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(54) Title: HYDROPHOBIZED PAPER OR PAPERBOARD COMPRISING ONE OR MORE PLIES

(57) Abstract: The invention relates to a paper or paperboard comprised of one or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose, and wherein said paper or paperboard has been subjected to grafting with a fatty acid halide such that ester bonds are formed between carbonyl groups of the fatty acid halide and hydroxyl groups of the cellulose fibers and the strength enhancement agent. The invention also relates to a method for manufacturing paper or paperboard.



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HYDROPHOBIZED PAPER OR PAPERBOARD COMPRISING ONE OR MORE PLIES

Technical field

The present invention relates to a paper or paperboard comprised of one or more plies wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose.

Background

It is known to use microfibrillated and nanofibrillated cellulose as wet end additives to improve mechanical properties, such as strength, for paper and paperboard materials. However, due to its highly hydrophilic properties and high water-absorption capacity, addition of MFC to a papermaking furnish may not be suitable when it is desired to produce hydrophobic cellulose-based materials.

Paper- and paperboard are usually treated with sizing agents to increase the resistance to penetration of water and other liquids into the paper or paperboard. A common sizing agent is AKD which is added to the pulp or furnish at the wet end of papermaking. Use of AKD is however associated with certain drawbacks such as migration and clogging that can result both in machine stops and/or possibly issues with the final product. This is due to that AKD does not covalently bind to the cellulose fiber to any higher extent. AKD can also have a negative effect on the mechanical properties due to a debonding effect where the AKD molecules interact and reduce the fiber-fiber connections that give the high mechanical properties to a cellulose-based substrate. This can happen since the AKD is added to the furnish prior to formation and drying in paper and paperboard production. To compensate for the weaker material, the grammage of paper and board is increased leading to higher carbon footprint due to overuse of wood fibers and higher transport weight at all stages downstream the production.

To improve the wet strength of the material, the internal sizing agent can be combined with a wet-strength agent. A wet-strength agent improves the tensile properties of the paper or paperboard in the wet state by for example covalently binding to the cellulose fibers and also by forming a crosslinked network between the

fibers that does not break upon wetting. Common wet-strength agents include urea-formaldehyde (UF), melamine-formaldehyde (MF) and polyamide-epichlorohydrin (PAE). Other wet strength agents can give wet-strength by other mechanisms, and some of these wet-strength agents can also have a temporary wet-strength function.

A problem with the addition of wet strength agents is that the repulpability of the material is severely reduced.

There is a need for a cellulose-based fiber material, such as paper or paperboard, with good strength properties and at the same time providing water-repellence, wet-strength function and edge-wick resistance, without interfering with the repulpability.

Summary of the invention

It is an object of the present invention to solve or at least alleviate the problems presented above, and provide a cellulose-based material, such as paper or paperboard, with hydrophobic properties and edge-wick resistance, and at the same time providing an improved wet-strength.

The objects of the invention are at least partially obtained by means of a paper or paperboard according to claim 1. Said paper or paperboard comprises one or more plies wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose, wherein said paper or paperboard has been subjected to grafting with a fatty acid halide such that ester bonds are formed between carbonyl groups of the fatty acid halide and hydroxyl groups of the cellulose fibers and the strength enhancement agent.

The inventors have surprisingly found that application of grafting technology onto a paper or paperboard material comprising a strength enhancement agent in the form of microfibrillated cellulose or highly refined cellulose leads to a material with the desired properties of being hydrophobic, having edge wick resistance, and at the same time providing for improved wet strength properties. Untreated paper or paperboard material, i.e. products without sizing, grafting and/or other additives,

disintegrates and/or breaks when subjected to a certain stress or load in a moist and/or wet environment. AKD itself may not give enough wet-strength since it is mainly physically interacting with the fibers. By grafting of fatty acid halides, however, covalent bonds can be formed with fibers in the substrate, giving an improved wet-strength of the grafted material and at the same time hydrophobizing the material.

