(11) EP 3 748 077 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

09.12.2020 Bulletin 2020/50

(21) Application number: 19020674.8

(22) Date of filing: 05.12.2019

(51) Int Cl.:

D21H 27/00 (2006.01) D21C 5/00 (2006.01) D21C 3/02 (2006.01)

D21C 3/20 (2006.01) D21H 11/12 (2006.01)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

(30) Priority: 03.06.2019 PT 2019115562

(71) Applicant: Raiz - Instituto De Investigação Da

Floresta E Papel 3800-783 Eixo, Aveiro (PT) (72) Inventors:

- DE OLIVEIRA RODRIGUES PINTO, Paula Cristina 3800-783 Eixo, Aveiro (PT)
- MARTINS SALGUEIRO CARTA, Ana Margarida 3800-783 Eixo, Aveiro (PT)
- FERREIRA BASTOS, Margarida 3800-783 Eixo, Aveiro (PT)
- SENA DA COSTA BRANCO, Pedro Miguel 3800-783 Eixo, Aveiro (PT)
- DE OLIVEIRA, Ricardo Jorge 3800-783 Eixo, Aveiro (PT)

(54) EUCALYPTUS GLOBULUS BARK PULP FOR TISSUE PRODUCTS

(57) The present invention relates to a *Eucalyptus globulus* bark pulp for the production of tissue papers with improved pulp properties.

The present invention further includes the process of producing the $Eucalyptus\ globulus\ bark\ pulp$, involving selection of bark chips, bark pre-extraction and chips cooking with NaOH and Na₂S for a time of not less than

200 minutes and a maximum temperature of 170 ° C.

The invention disclosed herein also considers the use of tissue paper sheets incorporating the *Eucalyptus globulus bark pulp* for the production of household and sanitary products, such as toilet paper, napkins and kitchen paper rolls.

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Description

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FIELD OF THE INVENTION

[0001] The present invention relates to a pulp of *Eucalyptus globulus* bark and its production process. Additionally the present invention further relates to the use of the *Eucalyptus globulus* bark pulp for the production of tissue products, tissue paper sheets incorporating the *Eucalyptus globulus* bark pulp, and their use for the production of household and sanitary products.

10 BACKGROUND OF THE INVENTION

[0002] The industrial process of pulp production can generally be described as involving the processes of preparation of the raw material and cooking, the later which can be chemical or mechanical. Wood is the main source of raw material for cellulose pulp production.

[0003] One of the steps in the preparation of the raw material is the stripping of the wood logs to remove the bark. Industrial pulp and paper producers remove bark from the raw material because it is low in fiber, has a high extractable content, is dark and usually incorporates large amounts of debris such as sand.

[0004] The resulting bark is used for energy production at biomass boilers usually present at pulp and paper mills.

[0005] The pulp produced through wood cooking is then converted into different products such as printing and writing papers, packaging boards and tissue papers.

[0006] The document CN102011334B describes a cooking method using *Eucalyptus* bark. In the described method, the *Eucalyptus* bark is subjected to grinding, to an alkaline treatment and milling of the resulting pulp. The pulp is also described as being used for the preparation of corrugated paper. The method described is intended to be an alternative for reducing the environmental impact of the pulp and paper production process. No paper properties of the corrugated paper produced are detailed.

[0007] The document CN109082929A discloses a method of using *Eucalyptus* bark for the preparation of pulp for paper production, characterized by a crushing step of the bark, followed by immersing it in an alkaline liquid for 30-48 hours, and mixing the resulting pulp with water and carrying out a final grinding. The method is described as simple, inexpensive and environmentally friendly. Additionally it is described in said document that the pulp produced is suitable for the production of corrugated paper. No paper properties of the corrugated paper produced are detailed.

[0008] Tissue papers are those used for hygienic and sanitary purposes, both at home and in public places. A tissue paper product, such as toilet paper, napkins, kitchen rolls or tissues, is characterized by key properties such as strength, absorption, softness and even visual appearance.

[0009] This type of products, in order to be preferentially chosen by the consumer, needs to have a positive balance of these different properties in order to achieve a product of overall higher quality. It is currently found that when actions are taken to increase the quality of a product property, other product characteristics are often negatively affected.

[0010] Different approaches for enhancing these properties of tissue papers can be found in the literature. EP0478045A1 describes a soft tissue paper having a suitable tensile strength, obtained by incorporating into its constitution cellulose pulps obtained by different chemical and mechanical methods, and which have different types of wood as their raw material. Adopting this solution to improve the mentioned paper characteristics will lead to changes on an existing industrial production process of paper products. Additional costs are easily associated with these significant changes to an industrial process.

[0011] Another possibility commonly adopted for tissue paper products to improve their characteristics would be the use of chemical additives, as explained in EP0347154A2, which describes a product incorporating starch and polysiloxane to achieve an acceptable balance between softness and tensile strength of tissue paper products.

