by compression and shearing, thereby rendering it more stretchable under load than an uncreped paper.

Typical properties of tissue paper include the ready ability to absorb tensile stress energy, their drapability, good textile-like flexibility, a high specific volume with a perceptible thickness, as high a liquid absorbency as possible and a suitable wet and dry strength as well as an interesting optical appearance of the outer product surface.

Background art

From US 2003/0121629 A1 is known the use of fractionated fiber furnishes in the manufacture of tissue products. Therein it is mentioned that strength and softness are important attributes in consumer paper products such as bathroom tissue, towels and napkins. Strength and softness are strongly influenced by the sheet structure of a paper product. The type and arrangement of fibers employed in the manufacture of paper products are important factors in determining the strength and softness of products made from such fibers. Strength and softness are usually inversely related. That is, the stronger a given sheet, the less softness that sheet is likely to provide. Likewise, a softer sheet is usually not as strong. Thus, this inverse relationship between strength and softness results in a constant endeavour in the industry to produce a sheet having a strength which is at least as great as conventional prior art sheets, but with improved softness. Also, a sheet which is at least as soft as known sheets, but with improved strength, is desirable.

It is common in the manufacture of paper products to provide two or more furnishes of fiber. Sometimes, a two-furnish system is used in which the first furnish is comprised of hard wood eucalyptus wood fibers, the second furnish is made of soft wood fibers. Hard wood fibers made from eucalyptus tend to be softer and more "fuzzy" to the touch and,

therefore, often these fiber types are provided on outer surfaces of a paper product.

Fractionation is the process by which cellulosic fibers are separated according to their properties. US 6,024,834 is directed to a process of separating, by fractionation, cellulosic fibers that exhibit desired properties such as fiber length and fiber coarseness values.

US 4,781,793 discloses a method in a paper manufacturing process for improving the properties of paper using fractionation. In the disclosure of the patent, the fiber slurry is separated into two components which are stated to contain substantially all of the fibers to be used for paper manufacture. One component contains mainly fiber longer than the average distribution of fiber length in the basic stock, and the other component contains primarily shorter fibers and fines.

Fines and short fibers usually are regarded as the least desirable fibers in most fiber slurries. Fines comprise short portions of cellulosic material that do not appreciably contribute to paper softness.

US 2002/0162635 A1 teaches a product and process of making an absorbent paper article such as paper products, towels, napkins and the like. It is mentioned that one may supply a single furnish, or slurry, of cellulose fibers. Then, it is possible to separate or fractionate the slurry into at least two portions based upon fiber length in the slurry. Fines are employed in the process of manufacturing the products, and fines are specifically incorporated into an inner layer of the final paper products. Fines, and/or short fibers are used in the process so they may contribute in a positive manner to the final paper product. This use of fines in the inner layers of the products reduces the manufacturing costs and waste produced in the process. A soft paper product with good

strength characteristics results from the process. According to the process, in one step, a cellulosic fiber mixture is provided for fractionating the first cellulosic fiber mixture into a second fiber mixture having relatively short fibers and fines, and a third fiber mixture having relatively long fibers. The third fiber mixture may be treated with chemical agents to soften the fibers. In a next step, the third fiber mixture is provided to a paper machine, thereby forming a paper sheet from the third fiber mixture on a wire former. Then, the step of adding the second fiber mixture to the upper surface of the paper sheet is provided.

According to US 2003/0121629 A1 a method of making a paper product comprises:

providing a first furnish of fibers; providing a second furnish of fibers; fractionating the first furnish into a long fiber fraction and a short fiber fraction; diverting the short fiber fraction to the second furnish to form a third furnish; forming a first and second exterior layer using the third furnish; forming a first interior layer using the long fiber fraction of the first furnish; and combining at least the first and second exterior layers with the first interior layer to form a first ply. Here, the first furnish comprises softwood fibers and the second furnish comprises hardwood fibers. The first furnish is used for a strength layer and the second furnish for a softness layer of the paper. The first furnish is fractionated and the separated short fiber fraction is added to the second furnish for the softness layer.

Therewith, a paper product or a tissue is provided having reduced levels of slough, with about the same or comparable level of softness.

Disclosure of the invention

It is the problem (object) of the invention to provide a method by which an absorbent structure as a multi-layer paper and especially a tissue paper can be manufactured in which the at least two layers comprise a strength layer of improved strength and a softness layer of improved softness.

This problem is solved by a method of making an absorbent structure as a paper, especially a tissue paper, consisting of at least two layers, at least one layer as an outer layer being preferably a soft layer (softness layer) and at least one layer as an inner layer or intermediate layer being preferably a layer of high strength (strength layer) comprising the steps of:

a) providing a first furnish of fibers for the strength layer
b) providing a second furnish of fibers for the softness layer
c) fractionating the second furnish such that the short fiber/fines fraction is separated from the furnish
d) adding this short fiber/fines fraction to the first furnish
e) leading the two furnishes separately to a headbox and from there to a forming section of the paper machine and forming a multi-layer paper.

Tissue paper products such as handkerchiefs, cosmetic wipes, toilet papers, serviettes/napkins or kitchen towels are being distinguished from other paper products by their low basis weight and its significantly improved tensile energy absorption index.

Preferably the tissue paper contains as main component (in particular at least 80% by weight, relative to the dry weight of the fibrous web) cellulosic fibres, in particular pulp, although a proportional use of modified pulp fibers (e.g.

from 10 to 50 weight %, relative to the total weight of the fibers) or the use of synthetic fibers suitable for web making (e.g. from 10 to 30% by weight, relative to the total weight of the fibers) is covered by the invention. The origin of these fibers may be native or recycled. The tissue paper may be creped or uncreped, the use of creped tissue paper being preferred. The tissue paper (or the final tissue paper product obtained therefrom) can be single-ply or multi-ply with two, three, four, five, six or even more plies. Preferred tissue paper products comprise between two and four plies.

The tissue paper may be homogeneous or layered, wet-pressed or blow-dried (TAD-dried). The tissue paper includes, but is not limited to, felt-pressed tissue paper, pattern-densified tissue paper, uncompacted tissue paper or compacted tissue paper.

The starting material for the production of the tissue paper usually is a fibrous cellulosic material, in particular pulp.

If, however, linters or cotton is used as raw material for the production of tissue paper, usually no further pulping steps are needed. Due to the morphological structure, the cellulose already exists in an open state.

The starting pulps used may relate to primary fibrous materials (raw pulps) or to secondary fibrous materials, whereby a secondary fibrous material is defined as a fibrous raw material recovered from a recycling process. The primary fibrous materials may relate both to a chemically digested pulp and to mechanical pulp such as thermo mechanical pulp (TMP), chemothermo mechanical pulp (CTMP) or high temperature chemithermomechanical pulp (HTCTMP). Synthetic cellulose-containing fibres can also be used. Preference is nevertheless given to the use of pulp from plant material, particularly wood-forming plants. Fibers of softwood (usually

originating from conifers), hardwood (usually originating from deciduous trees) or from cotton linters can be used for example. Fibres from esparto (alfa) grass, bagasse (cereal straw, rice straw, bamboo, hemp), kemp fibers, flax, and other woody and cellulosic fiber sources can also be used as raw materials. The corresponding fiber source is chosen in accordance with the desired properties of the end product in a manner known from the prior art. For example, the fibers present in hardwood, which are shorter than those of softwood, lend the final product a higher stability on account of the higher diameter/length ratio. If softness of the product is to be promoted, which is important e.g. for tissue paper, eucalyptus wood is particularly suitable as a fiber source.

With regard to softness of the products, the use of chemical raw pulps is also preferred, whereby it is possible to use completely bleached, partially bleached, and unbleached fibers. The chemical raw pulps suitable according to the invention include *inter alia*, sulphite pulps, kraft pulps (sulphate process).

Before a raw pulp is used in the tissue making process, it may also be advantageous to allow further delignification to occur in a separate process step or employ a bleaching process to achieve a more extensive removal of lignin after the cooking process and to obtain a completely cooked pulp.

A preferred production process for tissue paper uses

a a forming section (for wet-laying a slurry of cellulosic fibrous material, typically pulp) comprising a headbox and wire section portion, and
b the drying section (TAD (through air drying) and/or conventional drying on the Yankee cylinder) that also may include the crepe process for tissues.

This is typically followed by

c the converting area.

The tissue paper can be formed by placing the fibers, in an oriented or random manner, on one of between two continuously revolving wires of a paper-making machine while simultaneously removing the main quantity of water of dilution until dry-solid contents of usually between 12 and 35% are obtained. It is possible to include additives in the paper furnish to improve the wet-strength or dry-strength or other properties of the finished tissue paper.

Drying the formed primary fibrous web occurs in one or more steps by mechanical and thermal means until a final dry-solids content of usually about 93 to 97% is obtained. In the case of tissue making, this stage is followed by the crepe process which crucially influences the properties of the finished tissue product in conventional processes. The conventional dry crepe process involves creping on a drying cylinder having a diameter of usually 3.5 to 6 meter, the so-called Yankee cylinder, by means of a crepe doctor with the aforementioned final dry-solids content of the base ("raw tissue") paper (wet creping can be used if lower demands are made of the tissue quality). The creped, final dry base tissue paper is then available for further processing into the paper product or tissue paper product according to the invention.

In addition to this conventional tissue making process described above, tissue paper can also be manufactured by a special kind of drying within process section b and in this way an improvement in bulk softness of the resulting tissue paper is achieved. This pre-drying process, which exists in a variety of subtypes, is termed the TAD (through air drying) technique. It is characterized by the fact that the "primary" fibrous web (like a non-woven) that leaves the sheet making

stage is pre-dried to a dry-solids content of between 55 and 99% before final contact drying on the Yankee cylinder by blowing hot air onto the fibrous web and by contact drying of the web. The fibrous web is supported by an air-permeable wire or belt and during its transport is guided over the surface of an air-permeable rotating cylinder drum. Structuring the supporting imprinting fabric or belt makes it possible to produce any pattern of compressed and uncompressed zones achieved by deflection of the fibres in the moist state, followed by pre-drying of the fibres (TAD step) and leading the web through a pressure nip between a pressure roll and the Yankee cylinder surface, thereby resulting in increased mean specific volumes and consequently leading to an increase in bulk softness without decisively decreasing the strength of the fibrous web.

Another possible influence on softness and strength of base tissue lies in the production of a layering in which the primary fibrous web to be formed is built up by a specially constructed headbox in the form of physically different layers of fibrous material, these layers being jointly supplied as a pulp jet to the forming stage.

The one-ply intermediate products originating from the paper-making machine and made of lightweight paper usually dry-creped on a Yankee cylinder by means of a crepe doctor are generally described as “tissue paper” or more accurately base tissue paper. The one-ply base tissue may be built up of one or a plurality of layers respectively.

