** 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.

**[0062]** In one embodiment, the second ply side is impregnated with a higher amount of polymer than the first ply.

**[0063]** Otherwise, the embodiments of the first aspect discussed above apply to the second aspect *mutatis mutandis*.

**[0064]** As demonstrated in the Examples section below, the high-density paper of the first aspect is an excellent substrate for a coating, in particular an oxygen-barrier coating. As a third aspect of the present disclosure, there is thus provided a coated paper comprising a high-density paper according to the first aspect, wherein a surface of the high density 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/m<sup>2</sup>.

**[0065]** In an embodiment, the coated paper of the third aspect is not PECVD- or PVD-coated.

**[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 ajar, 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 high-density 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 high-density 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.

[0071] In an embodiment, the multi-layered material of the fourth aspect is not comprising a PECVD or PVD coating.

## EXAMPLES

### EXAMPLE 1

#### 1A: Paper substrate production

[0072] 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).

[0073] 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 (°SR) according to ISO 5267-1:1999 of ~30 °SR.

[0074] 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 (°SR) value of ~38 °SR.

[0075] 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/m<sup>2</sup> prior coating (i.e. 30 g/m<sup>2</sup> 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.

[0076] The two plies formed on the fourdrinier machine were couched together at a dryness of ~10% and further dewatered using vacuum foils boxes to ~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.

[0077] After wet pressing, the web was dried in a conventional multi-cylinder dryer to form a paper substrate having a moisture content of ~5%. Prior winding up, the paper substrate was calendered in a soft nip at a line load of 20 kN/m. Properties of the paper substrate are presented in table 1 below.

[0078] A SEM image of a surface portion of the paper substrate is shown in figure 1A.

#### 1B: Impregnation

[0079] 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 mPa\*s (measured at 60 °C). The applied amount of PVOH was 1 g/m<sup>2</sup> on the top side and 2 g/m<sup>2</sup> 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%. Properties of the dried PVOH-impregnated paper substrate are

presented in table 1 below.

**[0080]** Figure 1B is a SEM image of a surface portion of the PVOH-impregnated paper substrate. As shown in figure 1B, the PVOH has not formed a film on the surface portion. Instead, it has penetrated into the fiber web.

**[0081]** In another trial, the applied amount of PVOH was 1.5 g/m<sup>2</sup> on each side instead of 1 g/m<sup>2</sup> on the top side and 2 g/m<sup>2</sup> on the reverse/bottom side.

#### 1C: Supercalendering

**[0082]** The impregnated paper substrate from 1B 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 °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 450 kN/m. The total supercalendering nip impulse was ~800 kPa·s [#nips × line load / 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.

**[0083]** A SEM image of a surface portion of the high-density paper is shown in figure 1C. Further, figure 2 is SEM image of a cross section 20 of the high-density paper. The dark grey areas 21 are PVOH and light grey areas 22 are fibers. There are also unfilled pores 23. Consequently, the high-density paper is not saturated with PVOH. However, figure 2 shows that most of the PVOH is within the fiber web. Only minor portion of the PVOH is found on the surface.

#### 1D: 1<sup>st</sup> reference supercalendering

**[0084]** As a reference, a paper substrate produced according to 1A above, but with softwood kraft pulp and broke as the only pulps in both plies, was supercalendered as in 1C above (but not impregnated). Resulting properties are presented in table 1 below.

#### 1E: 2<sup>nd</sup> reference supercalendering

**[0085]** As a reference, a machine glazed (MG) paper formed from a mixture of hardwood pulp and softwood (dry weight ratio 40:60) pulp was supercalendered as in 1C above, but the total nip impulse was about 10% lower. Resulting properties are presented in table 1 below.

#### Resulting properties

**[0086]** For table 1, the following applies:

Grammage was measured according to ISO 536:2012 and has the unit g/m<sup>2</sup>. Density was measured according to ISO 534:2011 and has the unit kg/m<sup>3</sup>. Roughness means Bendtsen roughness, 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. Tear index was measured in the MD and the CD according to ISO 1974:2012 and has the unit mNm<sup>2</sup>/g. °SR was measured according to ISO 5267-1:1999 after repulping according to ISO 5263-1:2004. Canadian Standard Free-ness ("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. Fines content was measured with a L&W Fibretester+ (ABB, Lorentzen & Wettre, Sweden) after repulping according to ISO 5263-1:2004. Fines are defined as fibrous particles shorter than 0.2 mm. "Somerville residue" means residues retained in a Somerville shive and flake content analyzer having a slot plate width of 0.15 mm. The residue content was calculated as dry weight-% of originally introduced dry material (into the re-pulper). Dry has the meaning of having 0 % moisture content in the material tested, which is accordingly oven-dried before weighing. The Somerville method is described in further detail below. Oxygen Transmission Rate ("OTR") has the unit cm<sup>3</sup>/m<sup>2</sup>/24h, 0.2 atm (21%) oxygen. It was measured according to ASTM F1927-14 after lamination with 20 g/m<sup>2</sup> LDPE on the top side of the paper. Super Perga 1 and 2 are commercial greaseproof papers from Nordic Paper. Super Perga 1 was used as a paper substrate in WO 2017/089508.

Table 1.