[0012] Similarly, EP0981668A1 describes a tissue paper product wherein at least one inner surface of the paper contains a resistance enhancing polymeric agent.

[0013] US5316623A provides a method for obtaining a tissue paper product having good absorption capacity and strength, which consists on the use of a combination of alkaline or neutral resins, water soluble anionic polymers and tertiary amines.

[0014] Adopting these approaches, in addition to not guaranteeing an overall improved tissue paper characteristics, will always have an associated environmental cost with regard to possible negative effects on the environment.

[0015] There is thus a need for tissue paper products with a wide range of improved paper properties, which are valued by the consumers, such as strength, absorption and even visual appearance, which can be associated with the ideas of sustainability and environmental concern, produced through alternative raw materials, which do not involve complex sources and mixtures of materials, which can be used in existing industrial processes and without significant changes, allowing reducing the waste streams of industrial processes, fulfilling possible deficiencies in the amount of raw material available for pulp and paper production, and which make possible to reduce, in number and quantity, the use of chemical

additives for enhancing the characteristics of tissue papers. Such a problem is solved by the invention described herein.

SUMMARY OF THE INVENTION

5 [0016] The Eucalyptus globulus bark pulp disclosed in this invention unexpectedly allows the production of tissue products with a globally improved consumer-friendly pulp properties, such as strength, absorption and even visual appearance associated with sustainability ideas and environmental concerns. Additionally, it is advantageously produced through alternative raw materials, not involving complex sources and mixtures of raw materials, in existing industrial processes and without significant modifications, with a reduction of the waste streams associated with industrial processes, filling possible deficiencies in the amount of raw material available for pulp and paper production, and making it possible to reduce, in number and quantity, the use of chemical additives for enhancing the characteristics of tissue papers. [0017] The invention here disclosed describes a cellulose pulp for the production of tissue products comprising Eucalyptus globulus bark fibers.

[0018] The Eucalyptus *globulus* bark pulp is comprised of fibers having a length of not less than 0.8 mm, a width of not less than 20 μ m and a coarseness value of not less than 8 mg/100m. The *Eucalyptus globulus* bark pulp presents a viscosity of not less than 1100 mL/g and a carboxyl content of not less than 9%.

[0019] The *Eucalyptus globulus* bark pulp is produced by a method involving the steps of bark chip selection, bark pre-extraction with an ethanol:water mixture, and cooking of the chips with NaOH and Na₂S for a time of not less than 200 minutes and at a temperature from 17 to 170 °C.

[0020] The disclosed invention further includes sheets of tissue paper incorporating the *Eucalyptus globulus* bark pulp, and short and long cellulose fiber pulps. The sheets have improved paper properties compared to tissue sheets that incorporate only *Eucalyptus globulus* wood pulp in their composition.

[0021] In the production process of tissue products, the described *Eucalyptus globulus* bark pulp can be used in different forms, such as in the form of dried pulp bales and in the form of a slush, the later feed to the industrial process through pipeline systems.

[0022] The tissue paper sheets have bulk values greater than 1 cm 3 /g, more preferably from 2 to 7 cm 3 /g and a tensile index greater than 4 kN.m/kg, preferably from 10 to 30 kN.m /kg. An absorption capacity greater than 8 gH $_2$ O/g $_{paper}$ and softness values of not less than 70 HF were found.

[0023] The tissue paper sheets disclosed in this document have a tear index greater than 3 mN.m²/g, preferably greater than 8 mN.m²/g, a burst index of not less than 1 kPa.m²/g, a capillarity greater than 60 mm/10min, preferably greater than 70 mm/10min and an opacity greater than 75%, preferably greater than 90%.

[0024] The invention disclosed herein thus includes the use of the *Eucalyptus globulus* bark pulp for the production of tissue products and the use of tissue papers sheets, incorporating the *Eucalyptus globulus* bark pulp, for the production of household and sanitary products, such as toilet paper, napkins, kitchen paper rolls and tissues.

DETAILED DESCRIPTION OF THE INVENTION

1. Eucalyptus globulus bark cooking

[0025] Eucalyptus globulus bark cooking was performed in a time and temperature controlled rotary digester.

[0026] To carry out the cooking, a batch of bark chips with the most uniform size as possible was selected. Prior to each run, the bark was pre-extracted with an ethanol:water mixture (52:48).

[0027] The composition of the cooking liquor, prepared by dissolving previously calculated amounts of NaOH and Na₂S, was confirmed according to the standard SCAN-N 2-88, also known as the ABC Test.

[0028] This test is performed by three successive titrations with a hydrochloric acid solution to obtain real concentrations of the cooking liquor. The cooking conditions are shown in Table 1. The cooking results are shown in Table 2.