All one-ply or multi-ply final products made of base tissue and tailored to the end user’s needs, i.e. manufactured with a wide variety of requirements in mind, are known as “tissue products”.

When processing the fibrous web or base tissue paper into the final tissue product, the following procedural steps are

normally used individually or in combination: cutting to size (longitudinally and/or cross cutting), producing a plurality of plies, producing mechanical and/or chemical ply adhesion, volumetric and structural embossing, folding, imprinting, perforating, smoothing, stacking, rolling up. These procedural steps are usually carried out in the converting part (c) of the papermaking process.

To produce multi-ply tissue paper products an intermediate step preferably occurs with so-called doubling in which the base tissue in the finished product's desired number of plies is usually gathered on a common multiply master roll.

The processing step from the base tissue that has already been optionally wound up in several plies to the finished tissue product occurs in processing machines which include operations such as repeated smoothing of the tissue, edge embossing, to an extent combined with full area and/or local application of adhesive to produce ply adhesion of the individual plies (base tissue) to be combined together, as well as longitudinal cut, folding, cross cut, placement and bringing together a plurality of individual tissues and their packaging as well as bringing them together to form larger surrounding packaging or bundles. The individual paper ply webs can also be pre-embossed and then combined in a roll gap according to the foot-to-foot or nested methods.

As follows, in the wording "short fiber/fines fraction" shall be understood to mean only such a fiber fraction which provides the shorter mean fiber length after fractionating in comparison with the basic stock. The mean fiber length of the "short fiber/fines fraction" is preferably at ≤ 1,0 mm, more preferably ≤ 0,8 mm and most preferably ≤ 0,6 mm. The mean fiber length can be determined by using so-called optical fiber length analysers (described in TAPPI method T271). Optical fiber length analysers count the number of fibers that produce a discrete digital response from the measuring

sensors. It is pointed out here that a "short fiber/fines fraction" does not mean the same as the wording "short fiber pulp", by which usually "hardwood pulp" is to be understood. Moreover, the wording "short fiber/fines fraction" means such fibers which are present after fractionating in the "short fiber/fines fraction" irrespective from the fiber quality used in the basic stock. Generally speaking, each fibrous material consists of fibers of different lengths, wherein, by fractionating each fibrous material is separated in fractions of different lengths. In determining the fiber length of different single fibers of a fibrous material as a result, there is in any case a fiber length distribution, since the length of the individual fibers is not even constant when the type of wood and the pulping methods are the same. "Long fibers" usually are fibers of a length ≥ 1,8 mm and "short fibers" are fibers of a length of ≤ 1,0 mm. "Fines" are of a length of about 0,2 mm and less.

Softness, haptic, absorption speed, absorption capacity, thickness etc. are negatively influenced by fines. The positive impact fines can have is on strength. The fines are coming with a pulp or are additionally generated by e.g. refining of the pulp. Tissue, especially when it is layered can have two different functional layers, one layer is supposed to deliver strength to the tissue, normally this is a so-called hood-layer, because it is positioned near the hoodside of the tissue, the other layer is the so-called Yankee-layer, because it is positioned near the Yankee-side of the tissue and should improve softness, haptic, absorption speed and capacity, and thickness. As a matter of fact, all kind of pulp contains fines even without any refining. Also the best pulps for softness (e.g. eucalyptus fibers) or absorption (CTMP-fibers) may have quite high fines levels. To keep the fines in the tissue is desirable for quality and economic reasons. Therefore, it is an advantage to change the sheet structure of a layered tissue by concentrating the fines in the hood-layer or strength layer and to reduce the

fines level in the Yankee-layer or softness-layer. This is achieved by the above-mentioned fractionation and delivery of the short fiber/fines fraction to the strength layer. Thus, softness, haptic, absorption speed and capacity, thickness and strength are improved in the tissue paper product.

These advantages are furthermore improved when the short fibers/fines are concentrated in the strength layer and the short fibers/fines are reduced in the softness-layer.

If white water originating especially from the forming section is transferred back to the furnishes upstream the headbox for dilution the afore-mentioned advantageous effect of the present invention is again reduced. This is due to the fact that white water coming from a forming section is characterized by a high content of short fibers/fines (e.g. as a result of low retention), which results in an undesirable increase of these short fibers/fines in the furnishes upstream the headbox. Therefore, a realistic and surprising effect is achieved for improving strength and softness when a retention-aid is added to at least one of the two furnishes upstream of the headbox, whereby the short fibers/fines content in the white water is reduced. Preferably the retention-aid is added to the strength layer to increase the content of the short fibers/fines in this layer and to reduce the short fibers/fines content in the softness layer.

The term retention-aid refers to a process chemical compound supporting the retention of solid particles within a suspension on a sieve or wire, thereby improving the runability of the drying process and reducing abrasion of the material of the sieve or wire. Retention-aids are especially used during the process of papermaking in order to improve formation of the paper web. Useful retention-aids are e.g. inorganic products such as aluminium sulfate (Bentonit), natural products such as cationic starch or synthetic organic

polymers such as polyacrylic amide, polyethyleneimine, polyamido amine or polyethyleneoxide.

In this respect it is possible to add the retention-aid to both furnishes, however, it is more effective when added only to the first furnish.

Brief description of the drawings

Fig. 1 is a schematic view showing a method for manufacturing two-layer paper,
Fig. 2 shows a similar schematic view of a method for manufacturing two-layer paper according to another embodiment, and
Fig. 3-1, 3-2 and 3-3 graphs show by curves the fiber length distributions of long fiber furnish and short fiber furnish.

Fig. 1 and Fig. 2 are showing views being self-explanatory. As far as the methods for manufacturing paper and tissue are concerned the methods contain the usual paper and tissue manufacturing steps. Nevertheless, for simplicity reasons, the steps shown in Figs. 1 and 2 are only focussed on the essential features of the present invention.

Embodiments of the invention

The embodiments are illustrated for a two-layer paper and especially a two-layer tissue paper manufactured in a tissue paper-making machine optionally including wet creped or dry creped or through-air-drying (TAD)or any other manufacturing process. Normally two separate layers in the headbox are provided in the paper machine being supplied differently with furnish, e.g. by the first furnish and the second furnish as illustrated in Figs. 1 and 2. The first furnish is destined for the strength layer of the paper, independently on the fact whether a two-layer paper or a multi-layer paper with more than two layers is manufactured. The second furnish is

destined for the softness layer being an outer layer. For the first furnish primarily softwood pulp is used and primarily for the second furnish hardwood pulp is used. The second furnish is fractionated and the such achieved short fibers/fines fraction is added to the first furnish in order to achieve in the manufactured paper a strength layer of higher strength. This causes simultaneously the manufacture of a softness layer of higher softness. Fractionating can be accomplished by standard processes, e.g. by screening in a screen cylinder. Fractionating should be carried out using a suitable fractionating device such as e.g. low-consistence washers, intermediate-consistency washers, high-consistency washers flotation cells, flotation machines, centrifugal cleaners, pressure screens and gravity screens.

In Fig. 3-1 is illustrated the fiber length distribution of a hardwood furnish (second furnish) and a softwood furnish (first furnish). The hardwood furnish is fractionated leading to a short fiber/fines fraction and a long fiber fraction (Fig. 3-2). The short fiber/fines fraction is being transferred to the softwood furnish (first furnish),thereby resulting in a mixture of softwood refined and hardwood short fiber/fines fraction (Fig. 3-3). So Fig. 3-1, 3-2 and 3-3 show the essential features of the invention.

The following examples are presented for average fiber length of hardwood furnish and softwood furnish.

In Figs. 1 and 2 with respect to the schematically illustrated two-layer paper the hood side and the Yankee side are indicated, which relates to the Yankee dryer and the position of the strength layer and the softness layer respectively in relation to the hood surrounding the Yankee cylinder and the Yankee cylinder itself. If a TAD-dryer is present in the paper machine the hood side is similar to the air side and the Yankee side is similar to the dryer side

with respect to the TAD fabric running through the TAD drying section of the paper machine.

Experiments were made and the results are shown in Table 1.

	Lab number	Beating time [min.]	Desintegrator time [min.]	Basis weight [g/m²]	Dry tensile strength [N/15mm]	Dry breaking length [m]
Softwood refined	26-1	10	2	75,8	56,1	5028
Softwood refined plus Hardwood short fibers/fines fraction (10% from second furnish)	26-2	10	2	77,1	67,8	5978
Hardwood	26-5	–	–	76,1	34,6	3086
Hardwood long fiber fraction	26-6	–	–	77,1	26,0	2204

The Table is self-explanatory and is not to be described in all detail. Strength is presented by dry tensile strength and dry breaking length and the Table 1 shows different results under different circumstances. The desintegrator time indicates the time used for disintegrating the cellulose pulp. Softwood refers to is long fibrous pine sulfate and eucalyptus is hardwood pulp.

Table 1 shows that according to the invention (lab number 26-2) the addition of 10% hardwood short fiber/fines fraction from the second furnish (softness layer) to the first furnish (strength layer) leads to higher strength.

Together with the present invention is to be considered that by beating and disintegrating combined with beating time and disintegrating time strength can be changed for different kind of cellulose pulp, wherein generally softwood pulp is used for strength layer of paper and hardwood pulp for softness layer of a multi-layer paper, wherein strength layer means that strength is of priority and softness layer that softness is of priority.

Fig.2 is a schematic view similar to the view in Fig.1, added by two separate layers within one headbox for each furnish and a former of the paper machine. The white water from the former is returned to each furnish for dilution. A retention aid is added to the first furnish and optionally also to the second furnish. This is an essential feature in contrast to the method illustrated in Fig.1.

If white water is returned to the furnishes the result with respect to strength and softness and especially strength achieved according to the method illustrated in Fig.1 is lowered by return of white water to the furnishes, which will be explained later. This reduction of strength is compensated essentially by the retention-aid.

This is explained in more detail on the basis of Table 2.

Furnish		60% retention	Fractionated 60% retention	95% retention	Fractionated 95% retention
a) First Furnish (Strength Layer)	Fines Content %	7.3	7.3	7.3	7.3
b) Second Furnish (Softness Layer)	Fines Content %	7.8	7.8	7.8	7.8
c) First Furnish plus Short Fibre/Fines Fraction from Second Furnish	Fines Content %	--	11.8	--	11.8
d) Long Fibre Fraction of Second Furnish	Fines Content %	--	3.3	--	3.3
e) First Furnish plus Short Fibre/Fines Fraction from Second Furnish after dilution with White Water I	Fines Content %	40.7	43.3	11.4	15.7
f) Long Fibre Fraction of Second Furnish after dilution with White Water I	Fines Content %	40.2	37.4	11.8	7.5
Final Tissue paper in total	Fines Content %	7.4	7.3	7.5	7.5
Yankee Layer	Fines Content %	7.3	6.8	7.6	4.9
Hood Layer	Fines Content %	7.4	7.9	7.4	10.1

To keep the fines in a tissue paper is desirable for quality and economic reasons. Therefore, it is an advantage to change the sheet structure of a layered tissue by concentrating the fines in the so-called hood-layer and to reduce the fines level in the Yankee-layer. This is achieved by having the fractionation in the Yankee-layer and to add the short fiber/fines fraction to the hood-layer. As mentioned before, this is improving softness, haptic, absorption speed and capacity, thickness and strength.