	Paper substrate (1A)	PVOH-impreg. paper substrate (1B)	High-density paper (1C)	Ref. SC paper (1D)	Ref. SC MG paper (1E)	Ref. Super Perga 1	Ref. Super Perga 2
Grammage	60	63	63	60	50	329	45

(continued)

	Paper substrate (1A)	PVOH-impreg. paper substrate (1B)	High-density paper (1C)	Ref. SC paper (1D)	Ref. SC MG paper (1E)	Ref. Super Perga 1	Ref. Super Perga 2
Density	800	770	1100	1071	1114	865 <sup>§</sup>	832/905/938 <sup>§</sup>
Roughness (top side)	150	330	50	33	23	290	440
Roughness (bottom side)			26				
Tensile index (MD/CD)	115/57	122/64	133/70			94/41	93/40
Tear index (MD/CD)			4.6/5.5			3.9/4.5	4.0/4.8
°SR			40.5				74
CSF			277			53 *	
Fines content			26.7% <sup>‡</sup>				46.0%
Somerville residue 20 min			0.1%			86.2%	
Somerville residue 60 min						43.4%	
OTR 23°C, 50%RH, 0.2 atm O <sub>2</sub>	N/A	19.4	6.1 (4.5 <sup>‡</sup> )	~200	>2500		232 (194 <sup>**</sup> )
OTR 23°C, 80%RH, 0.2 atm O <sub>2</sub>	N/A	33.3	13.9 (15.3 <sup>‡</sup> )				
<sup>§</sup> According to the supplier's data sheet <sup>‡</sup> Tested on the high-density paper that had been impregnated with 1.5 g/m <sup>2</sup> PVOH on each side * The grammage was 38 g/m <sup>2</sup> instead of 32 g/m <sup>2</sup> ** After supercalendering according to example 1C (no PVOH-impregnation)							

**[0087]** As shown in table 1 above, neither supercalendering (high density) nor PVOH impregnation alone results in really low OTR values. As an example, supercalendering had very little effect on the OTR value of the non-impregnated paper Super Perga 2. In contrast, supercalendering of the PVOH-impregnated paper substrate from Example 1B reduced the OTR value (50% RH) by ~70% to well below 10 cm<sup>3</sup>/m<sup>2</sup>/24h.

**[0088]** 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.

**[0089]** Somerville method: The Valmet repulping method described above was first carried out to obtain a pulp. Quantification of the proportion of Somerville residues, as retained in Somerville shive and flake content analyzer with slot plate width 0.15 mm, was made by diluting the pulp to less than 1 % consistency. The diluted pulp was then analyzed in the Somerville analyzer to obtain the proportion of flake residues as weight-% calculated on oven dry material (i.e. moisture content 0%), initially introduced into the repulping operation.

## EXAMPLE 2

**[0090]** A single-ply paper made for a different purpose than that of Example 1, but by a process similar to that of Example 1, was provided. The single-ply paper was made from a pulp mixture comprising Kraft softwood pulp, Kraft hardwood pulp and a smaller amount of CTMP pulp, in an approximate dry weight ratio of 45:45:10.

**[0091]** During production, the single-ply paper had been impregnated with PVOH from the top side and subsequently supercalendered to a density of about 1100 kg/m<sup>3</sup>. The grammage of the single-ply paper was 57 g/m<sup>2</sup>. The top-side surface had a smoothness of 15 ml/min Bendtsen.

**[0092]** Further, a non-impregnated reference paper was provided. It had a top side surface smoothness of about 20 ml/min Bendtsen, a grammage of 39 g/m<sup>2</sup> and a density of 978 kg/m<sup>3</sup>.

**[0093]** The single-ply paper and the non-impregnated reference paper were coated twice with 1 g/m<sup>2</sup> of PVOH onto the top side of the paper substrate and dried after each coating operation. They were then laminated to packaging materials having the following layer structure:

/LDPE 12 g/m<sup>2</sup>/paperboard (80 mN geometric bending resistance)/LDPE 20 g/m<sup>2</sup>/paper substrate with 2× PVOH á 1 g/m<sup>2</sup>/Adh EAA copolymer 6 g/m<sup>2</sup>/blend LDPE+m-LLDPE 19 g/m<sup>2</sup>/

**[0094]** The oxygen transmission of the laminated materials was measured by a fluorescent method using an oxygen probe PSt9 from PreSens GmbH, Germany. According to this method, a flat sample to be analyzed is placed on a cell, which is flushed with dry nitrogen, in which the probe is also located. The area of the circular cell section is 68 cm<sup>2</sup> (0.0068 m<sup>2</sup>). The surface of the sample that is not directed towards the cell is facing ambient air, i.e. 21 % oxygen, at 23 °C and 50 % RH. By using the oxygen concentration reading from the probe, an oxygen transmission rate is calculated according to ASTM F3136-15. The unit is provided as ml/specimen.

**[0095]** By this alternative oxygen transmission measurement method, the oxygen barrier properties of a planar material may be investigated before and after having been folded and then unfolded. The folding angle was 165 degrees and the barrier layer was directed to be on the outside of the fold. Measured values are the average of five samples measured.

**[0096]** The results of such measurements are presented in figure 3, which shows that the unfolded laminated packaging material comprising the PVOH-coated (non-impregnated) reference paper substrate provides an oxygen barrier. This oxygen barrier is however lost after one round of folding and unfolding. In contrast, the oxygen barrier provided by the laminated packaging material comprising the impregnated paper is much less affected by the folding-unfolding action. This "folding resistant" oxygen barrier is an important property since the laminate will be folded in the packaging process.