The material according to the invention is suitable for use in a vast number of applications. A non-limiting list of examples include:

- structures utilized for (but not limited to) liquid packaging boards (LPB) for use in the packaging of liquids or liquid-containing products, as well as paper or paperboard for dry, fat, fresh and/or frozen food, and laminates thereof;
- cup material and laminates thereof for hot and cold food stuff;
- general packaging, luxury packaging, and graphical board for their designated applications;
- multiply products for non-food applications, such as flora and fauna products, pharma products, beauty and personal care products and multi-pack products;
- well and wrapping paper (food and non-food based);
- pouches;
- paper or paperboard for single-use items;
- labels, grease-proof paper, high-density paper and sack paper..

Grafting technology utilizes fatty acid halides (C16 or C18, preferably C16) in liquid, spray or gas phase to graft the available hydroxyl groups on cellulose-based substrates, i.e. the fatty acids will be covalently attached to the fibers to a certain degree. Upon the reaction with the hydroxyl groups on the substrate or with water in the substrate or in the air, hydrohalic acid, e.g. hydrochloric acid, is formed as a reaction byproduct. The grafting may preferably be followed by removal of the formed hydrohalic acid, and optionally by full or partial removal of the non-grafted residues. The grafting process may optionally be repeated, in order to increase the amount of grafted fatty acid. In case of repeating grafting, the substrate may be grafted both at the top- and bottom-side. The technology is applied on pre-made and dried paper and boards to limit the hydrolysis to occur. The moist content of the substrate should be below 20 %, preferably below 15 %, even more preferably below 10 %. Furthermore, since the hydrophobization is done on dried paper and paper board

substrates, the treatment with fatty acid chlorides does not interfere with the formed fiber-fiber bonds. The addition of MFC in the substrate also provide for an increased number of hydroxyl groups that the reagent can react with, increasing the covalent degree and reducing the amount of unbound fatty acids.

WO2012066015A1 describes a machine that treats a moving substrate containing hydroxyl groups with a grafting reagent. A gas-phase process to graft fatty acid halides has also been described in WO2017002005A1, where vacuum is applied to withdraw the gas through the board to render the whole cellulose-based substrate treated.

It is known that it is difficult to modify MFC in itself since it is produced as a water dispersion with very high water-content around: 80-99.9 %, depending on the production method. Also, if the MFC would be hydrophobized prior to addition to the fiber furnish in paper or paperboard making, it will severely impact the mixability with the fiber slurry and the needed interactions between MFC and fibers, as well as most probably give an inhomogeneous material with loss in mechanical properties. The addition of sizing chemicals like AKD will not have the same detrimental effect. However, thanks to the present invention, sizing chemicals can be completely avoided, while still providing a desirable hydrophobicity and strength to the end material.

According to one aspect of the invention, said paper or paperboard comprises two or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose.

According to yet another aspect of the invention, said cellulose fibers comprise fibers or a mix of fibers from softwood, hardwood, Kraft pulp (bleached or unbleached), sulphite pulp, dissolving pulp, chemical pulp, chemi-mechanical pulp (CMP), thermomechanical pulp (TMP), chemi- thermomechanical pulp (CTMP), high-temperature (HT)-CTMP or recycled fibers.