Part of this effect is decreased by diluting the pulps with the fines containing white water upstream the headbox. This dilution is increasing the fines content in both layers. Nevertheless, the fines content in the hood-layer is higher than the fines content in the Yankee-layer.

According to Table 2, calculating with a fines content of 3.3% in the Yankee layer (d)) and a fines content of 11.8% in the Hood layer (c)) both before dilution of the stock with white water I, and assuming a retention of 60%, there will be after dilution of the stock with white water I a fines content of 40.2% in the Yankee layer (now f)) and a fines content of 40.7% in the Hood layer (now e)). Layers a) to f) refer also to Fig. 2.

The increase of the fines content in the Yankee layer of from 3.3% to 40.2% (simultaneously of from 11.8% to 40.7% in the Hood layer) is due to the dilution of the stock with white water I, which contains high amounts of fines.

When increasing the retention from 60% to 95% by using retention-aids, the increase of the fines content in the Yankee layer caused by the dilution with white water I is from 3.3% (d) to 7.5% (f)). Accordingly, the fines content in the Hood layer increases from 11.8% (c)) to 15.7% (e)) due to the dilution of the stock with white water I.

As it becomes apparent from the fines content of the final tissue paper, fractionating according to the invention results in an increasing difference of the fines content between the Hood layer and the Yankee layer of 0.1% (7.4% - 7.3% : no fractionation) to 1.1% (7.9% – 6.8% : fractionation). This difference can further be increased by adding retention-aids thereby raising the retention of from 60% to 95%. The resulting difference is now 5.2% (10.1% – 4.9%) instead of 1.1% for a retention of 60%.

According to Fig.2, retention-aids can be added to the strength layer (c)) as well as to the softness layer (d)). However, in order to enhance concentrating the fines content in the strength layer (c)) retention-aids should preferably be added to the strength layer (c)). Retention-aids are normally added in an amount of approximately 100g up to 500g per ton of fibers.

Claims

1. A method of making an absorbent structure as a paper, especially a tissue paper, consisting of at least two layers, a least one layer as an outer layer being preferably a soft layer (softness layer) and at least one layer as an outer layer or an intermediate layer being preferably a layer of higher strength (strength layer), comprising the steps of:

   a) providing a first furnish of fibers for the strength layer,
   b) providing a second furnish of fibers for the softness layer,
   c) fractionating the second furnish such that the short fibers/fines fraction is separated,
   d) adding the short fiber/fines fraction to the first furnish, and
   e) leading the two furnishes separately to a headbox and from there to a forming section of a paper machine and forming a multi-layer paper.

2. Method according to claim 1, wherein the content of the short fibers/fines is increased in the strength layer and the content of the short fibers/fines is reduced in the softness layer.

3. Method according to claim 1 or 2, wherein a retention-aid is added to at least one of the two furnishes upstream of the headbox, increasing the content of short fiber/fines in the strength layer.

4. Method according to claim 3, wherein the retention-aid is added to both furnishes.

5. Method according to claim 3, wherein the retention-aid is added only to the first furnish.

6. Tissue paper manufactured according to any of claims 1 to 5.

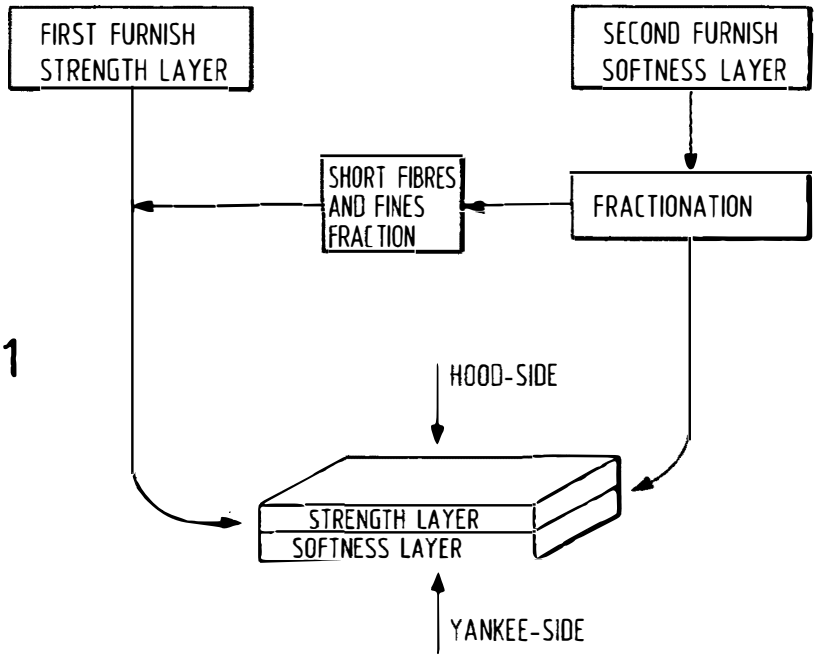


Fig. 1

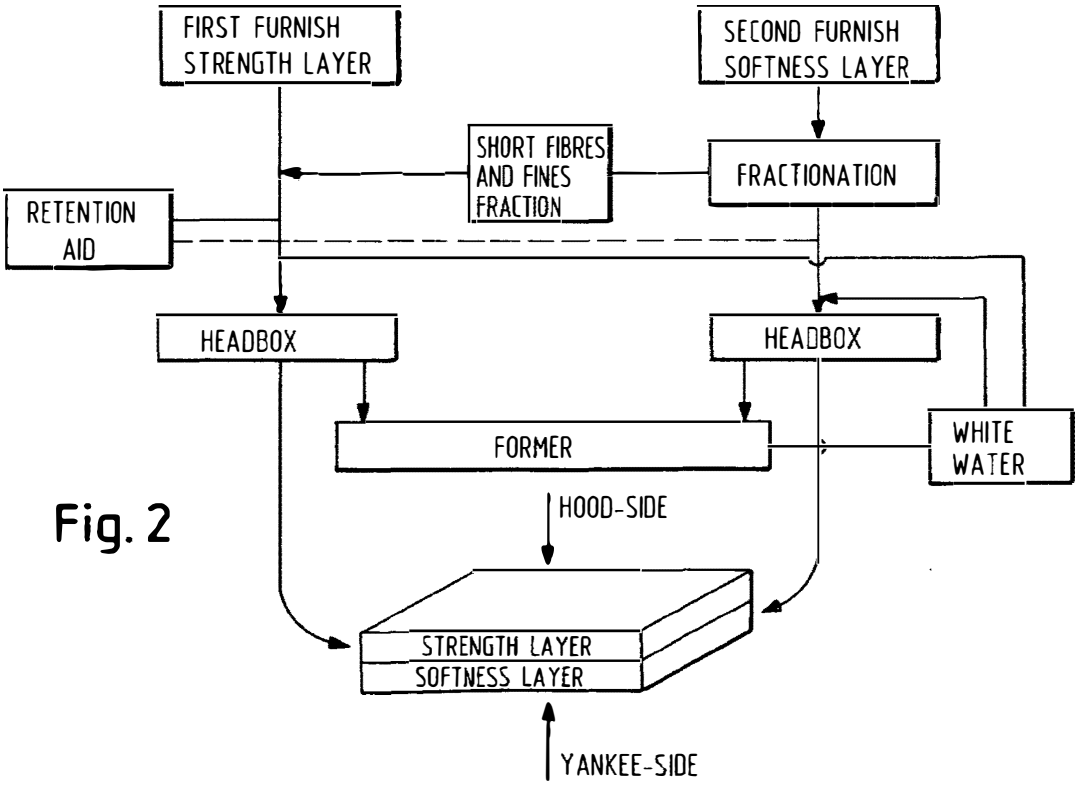
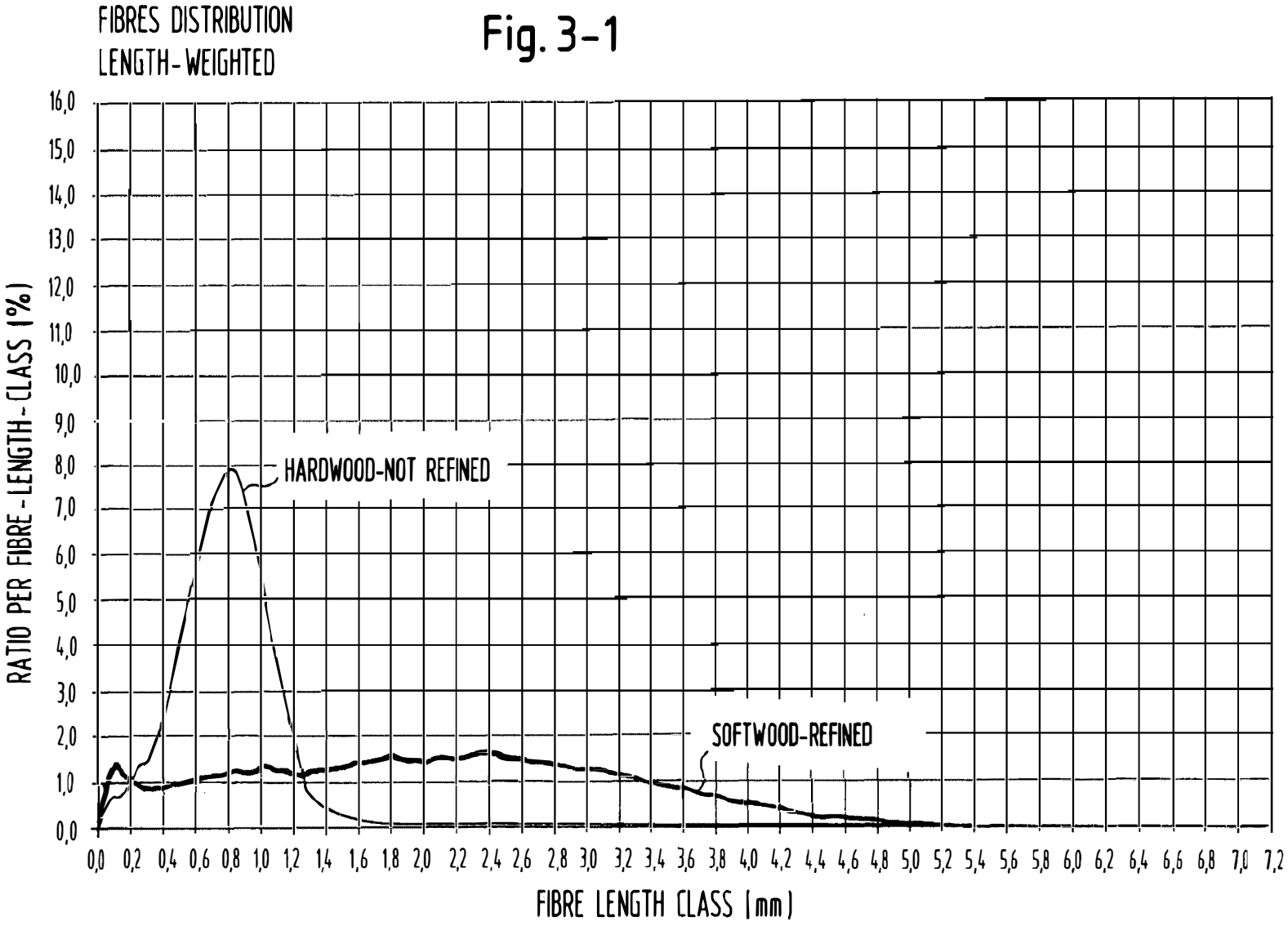


