

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

07 July 2022 (07.07.2022)



(10) International Publication Number

WO 2022/144682 A1

(51) International Patent Classification:

D21J 7/00 (2006.01) D21J 5/00 (2006.01)

C09D 101/02 (2006.01) C08L 1/02 (2006.01)

D21H 11/18 (2006.01) D21H 19/12 (2006.01)

D21J 3/00 (2006.01) D21H 21/18 (2006.01)

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(21) International Application Number:

PCT/IB2021/061939

(22) International Filing Date:

17 December 2021 (17.12.2021)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2051576-3 30 December 2020 (30.12.2020) SE

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: METHOD OF PRODUCING A CELLULOSE FIBER STRUCTURE AND A FIBER STRUCTURE

(57) Abstract: The invention discloses a method for producing a three-dimensional molded article from cellulose fibers, comprising the steps of: -providing a pulp molding composition; -molding a three-dimensional precursor structure from said composition wherein said structure comprises a dry content between 15-80wt%; -providing an aqueous suspension comprising microfibrillated cellulose; -applying the aqueous suspension onto at least one face of said precursor structure to create a surface barrier layer on said structure; and -dewatering and drying said molded precursor structure under elevated temperature >150°C to a dry content of ≥88wt%, preferably ≥94wt%, more preferably ≥96% to achieve the three-dimensional molded article comprising a surface barrier layer.



WO 2022/144682 A1

METHOD OF PRODUCING A CELLULOSE FIBER STRUCTURE AND A FIBER STRUCTURE

Technical field

The present invention relates to a method of producing a three-dimensional cellulose-based structure by means of fiber molding.

5

Background

There is a growing interest for producing cellulose based, three-dimensional (3D) products, e.g. for use as packaging applications for foodstuff, tableware, trays, technical products, electronic
10 equipment and/or consumer goods. Several advantages are associated with the use of natural fibers for manufacturing packages. Being a renewable resource, natural fibers provide a sustainable alternative to other packaging materials such as aluminum and plastics, and furthermore natural fibers are both
15 recyclable and biodegradable allowing for composting. Natural fibers include cellulose fibers of any natural origin, such as derived from wood pulp and/or plants.

Manufacturing molded fiber products and structures can be done by
20 wet forming, wherein an aqueous pulp composition is applied to a forming tool to form a fiber matt followed by compression-molding performed under elevated temperatures, resulting in a dried fiber product having a shape complementary to the shape of the mold. Typically, said tool is perforated or porous so that water can be
25 removed from the suspension or wet pulp during forming, such as in a dewatering/drying step.

It is common to add so called wet strength agents (WSA) to the furnish upon molding procedures. Wet strength chemicals improve the strength properties of the paper both in wet and dry state by crosslinking the cellulose fibres with covalent bonds that do not
5 break upon wetting. Wet strength agents also improve mechanical properties under humid conditions. A disadvantage associated with addition of WSA is that the repulpability of the material is decreased, i.e. the fraction of reusable fibers upon recycling is reduced, or harsher process condition than normally used at the
10 mill is required. Another disadvantage with WSA is that the chemical retention in the sheet or substrate is important in order to achieve the effects. One way is to combine WSA with a specific retention chemical in order to increase the fixation. The harsh dewatering conditions in fiber molding present challenging
15 conditions for obtaining good and efficient retention of the chemicals. To obtain sufficient wet strength, the preferred technical solution is to increase dosage of WSA and with higher dosage of retention chemicals. As a consequence, the use of higher concentration of WSA deteriorates disintegration of the molded
20 product and hence reduces repulpability.

Thus, there is a need for improvements when it comes to producing three dimensional products, and articles made from molded cellulose fibers, at least when it comes to improving repulpability.
25

Objects of the invention

It is an object of the present invention to provide an improved method for manufacturing a cellulose-based, three dimensional molded fiber article, resulting in a product having good wet
30 strength, grease resistance and water- and vapor resistance,

providing gas barrier and having an improved recyclability compared to known molded fiber products.

Summary

- 5 The objects of the invention are obtained by means of a method for producing a three-dimensional molded article from cellulose fibers according to claim 1.

Said method comprises at least the steps of:

- 10 -providing an aqueous pulp molding composition;
-wet molding a three-dimensional precursor structure from said composition, wherein said structure comprises a dry content between 15-80wt%;
-providing an aqueous suspension comprising microfibrillated
15 cellulose;
-applying the aqueous suspension onto at least one face of said precursor structure to create a surface barrier layer on said structure;
-dewatering and drying said molded precursor structure under
20 elevated temperature $>150^{\circ}\text{C}$ to a dry content of $\geq 88\text{wt}\%$, preferably $\geq 94\text{wt}\%$, more preferably $\geq 96\%$ to achieve the three-dimensional molded article.