Table 1. Operational conditions used for cooking *Eucalyptus globulus* bark.

| - | |
|--------------------------------|------|
| Ratio liquid/wood | 8 |
| Sulfide Index (%) | 28 |
| T _{initial} (°C) | 17.3 |
| T _{final} (°C) | 170 |
| Total time (min) | 213 |
| Time at T _{max} (min) | 153 |
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| Active alkali, %Na ₂ S | 22 |
|-----------------------------------|----|

Table 2. Eucalyptus globulus bark cooking results

| Bark humidity (%) | 73.87 |
|-----------------------|--------|
| Dry pulp produced (g) | 293.25 |
| Uncooked (g) | 6.97 |
| Uncooked (%) | 1.2 |
| Pulp yield (%) | 48.9 |
| Kappa index | 13.92 |

2. Biometric Characterization

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[0029] The biometric analysis of the fibers was performed in a Fiber Tester equipment (Lorentzen & Wettre), which is an instrument for advanced fiber analysis. The equipment measures, by 2D image analysis, a wide variety of properties such as length, width, fines content, coarseness, among others. Coarseness is defined as the weight per unit length of fiber expressed in milligrams per 100 meters. For that, 1 g (dry basis) of pulp was dispersed in 1 L of distilled water. Subsequently, all the suspensions were positioned for analysis by the equipment using available software. For each pulp three measurements were made, the final value of each parameter resulting from the arithmetic mean of the values obtained at the three measurements.

3. Chemical characterization

a. Extractable compounds content

[0030] Extractable compounds are hydrophobic (lipophilic) components present in wood and extracted by organic solvents.

[0031] The extractable compounds content was determined using ethanol/toluene in quantities enough for samples analysis preparation, as it requires a pulp pre-extraction. The extraction was carried out during approximately 4 hours (24 extraction cycles) of 2 g (dry basis) of pulp in a 100 mL capacity Soxhlet extraction apparatus, using 250 mL of a 1:2 (v/v) ethanol/toluene solution. The insoluble residue was filtered and washed with hot absolute ethanol, for removing any remaining toluene, and dried at room temperature, contrary to what is indicated at the standard TAPPI T 204 om-88, since washing with water, as described, could lead to the loss of pentosans and other polysaccharides of low molecular weight. The obtained extract was dried at a rotary evaporator equipment and the extractable content was determined gravimetrically.

b. Pentosans content

[0032] Pentosans content was determined according to the Tappi Test Method T 223 cm-10. This method is based on the action of hydrochloric acid on the pulp hemicelluloses, hydrolyzing them and, consequently, converting the xylose and other pentoses to furfural, which is collected with the distillate and, reacting with orcinol, forms a colored complex making therefore possible the content quantification by spectrophotometry.

[0033] About 0.5-1.0 g (dry basis) of unbleached pulp pre-extracted in ethanol/toluene (1:2), together with 20 g of NaCl and 100 mL of HCL 3.85 N, was inserted into a distillation flask. In a hopper, 250 mL of 3.85 N HCl was added and the acid distillation was started into a volumetric flask placed in an ice bath.

[0034] Finally, 5 mL of the distillate was pipetted, 25 mL of the orcinol ferric chloride reagent was added, and the mixture was kept in a thermostatic bath for 1 hour. Absolute ethanol was added and the volumetric flask was placed again in the thermostatic bath for another hour. The solution absorbance at 630 nm was then read, and measurements comparisons were carried out using a 5 mL blank of 3.85 N HCl.

[0035] The pentosans content was obtained with the aid of the calibration curve and equations as described below:

$$m_{xylan} (mg) = 0.88 \times m_{xylose} (mg)$$

$$Pentosans\ content\ (\%) = \frac{m_{pentosans\ in\ each\ sample}}{10\times w}$$

where w is the dry weight (g) of the sample.

10 c. Carboxyl content

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[0036] The content of carboxyl groups was determined according to the TAPPI T 237 om-93 standard method. About $2.5\pm0.1~g$ of disintegrated pulp was first weighed and 250 mL of a diluted hydrochloric acid solution (approximately 0.1~M) was added during 12 hours, ensuring that all existing carboxylic groups are in their protonated form. Subsequently, the pulp was filtered and washed with distilled water until the pH of the filtrate equaled the pH of the distilled water. To the pulp it was added 50 mL of an aqueous sodium bicarbonate-sodium chloride solution, the resulting mixture stirred for about 5 hours, filtered, and the filtrate twice titrated (25 mL in each titration) with a standard solution of hydrochloric acid (0.01 M) using methyl red as indicator. At the first color change the solution was boiled for 1 minute to release CO_2 . Titration is resumed ending only when the solution changes to pink. The blank was prepared by titrating 25 mL of sodium bicarbonate-sodium chloride solution with 0.01 M HCl. The content of carboxyl groups was determined with the following equation:

Content COOH
$$\left(\frac{mmol}{100 \ g}\right) = \left(b - a - \frac{C_w \times a}{50}\right) \times \left(\frac{50}{25 \times w}\right)$$

where a is the volume, in mL, of hydrochloric acid (0,01 M) spent during titration, b is the volume, in mL, of hydrochloric acid (0,01 M) consumed during the blank titration, C_w is the mass, in g, of the water in the pulp after filtration, and w is the weight, in g, of the dry pulp.

d. Pulp viscosity

[0037] The viscosity was determined according to the SCAN-test standards SCAN-CM 15:88, which consists on the determination of the viscosity of cellulose pulps by solubilization in a dilute copper-ethylenediamine (CED) solution.