Fig. 2

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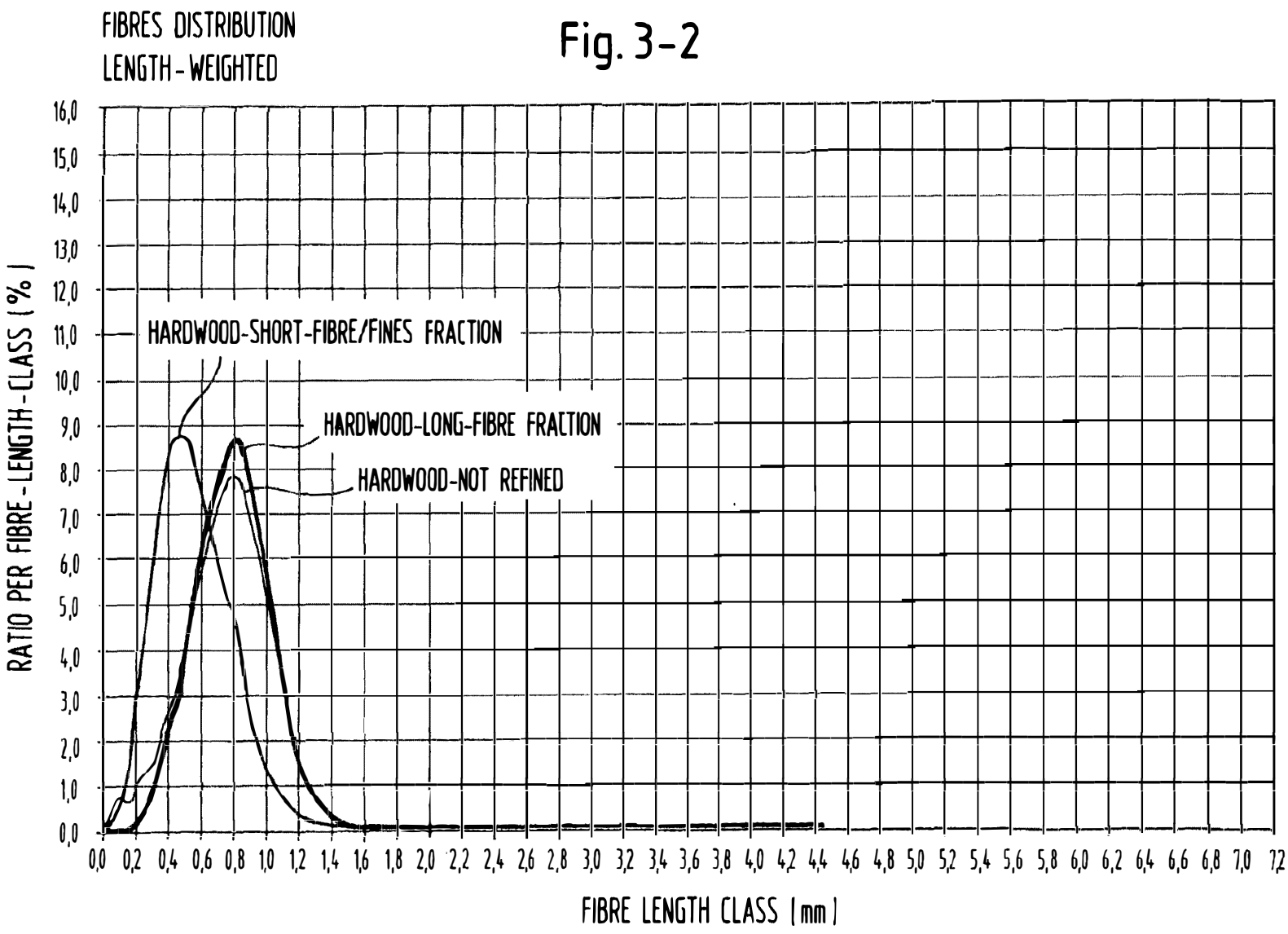
SUBSTITUTE SHEET (RULE 26)

Fig. 3-1



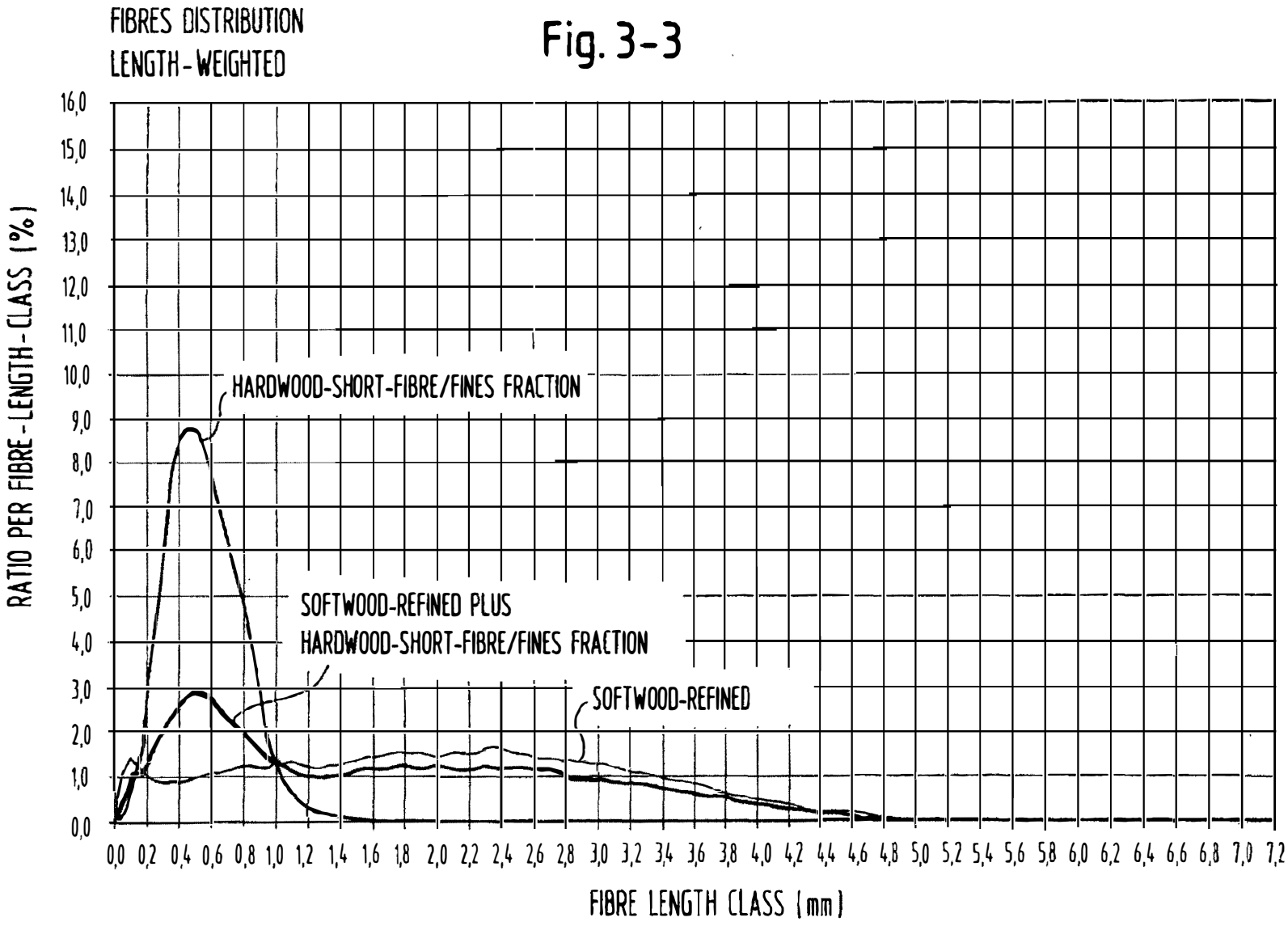
Kimberly Clark EX1002, p. 652
PGR2026-00078

Fig. 3-2



SUBSTITUTE SHEET (RULE 26)

Fig. 3-3



SUBSTITUTE SHEET (RULE 26)

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PGR2026-00078

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/006630

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H27/38
ADD. D21H27/00 B32B29/00

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)
D21H B32B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 781 793 A1 (HALME MATTI [FI]) 1 November 1988 (1988-11-01) cited in the application figure 1 column 1, line 7 - line 15 column 2, line 55 - line 60 column 4, line 25 - line 52 column 5, line 19 - line 29 column 5, line 62 - column 6, line 36 column 7, line 18 - line 25 -/--	1-5

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/006630

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/121629 A1 (HU SHENG-HSIN [US]) 3 July 2003 (2003-07-03) cited in the application figures 1,4 page 1, paragraph 1 - paragraph 14 page 2, paragraph 28 - paragraph 29 page 2, paragraph 33 page 3, paragraph 40 - paragraph 44 page 5, paragraph 60 - paragraph 62 page 6, paragraph 73 - paragraph 74	1,2,6
X	US 2002/162635 A1 (HSU JAY C [US] ET AL) 7 November 2002 (2002-11-07) cited in the application page 1, paragraph 1 - paragraph 12 page 2, paragraph 15 page 2, paragraph 17 page 2, paragraph 23 page 3, paragraph 34 page 4, paragraph 37 - paragraph 40	1,2,6
A	US 6 024 834 A1 (HORTON JR JAMES ELLIS [US] ET AL) 15 February 2000 (2000-02-15) cited in the application column 2, line 35 - line 51	1-6
A	US 5 785 813 A1 (SMITH MICHAEL JOHN [US] ET AL) 28 July 1998 (1998-07-28) figure 1	1-6