According to yet another aspect of the invention, said paper or paperboard is comprising at least a three plies, i.e. a three-ply structure, wherein at least a middle ply is arranged as a structural core layer with high bulk (bulk referring to the inverse of density), sandwiched between top and back plies according to an I-beam arrangement. The structural core layer preferably mainly comprises mechanical pulp fibers, such as CTMP, TMP or pressure groundwood (PGW), preferably at least 60 wt%, but may also include other fibers, preferably Kraft pulp can be included to a certain extent, preferably at most 40 wt% calculated on the total fiber weight of the ply. Said structural core layer (corresponding to a bulky middle ply) is arranged to provide bending stiffness to the overall structure. In this embodiment, at least said structural core layer comprises a strength enhancement agent in the form of microfibrillated cellulose (MFC) or highly refined cellulose. The structural core layer has also been subjected to grafting treatment, which means that also the flanging layers (top- and bottom) have been grafted. The skilled person knows that "bulky" refers to a thicker ply with lower density compared to the flanging plies (i.e. top and back ply) in the structure. Preferably, said middle ply exhibits a density of below 400 kg/m³, preferably of below 350 kg/m³, even more preferably of below 300 kg/m³. MFC may be added in an amount of between 0.1 - 10 wt%, preferably between 1 - 7 wt%, or between 1 - 5 wt% as calculated on the total solid content of the ply.

According to yet another aspect of the invention, said paper or paperboard has been subjected to grafting with a fatty acid halide through the entire thickness of said paper or paperboard.

According to yet another aspect of the invention, a surface of said paper or paperboard subjected to grafting with a fatty acid halide has a water contact angle above 90°, preferably above 100°.

According to another aspect of the invention, the fatty acid halide grafting results in a paper or paperboard having a Cobb60 value below 30 g/m² (as determined according to standard ISO 535:2014 after 60 seconds), preferably below 20 g/m², and more preferably below 15 g/m².

According to another aspect of the invention, the fatty acid halide grafting results in a paper or paperboard having an edge-wick index (Lactic acid 1% solution, 1 h at 23 °C and 50 % relative humidity) below 1.5 kg/m²h, preferably below 1 kg/m²h, and even more preferably below 0.5 kg/m²h.

According to yet another aspect of the invention, said paper or paperboard subjected to grafting with a fatty acid halide has a Z-strength of at least 150 kPa, preferably of at least 250 kPa, most preferably of at least 350 kPa as determined according to standard ISO 15754:2009.

According to yet another aspect of the invention, said paper or paperboard subjected to grafting with a fatty acid halide has a wet tensile strength in machine direction (MD) in the range of 0.5-10 kN/m, as determined according to standard 3781:2011.

According to yet another aspect of the invention, said paper or paperboard subjected to grafting with a fatty acid halide has a relative wet strength in machine direction (MD) in the range of 10-30 %, as determined according to standard ISO 3781:2011.

According to yet another aspect of the invention, said paper or paperboard subjected to grafting with a fatty acid halide has a relative wet tear strength in machine direction (MD) in the range of 20-100 %, as determined according to TAPPI T 496 sp-13 (T 496 cm-85) and ISO 1974:2012.

According to yet another aspect of the invention, the grammage of said paper or paperboard prior to grafting is in the range of 40-700 g/m².

According to yet another aspect of the invention, the thickness of said paper or paperboard prior to grafting is in the range of 40-1000 µm.

According to yet another aspect of the invention, the density of said paper or paperboard prior to grafting is in the range of 350-1300 kg/m³.

According to yet another aspect of the invention, the density of said paper or paperboard subjected to grafting with a fatty acid halide is in the range of 350-1300 kg/m³.

According to yet another aspect of the invention, said cellulose fibers comprise fibers or a mix of fibers from soft wood, hard wood, sulphate pulp, sulphite pulp, dissolving pulp, chemical pulp, thermomechanical pulp (TMP), chemi-thermomechanical pulp (CTMP) or high-temperature (HT)-CTMP.

According to one aspect of the invention, said strength enhancement agent is MFC. There are different acronyms for MFC such as cellulose microfibrils, fibrillated cellulose, nanofibrillated cellulose, fibril aggregates, nanoscale cellulose fibrils, cellulose nanofibers, cellulose nanofibrils, cellulose microfibers, cellulose fibrils, microfibrillar cellulose, microfibril aggregates and cellulose microfibril aggregates. MFC can also be characterized by various physical or physical-chemical properties such as large surface area or its ability to form a gel-like material at low solids (1-5 wt%) when dispersed in water. The cellulose fiber is preferably fibrillated to such an extent that the final specific surface area of the formed MFC is from about 1 to about 300 m²/g, such as from 1 to 200 m²/g or more preferably 50-200 m²/g when determined for a freeze-dried material with the BET method.