[0038] The pulp sample was reduced to small fragments in the amount indicated at the table provided by the method (Table 7, Annex C.1.) - 150 mg of pulp were weighed. Each sample was placed into a glass vial along with 25 mL of distilled water and some copper wires. The vials were then placed on a shaker for as long as necessary to ensure that the pulp was completely disintegrated. The procedure continued with adding 25 mL of 1 M CED solution, expelling all existing air and stirring until the sample is completely dissolved. Finally, the temperature of the viscometer bath and the sample's were adjusted to 25.0 ± 0.1 °C and, with the aid of a syringe, a portion of the solution was aspirated and allowed to flow unobstructed. The time it takes to travel the distance between the two viscometer marks was measured to within ± 0.2 s. At least 5 readings were taken for each sample.

[0039] With the flow time of each sample, t_n , it is possible to calculate its relative viscosity, η_{rel} , through the relationship shown in the equation:

$\eta_{rel} = h \times t_n$

where h represents the viscometer constant, obtained from the equipment calibration. From the table provided by the aforementioned standard, it is possible to read the value resulting from multiplying the viscosity value with the pulp concentration, $[\eta]C$.

[0040] Biometric and chemical measurements and comparisons were carried out for a pulp produced with *Eucalyptus globulus* wood (**SF**), characterized by containing short fibers, and for a pulp containing long cellulose fibers (**LF**), in addition to for the pulp produced with *Eucalyptus globulus* bark (**BP**) by the process described above.

4. Preparation of paper sheets

[0041] Tissue paper sheets with a weight of 20 g/m², and not subjected to any pressing procedure, were prepared

following an adaptation of the standard method ISO 5269-1:2005. Additionally, $60\,\mathrm{g/m^2}$ tissue paper sheets were prepared according to the same ISO.

[0042] The pulps described above, **SF**, **LF** and **BP** were used. The prepared formulations are described in Table 3. Reference formulations (**REF 1** and **REF 2**) consist on formulations used for the production of tissue paper sheets. The other formulations were based on the replacement of short fibers content by bark pulp (**BP1** and **BP2**).

[0043] The prepared sheets were stored according to the standard ISO 187:1990 for further analysis.

Table 3. Formulations used in sheet preparation.

| | Percentages (%) (w/w) | | | |
|--------------|-----------------------|-----|---------|----------|
| | References | | Formula | tions BP |
| Formulations | REF 1 REF 2 | | BP 1 | BP 2 |
| SF | 70 | 100 | 50 | 40 |
| LF | 30 | - | 30 | 30 |
| BP | - | - | 20 | 30 |

5. Paper properties of 20 g/m² tissue sheets

[0044] The 20 g/m² sheets were analyzed as indicated in Table 4.

Table 4. Paper properties analyzed for sheets of 20 g/m² and respective measure standards.

| Property | Standard | |
|---------------------|-------------------------|--|
| Weight | ISO 12625-6:2005 | |
| Bulk | ISO 12625-3:2014 | |
| Dry tensile index | ISO 12625-4:2005 | |
| Klemm capillarity | ISO 8787-1986 | |
| Absorption capacity | Adaptation 12625-8:2010 | |

[0045] The softness was analyzed on an Emtec TSA - Tissue Softness Analyzer. This device combines data from the three parameters that have the greatest influence on the human feel to the touch: fibers softness, smoothness, and sheet stiffness. The calculation method used by the device is an algorithm that calculates the hand feel (HF).

[0046] The water absorption of the tissue papers was determined according to the standard ISO 12625-8:2010, by the immersion absorption method. Approximately 2 g of paper was placed in a basket of certain dimensions, contrary to what is mentioned at the standard, which indicates the use of 5 g of paper.

6. Paper properties of 60 g/m² tissue sheets

[0047] The 60 g/m² sheets were analyzed as indicated in Table 5.

Table 5. Paper properties analyzed for sheets of 60 g/m² and respective measure standards.

| Property | Standard |
|----------------|-----------------|
| Weight | ISO 536:2012 |
| Bulk | ISO 534:2011 |
| Traction index | ISO 1924-2 |
| Burst index | ISO 2758:2014 |
| Extension | ISO 1924-2:2008 |
| Tear Index | ISO 1974:2012 |
| Opacity | ISO 2471 |

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| Property Standard | |
|-----------------------|-----------------|
| Gurley air resistance | ISO 5636-5:2013 |
| Capillarity | NP686:1990 |

[0048] Additionally, a Scott Test was carried out and the Gurley's air resistance was measured.