## EXAMPLE 3

**[0097]** The high-density paper obtained in Example 1C above was coated twice with intermediate and subsequent drying operations to provide a PVOH coat weight of 3 g/m<sup>2</sup> and 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/m<sup>2</sup>/paperboard (80 mN geometric bending resistance)/LDPE 20 g/m<sup>2</sup>/ high-density paper+PVOH+met./Adhesive EAA copolymer 6 g/m<sup>2</sup> + 29 g/m<sup>2</sup> blend LDPE + mLLDPE /

**[0098]** 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.

**[0099]** 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.

**[0100]** Laminates comprising a PVOH-coated greaseproof paper from Nordic Paper, identified as "Super Perga® WS Parchment" and having a grammage of 32 g/m<sup>2</sup>, were used as comparative examples:

/LDPE 12 g/m<sup>2</sup>/ paperboard (260 mN geometric bending resistance)/LDPE 20 g/m<sup>2</sup> /paper substrate (32 g/m<sup>2</sup>)+PVOH+met./LDPE 20 g/m<sup>2</sup>/LDPE+mLLDPE 20 g/m<sup>2</sup>; and

/LDPE 12 g/m<sup>2</sup>/paperboard (80 mN geometric bending resistance)/LDPE 20 g/m<sup>2</sup>/ paper substrate (32 g/m<sup>2</sup>)+PVOH+met./LDPE 40 g/m<sup>2</sup>/

**[0101]** These reference laminates are further described in table 2 below.

**[0102]** Oxygen transmission rate (OTR) of flat packaging material was measured using a coulometric detector according to the standard ASTM F1927-14. The relative humidity (RH) was either 50% or 80%. The unit was cm<sup>3</sup>/m<sup>2</sup>/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.

**[0103]** The oxygen transmission rate (OTR) 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 cm<sup>3</sup>/package/24h. The OTR testing was carried out 2-3 weeks after production of the filled and sealed packages.

**[0104]** The package was mounted on a special holder; inside the package nitrogen was purged; the outside of the package is exposed to the environment surrounding the instrument. When oxygen permeated through the package into the nitrogen carrier gas, it was transported to the coulometric sensor. The sensor read how much oxygen that was leaked into the nitrogen gas inside the package.

Table 2

Paper substrate	Comparative example: Super Perga 32 g/m <sup>2</sup>	Comparative example: Super Perga 32 g/m <sup>2</sup>	HD paper of Example 1C ***
Principal laminate structure: /LDPE/ paperboard /LDPE/ paper substrate +PVOH+met/ inside PE polymers/	260 mN paperboard;  1 g/m <sup>2</sup> PVOH; Met. to OD 2.5;	80 mN paperboard  1.5 g/m <sup>2</sup> PVOH Met. to OD ~2.3	80 mN paperboard 3 g/m <sup>2</sup> PVOH Met. to OD ~2
Package format	Tetra Brik® Aseptic1000B	Tetra Brik(R) Aseptic200S	Tetra Brik® Aseptic200S
Package volume	1000 ml	200 ml	200 ml
Laminate area per package	0.077	0.030	0.030
Flat laminate OTR 1 atm, 23 °C, 50% RH	0.4 measured	1.3 measured	
Flat laminate OTR 1 atm, 23 °C, 80% RH	0.4 measured	1.3 measured	
Flat laminate OTR 0.2 atm, 23 °C, 50% RH	0.080 calculated	0.26 calculated	0.165 measured
Flat laminate OTR 0.2 atm, 23 °C, 80% RH	0.080 calculated	0.26 calculated	0.245 measured
<b>Calculation of loss:</b>			
Calculated, theoretical OTR per package, 0.2 atm, 23 °C, 50% RH	0.0062	0.0078	0.0050
Calculated, theoretical OTR per package, 0.2 atm, 23 °C, 80% RH	0.0062	0.0078	0.0074
Measured OTR per package 0.2 atm, 23 °C, 50% RH	0.06	0.075	0.029
Measured OTR per package 0.2 atm, 23 °C, 80% RH			0.028
Loss factor measured/theoretical, 23 °C, 50% RH	9.7	9.6	5.8
Loss factor measured/theoretical, 23 °C, 80% RH			3.8

**[0105]** Although, there is a difference between the comparative examples and the laminate based on the HD paper of Example 1C in the amount of polyethylene of the layers facing the inside of the package, i.e. 40 g/m<sup>2</sup> and 35 g/m<sup>2</sup>, respectively, this has no practical influence for the comparison of oxygen transmission rate since polyethylene is a poor oxygen barrier in relation to the HD paper and the applied coating. Typical oxygen transmission rate for LDPE of 40 μm thickness is 600-900 cm<sup>3</sup>/m<sup>2</sup>/24h/0.2 atm at 23 °C.

**[0106]** As shown in table 2, the filled 200 ml package made from the laminate comprising the impregnated high-density paper according to the present disclosure has a very low level of oxygen transmission (0.03 cm<sup>3</sup>/m<sup>2</sup>/day/0.2 atm at 23 °C and 50%RH). Furthermore, the oxygen barrier remained as effective in a more humid environment (23 °C and 80 % RH). In the reference laminate comprising the Super Perga paper substrate, the OTR value was 0.075 at 23°C and 50%RH, which means 2-3 times shorter shelf life for an oxygen sensitive product in a 200 ml package. It is thus shown that the impregnated high-density paper according to the present disclosure enables a higher fiber-based content in a packaging material for packaging of oxygen-sensitive products.