According to yet another aspect of the invention, said strength enhancement agent is highly refined cellulose. Preferably, said highly refined cellulose is cellulose refined to an SR value in the range of 70-94, preferably in the range of 70-90, and wherein the cellulose fibers have a length of <1mm. The Schopper-Riegler value can be obtained through the standard method defined in EN ISO 5267-1. This SR value is determined for a pulp, with or without additional chemicals, thus the fibers have not consolidated into a film or started any hornification or such. The dry solid content of this kind of web, before disintegrated and measuring SR, is less than 50 % (w/w). To determine the Schopper Riegler value it is preferable to take a sample just after the wire section where the wet web consistency is relatively low. The skilled person understands that paper making chemicals, such as retention agents or dewatering agents, have an impact on the SR value. The SR value specified herein, is to be

understood as an indication but not a limitation, to reflect the characteristics of the material itself.

A combination of MFC and highly refined pulp can also be utilized as strength enhancement agent.

According to yet another aspect of the invention, the dry weight ratio between said cellulose fibers and said strength enhancement agent in the at least one ply is in the range of 80:20 to 99.9:0.1, preferably in the range of 90:10 to 99:0.5.

The present invention also relates to a method for manufacturing paper or paperboard, said method comprising at least the steps of:

a) providing a paper or paperboard substrate comprised of one or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose, and

b) subjecting said paper or paperboard to grafting with a fatty acid halide such that ester bonds are formed between carbonyl groups of the fatty acid halide and hydroxyl groups of the cellulose fibers and the strength enhancement agent.

According to one aspect of the method of the invention, said paper or paperboard comprises two or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC), and highly refined cellulose.

According to yet another aspect of the invention, said paper or paperboard is subjected to grafting with a fatty acid halide through the entire thickness of said paper or paperboard.

According to another aspect of the invention, the applied amount of fatty acid halide is between 0.1-4 g/m² of total dry weight of the substrate, preferably between 0.5-2 g/m². The method for analyzing the amount of free and grafted fatty acids in the treated substrate is based on the method for AKD analysis. Free fatty acids are extracted from the board sample with an organic solvent and analyzed with GC-FID

after silylation. The same board sample is subsequently submitted to alkaline hydrolysis for breaking the ester bonds to cellulose and the released fatty acids are thereafter extracted and analyzed with GC-FID after silylation. The sum of the analyzed free and bound fatty acids constitutes the total amount of fatty acid halide.

The present invention also relates to the use of a fatty acid halide for hydrophobization of a paper or paperboard comprised of one or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose.

Detailed description of the invention

The material according to the invention will now be further described in the following. However, the embodiments referred to in this description are not to be seen as limiting the scope of the invention in any way, but are merely provided for a better understanding of the invention.

As previously described, the present invention relates to a paper or paperboard comprised of one or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose, and wherein said paper or paperboard has been subjected to grafting with a fatty acid halide such that ester bonds are formed between carbonyl groups of the fatty acid halide and hydroxyl groups of the cellulose fibers and the strength enhancement agent. Paper and paperboard structures can be built up by one or more plies. A structure comprising more than one ply is referred to as multiply structures. Some boards structures are built up by a three-layer fiber construction, i.e. in three plies. The top and the back ply can be based on bleached and/or unbleached sulphate pulp and the middle ply can consist of CTMP. The middle ply can also consist of CTMP and bleached and/or unbleached sulphate pulp. A reverse layer can also be utilized of unbleached sulphate pulp. Multiply structures with more than three plies, such as five plies or more, are also within the scope of the present invention.