- Said achieved three-dimensional molded article thus comprises a
25 base substrate originating from the aqueous pulp molding composition, and a surface barrier layer (herein sometimes also referred to as "top layer" or "top barrier layer") originating from the aqueous suspension.

It is to be understood that the procedure of "molding a three-dimensional precursor structure" in this context may include the steps of providing a forming tool having a three dimensional shape and comprising a forming portion; and bringing said forming portion
5 into contact with the aqueous composition so that said forming portion is covered with a wet layer of pulp from the pulp molding composition.

It is also to be understood that said "precursor structure" refers to
10 an intermediate, not-yet ready structure, that in the present case has been formed into a three-dimensional shape, and which is still in a wet state (dry content between 15-80wt%).

Moreover, the term "recycling" used herein refers to the process of
15 converting waste cellulose-based materials into new cellulose-based materials and products. The recyclability of a material depends on its ability to reacquire the properties it had in its virgin state. During recycling of cellulose based products, the fibers are converted back into pulp in a so called "repulping" procedure. In
20 other words, recyclability and repulpability means that pre-consumer waste can be collected, disintegrated and reused for example when making new formed fiber products. Post-consumer waste can be collected and treated in various ways before being reused in e.g. molded pulp. The treatment before reuse depends on
25 the packed product and level of contaminants. Repulpability can be determined according to the PTS standard (PTS RH 021/97).

According to a preferred aspect of the invention, said aqueous pulp molding composition used for molding the precursor structure is
30 free from wet strength agent.

According to the present invention, a top barrier layer is formed on a surface of the molded article. It has surprisingly been found that a top layer comprising MFC, applied onto a wet precursor molded fiber substrate, which is subsequently dried under heat provides a final product with a dense top layer providing excellent grease barrier properties as well as improved wet rub resistance. Furthermore, applying the aqueous suspension onto a wet precursor substrate ensures better economy, better infiltration of MFC and chemicals into the base substrate, and significantly better chemical retention.

In one embodiment, the MFC content of the top barrier layer may be in the range of 70 to 99 weight%, in the range of 80 to 99 weight%, or in the range of from 90 to 99 weight% of the solids of the top barrier layer.

Microfibrillated cellulose (MFC) shall in the context of the patent application mean a nano scale cellulose particle fiber or fibril with at least one dimension less than 1000 nm. MFC comprises partly or totally fibrillated cellulose or lignocellulose fibers.

The liberated fibrils have a diameter less than 1000 nm, whereas the actual fibril diameter or particle size distribution and/or aspect ratio (length/width) depends on the source and the manufacturing methods.

The smallest fibril is called elementary fibril and has a diameter of approximately 2-4 nm (see e.g. *Chinga-Carrasco, G., Cellulose fibres, nanofibrils and microfibrils, The morphological sequence of*

- MFC components from a plant physiology and fibre technology point of view, Nanoscale research letters 2011, 6:417*), while it is common that the aggregated form of the elementary fibrils, also defined as microfibril (*Fengel, D., Ultrastructural behavior of cell wall polysaccharides, Tappi J., March 1970, Vol 53, No. 3.*), is the main product that is obtained when making MFC e.g. by using an extended refining process or pressure-drop disintegration process. Depending on the source and the manufacturing process, the length of the fibrils can vary from around 1 to more than 10 micrometers. A coarse MFC grade might contain a substantial fraction of fibrillated fibers, i.e. protruding fibrils from the tracheid (cellulose fiber), and with a certain amount of fibrils liberated from the tracheid (cellulose fiber).
- There are different acronyms for MFC such as cellulose microfibrils, fibrillated cellulose, nanocellulose, fibril aggregates, 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 the invention, the MFC should preferably be a mechanically fibrillated fiber from either non-mechanically pre-treated or mechanically pre-treated pulp. The pulp can also be enzymatically pre-treated before fibrillation step. Further, the MFC

- should preferably have the following characteristics: FS5 fines should preferably lower than 100%, and preferably lower than 90% (as determined the Valmet FS5 fiber image analyzer). "FS5 fines" here refers to the projection area of particles with a size under
- 5 0.2mm of the total surface area of all measured objects $\times 100\%$. FS5 fibrillation level (P14) should preferably be higher than 1.5% and more preferably higher than 1.8% and more preferably higher than 2%.
- 10 According to one aspect of the invention, the MFC is fine fibrils derived from enzymatically treated and fluidized chemical pulp or homogenized pulp or disintegrated by Aqueous counter collision (ACC) or high pressure drop methods or treated in a high shear rotor stator mixer. Before subjecting the enzymatically pre-treated
- 15 pulp to high shear disintegration, the pulp can be mechanically activated or fibrillated in one or several steps. The enzymatically treated pulp can be provided as never-dried, dewatered or dried before further subjecting to the activation and fibrillation step.
- 20 According to another aspect of the present invention, said MFC is coarse fibril, derived from fibrillated chemical pulp, said fibril coarse having a Shopper Riegler value between 50-95, more preferably between 60-93. The Schopper-Riegler value can be determined through the standard method defined in EN ISO 5267-1.
- 25
- According to one aspect of the present invention, in addition to MFC the aqueous suspension also comprises wet strength agent of an amount between 1-100kg/tn, more preferably 5-75kg/tn and most preferably 10-50kg/tn (measured in dry weight of the top layer). As

previously explained, the aqueous suspension is applied onto a surface of the molded precursor substrate thus forming a top layer.