**[0107]** The OTR of a laminate based on the impregnated high-density paper according to the present disclosure is at

least as good as similar paper-based barrier laminates of the prior art. Most importantly, it does not exhibit the same level of loss of oxygen barrier properties when converted into a filled, formed and heat-sealed packaging container. It is thus shown above that the impregnated high-density paper according to the present disclosure provides a robustness against the stresses that a packaging material typically experiences during conversion and use.

#### EXAMPLE 4

**[0108]** The proportion of coarse reject, i.e. the non-fibrous recyclable part of the laminated materials (polymers, aluminum foil and some non-detachable fibers), was determined after re-pulping by a Valmet re-pulper. The re-pulping was carried out in the same way as described above in connection with CSF and Somerville measurements, except that the laminated packaging material to be re-pulped and analyzed was first cut into pieces of 30 by 90 mm. The coarse reject was screened (separated) using a plate with holes (diameter: 10 mm) and then dried to 0% moisture content. The proportion of coarse reject was then calculated as weight percent of dry (0% moisture) material introduced into the re-pulper.

**[0109]** The coarse reject as determined by a contracted global industrial supplier of equipment for fiber processing and recycling was made in a similar way. In this alternative method, however, 20 g of laminated material was mixed into 21 of water and disintegration was carried out at a consistency of about 1% for time cycles of 18 minutes. The water temperature was kept at 57 °C also in this test.

**[0110]** The results are presented in table 3 below.

Table 3

Laminate	Reference laminate comprising a 6.3 $\mu\text{m}$ aluminum foil <sup>a</sup>	Reference laminate comprising 38 g/m <sup>2</sup> Super Perga paper coated with 1 g/m <sup>2</sup> PVOH and metallized to OD 2.5 <sup>aa</sup>	Laminate comprising the HD paper of example 1C coated with 3 g/m <sup>2</sup> PVOH and metallized to OD ~2 <sup>aa</sup>
Coarse reject (wt-%) as repulped by Valmet re-pulper, 20 min	29	-	26 (18 after 50 minutes)
Coarse reject (wt-%) as re-pulped by the alternative method	39.8	40.2	-
<sup>a</sup> /LDPE 12 g/m <sup>2</sup> /paperboard (80 mN geometric bending resistance)/LDPE 20 g/m <sup>2</sup> /Al-foil 6.3 $\mu\text{m}$ /Adhesive EAA copolymer 6 g/m <sup>2</sup> + 19 g/m <sup>2</sup> blend LDPE + mLLDPE/ <sup>aa</sup> /LDPE 12 g/m <sup>2</sup> /paperboard (80 mN geometric bending resistance)/LDPE 20 g/m <sup>2</sup> /paper substrate +PVOH+met/Adhesive EAA copolymer 6 g/m <sup>2</sup> + 19 g/m <sup>2</sup> blend LDPE + mLLDPE/			

**[0111]** The results in table 3 indicate that the impregnation of the HD paper of the present disclosure does not result in worse repulpability/recyclability than the previously tested, non-impregnated, Super Perga paper.

#### Claims

1. A high-density paper having a grammage measured according to ISO 536:2012 of 30-75 g/m<sup>2</sup> and a density measured according to ISO 534:2011 above 1000 kg/m<sup>3</sup> and wherein the high-density paper is impregnated on each side with 0.3-4.0 g/m<sup>2</sup>, such as 0.5-3.0 g/m<sup>2</sup>, of a polymer selected from the group consisting of polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH), carboxymethylated cellulose (CMC), nanocrystalline cellulose (NCC) and carboxy methyl starch (CMS).
2. The high-density paper of claim 1, which is formed from at least 50% by dry weight kraft pulp, such as at least 75% by dry weight kraft pulp, such as at least 85% by dry weight kraft pulp, such as at least 95% by dry weight kraft pulp.
3. The high-density paper of claim 1 or 2, wherein 20-65 % by dry weight, such as 30-60 % by dry weight, of the pulp used to form the high-density paper is hardwood pulp.

4. The high-density paper of any one of the preceding claims, wherein 35-80 % by dry weight, such as 40-70 % by dry weight, of the pulp used to form the high-density paper is softwood pulp, preferably softwood that has been subjected to high consistency (HC) refining.
5. The high-density paper of any one of the preceding claims having a top ply and a bottom ply.
6. The high-density paper of any one of the preceding claims, wherein the grammage measured according to ISO 536:2012 is 35-65 g/m<sup>2</sup>.
7. The high-density paper of any one of the preceding claims, which has a Schopper-Riegler (°SR) number measured according to ISO 5267-1:1999 of 33-50, such as 35-45, after repulping according to ISO 5263-1:2004.
8. The high-density paper of any one of the preceding claims, which has a fines content measured with a L&W Fibre-tester+ (ABB, Lorentzen & Wettre, Sweden) of less than 40%, such as less than 34%, such as less than 32%, after repulping according to ISO 5263-1:2004, wherein fines are defined as fibrous particles shorter than 0.2 mm.
9. A method of forming a high-density paper having a grammage measured according to ISO 536:2012 of 30-75 g/m<sup>2</sup> and a density measured according to ISO 534:2011 of above 1000 kg/m<sup>3</sup>, said method comprising the steps of:
  - impregnating each side of a paper substrate with 0.3-4.0 g/m<sup>2</sup>, such as 0.5-3.0 g/m<sup>2</sup>, of a polymer selected from the group consisting of polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH), carboxymethylated cellulose (CMC), nanocrystalline cellulose (NCC) and carboxy methyl starch (CMS) to obtain an impregnated substrate; and
  - supercalendering the impregnated substrate to obtain the high-density paper.
10. The method of claim 9, wherein the polymer is PVOH having a weight average molecular weight (M<sub>w</sub>) below 100,000 g/mol.
11. The method of claim 9 or 10, wherein the impregnating step comprises adding an aqueous composition comprising the polymer to each side of the paper substrate and the viscosity measured at 60°C of the aqueous composition is 55-90 mPa\*s.
12. The method of any one of claims 9-11, wherein the impregnated substrate entering the supercalendering step has a moisture content of 11.0%-20.0%, preferably 12.0%-19.0%, more preferably 13.5%-18.0%.
13. The method of any one of claims 9-12, wherein the impregnating step is carried out by means of a film press.
14. A coated paper comprising a high-density paper according to any one of claims 1-8, wherein a surface of the high density paper is provided with a barrier coating 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. 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 high-density paper according to any one of claims 1-8, provided that the food product is not a liquid, semi-liquid or viscous food product.