[0049] Mechanical strength properties of pulp furnishes ultimately contribute to the strength characteristics of the outcoming material, as paper sheets are subjected to considerable stresses during processing and use. The Scott Test is related to the internal fibers bonding strength of the paper when subjected to delamination. It allows the determination of the energy (or force) required to delaminate a sheet of paper in the z-direction. In this method (TAPPI T 569 standard) the paper sheet is delaminated under the action of a pendulum of controlled mass and velocity. The internal strength of the fibers is affected by the paper sheets formation (bonding between layers) and also by the process of pulp refining. **[0050]** The Gurley's air resistance is a structural property that quantifies the time required for a certain volume of air (100 mL) to pass through a given area of paper under constant pressure, ISO 5636-5:2013 standard. It is an indirect measure of the porosity of the fibrous matrix.

[0051] Both tests were performed under the same atmospheric conditions used for sample conditioning and sample preparation (T = 23 $^{\circ}$ C \pm 1 $^{\circ}$ C and Relative Humidity (RH) = 50% \pm 2%, according to the ISO 187:1990 standard.

Examples

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a. Biometric and Chemical Properties

[0052] The biometric properties of the 3 pulps, SF, LF, BP, were analyzed and the results are shown in Table 6.

Table 6. Biometric properties of SF, LF and BP pulps.

| | - 1 - 1 | · · · · · · · · · · · · · · · · · · · | <u> </u> |
|---------------------------------|------------|---------------------------------------|--------------|
| | SF | LF | BP |
| Fiber length, mm | 0.79 ±0.00 | 2.15 ±0.01 | 0.8 ± 0.00 |
| Fiber width, μm | 18.6 ± 0.1 | 32.4 ± 0.1 | 20.80 ± 0.08 |
| N.° fibers/g, ×10 ⁻⁶ | 18.7 ± 0.1 | 4.30 ±0.07 | 15.6 ± 0.6 |
| Coarseness, mg/100m | 6.3 ± 1.20 | 15.1 ± 0.4 | 8.4 ± 0.3 |
| Fines (0,0-0,200 mm), % | 4.2 ± 0.1 | 5.7 ± 0.1 | 3.8 ±0.1 |
| Shape, % | 90.7 ± 0.1 | 88.2 ±0.07 | 92.73 ± 0.05 |
| Curl, % | 9.2 ± 0.1 | 13.4 ± 0.1 | 7.8 ± 0.1 |
| Mean kink index | 1.3 ± 0.0 | 0.90 ±0.00 | 0.84 ± 0.00 |

[0053] Considering the obtained results, it is verified that the fiber length values are within the expected. Concerning the width results, it was found that the **BP** fibers have higher values than the other short fibers. When it comes to coarseness, **LF** fibers have the highest value. Regarding the other fibers, **BP** showed the highest value, followed by **SF**. [0054] The chemical characterization of the pulps under study was also performed (Table 7).

Table 7. Chemical properties of SF, LF and BP pulps.

| | SF | LF | BP |
|-----------------|-----------------|---------------|---------------|
| Viscosity, mL/g | 716 ± 3 | 699 ± 14 | 1171.9 ± 0.0 |
| Carboxylic, % | 7.03 ± 0.05 | 8.92 ± 0.23 | 9.89 ± 0.12 |
| Pentosans, % | 19.6 ± 0.25 | 8.1 ± 0.02 | 14.04 ± 0.18 |
| Extractable, % | 0.21 ± 0.00 * | 0.40 ± 0.22 * | 0.47 ± 0.04** |

^{*}Extractable in acetone

^{**}Extractable in ethanol:toluene(1:2)

[0055] Considering the viscosity results, **BP** revealed a considerably higher value than the **SF**'s (homologous), meaning the degree of cellulose polymerization was preserved.

[0056] Regarding the carboxyl content, this is higher in **BP** compared to other pulps'.

[0057] The pentosans content (measured by the xylan content, the majority of hemicelluloses in short fiber pulps) is within the typical range and considered as favorable.

b. Paper properties - 20 g/m² tissue paper sheets

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[0058] The paper sheets produced for the reference formulation REF 1 (70:30:0) and REF 2 (100:0:0) and the paper sheets with incorporation of bark pulp BP 1 (50:30:20) and BP 2 (40:30:30) were analyzed and the main results are shown in Table 8.

Table 8. Results obtained for the properties of sheets of 20 g/m², reference and with *Eucalyptus globulus* bark pulp (formulation = %SF : %LF : %BP).