It is within the scope of the present invention to mix fine and
5 coarse MFC and apply together with WSA as said aqueous solution to form the top barrier layer.

According to another aspect of the present invention, said wet strength agent is selected from the group comprising: polyamide
10 epichlorohydrin, polyethylene imine, dialdehyde starch, polyacryl amides, glyoxal or melamine formaldehyde, polyamidoamine-epichloro hydrin and urea formaldehyde melamine or a combination thereof.

15 According to another aspect of the present invention, said microfibrillated cellulose and WSA have been co-fibrillated and/or co-mixed before applied onto said precursor structure as an aqueous suspension. Co-fibrillation and/or co-mixing leads to facilitated preparation of the aqueous solution, e.g. due to that MFC
20 alone is sometimes difficult to mix with water. The mixing is even more difficult if the WSA is added with a retention agent or if the WSA has cationic or cellulose fibril reactive sites since this can causes substantial increase in gel viscosity or formations or flocs. Thus, in one aspect of the invention, WSA is added together with
25 additional functional chemicals such as retention agents to fiber before subjecting the resulting mixture to fibrillation treatment.

According to another aspect of the invention, said aqueous suspension further comprises a sizing agent, preferably selected
30 from the group comprising: alkyl ketene dimer (AKD), rosin sizes

such as soap or rosin emulsions, alkyl succinic anhydride (ASA), polyurethane or styrene maleic anhydrides. In a preferred aspect, the sizing agent is AKD. Preferably, the amount of AKD is between 0.05 -100 kg/tn, more preferably 0.1-50 kg/tn, and even more
5 preferably 0.5-40 kg/tn and more preferably 2-20 kg/tn based on the dry content of the top layer.

According to another aspect of the invention, said aqueous suspension further comprises dye and/or pigment to achieve a
10 shaded/colored product providing possibilities of controlling the appearance of the molded article.

According to another aspect of the invention, the viscosity of the aqueous suspension is 5-2000 mPas, such as 10-500 mPas as
15 determined with Brookfield, i.e. Brookfield viscosity determined at 100 rpm according to standard SCAN-P 50:84.

According to yet another aspect of the present invention, said aqueous suspension is applied onto the precursor structure by
20 means of a non-contact application method, e.g. by spraying liquid droplets onto the surface of the precursor structure, or by means of curtain coating. Non-contact application onto the precursor structure may be repeated several times in order to reach the desired grammage of the top layer, preferable in at least two
25 consecutive steps, or at least ten steps. Spraying of aqueous suspension can be carried out using methods known in the art. The spraying can for example be electrostatically assisted or ultrasound assisted. It can also be performed by a co-axial spray nozzle, as steam, high air pressure or by use of a rotary disk atomizer.

It is also within the scope of the present invention to apply said aqueous suspension onto the precursor structure by means of contact applications, such as immersing the precursor structure into a bath of aqueous suspension comprising MFC and optionally WSA.

5

According to another aspect of the present invention, the pulp molding composition for wet molding the precursor structure is an aqueous composition having a solid content between 0.05 – 10wt%, preferably between 0.2-1.5wt%.

10

According to another aspect of the present invention, the pulp molding composition comprises cellulose fibers or a mix of cellulose fibers selected from the group comprising: wood pulps, non-wood pulps, unbleached chemical pulp, defibrated fiber material, bagasse, straws, bamboo, spruce CTMP, eucalyptus CTMP, spruce HT CTMP, sulphate, sulphite, PGW, GW, DIP, recycled paper and board, broke, RMP, TMP, CMP, NSSC, dissolving pulp, and regenerated fibers and mixtures thereof. In a preferred aspect, the pulp molding composition is based on CTMP. CTMP comprise bulky and stiff fibers and provide more rigidity to the final structure. CTMP pulp can also be deficient of fines e.g. by fractionation or washing. Less fines in the bulk layer leads to faster dewatering during production of the molded structure.

25 According to yet another aspect of the present invention, the grammage of the three-dimensional molded article is 50 - 500 gsm in dry weight.

Preferably, dewatering and drying the precursor structure comprising the top barrier layer is performed by pressing the wet

30

fiber layer under applied heat, optionally with vacuum suction for removing water/steam.

According to another aspect of the present invention, dewatering
5 and drying said molded precursor structure is performed as a one-sided dewatering. In case of dewatering and drying by means of vacuum suction, one-sided dewatering is performed by applying the vacuum on the non-coated side of the structure. This leads to that the top barrier layer is to some extent drawn into the base
10 substrate, leading to improved retention and integration of the MFC and WSA.