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4781793 A1		NONE	
US 2003121629 A1	03-07-2003	US 2003127203 A1	10-07-2003
US 2002162635 A1	07-11-2002	MX PA01006787 A US 6413363 B1	30-07-2004 02-07-2002
US 6024834 A1		NONE	
US 5785813 A1		NONE	

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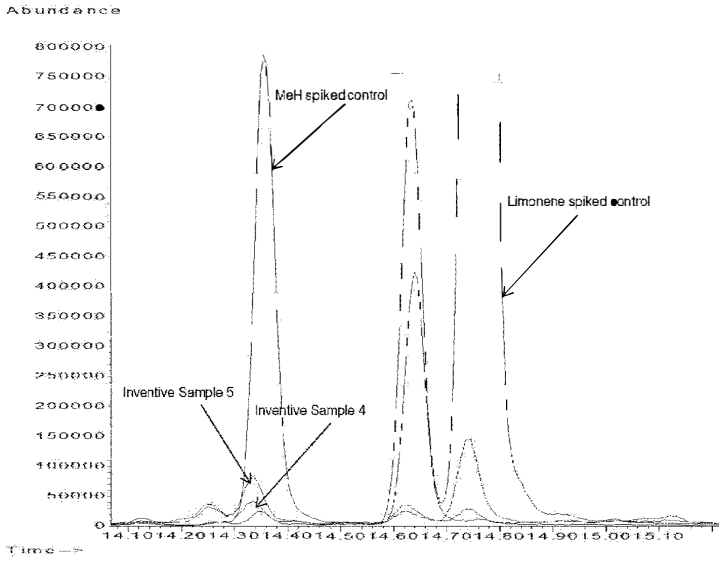


FIG. 1

(57) Abstract: The disclosure provides fibrous structures and tissue products comprising a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one. The volatile agave compounds may be provided by forming the structures at least in-part from agave fiber, such as Agave tequilana fiber. In other embodiments the volatile agave compounds may be incorporated in the fibrous structures by adding the compounds during formation of the fibrous structure, such as by adding the compounds to the furnish, or by topically applying the compounds to the fibrous structure after formation, in order to provide a lemon-like scent to the fibrous structure.

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FIBROUS STRUCTURES COMPRISING VOLATILE AGAVE COMPOUNDS

BACKGROUND

Manufacturers of fibrous structures have long sought to introduce compositions having a scent, such as a perfume, fragrance-emitting substance, and the like to their products to enhance their appeal to consumers and to provide a more favorable consumer experience. The manufacturers of tissue, and rolled tissue products, such as bath tissue and paper towels, in particular, have concerned themselves with adding scents to the core or to the dispensing mechanism. For example, US Patent Nos. 3,017,117, 5,857,621, 6,425,530 and 6,688,551 are directed to various roll holder and dispensing systems for rolled bath tissue that deliver a scent in-use. In each instance the user must purchase and install some additional component to provide scent to a roll of bath tissue. Requiring users to purchase and install additional components adds complexity and cost to delivering a scented tissue product. Moreover, the foregoing systems are generally limited to the storage and dispensing of rolled tissue products and not readily adapted to storing and dispensing folded tissue products, such as facial tissue.

In other instances a scent may be applied to the core during manufacture of the rolled tissue product such as disclosed in US Patent Publication No. 2014/0230950. Adding a scent directly to the core eliminates the need for a user to purchase a separate scented dispenser, but adds complexity to the manufacturing process and may not deliver a long-lasting scent. Further, the scent may not be perceived in-use by the consumer as it is not incorporated in the tissue sheet itself.

Therefore there remains a need in the art for a tissue product comprising a scent, where the scent is incorporated in the tissue sheet itself, is long lasting and provides the consumer with a sensory cue.

SUMMARY

The present inventors have now discovered that agave fiber is suitable for forming fibrous structures, such as rolled bath tissue and towels, having favorable physical characteristics such as low stiffness and good bulk. In addition to having favorable physical properties, the tissue products have a pleasant odor, which consumers describe as citrusy, grassy and fatty. These scents, in-turn, may act as a sensory cue to convey to a consumer product benefits and attributes such as natural, freshness and cleanliness. Thus, the present invention provides fibrous structures comprising volatile agave compounds, particularly compounds selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-heptene-2-one.

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Accordingly, in one embodiment the present invention provides a fibrous structure comprising agave fiber and at least one volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one.

In another embodiment, the present invention provides a tissue product comprising agave fiber and a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof.

In other embodiments, the present invention provides a tissue product comprising at least about 1.0 percent, by weight of the tissue product, agave fiber and a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof, wherein the tissue product contains at least 10 ppb of the volatile agave compound.

In still other embodiments, the present invention provides manufacturing a tissue web having a lemon-like odor note comprising the steps of forming a fiber slurry comprising agave fiber and wood pulp fiber, forming a tissue web from the fiber slurry, the web having a first and a second side; depositing on at least a first side of the web a formulation comprising a sensorily effective amount of a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof and a carrier.

DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts the total ion chromatogram (TIC) obtained by SPME GC/MS of two tissue products comprising agave fiber and two volatile agave compound standards;

FIG. 2 depicts mass spectra obtained from limonene standard (top) and a tissue product comprising 40 weight percent agave fiber (bottom); and

FIG. 3 depicts mass spectra obtained from 6-methyl 5-heptene-2-one standard (top) and a tissue product comprising 40 weight percent agave fiber (bottom).

DETAILED DESCRIPTION

The present invention provides fibrous structures adapted for use in tissue products such as facial tissues, bathroom tissues, toilet tissues and the like comprising a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one. In certain embodiments fibrous structures may be provided with volatile agave compounds by forming the structures at least in-part from agave fiber. In other embodiments the volatile agave compounds may be incorporated in the fibrous structures of the present invention by adding the compounds during formation of the fibrous structure, such as by adding the compounds to the furnish, or by topically applying the

compounds to the fibrous structure after formation. For example, the volatile agave compounds may be incorporated into a formulation and topically applied to a fibrous structure to provide the fibrous structure with a sensory cue in-use. Alternatively, one or more volatile agave compounds may be formulated in a lotion, which may in-turn be applied to the external surface of the fibrous structure or otherwise, as desired.

Volatile agave compounds useful in the present invention are selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one. The foregoing compounds have been found in agave fiber, which may be useful in forming fibrous structures according to the present invention. The compounds provide the fibrous structures with a pleasant odor, which may act as a sensory cue to users and reinforce properties of the fibrous structures. In other instances the sensory cue may reinforce the user's perception of cleanliness and freshness.

In certain embodiments the invention provides a tissue product comprising limonene (1-methyl-4-(1-methylethenyl)-cyclohexene) having the formula $C_{10}H_{16}$, which is preferably provided as d-limonene and which may impart the tissue product with a citrus, lemon or piney odor. In other embodiments the invention provides a tissue product comprising hexanaldehyde, also known as hexanal, and having the chemical formula $C_6H_{12}O$, which may impart the tissue product with a grassy odor. In still other embodiments the invention provides a tissue product comprising 6-Methyl-5-hepten-2-one having the chemical formula $C_8H_{14}O$, which may impart the tissue product with a fatty, green and citrus odor.

Fibrous structures may comprise a single volatile agave compound, or may comprise a combination of two or more volatile agave compounds. Further, the amount of volatile agave compound may vary depending on the desired physical properties of the fibrous structure. As such, the tissue products may comprise at least one volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one, the volatile agave compound having a concentration of at least about 5 parts per billion (ppb), more preferably at least about 10 ppb and still more preferably at least about 15 ppb, such as from about 5 to about 500 ppb and more preferably from about 10 to about 300 ppb.

In certain embodiments the volatile agave compound is provided in an amount that exceeds its odor thresholds. Generally, when a compound is provided in excess of its odor threshold, the compound is said to be present in a "sensorily effective amount." For example, the fibrous structure may comprise at least about 10 ppb limonene, such as from about 10 to about 500 ppb. In other embodiments the fibrous structure may comprise at least about 2,500 ppb hexanaldehyde, such as from about 2,500 to about 5,000 ppb. In still other embodiments the fibrous structure may comprise at least about 50 ppb 6-Methyl-5-hepten-2-one such as from about 50 to about 500 ppb.

The volatile agave compounds may be incorporated in a wide range of fibrous structures. Suitable fibrous structures include, for example, a web, such as a wet laid tissue web or air laid web, gauze, swab, pad or the like. Particularly preferred fibrous structures include fibrous webs, including flushable and non-flushable cellulosic webs and nonwoven webs of synthetic fibrous material. Useful webs may be wet laid, air laid, meltblown, or spunbonded. Suitable synthetic fibrous material includes meltblown polyethylene, polypropylene, copolymers of polyethylene and polypropylene, bicomponent fibers including polyethylene or polypropylene, and the like. Useful nonwoven webs may be meltblown, coform, spunbond, airlaid, hydroentangled nonwovens, spunlace, bonded carded webs.

In one particularly preferred embodiment the volatile agave compounds are incorporated in tissue webs and products. Tissue webs useful in the present invention may be manufactured using any number of different techniques for manufacturing tissue webs, including but not limited to known wet-laid papermaking processes and air-laid papermaking processes. Such processes typically include steps of preparing a fiber composition in the form of a suspension in a medium, either wet, more specifically aqueous medium, or dry, more specifically gaseous, i.e. with air as medium. The aqueous medium used for wet-laid processes is oftentimes referred to as a fiber slurry. The fibrous slurry is then used to deposit a plurality of fibers onto a forming wire or belt such that an embryonic tissue product is formed, after which drying and/or bonding the fibers together results in a tissue product.

In particularly preferred embodiments the tissue webs and products of the present invention are formed by through-air drying and may be either creped or uncreped. For example, in one embodiment, at least one web of the tissue product is formed by an uncreped through-air drying process, such as the process described, for example, in US Patent Nos. 5,656,132 and 6,017,417, both of which are hereby incorporated by reference herein in a manner consistent with the present disclosure. Alternatively, at least one web of the tissue product is formed by the creped through-air dried process.

Further processing of the tissue product may be carried out such that a finished tissue product is formed. For example, in typical papermaking processes, the finished tissue product is the tissue product that is wound on the reel at the end of papermaking, and may subsequently be converted into a finished product, such as a rolled tissue product or a folded and stacked tissue product. Rolled tissue products may comprise a plurality of individual sheets separated from one another by perforations, which connect the sheets but allow individual sheets to be dispensed for use.