#### Patentansprüche

1. Hochdichtes Papier mit einer gemäß ISO 536:2012 gemessenen Grammatik von 30-75 g/m<sup>2</sup> und einer gemäß ISO 534:2011 gemessenen Dichte von über 1000 kg/m<sup>3</sup>, wobei das hochdichte Papier auf jeder Seite mit 0,3-4,0 g/m<sup>2</sup>, beispielsweise 0,5-3,0 g/m<sup>2</sup>, eines Polymers imprägniert ist, das aus der Gruppe ausgewählt ist, die aus Polyvinylalkohol (PVOH), Ethylenvinylalkohol (EVOH), carboxymethylierter Cellulose (CMC), nanokristalliner Cellulose (NCC) und Carboxymethylstärke (CMS) besteht.
2. Hochdichtes Papier nach Anspruch 1, das zu mindestens 50 % des Trockengewichts aus Kraftzellstoff, beispielsweise zu mindestens 75 % des Trockengewichts aus Kraftzellstoff, beispielsweise zu mindestens 85 % des Trockengewichts aus Kraftzellstoff, beispielsweise zu mindestens 95 % des Trockengewichts aus Kraftzellstoff gebildet ist.

3. Hochdichtes Papier nach Anspruch 1 oder 2, wobei 20-65 % des Trockengewichts, beispielsweise 30-60 % des Trockengewichts, des zur Bildung des hochdichten Papiers verwendeten Zellstoffs Hartholzzellstoff ist.
- 5 4. Hochdichtes Papier nach einem der vorhergehenden Ansprüche, wobei 35-80 % des Trockengewichts, beispielsweise 40-70 % des Trockengewichts, des zur Bildung des hochdichten Papiers verwendeten Zellstoffs Weichholzzellstoff ist, vorzugsweise Weichholz, das einer Hochkonsistenzveredelung (HC) unterzogen wurde.
5. Hochdichtes Papier nach einem der vorhergehenden Ansprüche mit einer oberen Lage und einer unteren Lage.
- 10 6. Hochdichtes Papier nach einem der vorhergehenden Ansprüche, wobei die Grammatur, gemessen gemäß ISO 536:2012, 35-65 g/m<sup>2</sup>, beträgt.
7. Hochdichtes Papier nach einem der vorhergehenden Ansprüche, das nach einem Wiederaufbereiten gemäß ISO 5263-1:2004 eine gemäß ISO 5267-1:1999 gemessene Schopper-Riegler-Zahl (°SR) von 33-50, beispielsweise 35-45, aufweist.
- 15 8. Hochdichtes Papier nach einem der vorhergehenden Ansprüche, das nach einem Wiederaufbereiten gemäß ISO 5263-1:2004 einen mit einem L&W Fibretester+ (ABB, Lorentzen & Wettre, Schweden) gemessenen Feinanteil von weniger als 40 %, beispielsweise weniger als 34 %, beispielsweise weniger als 32 %, aufweist, wobei Feinanteile als faserige Partikel, die kürzer als 0,2 mm sind, definiert sind.
- 20 9. Verfahren zur Bildung eines hochdichten Papiers mit einer gemäß ISO 536:2012 gemessenen Grammatur von 30-75 g/m<sup>2</sup> und einer nach ISO 534:2011 gemessenen Dichte von über 1000 kg/m<sup>3</sup>, wobei das Verfahren die Schritte aufweist:
  - 25 - Imprägnieren jeder Seite eines Papiersubstrats mit 0,3-4,0 g/m<sup>2</sup>, beispielsweise 0,5-3,0 g/m<sup>2</sup>, eines Polymers, ausgewählt aus der Gruppe bestehend aus Polyvinylalkohol (PVOH), Ethylenvinylalkohol (EVOH), carboxymethylierter Cellulose (CMC), nanokristalline Cellulose (NCC) und Carboxymethylstärke (CMS), um ein imprägniertes Substrat zu erhalten; und
  - 30 - Superkalandrieren des imprägnierten Substrats, um das hochdichte Papier zu erhalten.
10. Verfahren nach Anspruch 9, wobei das Polymer PVOH mit einem gewichtsmittleren Molekulargewicht (Mw) unter 100000 g/mol ist.
- 35 11. Verfahren nach Anspruch 9 oder 10, wobei der Imprägnierungsschritt Hinzufügen einer wässrigen Zusammensetzung, die das Polymer aufweist, zu jeder Seite des Papiersubstrats aufweist, und die bei 60°C gemessene Viskosität der wässrigen Zusammensetzung 55-90 mPa\*s beträgt.
- 40 12. Verfahren nach einem der Ansprüche 9-11, wobei das imprägnierte Substrat, das in den Superkalandrierungsschritt eintritt, einen Feuchtigkeitsgehalt von 11,0 %-20,0 %, vorzugsweise 12,0 %-19,0 %, noch bevorzugter 13,5 %-18,0 %, aufweist.
- 45 13. Verfahren nach einem der Ansprüche 9-12, wobei der Imprägnierungsschritt mittels einer Filmpresse durchgeführt wird.
- 50 14. Beschichtetes Papier, aufweisend ein hochdichtes Papier nach einem der Ansprüche 1-8, wobei eine Oberfläche des hochdichten Papiers mit einer Barrierebeschichtung versehen ist, die Polyvinylalkohol (PVOH), Ethylenvinylalkohol (EVOH), Stärke oder Stärkederivat, nano- oder mikrofibrilläre Cellulose, Polyvinylidenchlorid (PVDC) oder ein Polyamid aufweist.
- 55 15. Verwendung eines mehrschichtigen Materials zum Verpacken eines Lebensmittelprodukts oder eines anderen sauerstoffempfindlichen Produkts, wobei eine Schicht des mehrschichtigen Materials ein hochdichtes Papier nach einem der Ansprüche 1-8 ist, insofern das Lebensmittelprodukt kein flüssiges, halbflüssiges oder viskoses Lebensmittelprodukt ist.