According to yet another aspect of the invention, the top barrier layer has a grammage between 5-50gsm, preferably 10-30gsm,
15 preferably between 7-20gsm.

According to yet another aspect of the invention, the top barrier layer comprises <10 pinholes/m², preferably <5 pinholes/m², more preferably pinhole free according to standard EN13676:2001.
20

According to yet another aspect of the invention, the surface barrier side of the three-dimensional molded article has a water Cobb₆₀ value (as determined according to standard ISO 535:2014 after 60 seconds) below 50 g/m², preferably below 30 g/m². According to
25 yet another aspect, the substrate comprises internal sizing such as AKD, and the three-dimensional molded article has a Cobb₆₀ value below 30 g/m².

According to yet another aspect of the invention, the three-
30 dimensional molded article has an oil Cobb₃₀ value (as determined

according to standard SCAN-P 37:77 after 30 seconds) below 9 g/m², preferably below 5 g/m².

According to yet another aspect of the invention, the three-
5 dimensional molded article has a KIT barrier >5, preferably >10 such as 12 (TAPPI method 559, 3M KIT test).

According to yet another aspect of the invention, the three-
dimensional molded article has an air permeance, L&W Code 168
10 air permeance tester (pm/Pa s at 20 kPa), less than 1000 and more preferably less than 500 and most preferably less than 210 (SCAN P26 or ISO 5636-1).

According to yet another aspect of the invention, the three-
15 dimensional molded article has a Gurley Hill value (L&W Code 166) >20 000, more preferably >30 000 and most preferably >40 000 s/100 ml (determined according to the standard ISO 5636/6).

According to yet another aspect of the present invention, said
20 three-dimensional molded article has an average density between 350-1500 kg/m³, preferably 400-1200 kg/m³ or more preferably 500-900 kg/m³.

According to yet another aspect of the present invention, said
three-dimensional molded article comprises a top side comprising
25 said top barrier layer, and a back side opposite to said top side.
According to this aspect, the density at said top side is >800 kg/m³, more preferably > 850 kg/m³, and the density at said back side is 300 – 800 kg/m³.

According to yet another aspect of the present invention, said dried three-dimensional molded article has a repulpability characterized by a reject rate (as determined according to the PTS RH 021/97 test method) below 10%, preferably below 5%. Hereby, the molded
5 article according to the invention is suitable for recycling, since a vast majority of its fiber content can be re-used.

According to yet another aspect of the present invention, said three-dimensional molded article has a wet strength $>1\%$, preferably between 2-10% measured as percent wet strength over
10 dry strength.

According to yet another aspect of the present invention, said three-dimensional molded article has a wet rub turbidity between 1-25 Nephelometric Turbidity Units (NTU) measured with a
15 nephelometer (ISO 7027) after 20 s of wet rub.

The present invention further comprises a three-dimensional molded pulp article comprising more than one layer, whereof at least one layer is made by means of a method according to the
20 invention, further where said top barrier layer is arranged as an outer layer of said multilayer article.

Detailed description

The present description is directed to production of three-
25 dimensional molded pulp articles with grease barrier properties and improved repulpability. Examples of three-dimensional molded pulp articles include in a non-limiting way bowls, cups, capsule, pots, containers, trays and packages.

The present description relates to the context of wet molding procedures.

According to the invention, applying MFC in an aqueous suspension
5 onto the surface of a wet molded 3D fiber structure, where application of MFC is performed onto a fiber structure which comprises a dry content between 15-80wt%, and thereafter dewatering the structure under heat, leads to a product with good grease barrier as well as wet rub resistance.

10

In one embodiment, the molded article is intended to contain foodstuff. In such a variant, the surface comprising the top barrier layer is arranged at the food-contact side of the product.

15 It is thus within the ambit of the present invention to provide a 3D molded fiber article comprising at least one outer surface, or a portion of an outer surface, which has been subjected to application (e.g. spraying, coating or immersion) of an aqueous suspension comprising MFC and optionally WSA. Said aqueous suspension is to
20 be applied onto a substrate in wet state (i.e. dry content between 15-80wt%), whereafter the article is subjected to drying and dewatering under heat treatment, preferably in combination with applied pressure.

25 In the following, an example of a wet molding method for manufacturing a three-dimensional molded fiber article with barrier properties will be described in a non-limiting way.

An aqueous pulp composition is provided with consistency between
30 0.05-10wt%. The pulp may be any one of wood pulps, non-wood

pulps, unbleached chemical pulp, defibrated fiber material, bagasse, straws, bamboo, spruce CTMP, eucalyptus CTMP, spruce HT CTMP, sulphate, sulphite, PGW, GW, DIP, recycled paper and board, broke, RMP, TMP, CMP, NSSC, dissolving pulp, and regenerated fibers or
5 mixtures thereof. Preferably, the pulp is CTMP.