| | • | , | | |
|--|--------------------------|--------------------------|--------------------------|--------------------------|
| | REF 1 (70:30: <u>0</u>) | REF 2 (100:0: <u>0</u>) | BP 1 (50:30: <u>20</u>) | BP 2 (40:30: <u>30</u>) |
| Weight, g/m ² | 21.1 ± 0.3 | 21.1 ± 0.4 | 21.0 ± 0.4 | 20.7 ± 0.3 |
| Thickness, μm | 135.4 ± 7.0 | 127.3 ± 5.6 | 134.7 ± 4.5 | 137 ± 2.1 |
| Bulk, cm ³ /g | 6.4 ± 0.4 | 6.0 ± 0.3 | 6.4 ± 0.2 | 6.6 ± 0.1 |
| Tensile index, Nm/g | 4.4 ± 0.3 | 4.42 ± 0.3 | 10.8 ± 0.3 | 9.5 ± 0.9 |
| Absorption capacity, g_{H2O}/g_{paper} | 8.05 ± 0.04 | 7.54 ± 0.3 | 8.25 ± 0.60 | 8.49 ± 0.17 |
| Air permeability, L/m ² /s | 840 ± 84 | 741 ± 86 | 690 ± 25 | 818 ± 54 |
| Softness, HF | 80.5 ± 1.9 | 80.5 ± 2.5 | 70.2 ± 1.4 | 74.5 ± 0.9 |
| Softness, TS7 | 13 ± 1 | 13.4 ± 1.4 | 18.68 ± 0.73 | 16.33 ± 0.48 |
| Softness, TS750 | 13.3 ± 1.3 | 11.6 ± 0.4 | 17.9 ± 1.2 | 16.3 ± 1.1 |
| | Klemm | Capillarity, mm | | |
| 10 s | 27.5 ± 3.5 | 25.0 ± 2.8 | 24.5 ± 1.5 | 28.0 ± 1.4 |
| 20 s | 38.5 ± 2.7 | 33.8 ± 1.1 | 33.5 ± 1.5 | 38.0 ± 1.6 |
| 30 s | 45.8 ± 1.3 | 40.8 ± 2.5 | 41.0 ± 1.0 | 43.7 ± 0.9 |
| 60 s | 59.5 ± 1.5 | 54.8 ± 3.4 | 56.3 ± 2.1 | 59.3 ± 1.3 |
| 180 s | 91.3 ± 1.1 | 87.0 ± 4.1 | 91.0 ± 3.0 | 93.7 ± 2.5 |
| 300 s | 112.0 ± 0.7 | 105.3 ± 5.4 | 111.3 ± 2.9 | 112.5 ± 1.5 |

[0059] The paper sheets with higher **BP** incorporation, especially the **BP 2** formulation, revealed a higher thickness, for the same grammage and, consequently, a higher bulk, comparing to **REF 1** and **REF 2**.

[0060] The results for the air permeability (L/m²/s), sheet permeable air flow per unit of time, indirect measure of porosity, show a slight decrease in porosity. However, it is noted that the measured variations are within the deviation values ranges.

[0061] The tensile index increased with the incorporation of bark pulp.

[0062] In terms of water absorption properties, capillarity and absorption capacity were evaluated, and the results indicated that incorporation of **BP** fibers led to an increase of the absorption capacity (when compared to **REF 1** and **REF 2**) and little significant variations were found in terms of capillarity.

[0063] Concerning softness, the increase in **BP** led to a decrease in softness compared to reference **REF 1** and **REF 2**. However, these correspond to a minimum loss of 6 HF points.

c. Paper properties - 60 g/m² tissue paper sheets

[0064] 60 g/m 2 paper sheets were also produced from the **BP** incorporation formulations. These were analyzed and the results are shown in Table 9.

Table 9. Results obtained for the properties of sheets of 60 g/m² with *Eucalyptus globulus* bark pulp (formulation = %SF: %LF: %BP).

| 5 | | REF 1 (70:30: <u>0</u>) | REF 2 (100:0: <u>0</u>) | BP 1 (50:30: <u>20</u>) | BP 2 (40:30: <u>30</u>) |
|------|------------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Ü | Weight, g/m ² | 64.5 ± 0.02 | 64.7 ± 0.01 | 62.9 ± 0.02 | 64.5 ± 0.02 |
| | Thickness, μm | 97. 8 ± 7.9 | 113.9 ± 13.4 | 113.3 ± 4.9 | 116.9 ± 12.5 |
| | Bulk, cm ³ /g | 1.25 ± 0.02 | 1.76 ± | 1.80 ± 0.03 | 1.81 ± 0.02 |
| 10 | Tensile index, Nm/g | 19.0 ± 0.2 | 21.0 ± 1.6 | 26.0 ± 1.6 | 28.0 ± 1.6 |
| • | Tear index, mN.m ² /g | 6.4 ± 0.7 | 3.10 ± 0.7 | 8.9 ± 1.2 | 8.6 ± 1.1 |
| 15 . | Burst index, kPa.m ² /g | 1.30 ± 0.1 | 0.95 ± 0.1 | 1.31 ± 0.1 | 1.31 ± 0.1 |
| | Extension, % | 1.2 ± 0.1 | 1.1 ± 0.2 | 1.5 ± 0.1 | 1.5 ± 0.1 |
| | Opacity, % | 76.9 ± 0.5 | 78.6 ± 0.4 | 91.8 ± 2.5 | 93.9 ± 0.7 |
| | Gurley air resistance, s | 3.6 ± 0.3 | 0.90 ± 0.1 | 1.10 ± 0.1 | 1.10 ± 0.1 |
| _ | Scott Test, J/m ² | 326 ± 40 | 103 ± 8 | 114 ± 11 | 129 ± 14 |
| 20 | Capillarity, mm/10min | 61.0 ± 2.4 | 92.0 ± 3.0 | 86.0 ± 1.2 | 79.0 ± 1.6 |
| | | | | | |

[0065] Analyzing the depicted results it is observed that, similarly to the results with the 20 g/m² paper sheets, the incorporation of **BP** leads to a bulk increase. Additionally, the incorporation of **BP** led to an increase in the tensile and tear indexes, comparing to the references. As for the burst index, it did not change significantly.