## Revendications

- 5 1. Papier à haute densité ayant un grammage mesuré selon la norme ISO 536:2012 allant de 30 à 75 g/m<sup>2</sup> et une densité mesurée selon la norme ISO 534:2011 supérieure à 1 000 kg/m<sup>3</sup> et dans lequel le papier à haute densité est imprégné sur chaque face de 0,3 à 4,0 g/m<sup>2</sup>, tel que de 0,5 à 3,0 g/m<sup>2</sup>, d'un polymère choisi dans le groupe constitué de l'alcool polyvinylique (PVOH), de l'alcool éthylène vinylique (EVOH), de la cellulose carboxyméthylée (CMC), de la cellulose nanocristalline (NCC) et de l'amidon carboxy-méthylque (CMS).
- 10 2. Papier à haute densité selon la revendication 1, qui est formé à partir d'au moins 50 % de pâte kraft en poids sec, par exemple d'au moins 75 % de pâte kraft en poids sec, d'au moins 85 % de pâte kraft en poids sec, d'au moins 95 % de pâte kraft en poids sec.
- 15 3. Papier à haute densité selon la revendication 1 ou la revendication 2, dans lequel de 20 à 65 % en poids sec, par exemple de 30 à 60 % en poids sec, de la pâte utilisée pour former le papier à haute densité est de la pâte de feuillus.
4. Papier à haute densité selon l'une quelconque des revendications précédentes, dans lequel de 35 à 80 % en poids sec, par exemple de 40 à 70 % en poids sec, de la pâte utilisée pour former le papier à haute densité est de la pâte de résineux, de préférence de résineux ayant été soumis à un raffinage à haute consistance (HC).
- 20 5. Papier à haute densité selon l'une quelconque des revendications précédentes, comportant un pli supérieur et un pli inférieur.
- 25 6. Papier à haute densité selon l'une quelconque des revendications précédentes, dans lequel le grammage mesuré selon la norme ISO 536:2012 est compris entre 35 et 65 g/m<sup>2</sup>.
7. Papier à haute densité de l'une quelconque des revendications précédentes, qui présente un indice de Schopper-Riegler (0 SR) mesuré selon la norme ISO 5267-1:1999 allant de 33 à 50, tel qu'allant de 35 à 45, après repulpage selon la norme ISO 5263-1:2004.
- 30 8. Papier à haute densité selon l'une quelconque des revendications précédentes, qui présente une teneur en matières fines mesurée à l'aide d'un L&W Fibretester+ (ABB, Lorentzen & Wettre, Suède) inférieure à 40 %, telle qu'inférieure à 34 %, telle qu'inférieure à 32 %, après repulpage conformément à la norme ISO 5263-1:2004, dans lequel les matières fines sont définies comme étant des particules fibreuses d'une longueur inférieure à 0,2 mm.
- 35 9. Procédé de formation d'un papier à haute densité ayant un grammage mesuré selon la norme ISO 536:2012 allant de 30 à 75 g/m<sup>2</sup> et une densité mesurée selon la norme ISO 534:2011 supérieure à 1 000 kg/m<sup>3</sup>, ledit procédé comprenant les étapes suivantes :
  - 40 - imprégnation de chaque face d'un substrat de papier allant de 0,3 à 4,0 g/m<sup>2</sup>, tel qu'allant de 0,5 à 3,0 g/m<sup>2</sup>, d'un polymère choisi dans le groupe constitué de l'alcool polyvinylique (PVOH), de l'alcool éthylène vinylique (EVOH), de la cellulose carboxyméthylée (CMC), de la cellulose nanocristalline (NCC) et de l'amidon carboxy méthylque (CMS) afin d'obtenir un substrat imprégné ; et
  - supercalandrage du substrat imprégné pour obtenir le papier à haute densité.
- 45 10. Procédé selon la revendication 9, dans lequel le polymère est du PVOH ayant un poids moléculaire moyen (Mw) inférieur à 100 000 g/mol.
- 50 11. Procédé selon la revendication 9 ou la revendication 10, dans lequel l'étape d'imprégnation comprend l'ajout d'une composition aqueuse comprenant le polymère sur chaque face du substrat de papier et la viscosité mesurée à 60 °C de la composition aqueuse est comprise entre 55 et 90 mPa\*s.
- 55 12. Procédé selon l'une quelconque des revendications 9 à 11, dans lequel le substrat imprégné entrant dans l'étape de surcalandrage a un taux d'humidité allant de 11,0 % à 20,0 %, de préférence allant de 12,0 % à 19,0 %, plus préférentiellement allant de 13,5 % à 18,0 %.
13. Procédé selon l'une quelconque des revendications 9 à 12, dans lequel l'étape d'imprégnation est réalisée au moyen d'une presse à film.