A 3D shaped forming tool comprising a forming portion is brought into contact with the pulp composition, for instance by immersing said tool into the slurry bath. Said forming portion is arranged to
10 represent a 3D mirror image of the article to be formed. Pulp is drawn onto the forming portion e.g. by means of vacuum suction until a layer of desired thickness has been formed, whereupon the forming tool is removed from the slurry. Next, the wet layer of pulp is dewatered to a dry content between 15-80wt%. Hereby, an
15 intermediate precursor structure has been obtained, which is still supported by the shape of the forming tool.

In a next step, an aqueous suspension is provided, comprising microfibrillated cellulose and optionally wet strength agent mixed
20 with each other to a homogenous mixture. The aqueous suspension is applied onto at least one face of said precursor structure e.g. by means of a non-contact application method to create a layer on said structure. An example of a non-contact application method is spraying liquid droplets onto the precursor structure. Application of
25 the aqueous suspension can be performed in many consecutive sessions, e.g. spraying sessions, e.g. such as spraying at least two times on the same surface, or at least five times or at least twenty times, until a desired thickness of the sprayed layer is achieved. The top layer originating from the aqueous suspension will provide

barrier properties, and the wet strength agent present in the suspension will contribute to make the article stable and rigid.

The precursor structure having been covered with a top barrier layer is then to be further dewatered and dried. Preferably, dewatering of said molded precursor structure is performed as a one-sided dewatering by means of applying suction at the non-coated side of the structure. Sucking from the untreated side leads to that the top layer components are partially drawn into the substrate and gets integrated therewith, and binding of the top surface components onto the substrate is improved. Preferably, the side of the structure comprising the barrier layer is pressed against a support arrangement, e.g. a mesh. As a result, a dense and stable top barrier layer is achieved.

Dewatering and/or drying can be done in various ways. In a wet curing procedure, the wet layer is pressed under elevated temperatures to be compressed and dried to a certain thickness, thereby yielding a smooth external surface for the end structure. In a dry curing process, the wet layer is subjected to heated air thereby removing moisture, which results in an end structure with a more textured finish.

According to the invention, the hot press temperature range for a wet molded procedure is between 150-220 °C, with a press range between 1-10 bar. This way, a single layer 3D molded fiber article is formed, having a dry content of $\geq 88\text{wt}\%$, preferably $\geq 94\text{wt}\%$, more preferably $\geq 96\%$.

It is conceivable to produce multilayered molded fiber products. Manufacturing multilayered molded fiber products can be accomplished for instance by applying more than one fibrous layer on top of each other in consecutive molding production steps. The various layers of a multilayered product may hereby provide different functions, such as rigidity, barrier properties, etc. In a multilayered product according to the present invention, the food-contact layer of the end-product is arranged to comprise the top barrier layer described herein.

10

The present invention has been described with regards to preferred embodiments. However, it will be obvious to a person skilled in the art that a number of variations and modifications can be made without departing from the scope of the invention as described herein.

15

Examples

Materials used

20

Pulp – CTMP pulp was used with and without additives, i.e. internal sizing agent and/or wet strength agent (WSA).

25

Fine fibril – This was a chemical pulp that was enzymatically treated and then fluidized. Among the characteristic properties of this material is high water retention value, but due to its fineness, it is difficult to retain on a wire. If blended with a furnish/pulp, it will pass through the wire or holes in the dewatering unit. The material is gel like at low solid contents 2-4 wt%.

30

- Coarse fibril – This is a fibrillated fiber prepared from a chemical pulp. The characteristic properties of this is that it is easier to retain mechanically in a fiber matrix or on a dewatering wire. On the other hand, it increases also drainage resistance. The preferred Shopper
- 5 Riegler level is 50-95 and more pref. 60-93. The SR for fibril coarse used here was about 93.

The internal sizing agent used was alkyl ketene dimer (AKD).

- 10 The wet strength agent (WSA) used here was polyamide epichlorohydrin.

Measurement and evaluation methods

- 15 The following methods and standards apply both to the definitions of the appended claims and to the measurements performed in the examples below.

- Twelve cellulose-based test sheets (referred to below) were
- 20 prepared and analyzed with regards to the following properties:

- Oil Cobb30 (gsm)
- Water Cobb60 (gsm) (ISO 535:2014)
- KIT (TAPPI method 559, 3M KIT test)

25 -WVTR (g/m² 24h) (ASTM F1249)

- OTR (g/m² 24h) (ASTM D-3985)
- Wet rub (30s, turbidity NTU)
- Wet rub (20s, turbidity NTU)
- Wet strength (expressed as the ratio of wet to dry tensile force at

30 break)

-PTS repulpability

With regards to evaluation of wet rub, measurements were performed using a conventional rotational wet abrasion tester to determine wet rub resistance of the coatings. A volume of 50 ml distilled water was poured over the respective sample, and after 30s wetting time, the rotational wet abrasion of the sample is started. After 40s and 20s respectively, the rotation was stopped and water was poured off from the sample. Turbidity of the water was then measured using a nephelometer (ISO 7027).