The tissue products may be single-ply or may be multi-ply. In those embodiments where the tissue product comprises more than one ply, each ply may be made of different materials or can have been manufactured in different ways. As used herein, the term “single-ply tissue product” means that it is comprised of one ply of tissue; the ply can be substantially homogeneous in nature or it can be a multi-

layered tissue paper web. As used herein, the term “multi-ply tissue product” means that it is comprised of more than one ply of tissue. The plies of a multi-ply tissue product can be substantially homogeneous in nature or they can be multi-layered tissues. Further, the plies can be of the same construction and content or include different materials or processing steps prior to their combination.

The tissue product of the present invention may have a basis weight from about 10 to about 120 gsm, more preferably from about 10 to about 80 gsm and still more preferably from about 10 to about 60 gsm. Basis weight, as used herein, generally refers to the bone dry weight per unit area of a tissue and is generally expressed as grams per square meter (gsm). Basis weight is measured using TAPPI test method T-220. In particularly preferred embodiments the tissue products comprise one or more plies and have a basis weight from about 10 to about 80 gsm and still more preferably from about 15 to about 60 gsm.

The tissue product of the present invention may have a geometric mean tensile (GMT) greater than about 400 g/3”. GMT refers to the square root of the product of the machine direction tensile strength and the cross-machine direction tensile strength of the tissue product, measured as described in the test methods section below and having units of grams per three inches (g/3”). In particularly preferred embodiments the tissue products may have a GMT from about 400 to about 3,000 g/3” and more preferably from about 600 to about 2,500 g/3”. In certain preferred embodiments the tissue product may have a basis weight from about 30 to about 60 gsm and a GMT from about 700 to about 1,200 g/3”. In another embodiment the tissue product may have a basis weight from about 45 to about 70 gsm and a GMT from about 1,200 to about 2,500 g/3”.

The tissue product of the present invention may have a sheet bulk greater than about 5.0 cc/g. Sheet bulk refers to the quotient of the caliper (μm) divided by the bone dry basis weight (gsm). The resulting sheet bulk is expressed in cubic centimeters per gram (cc/g). Tissue products prepared according to the present invention generally have a sheet bulk greater than about 5.0 cc/g, more preferably greater than about 8.0 cc/g and still more preferably greater than about 10.0 cc/g, such as from about 5.0 to about 20.0 cc/g and more preferably from about 8.0 to about 15.0 cc/g.

In a particularly preferred embodiment the present invention provides a through-air dried tissue product comprising agave fiber, and more preferably high yield agave fiber, and at least one volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one, the product having a GMT greater than about 400 g/3” and a sheet bulk greater than about 8.0 cc/g.

In certain embodiments the addition of volatile agave compounds to the tissue products may be achieved by forming the tissue product at least in-part from fiber derived from non-wood plants of the

genus Agave, of the family Asparagaceae, such as *Agave tequilana, Agave sisalana* and *Agave fourcroydes*. Where the compounds are provided by forming the tissue product in-part from agave fiber, it is generally preferred that the tissue product comprise at least about 0.5 percent, by weight of the product, agave fiber and more preferably at least about 1.0 percent, and still more preferably at least about 5.0 percent, such as from about 0.5 to about 50 percent agave fiber and more preferably from about 1.0 to about 20 percent and still more preferably from about 5 to about 15 percent. In particularly preferred embodiments the agave fibers are incorporated into the instant tissue products as a replacement for a portion of the long fiber fraction of the papermaking furnish, such as Northern Softwood Kraft (NSWK) or Southern Softwood Kraft (SSWK).

In a particularly preferred embodiment the present invention provides a three layered web where the agave fiber is selectively disposed in the middle layer and the two outer layers consist essentially of hardwood kraft fibers, such as Eucalyptus Hardwood Kraft (EHWK) and are substantially free of agave fiber. In addition to agave fiber, the middle layer also comprises wood pulp fibers having an average fiber length greater than about 2.0 mm. As used herein, the term "average fiber length" generally refers to the length weighted average length of fibers determined utilizing a fiber analyzer such as those commercially available from Kajaani Oy Electronics (Kajaani, Finland). The agave fiber comprises at least about 1.0 percent by weight of the middle layer, and more preferably at least about 5.0 percent and sill more preferably at least about 10 percent, such as from about 1.0 to about 75 percent by weight of the middle layer. In the foregoing example, the agave fiber may comprise from about 0.5 to about 30 percent, by weight of the tissue product, and the product may comprise from about 1.0 to about 30 percent, by weight of the product, less wood pulp fibers having an average fiber length greater than about 2.0 mm, such as NSWK or SSWK.

In still other embodiments the agave fiber may replace substantially all of the long fiber fraction of the papermaking furnish, such that the tissue product is substantially free from wood pulp fibers having an average fiber length greater than about 2.0 mm. In such embodiments the agave fiber may be selectively incorporated into the middle layer of a three layered tissue web such that the middle layer consists essentially of agave fiber and the two outer layers comprise wood pulp fibers having an average fiber length less than about 2.0 mm.

Further, in certain embodiments it may be desirable to provide a layered tissue web where the agave fiber is selectively disposed in a layer of the tissue which is not brought into contact with a dryer, such as a Yankee dryer during manufacture. Without being bound by any theory, selectively disposing the agave fiber in a layer that is not contacted by a dryer may preserve the volatile agave compound and ensure that the resulting tissue web and products have a pleasant odor.

The tissue webs may be incorporated into tissue products that may be either single- or multi-ply, where one or more of the plies may be formed by a multi-layered tissue web having agave fibers selectively incorporated in one of its layers. In one embodiment the tissue product is constructed such that the agave fibers are not brought into contact with the user's skin in-use. For example, the tissue product may comprise two multi-layered through-air dried webs wherein each web comprises a first fibrous layer substantially free from agave fibers and a second fibrous layer comprising agave fibers. The webs are plied together such that the outer surface of the tissue product is formed from the first fibrous layer of each web and the second fibrous layer comprising the agave fibers is not brought into contact with the user's skin in-use.

Generally agave fibers useful in the present invention are derived from non-woody plants in the genus Agave of the family Asparagaceae. Suitable species within the genus Agave include, for example, *Agave tequilana*, *Agave sisalana* and *Agave fourcroydes*.

In certain embodiments the agave fibers are processed by a high yield pulping process, such as mechanically treating the fibers. High yield pulping processes include, for example, mechanical pulp (MP), refiner mechanical pulp (RMP), pressurized refiner mechanical pulp (PRMP), thermomechanical pulp (TMP), high temperature TMP (HT-TMP), RTS-TMP, thermopulp, groundwood pulp (GW), stone groundwood pulp (SGW), pressure groundwood pulp (PGW), super pressure groundwood pulp (PGW-S), thermo groundwood pulp (TGW), thermo stone groundwood pulp (TSGW) or any modifications and combinations thereof. Processing of agave fibers using a high yield pulping process generally results in a pulp having a yield of at least about 50 percent, more preferably at least about 65 percent and still more preferably at least about 85 percent, such as from about 50 about 95 percent and more preferably from about 65 to about 90 percent.

The high yield pulping process may comprise heating the agave fiber above ambient, such as from about 70 to about 200ºC, and more preferably from about 90 to about 150ºC while subjecting the fiber to mechanical forces. Caustic or an oxidizing agent may be introduced to the process to facilitate fiber separation by the mechanical forces. For example, in one embodiment, a solution of 3 to about 8 percent NaOH and a solution of 3 to about 8 percent peroxide may be added to the fiber during mechanical treatment to facilitate fiber separation.

In other embodiments the high yield pulping process may comprise treating agave leaves with an alkaline pulping solution such as that disclosed in US Patent No. 6,302,997, the contents of which are incorporated herein in a manner consistent with the present disclosure. Alkaline treatment may be carried out at a pressure from about atmospheric pressure to about 30 psig and at a temperature ranging from about ambient temperature to about 150°C. The alkaline hydroxide may be added, based upon the

oven dried mass of the agave leaves, from about 10 to about 30 percent. Suitable alkaline pulping solutions include, for example, sodium hydroxide, potassium hydroxide, ammonium hydroxide, calcium hydroxide and combinations thereof. After alkaline treatment, the agave is mechanically worked and then treated with an acid solution to reduce the pH to an acid pH.

In other embodiments the high yield pulping process may comprise impregnating agave leaves with a solution of nitric acid and optionally ammonium hydroxide at ambient temperatures under atmospheric pressure, such as described in US Patent No. 7,396,434, the contents of which are incorporated herein in a manner consistent with the present invention. The impregnated leaves are then heated to evaporate the nitric acid followed by treatment with an alkaline solution before being cooled.

Although a caustic, such as NaOH, or oxidizing agent, such as nitric acid or peroxide, may be added during processing, it is generally preferred that the agave fiber is not pretreated with a sodium sulfite or the like prior to processing. For example, high yield agave pulps are generally prepared without pretreatment of the fiber with an aqueous solution of sodium sulfite or the like, which is commonly employed in the manufacture of chemi-mechanical wood pulps.

The use of agave fiber, and in a particularly preferred embodiment high yield agave pulp fibers, results in tissue webs and products having one or more volatile agave compounds selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one. The volatile agave compounds may provide the tissue products with an odor, which consumers may find desirable and provide the consumer with a sensory cue. Thus, the present invention may provide a sensory cue that can remain with the consumer for a period of time, does not rely on the consumer viewing or reading packaging content, may be more impactful than a visual cue and may provide a more lasting impression.

While in certain embodiments the volatile agave compounds may be provided by forming the fibrous structure at least-in part from agave fiber, in other embodiments the volatile agave compounds may be formulated and added to a fibrous structure to enhance the sensory cue and reinforce to a user the presence and benefits of agave fiber in the fibrous structure. In such embodiments the fibrous structure may comprise less than about 10 percent, by weight, agave fiber, such as less than about 5.0 percent, and in certain instances less than about 2.0 percent, such as from about 0.1 to about 10 percent and more preferably from about 1.0 to about 5.0 percent and the web may further comprise a formulation comprising a volatile agave compound and a carrier disposed thereon.

Suitable formulations may comprise a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof and a carrier. Amounts of the volatile agave compounds in the foregoing formulation may range from 0.000001 to 2 percent, by weight of the formulation, more preferably from 0.00001 to 1 percent, and still more

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preferably from 0.0001 to 0.5 percent, and optimally from 0.001 to 0.1 percent. Amounts of the carrier may range from 1 to 99.9 percent, by weight of the formulation, preferably from 70 to 95 percent, optimally from 80 to 90 percent. Among the useful carriers are water, emollients, fatty acids, fatty alcohols, humectants, thickeners and combinations thereof. The carrier may be aqueous, anhydrous or an emulsion. Preferably the formulations are aqueous, especially water and oil emulsions. Water when present may be in amounts ranging from 5.0 to 90 percent, by weight of the formulation, preferably from 20 to 70 percent, optimally from 35 to 60 percent. Alternatively, emollient materials may serve as carriers. These may be in the form of silicone oils, synthetic esters and hydrocarbons. Amounts of the emollients may range anywhere from 0.1 to 95 percent, by weight of the formulation, preferably between 1 and 50 percent.