14. Papier revêtu comprenant un papier à haute densité selon l'une quelconque des revendications 1 à 8, dans lequel une surface du papier à haute densité est pourvue d'un revêtement barrière comprenant de l'alcool polyvinylique (PVOH), de l'alcool éthylène vinylique (EVOH), de l'amidon ou un dérivé de l'amidon, une cellulose nano ou micro-fibrillaire, du chlorure de polyvinylidène (PVDC) ou un polyamide.

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15. Utilisation d'un matériau multicouche pour l'emballage d'un produit alimentaire ou d'un autre produit sensible à l'oxygène, dans lequel une couche du matériau multicouche est un papier à haute densité selon l'une quelconque des revendications 1 à 8, à condition que le produit alimentaire ne soit pas un produit alimentaire liquide, semi-liquide ou visqueux.

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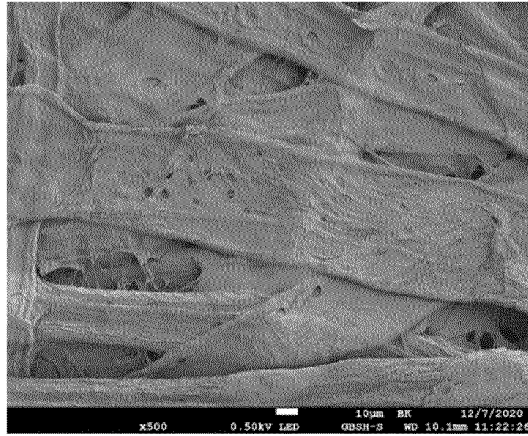
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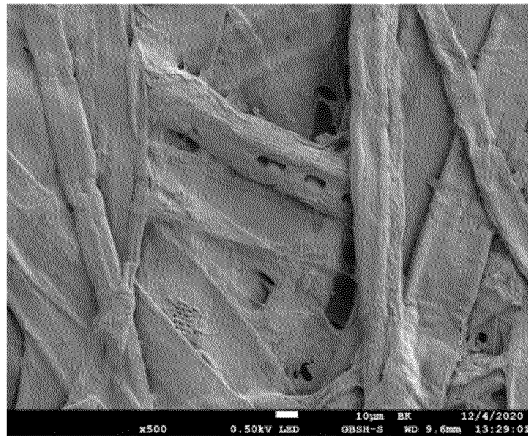
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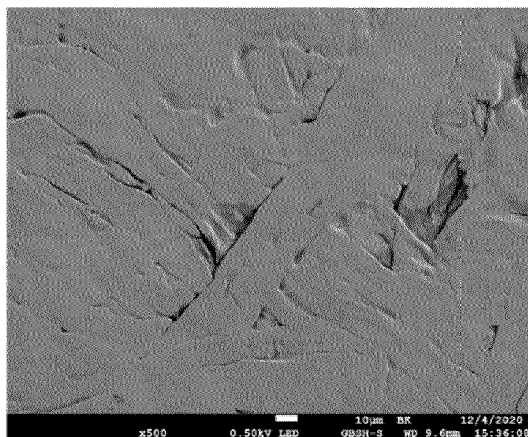
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(A)



(B)



(C)