The results from the performed tests for the respective sheet are summarized in Table 1, appended herewith.

Results

The sheets numbered 1 – 12 are described in the following.

1. Base sheet (comparative example)

A 300 gsm sheet was prepared on a 2D molding wire using vacuum suction. The wet sheets were dried using a hot plate (under pressure) at 180 C. No barrier properties were obtained.

2. Base sheet with WSA and internal sizing (comparative example)

Same as #1 but with added AKD and WSA. Clear improvement especially in water cobb (water uptake) but the sheet has still poor wet resistance. Due to the presence of WSA, this grade will have limited repulpability.

3. Base sheet with integrated fine fibril top layer and WSA

After wet forming the base, a 10 gsm (dry weight) wet layer of fine fibril pre-mixed with WSA was applied by spraying, and then the product was further dewatered and dried. This recipe shows a significant reduction in oil uptake (Oil Cobb). The amount of WSA corresponds to 0.86 kg/tn of the whole product, i.e. a reduction with more than 50% compared to #2.

4. Base sheet with integrated fine fibril top layer

This is a corresponding test point to #3 but without the WSA. The oil absorbency confirms that the fine fibril gives a significant reduction on oil uptake and also in water uptake. The oil and grease resistance show also excellent KIT value (max value) confirming that the coating is uniform and forms a dense layer with good adhesion to the base substrate. The gas and water vapor barriers are also detectable showing that the film is dense and not destroyed during coating, which is probably due to the fact that steam and water is removed in one side direction, i.e. a one-sided dewatering was performed.

20

5. Base sheet with integrated top layer comprising fine fibril and sizing agent

This sample shows the benefit of adding sizing agent to the integrated top layer instead of adding the chemical to the bulk furnish. Compared to the reference #1, an increased wet rub resistance is obtained.

6. Base sheet with integrated top layer comprising fine fibril, AKD and WSA

In this trial, high barrier level is obtained and especially for KIT. Surprisingly high WVTR is obtained which indicates that the specific manufacturing technique is actually densifying the top layer structure without causing blistering and pinholes. Very low wet rub resistance value, i.e. very low amount of material is released confirming high surface strength.

7. Base sheet with top layer comprising fine fibril, AKD and WSA

10 Same as the #6 but the top layer grammage has been increased to about 20 gsm. In this case, very low OTR and WVTR was obtained which is surprising.

8. Base sheet with top layer comprising fine fibril, AKD and WSA

15 Same as the #6 but the top layer grammage has been increased to about 30 gsm. In this case, very low OTR and WVTR was obtained which is surprising.

9. Base sheet with top layer comprising fine fibril, AKD and WSA and dispersing agent

20 Same as the #8 but the top layer recipe has been modified with a dispersing agent for enhancing runnability and flow behavior. WVTR and KIT are almost on same level whereas OTR is increased (less gas barrier).

10. Base sheet with top layer comprising coarse fibril, AKD and WSA

30 This corresponds to sample #6 with the exception that the fibril grade is coarser. At 10 gsm amounts, no barrier was obtained.

11. Base sheet with top layer comprising coarse fibril, AKD and WSA

This corresponds to #10 with the exception that the coating weight
5 is about 30 gsm.

12. Base sheet with top layer comprising coarse fibril, AKD and WSA and dispersing agent

This corresponds to #11 with the exception that the top layer
10 contains a dispersing agent (low molecular weight CMC). The oil barrier and oil uptake values are very good.

Comments

The results show that applying MFC in a coating layer (see
15 examples No. 4 and 5) improves grease barrier as well as wet rub resistance.

Combination of WSA and AKD respectively with MFC in the top barrier layer provides additional advantages showing synergistical
20 effects that is not obtained with AKD and WSA separately.

CLAIMS

1. A method for producing a three-dimensional molded article from cellulose fibers, comprising the steps of:
 - 5 -providing a pulp molding composition;
 - molding a three-dimensional precursor structure from said composition wherein said structure comprises a dry content between 15-80wt%;
 - providing an aqueous suspension comprising microfibrillated
10 cellulose;
 - applying the aqueous suspension onto at least one face of said precursor structure to create a surface barrier layer on said structure; and
 - dewatering and drying said molded precursor structure under
15 elevated temperature $>150^{\circ}\text{C}$ to a dry content of $\geq 88\text{wt}\%$, preferably $\geq 94\text{wt}\%$, more preferably $\geq 96\%$ to achieve the three-dimensional molded article comprising a surface barrier layer.
- 20 2. A method according to claim 1, wherein said aqueous suspension further comprises a wet strength agent at a concentration between 1-100 kg/tn, more preferably 5-75 kg/tn, even more preferably 10-50 kg/tn based on the dry content of the surface barrier layer.
- 25 3. A method according to any one of claims 1-2, wherein said wet strength agent is selected from the group comprising:
polyamide epichlorohydrin, polyethylene imine, dialdehyde starch, polyacryl amides, glyoxal or melamine formaldehyde,
30 and urea formaldehyde melamine or a combination thereof.