Another option is to have a three-layered structure with chemical pulp, optionally combined with CTMP in one or more plies as well as additional layers with surface sizing and/or single, double and/or triple mineral coating. Yet another option is multilayer Kraft back board which is built up of three plies with bleached or unbleached chemical pulp in outer plies and unbleached chemical pulp and CTMP in mid ply, possibly combined with a double coating.

The strength enhancement agent can be added to one, several or all of the plies of a multiply structure, preferably it is placed in the middle ply(ies) for the substrates that have more than one ply. It is generally the mid ply that is the bulkiest ply, giving an increase in the bending stiffness. By adding MFC to this bulky mid-layer, the Z-strength is improved.

According to the invention, the grafting technology used onto a paper or paperboard material comprising a strength enhancement agent (MFC or highly refined cellulose) leads to a material with the properties of being hydrophobic, having edge wick resistance, and at the same time providing for improved wet strength properties. The grafting technology is based on the concept of applying a fatty acid halide onto a cellulose substrate such that the fatty acid penetrates the cellulose substrate and resulting in a hydrophobization thereof. Grafting can be accomplished in various ways. According to one example, grafting is performed by firstly drying a cellulose substrate to a dry content above 80%, and thereafter adding a vaporized fatty acid halide to the first side of the cellulose substrate, and, at the same time perform vacuum sucking at the second side of the cellulose substrate, such that the vaporized fatty acid penetrates the cellulose substrate in a predetermined direction through the substrate.

In one aspect of the invention, said substrate can comprise at least one outer polymer layer forming an outer surface of said substrate, wherein said polymer comprises any of the following; polyethylene (PE), polyethylene terephthalate (PET), polyvinyl alcohol (PVOH), polyvinyl acetate (PVA), polypropylene (PP), polylactic acid (PLA) and/or polyamide (PA).

According to the invention it is also conceivable to replace or minimize the grammage of one or two polymer layers at the front- and/or backside of the substrate/laminate, especially with regards to the outer layer utilized for condensation.

Examples

Two grades of MFC were employed, one finer grade that has been passed through a homogenizer for five passages and one coarser grade that only has been highly refined corresponding to a highly refined fiber with SR>80.

Formette lab sheets were prepared of CTMP fibers with MFC and/or AKD, see Table 1. Drying of the sheets was performed with a pressure that was varied between 1 to 5 bar at a temperature of 100 °C.

The sheets that did not contain any AKD were treated with palmitoyl chloride (PTC) by spraying the reagent onto one side of the substrate with a spray gun with max 100 ml volume and an operating pressure of 1.5 bar, followed by infrared (IR) heat-treatment of the same surface. The corresponding grafted samples are presented in Table 1.

Table 1. Recipes of Formette lab sheets.

	Retention aid	MFC fine (Conc. 4.5 g/L)	MFC coarse (Conc. 4.1 g/L)	AKD	Grammage (g/m ²)	Density (kg/m ³)
Ref-PTC-FS – No MFC	0.8 kg/ton	No	No	No	100	350
PTC-FS-MFC fine	0.8 kg/ton	50 kg/ton	No	No	110	400
PTC-FS-MFC coarse	0.8 kg/ton	No	50 kg/ton	No	110	390
Ref-AKD-FS – No MFC	0.8 kg/ton	No	No	3 kg/ton		
AKD-FS-MFC fine	0.8 kg/ton	50 kg/ton	No	3 kg/ton	100	400
AKD-FS-MFC coarse	0.8 kg/ton	No	50 kg/ton	3 kg/ton	100	370

The method for measurement of contact angle (CA) is based on the standard ISO TC 6/SC 2/WG 41: Paper and board - Measurement of water contact angle by optical methods. Contact angle was measured for 10 seconds and values for each second and at 0.1 s were noted. The values are an average from 5 drops. The liquid

used was Milli-Q water, drop size was 4 μ l and drops were evaluated by the software calculation program Circle.

The tensile strength was measured according to standard ISO 1924-3:2005.

The Z-strength was measured according to standard ISO 15754:2009.