Fig. 1

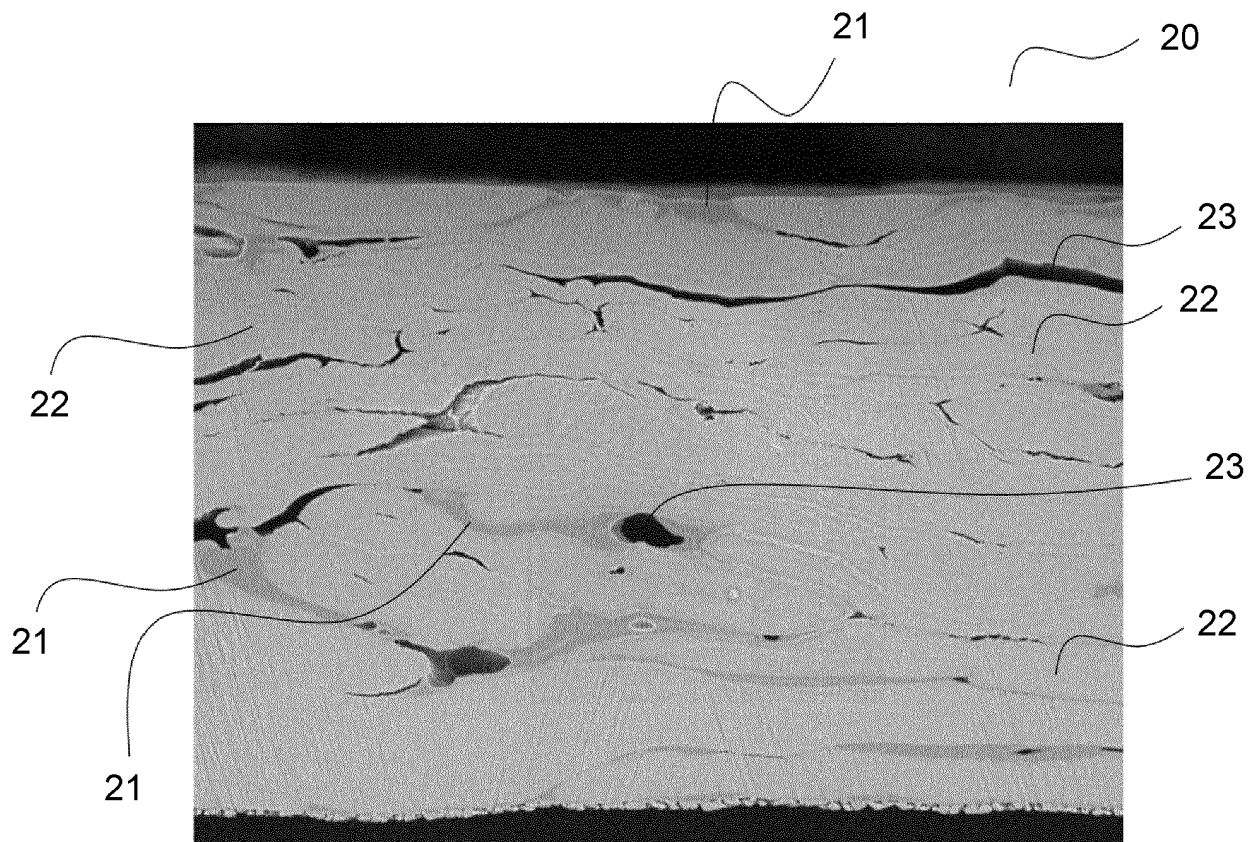


Fig. 2

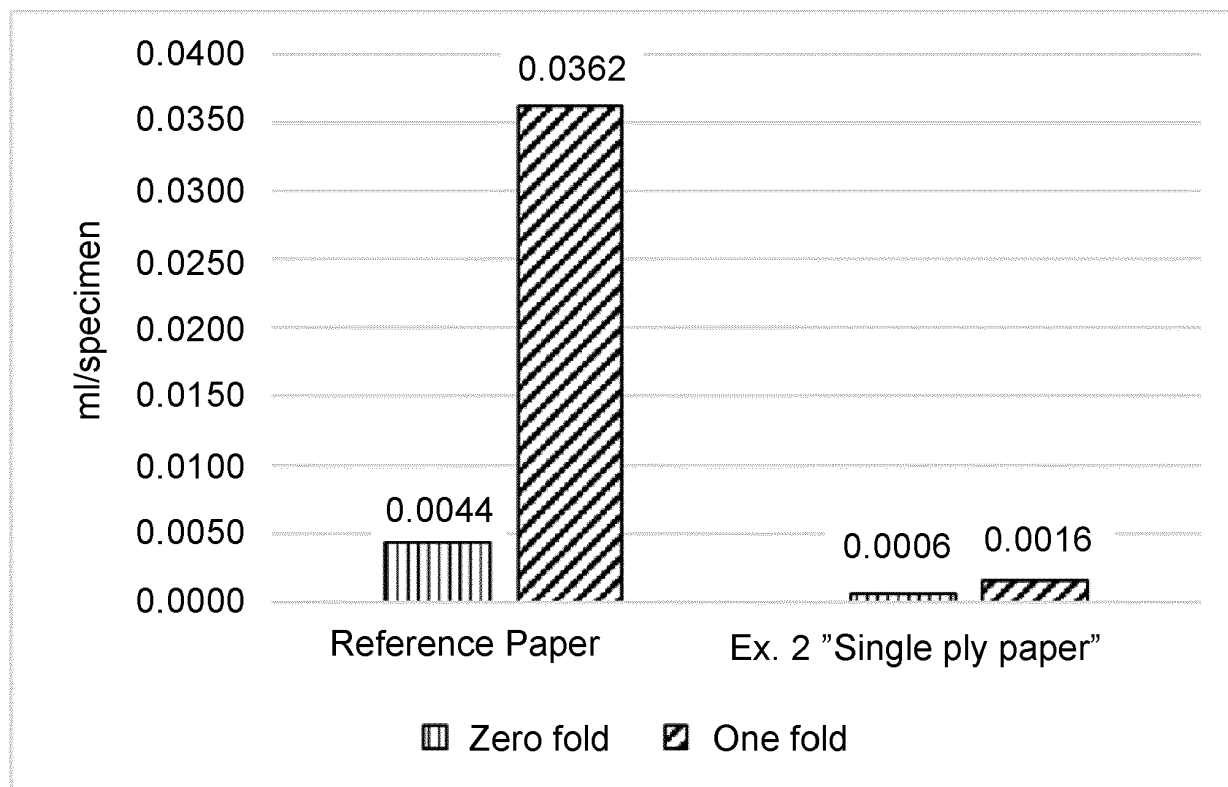


Fig. 3

**REFERENCES CITED IN THE DESCRIPTION**

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