4. A method according to any one of claims 1-3, wherein said microfibrillated cellulose is fine fibril derived from enzymatically treated and fluidized chemical pulp or homogenized pulp or
5 disintegrated by aqueous counter collision (ACC) or high pressure drop methods or treated in a high shear rotor stator mixer.
5. A method according to any one of claims 1-3, wherein said
10 microfibrillated cellulose is coarse fibril, derived from fibrillated chemical pulp, said fibril coarse having a Shopper Riegler value between 50-95, more preferably between 60-93.
6. A method according to any one of claims 2 - 5, wherein said
15 microfibrillated cellulose and wet strength agent have been co-fibrillated or co-mixed before applied onto said precursor structure as an aqueous suspension.
7. A method according to any one of the previous claims, wherein
20 the aqueous suspension further comprises a sizing agent, preferably selected from the group comprising alkyl ketene dimer (AKD), rosin sizes such as soap or rosin emulsions, alkyl succinic anhydride (ASA), polyurethane and styrene maleic anhydrides.
25
8. A method according to any one of the previous claims, wherein
the pulp molding composition is an aqueous composition having a dry content between 0.05 – 10wt%, preferably between 0.2-1.5wt%.

9. A method according to any one of the previous claims, wherein the pulp molding composition comprises cellulose fibers or a mix of cellulose fibers selected from the group comprising wood pulps, non-wood pulps, unbleached chemical pulp, defibrated fiber material, bagasse, straws, bamboo, spruce CTMP, eucalyptus CTMP, spruce HT CTMP, sulphate, sulphite, PGW, GW, DIP, recycled paper and board, broke, RMP, TMP, CMP, NSSC, dissolving pulp, and regenerated fibers and mixtures thereof.
10. A method according to any one of the previous claims, wherein the grammage of the three-dimensional molded article is 50 - 500 gsm in dry weight.
11. A method according to any one of the previous claims, wherein the dewatering and drying of said molded precursor structure is performed as a one-sided dewatering.
12. A method according to any one of the previous claims, wherein the surface barrier layer of the three-dimensional molded article has a basis weight between 5-50gsm, preferably 10-30gsm, preferably between 7-20gsm.
13. A method according to any one of the previous claims, wherein applying the aqueous suspension is non-contact application, preferably a series of non-contact application steps of aqueous suspension onto the precursor structure, preferable at least two consecutive application steps.

14. A method according to claim 13, wherein said non-contact application is performed by spraying liquid droplets onto the surface of the precursor structure.
- 5 15. A method according to any one of the previous claims, wherein said three-dimensional molded article has a repulpability of a reject rate (as determined according to the PTS RH 021/97 test method) below 10%, preferably below 5%.
- 10 16. A method according to any one of the previous claims, wherein the three-dimensional molded article has a water Cobb₆₀ value (as determined according to standard ISO 535:2014 after 60 seconds) below 50 g/m², preferably below 30 g/m².
- 15 17. A method according to any one of the previous claims, wherein the three-dimensional molded article has an oil Cobb₃₀ value (as determined according to standard SCAN-P 37:77 after 30 seconds) below 9 g/m², preferably below 5 g/m², preferably below 1 g/m².
- 20
18. A method according to any one of the previous claims, wherein the three-dimensional molded article has a KIT barrier >5, preferably >10 (TAPPI method 559, 3M KIT test).
- 25 19. A method according to any one of the previous claims, wherein the three-dimensional molded article has an air permeance, L&W Code 168 air permeance tester (pm/Pa s at 20 kPa), less than 1000 and more preferably less than 500 and most preferably less than 210 (SCAN P26 or ISO 5636-1).

20. A method according to any one of the previous claims,
wherein the three-dimensional molded article has a Gurley Hill
value (L&W Code 166) >20 000, more preferably >30 000 and
most preferably >40 000 s/100 ml (determined according to
5 the standard ISO 5636/6).
21. A method according to any one of the previous claims, wherein
said three-dimensional molded article has an average density
between 350-1500 kg/m³, preferably 400-1200 kg/m³ or
10 more preferably 500-900 kg/m³.
22. A method according to any one of the previous claims, wherein
said three-dimensional molded article comprises a top side
with the surface barrier layer, and a back side opposite to said
15 top side, wherein the density of said top side is >800 kg/m³,
more preferably > 850 kg/m³, and the density of said back
side is 300 – 800 kg/m³.
23. A method according to any one of the previous claims, wherein
20 said three-dimensional molded article comprises a wet strength
>1%, preferably between 2-10%.
24. A three-dimensional molded pulp article made by means of a
method according to any one of claims 1 – 23, comprising a
25 wet tensile strength >1%, preferably between 2-10%, and a
repulpability characterized by a reject rate (as determined
according to the PTS RH 021/97 test method) below 10%,
preferably below 5%.
- 30 25. A three-dimensional molded pulp article according to claim 24,
wherein the surface barrier layer comprises 1-100 kg/tn wet

strength agent, more preferably 5-75 kg/tn, even more preferably 10-50 kg/tn based on the dry content of the surface barrier layer, and wherein the substrata layer is void of any wet strength agent.