The wet strength was measured according to ISO 3781:2011 for the hydrophobized sheets with fatty acid grafting or AKD sizing. The relative wet strength is the difference between the tensile strength and the wet strength in percentage.

The edge wick penetration testing was performed with lactic acid (LA) (1 %) for 1 h at conditioned climate of 23 °C and 50 % RH. The thickness of the sheets was determined and the surfaces were masked with a plastic film on both sides prior to cutting them into five pieces to reveal raw edges. These were thereafter immersed into the LA bath for 1 h, and the amount of absorbed liquid was subsequently weighed. Thereafter the edge penetration wick index can be calculated in kg/m².

The Cobb₆₀ value was determined according to standard ISO 535:2014 after 60 seconds for the hydrophobized sheets with fatty acid grafting or AKD sizing.

The hydrophobicity of the fatty acid grafted sheets was greatly enhanced compared to the unsized sheets, which could be validated by their high (water) contact angles; values between 120-130 °C were achieved. Also, the contact angles for the AKD sized sheets were in the same range. The Formette sheet without any hydrophobation agent absorbed the water droplet immediately.

The tensile strength as well as the Z-strength were measured for all sheets and as can be seen in Table 2, the addition of MFC had an enormous effect on both strength parameters.

Another important feature for many paper and board products is the wet strength. Formette lab sheets without any additives have a very low wet strength and have therefore not been measured. The addition of AKD to the sheets with MFC gave

a wet strength of 0.75 and 0.72 kN/m for the fine and the coarse MFC, respectively, see Table 2. However, for the fatty acid grafted samples, the wet strength became more than twice as high: 1.81 and 1.63 kN/m for the fine and the coarse MFC, respectively, which is a very impressive value for weak Formette sheets.

The LA wick tests also showed an improvement of applying the grafting technique compared to AKD sizing, and values as low as 0.19 and 0.20 kg/m²h were achieved for the grafted MFC sheets with fine and coarse MFC, respectively, see Table 2. These values are also in line with the grafted reference samples without MFC.

The Cobb₆₀ measurements of the Formette sheets displayed an improved surface hydrophobicity for all samples, which also supports the CA measurement.

These results confirm that despite the hydrophilic nature of MFC, it is possible to improve both the wet strength and the edge wick penetration by grafting of fatty acid halides. It has also been shown how these characteristics can be in the same range or even further improved compared to AKD utilization.

Table 2. Results for the MFC strength enhanced sheets.

	Tensile strength MD (kN/m)	Z-strength (kN/m²)	Wet strength MD (kN/m)	Relative wet strength MD (%)	LA wick (kg/m²h)	Cobb₆₀ (g/m²)
Ref-PTC- FS – No MFC	4.6	110	1.2	25	0.21	14.6
PTC-FS- MFC fine	7.0	220	1.8	26	0.19	10.0
PTC-FS- MFC coarse	6.2	200	1.6	26	0.20	9.7
Ref-AKD- FS – No MFC	4.7	120	0.45	10	0.25	14.2
AKD-FS- MFC fine	7.4	260	0.75	10	0.31	14.2
AKD-FS- MFC coarse	5.8	190	0.72	12	0.25	14.6

CLAIMS

1. Paper or paperboard comprised of one or more plies,

wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose,

wherein said paper or paperboard has been subjected to grafting with a fatty acid halide such that ester bonds are formed between carbonyl groups of the fatty acid halide and hydroxyl groups of the cellulose fibers and the strength enhancement agent.

2. Paper or paperboard according to claim 1, wherein said paper or paperboard comprises two or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose.

3. Paper or paperboard according to any one of the preceding claims, wherein said paper or paperboard has been subjected to grafting with a fatty acid halide through the entire thickness of said paper or paperboard.

4. Paper or paperboard according to any one of the preceding claims, wherein a surface of said paper or paperboard subjected to grafting with a fatty acid halide has a water contact angle above 90°, preferably above 100°.