In other embodiments the volatile agave compounds may be incorporated in a lotion and applied to a tissue web or product. In certain embodiments, particularly those in which the composition is applied to a web, it may be desirable that the composition provide certain physical attributes, such as having a smooth, lubricious, non-greasy feel; the ability to at least partially transfer from the web to the user's skin; the capability to be retained on the web at about room temperature; or the ability to be compatible with the web manufacturing process. In certain embodiments it is preferred that at least a portion of the composition is transferred from the tissue to the user's skin in-use.

Incorporating volatile agave compounds into lotions and applying the same to a tissue product provides the added advantage of transferring the volatile agave compounds to a user's skin in the region where the effect is mostly intended. For example, the tissue product may be in the form a facial tissue product intended for nose blowing and wiping, and in-use the lotion is transferred to the user's skin near the nose enabling highly effective transport of the compounds to receptor sites of the mucous skin in the nasal cavity. According to the present invention the lotion can be the carrier for the volatile agave compounds.

As used herein, the term "lotion" generally refers to a composition added to the tissue in order to improve its softness or handfeel of the tissue and which may be transferred to the user's skin in-use. The lotion may comprise tissue softening and/or debonding agents, emollients, immobilizing agents and mixtures thereof. Suitable softening and/or debonding agents include quaternary ammonium compounds, polysiloxanes, and mixtures thereof. Suitable emollients include propylene glycol, glycerin, triethylene glycol, spermaceti or other waxes, petrolatum, fatty acids, fatty alcohols and fatty alcohol ethers or esters having from 12 to 28 carbon atoms in their fatty acid chain, mineral oil and mixtures thereof. Suitable immobilizing agents include waxes, fatty alcohols, fatty acids, polyhydroxy fatty acid

esters, polyhydroxy fatty acid amides, and mixtures thereof. In most cases, the lotions contain at least one immobilizing agent and an emollient. Lotions can be emulsions or dispersions.

Thus, in certain embodiments a lotion useful in the present invention may consist essentially of a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one, a cationic softening compound, such as a quaternary ammonium compound, a polyhydroxy compound having a molecular weight at least about 1,000 and optionally a silicone or glycerin, or mixtures thereof. For example, the softening composition may consist essentially of a quaternary ammonium compound, a polyhydroxy compound having a molecular weight at least about 1,000, a silicone and glycerin.

Other chemicals commonly used in papermaking can be added to the softening composition described herein, or to the papermaking furnish so long as they do not significantly and adversely affect important tissue product properties, such as strength or absorbency of the tissue product, or negatively effect the softening provided by the softening compositions of the present invention. For example, dry strength additives such as starch or carboxymethyl cellulose may be added to the furnish to improve the tensile strength of the tissue products. In other embodiments wet strength resins, such as polyamide-epichlorohydrin resins may be added to the furnish to improve the tensile strength of the tissue product when wet. In still other embodiments a temporary wet strength agent may be added to the furnish, such as modified starch and more particularly cationic starches.

Other additives may include humectants and skin protectants. Suitable humectants include lactic acid and its salts, sugars, ethoxylated glycerin, ethoxylated lanolin, corn syrup, hydrolyzed starch hydrolysate, urea, and sorbitol. Suitable skin protectants include allantoin, kaolin, zinc oxide, aloe vera, vitamin E, petrolatum and lanolin. Again, the foregoing additives are generally complementary to the volatile agave compound containing lotion and generally do not significantly and adversely affect important tissue product properties, such as strength or absorbency of the tissue product, or negatively effect the sensory cue provided by the volatile agave compounds.

The formulations and lotions comprising volatile agave compounds described above, may be added to the tissue web at any point after the web has been formed and at least partially dewatered. In a particularly preferred embodiment a formulation or lotion comprising volatile agave compound is applied to the web after it has been dried to final dryness, such as a moisture content less than about 10 percent (by weight of the tissue web) and more preferably less than about 5 percent. For example, a lotion may be applied after the drying section of the tissue machine where the tissue sheet has a consistency of from about 90 to about 100 percent. Formulations and lotions may also be applied via a

secondary post treatment process where the tissue sheet has a consistency of from about 90 to about 100 percent.

The method by which the formulation or lotion is applied to the tissue sheet may be accomplished by any method known in the art. For example, in one embodiment a formulation or lotion may be applied by contact printing methods such as gravure, offset gravure, flexographic printing and the like. In other embodiments, non-contact printing methods such as ink jet printing, digital printing of any kind, and the like may be used.

In other embodiments the formulation or lotion may be sprayed onto the tissue sheet. For example, spray nozzles may be mounted over a moving tissue sheet to apply a desired dose of a solution to the tissue sheet. Nebulizers may also be used to apply a light mist to a surface of a tissue sheet. In other embodiments the lotion may be applied to a moving belt or fabric by spray or other means and the belt or fabric may in-turn contact the tissue sheet to apply the lotion to the tissue sheet.

In still other embodiments the lotion may also be applied by coating onto the tissue sheet by slot coating, blade coating, air knife coating, short dwell coating, cast coating, and the like. Preferred methods of application include gravure printing, flexographic printing, WEKO and spraying. A particularly preferred method of application is rotogravure printing such as described in US Patent No. 5,665,426, the contents of which are incorporated by reference in a manner consistent with the present disclosure.

In one embodiment the lotion may be applied by an indirect application process where the lotion is applied to the web via a transfer/applicator roll. For example, the web to be treated may be threaded from an unwind roll through a nip between the transfer/applicator roll and a backing roll. The lotion is added to a second nip created between a Mayer rod and the transfer/applicator roll. Mayer rods are well known in the art and are provided in a number of different configurations that allow different volumes of fluid to be put onto the transfer/applicator roll. The lotion applied to the transfer/applicator roll by the Mayer rod is subsequently disposed on the web.

The foregoing application method generally only applies the lotion to one side of the web. However, there is also an option to coat both sides of the web with a machine configuration change where the backing roll is replaced with a transfer/applicator roll.

The lotion may be applied to only a single surface of the tissue or may be applied to both the upper and opposed lower surfaces. The add-on amount of the lotion can be from about 0.5 to about 6 dry weight percent based on the weight of the tissue, more specifically from about 1 to about 5 dry weight percent, and still more specifically from about 2 to about 4.5 dry weight percent. The higher add-on amounts are more likely to leave behind a detectable residue on the skin, whereas the lower add-on

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amounts are less likely to do so. Surprisingly, the instant lotion may be added at relatively low levels, such as less than about 10 dry weight percent, and more preferably less than about 4 dry weight percent, such as from about 0.5 to about 6 dry weight percent, and still provide a significant sensory cue to the user.

When applied to the tissue web, the lotion can cover the entire surface area of the web or a portion of the web. For example, the composition can be applied so as to cover from about 20 to about 80 percent of the surface area of the web, and particularly from about 30 to about 60 percent of the surface area of the web. In certain embodiments, depending on the composition of the lotion, leaving untreated areas on the web, the web remains easily wettable, which can be a concern when applying hydrophobic additives.

Thus, in one embodiment, the present invention provides a method of making a soft, single- or multi-ply tissue product wherein one or more of the plies of the tissue product comprises a lotion disposed on its outer surface, the composition comprising a cationic softener, such as a quaternary ammonium compound, a polyhydroxy compound, a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof and optionally a silicone or glycerin. Methods of forming the foregoing tissue web generally comprise (a) forming a fiber slurry comprising agave fiber and wood pulp fiber; (b) depositing the fiber slurry onto a forming fabric to form a wet tissue sheet; and, (c) dewatering the wet tissue sheet to form a dewatered tissue sheet; (d) drying the dewatered tissue sheet to form a dried tissue sheet; and, (e) topically applying a lotion on the dried tissue sheet, the composition comprising a cationic softener, such as a quaternary ammonium compound, a polyhydroxy compound, a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof, and optionally a silicone or glycerin.

TEST METHODS

Gas Chromatography/Mass Spectrometry

Samples of tissue products were prepared by cutting and weighting 2.5 g of each tissue product and placing into a 60 mL vial. The tissue samples were then sampled by poking a small hole through the vial cap septa using a needle. Through the hole, a SPME fiber was inserted and the fiber exposed for one hour at 85°C to collect the volatiles for analysis. The SPME fiber used was:

- 85 µm Carboxen/polydimethylsilicone (Supelco catalog No. 57334-U, light blue) recommended for gases and low molecular weight compounds (MW 30-225).
- 57330-U manual fiber holder.

Control samples were spiked with standards and analyzed similarly to the samples. Area counts generated from the standards were used to calculate amounts present in the sample. Three replicates were run for each sample.

Analysis was carried out using a series 5973N quadrupole mass spectrometer (Agilent Technologies Inc., Santa Clara, CA). The gas chromatograph was equipped with an Agilent J&W DB-624MS column (30m, 0.25mm ID, 1.8 µ film). Helium was used as the carrier gas. The helium flow rate was 1.5 mL/minute. The gas chromatograph temperature was programmed as follows:

Level	Rate (°C/min)	Final Temp (°C)	Final Time (min)
Initial	-	0	1
1	7.5	100	0
2	10	240	-

The temperature of the GC inlet was 240°C and the split ratio was 5:1. Mass spectra and reconstructed chromatograms (total ion current "TIC") were obtained by automatic scanning in the mass range from 35 to 350 Daltons with a threshold of 200 Daltons. GC/MS data were processed with Agilent ChemStation software and the Wiley NIST11 mass spectra library.

Sheet Bulk

Sheet Bulk is calculated as the quotient of the dry sheet caliper (µm) divided by the basis weight (gsm). Dry sheet caliper is the measurement of the thickness of a single tissue sheet measured in accordance with TAPPI test methods T402 and T411 om-89. The micrometer used for carrying out T411 om-89 is an Emveco 200-A Tissue Caliper Tester (Emveco, Inc., Newberg, OR). The micrometer has a load of 2 kilo-Pascals, a pressure foot area of 2500 square millimeters, a pressure foot diameter of 56.42 millimeters, a dwell time of 3 seconds and a lowering rate of 0.8 millimeters per second.