5

26. A three-dimensional molded pulp article comprising more than one layer, whereof at least one layer is made by means of a method according to any one of claims 1 - 23, further where said layer is arranged as an outer layer of said multilayer
- 10 article.

Sample id	1 (Ref)	2 (Ref)	3	4	5	6	7	8	9	10	11	12
Furnish %	100 CTMP	100 CTMP	100 CTMP	100 CTMP	100 CTMP	100 CTMP	100 CTMP	100 CTMP	100 CTMP	100 CTMP	100 CTMP	100 CTMP
Grammage	300	300	300	300	300	300	300	300	300	300	300	300
WSA		2 kg/tn			2 kg/tn							
Internal sizing		2 kg/tn										
Top layer (barrier)												
Grammage			10	10,2	12	10,5	19,4	30	33,3	11,2	31,1	32,9
Fibril - coarse %										100	100	100
Fibril - fine %			100	100	100	100	100	100	100			
WSA, 20 kg/tn			20			10	10	10	10	10	10	10
Internal sizing					20	10	10	10	10	10	10	10
Drying time, sec	40		40	40		40	50	60	60	40	60	60
Oil Cobb30, gsm	220	197	0,7	0,5		1,6	1,3	0,8	1,3	8,2	0,8	0,5
Water Cobb60, gsm	220	26	52	40,7		25,4	29,5	29,9	32,5	25,8	30,5	33,5
KIT	<1			12		12	12	12	11	1	12	12
WVTR, (g/m2) 24h				118		118	63	51	95	195	85	73
OTR, g/(m*24h)				2000		2000	6	5	2000	2000	1826	2000
Density, kg/m3	434		445	465	437	438						
Tensile Strength Index, Nm/g	31,4		36,2	36,7	41,3	36,8						
Wet strength, %	0		4,7	0	19,4	3,9						
Wet rub 30s, turbidity NTU	48,500	29,067	6,557	11,227	4,387	10,467	12,100	20,433	26,167	4,387	4,030	3,040
Wet rub 20s, turbidity NTU	5,637	5,680	2,747	2,470	4,355	2,653	3,440	5,390	4,033	1,087	1,237	1,310

Table 1

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/IB2021/061939

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: C08L, C09D, D21H, D21J

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, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2018078558 A1 (STORA ENSO OYJ), 3 May 2018 (2018-05-03); page 1, line 4 - line 5; page 3, line 19 - line 22; page 4, line 24 - page 5, line 1; page 5, line 5 - line 23; page 6, line 4 - line 5; page 6, line 25 - line 27; page 7, line 11 - line 15; page 7, line 26 - line 34; page 11, line 27 - line 28; page 13, line 5 - line 15; Table 2	1, 4-5, 7-15, 17-24, 26
Y	--	2-3, 6, 16, 25
Y	WO 2017046755 A1 (STORA ENSO OYJ), 23 March 2017 (2017-03-23); page 2, line 13 - line 15; page 2, line 31 - line 34; page 3, line 11 - line 13; page 3, line 23 - line 26; page 3, line 30 - line 35; page 8, line 24 - line 28; page 8, line 31 - line 33; Table 1, Table 2	2-3, 6, 16, 25
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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

25-02-2022

Date of mailing of the international search report

28-02-2022

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2021/061939

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016097964 A1 (STORA ENSO OYJ), 23 June 2016 (2016-06-23); whole document --	1-26
A	CN 111519476 A (HANGZHOU XIHONGSHI ENVIRONMENTAL PROTECTION TECH CO LTD), 11 August 2020 (2020-08-11); whole document --	1-26
A	US 20200277738 A1 (CHUNG YOKE DOU ET AL), 3 September 2020 (2020-09-03); whole document -- -----	1-26

Continuation of: second sheet

International Patent Classification (IPC)

D21J 7/00 (2006.01)

C09D 101/02 (2006.01)

D21H 11/18 (2006.01)

D21J 3/00 (2006.01)

D21J 5/00 (2006.01)

C08L 1/02 (2006.01)

D21H 19/12 (2006.01)

D21H 21/18 (2006.01)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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			NONE		
US	20200277738 A1	03/09/2020	NONE		