5. Paper or paperboard according to any one of the preceding claims, wherein said paper or paperboard subjected to grafting with a fatty acid halide has a wet tensile strength in machine direction in the range of 0.5-10, or more preferably 0.8-4 kN/m, as determined according to standard ISO 3781:2011.

6. Paper or paperboard according to any one of the preceding claims, wherein the grammage of said paper or paperboard prior to grafting is in the range of 50-700 g/m², more preferably between 60-500 g/m².

7. Paper or paperboard according to any one of the preceding claims, wherein the grammage of said paper or paperboard subjected to grafting with a fatty acid halide is in the range of 40-700 g/m², more preferably between 60-500 g/m².

8. Paper or paperboard according to any one of the preceding claims, wherein said cellulose fibers are from soft wood, hard wood, sulphate pulp, sulphite pulp, dissolving pulp, chemical pulp, thermomechanical pulp (TMP), chemi-thermomechanical pulp (CTMP) or high-temperature (HT)-CTMP, or a mixture thereof.

9. Paper or paperboard according to any one of the preceding claims, wherein said strength enhancement agent is MFC.

10. Paper or paperboard according to claim 9, wherein MFC is added in an amount of between 0.1 - 10 wt%, preferably between 1 - 7 wt%, or between 1 - 5 wt% as calculated on the total solid content of the ply.

11. Paper or paperboard according to any one of claims 1-8, wherein said strength enhancement agent is highly refined cellulose.

12. Paper or paperboard according to claim 11, wherein said highly refined cellulose is cellulose refined to an SR value in the range of 70-94, preferably in the range of 70-90, as determined according to standard method defined in EN ISO 5267-1.

13. Paper or paperboard according to any one of the preceding claims, wherein the dry weight ratio between said cellulose fibers and said strength enhancement agent in the at least one ply is in the range of 80:20 to 99.9:0.1, preferably in the range of 90:10 to 99:0.5.

14. Paper or paperboard according to any one of the preceding claims, having a Cobb60 value below 30 g/m² preferably below 20 g/m², and more preferably below 15 g/m².

15. Paper or paperboard according to any one of the preceding claims, wherein the paper or paperboard has a structure comprising at least three plies, wherein at least the middle ply:

- comprises a mixture of cellulose fibers and a strength enhancement agent; and
- has been subjected to grafting with a fatty acid halide such that ester bonds are formed between carbonyl groups of the fatty acid halide and hydroxyl groups of the cellulose fibers and the strength enhancement agent.

16. Paper or paperboard according to claim 15, wherein said middle ply comprises $\geq 60\%$ mechanical fibers and $\leq 40\text{wt}\%$ chemical pulp calculated on the total fiber weight of the ply.

17. Paper or paperboard according to any one of the preceding claims, further comprising at least one outer polymer layer forming an outer surface of said paper or paperboard, wherein said polymer comprises any of the following; polyethylene (PE), polyethylene terephthalate (PET), polyvinyl alcohol (PVOH), polyvinyl acetate (PVA), polypropylene (PP), polylactic acid (PLA) and/or polyamide (PA).

18. A method for manufacturing paper or paperboard, said method comprising:

a) providing a paper or paperboard substrate comprised of one or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC) and highly refined cellulose, and

b) subjecting said paper or paperboard to grafting with a fatty acid halide such that ester bonds are formed between carbonyl groups of the fatty acid halide and hydroxyl groups of the cellulose fibers and the strength enhancement agent.

19. The method according to claim 18, wherein said paper or paperboard comprises two or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC), and highly refined cellulose.

20. The method according to any one of claims 18-19, wherein said paper or paperboard is subjected to grafting with a fatty acid halide through the entire thickness of said paper or paperboard.

21. The method according to any one of claims 18-20, wherein a surface of said paper or paperboard subjected to grafting with a fatty acid halide has a water contact angle above 90°, preferably above 100°.