[0066] With regard to capillarity, the incorporation of **BP** fibers resulted in increased capillarity, especially when compared to **REF 1**. The opacity of the fibrous structures also increases with the incorporation of **BP**.

Claims

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- 1. A pulp for tissue products production comprising *Eucalyptus globulus* bark fibers.
- The pulp according to claim 1, having a viscosity of not less than 1100 mL/g and a carboxyl content of not less than 9%, and comprising fibers having a length of not less than 0.8 mm, a width of not less than 20 μm and a coarseness of not less than 8 mg/100m.
 - 3. A process for the manufacture of the pulp described in any of the preceding claims, comprising the following steps:
 - selection of uniform size Eucalyptus globulus bark chips;
 - bark pre-extraction with an ethanol:water mixture;
 - cooking of chips with NaOH and Na $_2$ S, a sulfide index of 28 %, an active alkali of 22 % Na $_2$ S, for a time of not less than 200 minutes and at a temperature from 17 to 170 °C.
- 45 **4.** Use of the pulp described in any of the claims 1 and 2 for the production of tissue products.
 - **5.** Tissue paper sheets comprising the pulp described in any of the claims 1 and 2.
 - **6.** The tissue paper sheets according to claim 5, comprising a minimum of 20 % (w/w) of the pulp described in any of the claims 1 and 2.
 - 7. The tissue paper sheets according to any of the claims 5 and 6, having a bulk greater than 1 cm³/g, a tensile index greater than 4 kN.m/kg, an absorption capacity greater than 8 g_{H2O}/g_{paper} and a softness of not less than 70 HF.
- 55 **8.** The tissue paper sheets, according to any of the claims 5 to 7, having a bulk from 2 to 7 cm³/g and a tensile index from 10 to 30 kN.m/kg.
 - 9. The tissue paper sheets according to any of the claims 5 to 8, having a tear index greater than 3 mN.m²/g, a burst

index of not less than 1 kPa.m²/g, a capillarity greater than 60 mm/10min and an opacity greater than 75%.

| 5 | 10. | The tissue paper sheets according to any of the claims 5 to 9, having a tear index greater than 8 mN.m 2 /g, a capillarity greater than 70 mm/10 min and an opacity greater than 90%. |
|----|-----|--|
| J | 11. | Use of the tissue paper sheets described in any of the claims 5 to 10 for the production of household and sanitary products. |
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EUROPEAN SEARCH REPORT

Application Number EP 19 02 0674

| | Category | Citation of document with in of relevant passa | dication, where appropriate, | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) | | |
|-----|---|---|---|----------------------|--|--|--|
| 10 | X | JP 2011 047083 A (0 10 March 2011 (2011 * claims 1-7; examp | -03-10) | 1,2 | INV. D21H27/00 D21C3/20 | | |
| 15 | X | JP 2010 136646 A (0 24 June 2010 (2010- * claims 1-4; examp | 06-24) | 1,2 | D21C5/00 D21H11/12 D21C3/02 | | |
| 20 | X | CN 102 011 334 B (L 10 April 2013 (2013 * claims 1-5 * | | 1-11 | | | |
| | X,D | CN 109 082 929 A (L 25 December 2018 (2 * claims 1-6 * | | 1,2 | | | |
| 25 | Y | US 6 296 736 B1 (HS AL) 2 October 2001 * claims 1-20 * | U JAY CHIEHLUNG [US] ET (2001-10-02) | 1-11 | | | |
| 30 | Y | JP 2011 193981 A (J 6 October 2011 (201 * paragraph [0030]; | 1-10-06) | 1-11 | TECHNICAL FIELDS SEARCHED (IPC) D21C D21H | | |
| 0.5 | A | WO 00/19005 A1 (KIM 6 April 2000 (2000- * the whole documen | | 1-11 | DZIN | | |
| 35 | A | US 2013/029106 A1 (AL) 31 January 2013 * the whole documen | | 1-11 | | | |
| 40 | Y | US 2010/305241 A1 (YUREVICH [CA] ET AL 2 December 2010 (20 * claims 1-22 * |) | 3 | | | |
| 45 | | | | | | | |
| 1 | L | The present search report has b | | | | | |
| 50 | (401) | Place of search Munich | Date of completion of the search 1 July 2020 | Kar | lsson, Lennart | | |
| | X · par | ATEGORY OF CITED DOCUMENTS | T : theory or principle | underlying the in | nvention | | |
| 55 | X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ** member of the same patent family, corresponding document document | | | | | | |