22. The method according to any one of claims 18-21, wherein the applied amount of fatty acid halide is between 0.1-4 kg/ton of total dry weight of the paper or paperboard, preferably between 0.5-2 g/m².

23. The method according to any one of claims 18-22, wherein said paper or paperboard subjected to grafting with a fatty acid halide has a wet tensile strength in machine direction in the range of 0.5-10, or more preferably 0.8-4 kN/m, as determined according to standard ISO 3781:2011.

24. The method according to any one of claims 18-23, wherein grammage of said paper or paperboard prior to grafting is in the range of 40-700 g/m², more preferably between 60-500 g/m².

25. The method according to any one of claims 18-24, wherein the grammage of said paper or paperboard subjected to grafting with a fatty acid halide is in the range of 40-700 g/m², more preferably between 60-500 g/m².

26. The method according to any one of claims 18-25, wherein said cellulose fibers are from soft wood, hard wood, Kraft pulp, sulphite pulp, dissolving

pulp, chemical pulp, thermomechanical pulp (TMP), chemi-thermomechanical pulp (CTMP) or high-temperature (HT)-CTMP, or a mixture thereof.

27. The method according to any one of claims 18-26, wherein said strength enhancement agent is MFC.

28. The method according to claim 27, wherein the final specific surface area of the formed MFC is from about 1 to about 500 m²/g, such as from 10 to 400 m²/g or more preferably 50-300 m²/g when determined for a solvent exchanged and freeze-dried material with the BET method.

29. The method according to any one of claims 18-26, wherein said strength enhancement agent is highly refined cellulose.

30. The method according to claim 29, wherein said highly refined cellulose is cellulose refined to an SR value in the range of 70-94, preferably in the range of 70-90, as determined according to standard method defined in EN ISO 5267-1.

31. The method according to any one of claims 18-30, wherein the dry weight ratio between said cellulose fibers and said strength enhancement agent in the at least one ply is in the range of 80:20 to 99:1, preferably in the range of 90:10 to 99:1.

32. Use of a fatty acid halide for hydrophobization of a paper or paperboard comprised of one or more plies, wherein at least one ply comprises a mixture of cellulose fibers and a strength enhancement agent selected from the group consisting of microfibrillated cellulose (MFC), and highly refined cellulose.

33. A product produced from the paper or paperboard substrate according to any of the claims 1-17, wherein the product is any one of the products from the group comprising:
laminate structures for boards utilized for liquid packaging boards (LPB) for use in the packaging of liquids or liquid-containing products, as well as board for dry, fat, fresh and/or frozen food;

- cup material for hot and cold food stuff, and general packaging, graphical board and luxury packaging;
- products for non-food applications, such as flora and fauna products, graphical products, pharma products, beauty and personal care products and multi-pack products;
- well and wrapping paper;
- paper or paperboard for single-use items;
- labels and pouches; and
- grease-proof paper, high-density paper, sack paper and well structures

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2020/056061

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: B32B, D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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L	US 20150167243 A1 (BILODEAU MICHAEL A ET AL), 18 June 2015 (2015-06-18); paragraph [0085]; cross-reference cited in US'073 above --	1-33
Y	EP 1936032 A1 (AKZO NOBEL NV), 25 June 2008 (2008-06-25); paragraphs [0031], [0041]-[0044]; claims 1-18 --	1-33

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"D" document cited by the applicant in the international application	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"E" earlier application or patent but published on or after the international filing date	"&" document member of the same patent family
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 31-08-2020	Date of mailing of the international search report 02-09-2020
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Continuation of: second sheet

International Patent Classification (IPC)

D21H 21/16 (2006.01)

D21H 11/18 (2006.01)

D21H 17/18 (2006.01)

D21H 21/18 (2006.01)

D21H 27/30 (2006.01)

B32B 27/10 (2006.01)

B32B 29/00 (2006.01)

D21H 17/11 (2006.01)

D21H 17/14 (2006.01)

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