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

EP 19 02 0674

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 5

01-07-2020

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|----|------------------|--|--|
| JP 2011047083 | Α | 10-03-2011 | JP 5267387 B2 JP 2011047083 A | 21-08-2013 10-03-2011 |
| JP 2010136646 | Α | 24-06-2010 | NONE | |
| CN 102011334 | В | 10-04-2013 | NONE | |
| CN 109082929 | Α | 25-12-2018 | NONE | |
| US 6296736 | В1 | 02-10-2001 | NONE | |
| JP 2011193981 | Α | 06-10-2011 | JP 5666155 B2 JP 2011193981 A | 12-02-2015 06-10-2011 |
| WO 0019005 | A1 | 06-04-2000 | AR 022102 A1 AU 763350 B2 CA 2344820 A1 CO 4980908 A1 EP 1137841 A1 JP 2002525452 A KR 20000022000 A PE 20001203 A1 TW 548362 B US 6387210 B1 WO 0019005 A1 | 04-09-2002 17-07-2003 06-04-2000 27-11-2000 04-10-2001 13-08-2002 25-04-2000 06-11-2000 21-08-2003 14-05-2002 06-04-2000 |
| US 2013029106 | A1 | 31-01-2013 | CA 2843522 A1 EP 2737131 A1 EP 2940210 A1 HK 1194444 A1 HK 1210630 A1 PT 2737131 E PT 2940210 T RU 2014107739 A US 2013029106 A1 US 2016115648 A1 US 2016340835 A1 US 2017328012 A1 WO 2013016311 A1 | 31-01-2013 04-06-2014 04-11-2015 08-07-2016 29-04-2016 16-03-2016 04-10-2017 10-09-2015 31-01-2013 28-04-2016 24-11-2016 16-11-2017 31-01-2013 |
| US 2010305241 | A1 | 02-12-2010 | BR PI1012286 A2 BR PI1014395 A2 BR PI1014400 A2 BR PI1014694 A2 CA 2798158 A1 CA 2798160 A1 | 22-09-2015 25-08-2015 25-08-2015 12-11-2019 02-12-2010 02-12-2010 |

 $\stackrel{ ext{O}}{ ext{L}}$ For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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page 1 of 2

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

EP 19 02 0674

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 5

01-07-2020

| Patent document cited in search report | Publication date | | Patent family member(s) | Publication date |
|--|---------------------|----|-------------------------|------------------|
| | | CA | 2798161 A1 | 02-12-20 |
| | | CA | 2798196 A1 | 02-12-20 |
| | | CA | 2798256 A1 | 02-12-20 |
| | | CA | 2989498 A1 | 02-12-20 |
| | | CN | 102459424 A | 16-05-20 |
| | | CN | 102459425 A | 16-05-20 |
| | | CN | 102459426 A | 16-05-20 |
| | | CN | 102803281 A | 28-11-20 |
| | | EP | 2435453 A1 | 04-04-20 |
| | | EP | 2435454 A1 | 04-04-20 |
| | | EP | 2435455 A1 | 04-04-20 |
| | | EP | 2435456 A1 | 04-04-20 |
| | | EP | 2435458 A1 | 04-04-20 |
| | | US | 2010305241 A1 | 02-12-20 |
| | | ÜS | 2010305242 A1 | 02-12-20 |
| | | ÜS | 2010305243 A1 | 02-12-20 |
| | | US | 2010305244 A1 | 02-12-20 |
| | | US | 2012247617 A1 | 04-10-20 |
| | | ÜS | 2013197135 A1 | 01-08-20 |
| | | ÜS | 2013228298 A1 | 05-09-20 |
| | | ÜS | 2013253075 A1 | 26-09-20 |
| | | US | 2014206799 A1 | 24-07-20 |
| | | US | 2014346395 A1 | 27-11-20 |
| | | ÜS | 2015299951 A1 | 22-10-20 |
| | | US | 2015345078 A1 | 03-12-20 |
| | | US | 2016145399 A1 | 26-05-20 |
| | | US | 2017226344 A1 | 10-08-20 |
| | | WO | 2010135804 A1 | 02-12-20 |
| | | WO | 2010135805 A1 | 02-12-20 |
| | | WO | 2010135806 A1 | 02-12-20 |
| | | WO | 2010135807 A1 | 02-12-20 |
| | | WO | 2010135833 A1 | 02-12-20 |
| | | | | |
| | | WO | 2010135807 A1 | |
| | | | | |
| | | | | |
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| | | | | |
| | | | | |
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| | | | | |

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

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page 2 of 2

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CN 102011334 B [0006]
- CN 109082929 A [0007]
- EP 0478045 A1 **[0010]**

- EP 0347154 A2 [0011]
- EP 0981668 A1 [0012]
- US 5316623 A [0013]