Tensile

Tensile testing was done in accordance with TAPPI test method T-576 "Tensile properties of towel and tissue products (using constant rate of elongation)" wherein the testing is conducted on a tensile testing machine maintaining a constant rate of elongation and the width of each specimen tested is 3 inches. More specifically, samples for dry tensile strength testing were prepared by cutting a 3 ± 0.05 inch (76.2 ± 1.3 mm) wide strip in either the machine direction (MD) or cross-machine direction (CD) orientation using a JDC Precision Sample Cutter (Thwing-Albert Instrument Company, Philadelphia, PA, Model No. JDC 3-10, Serial No. 37333) or equivalent. The instrument used for measuring tensile strengths was an MTS Systems Sintech 11S, Serial No. 6233. The data acquisition software was an MTS TestWorks® for Windows Ver. 3.10 (MTS Systems Corp., Research Triangle Park,

NC). The load cell was selected from either a 50 Newton or 100 Newton maximum, depending on the strength of the sample being tested, such that the majority of peak load values fall between 10 to 90 percent of the load cell's full scale value. The gauge length between jaws was 4 ± 0.04 inches (101.6 ± 1 mm) for facial tissue and towels and 2 ± 0.02 inches (50.8 ± 0.5 mm) for bath tissue. The crosshead speed was 10 ± 0.4 inches/min (254 ± 1 mm/min), and the break sensitivity was set at 65 percent. The sample was placed in the jaws of the instrument, centered both vertically and horizontally. The test was then started and ended when the specimen broke. The peak load was recorded as either the "MD tensile strength" or the "CD tensile strength" of the specimen depending on direction of the sample being tested. Ten representative specimens were tested for each product or sheet and the arithmetic average of all individual specimen tests was recorded as the appropriate MD or CD tensile strength of the product or sheet in units of grams of force per 3 inches of sample. The geometric mean tensile (GMT) strength was calculated and is expressed as grams-force per 3 inches of sample width. Tensile energy absorbed (TEA) and slope are also calculated by the tensile tester. TEA is reported in units of gm•cm/cm^2. Slope is recorded in units of kg. Both TEA and Slope are directional dependent and thus MD and CD directions are measured independently. Geometric mean TEA and geometric mean slope are defined as the square root of the product of the representative MD and CD values for the given property.

Multi-ply products were tested as multi-ply products and results represent the tensile strength of the total product. For example, a 2-ply product was tested as a 2-ply product and recorded as such. A basesheet intended to be used for a two ply product was tested as two plies and the tensile recorded as such. Alternatively, a single ply may be tested and the result multiplied by the number of plies in the final product to get the tensile strength.

EXAMPLE

Single-ply uncreped through-air dried (UCTAD) tissue webs were made generally in accordance with US Patent No. 5,607,551. The tissue webs and resulting tissue products were formed from various fiber furnishes including, EHWK pulp, NSWK pulp, and high yield agave (HYA) pulp.

HYA was produced by processing *Agave Tequilana* leafs using a three stage non-wood pulping process commercially available from Taizen America (Macon, GA). The resulting HYA pulp had an average fiber length of about 1.1 mm and a fiber coarseness of about 12.74 mg/100 m.

The EHWK furnish was prepared by dispersing about 120 pounds (oven dry basis) EHWK pulp in a pulper for 30 minutes at a consistency of about three percent. The fiber was then transferred to a machine chest and diluted to a consistency of 1 percent. The NSWK furnish was prepared by dispersing about 50 pounds (oven dry basis) of NSWK pulp in a pulper for 30 minutes at a consistency of about

three percent. The fiber was then transferred to a machine chest and diluted to a consistency of 1 percent. The HYA was prepared by dispersing about 50 pounds (oven dry basis) HYA pulp in a pulper for 30 minutes at a consistency of about 3 percent. The fiber was then transferred to a machine chest and diluted to a consistency of 1 percent.

Stock solutions were diluted to 0.75 percent consistency and pumped to a 3-layer headbox to form a three layered web. The relative weight percentage and composition of the layers is summarized in Table 1 below. In those instances where starch was added, it was added on as a kilogram per ton of furnish basis as indicated in Table 1 and added to all layers.

TABLE 1

Sample	Furnish Layering (wt %)	Redibond 2038 A (kg/ton)	Middle Layer Furnish Refining (min)
Control 1	30 EHWK / 40 NSWK / 30 EHWK	0	0
Control 2	30 EHWK / 40 NSWK / 30 EHWK	3	0
Control 3	30 EHWK / 40 NSWK / 30 EHWK	6	0
Inventive 1	30 EHWK / 30 NSWK 10 HYA / 30 EHWK	0	2
Inventive 2	30 EHWK / 30 NSWK 10 HYA / 30 EHWK	2	2
Inventive 3	30 EHWK / 30 NSWK 10 HYA / 30 EHWK	4	2

The formed web was non-compressively dewatered and rush transferred to a transfer fabric traveling at a speed about 28 percent slower than the forming fabric. The web was then transferred to a T-1205-2 TAD fabric (commercially available from Voith Fabrics, Appleton, WI and previously disclosed in US Patent No. 8,500,955, the contents of which are incorporated herein in a manner consistent with the present disclosure). The web was then dried and wound into a parent roll. The effect of agave fibers on various tissue properties, including tensile, durability and softness, is summarized in the tables below.

TABLE 2

Sample	Basis Weight (gsm)	Sheet Bulk (cc/g)	GMT (g/3")	GM Slope (kg)	CD Tensile (g/3")	CD TEA (g•cm/cm^2)	CD Stretch (%)
Control 1	36.1	14.5	587	4.96	392	3.35	8.7
Control 2	35.8	13.4	856	6.51	607	5.40	9.7
Control 3	35.9	14.5	983	6.84	709	6.46	10.2
Inventive 1	36.9	13.7	735	6.34	514	4.14	9.0
Inventive 2	35.9	13.0	829	6.11	589	5.31	10.9
Inventive 3	37.3	13.9	1024	7.00	742	6.74	11.3

TABLE 3

Sample	Stiffness Index	Dry Burst (gf)	Burst Index	GM Tear (gf)	CD Tear (gf)	CD Durability Index
Control 1	8.46	521	8.89	8.30	9.9	19.72
Control 2	7.60	727	8.50	13.90	16.5	21.30
Control 3	6.96	832	8.46	15.25	18.5	21.93
Inventive 1	8.63	623	8.48	10.61	12.0	19.35
Inventive 2	7.38	687	8.28	10.59	12.5	22.03
Inventive 3	6.84	919	8.97	14.29	16.2	22.52

To further assess the quantity of volatile agave compounds present in the inventive products, additional tissue products comprising 20 and 40 percent, by weight of the tissue product, HYA pulp were produced as described above. The tissue products were analyzed by solid phase micro extraction (SPME) and high resolution gas chromatography coupled to mass spectrometry (GC-MS) to quantify odor compounds limonene and 6-methyl-heptene-2-one (MeH), as described in the Test Methods section above. FIG. 1 illustrates the SPME analysis of limonene and MeH for tissue products comprising 20 and 40 percent, by weight of the tissue product, agave fiber, compared to limonene and MeH standards. FIG. 2 illustrates the profile of volatile hydrocarbons obtained by the separations shown in FIG. 1. The amount of limonene and MeH in the various tissue product samples is summarized in the table below.

TABLE 4

Sample	HYA (wt %)	MeH (ppb)	Limonene (ppb)
Inventive 4	40	29.58	13.07
Inventive 5	20	22.89	9.92

While tissue webs, and tissue products comprising the same, have been described in detail with respect to the specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto and the foregoing embodiments:

In a first embodiment the present invention provides a fibrous structure comprising at least about 0.5 percent, by weight of the fibrous structure, agave fiber and a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof.

In a second embodiment the present invention provides the fibrous structure of the first embodiment comprising at least about 10 ppb limonene.

In a third embodiment the present invention provides the fibrous structure of the first or the second embodiments comprising from about 10 to about 200 ppb limonene and from about 10 to about 500 ppb 6-Methyl-5-hepten-2-one.

In a fourth embodiment the present invention provides the fibrous structure of any one of the first through the third embodiments having a geometric mean tensile (GMT) greater than about 400 g/3", such as from about 400 to about 2,500 g/3".

In a fifth embodiment the present invention provides the fibrous structure of any one of the first through the fourth embodiments having a basis weight greater than about 10 grams per square meter (gsm) and a sheet bulk greater than about 5 cc/g.

In a sixth embodiment the present invention provides the fibrous structure of any one of the first through the fifth embodiments comprising from about 1.0 to about 40 percent, by weight, agave fiber and from about 5.0 to about 30 percent, by weight of the product, wood pulp fibers having an average fiber length greater than about 2.0 mm.

In a seventh embodiment the present invention provides the fibrous structure of any one of the first through the sixth embodiments wherein the fibrous structure comprises high yield agave pulp fibers.

In an eighth embodiment the present invention provides the fibrous structure of any one of the first through the seventh embodiments comprising from about 1.0 to about 40 percent, by weight of the fibrous structure, agave fibers and substantially free from wood pulp fibers having an average fiber length greater than about 2.0 mm.

In a ninth embodiment the present invention provides the tissue product of any one of the first through the eighth embodiments wherein the agave fibers are high yield agave pulp fibers having a lignin content from about 10 to about 15 weight percent.

In a tenth embodiment the present invention provides the fibrous structure of any one of the first through the ninth embodiments wherein the fibrous structure comprises at least one multi-layered tissue web having a middle layer and two outer layers wherein the agave fiber is selectively disposed in the middle layer and the two outer layers are substantially free of agave fiber.

In an eleventh embodiment the present invention provides the fibrous structure of any one of the first through the tenth embodiments wherein the fibrous structure comprises a through-air dried fibrous structure. In particularly preferred embodiments the fibrous structure is an uncreped through-air dried fibrous structure and in other embodiments it is a creped through-air dried fibrous structure.

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In a twelfth embodiment the present invention provides the fibrous structure of any one of the first through the eleventh embodiments wherein the fibrous structure comprises a single-ply uncreped through-air dried fibrous structure.

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WHAT IS CLAIMED IS:

1. A fibrous structure comprising at least about 0.5 percent, by weight of the fibrous structure, agave fiber and a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof.

2. The fibrous structure of claim 1 wherein the fibrous structure comprises at least about 10 ppb limonene.

3. The fibrous structure of claim 1 wherein the fibrous structure comprises from about 10 to about 200 ppb limonene and from about 50 to about 500 ppb 6-Methyl-5-hepten-2-one.

4. The fibrous structure of claim 1 wherein the fibrous structure comprises from about 1.0 to about 40 percent, by weight of the fibrous structure, agave fiber and from 60 to about 99 percent, by weight of the fibrous structure, wood pulp fibers.

5. The fibrous structure of claim 4 wherein the agave fibers are high yield agave pulp fibers.

6. The fibrous structure of claim 1 wherein the fibrous structure comprises a throughdried fibrous structure.

7. The fibrous structure of claim 1 wherein the fibrous structure comprises an uncreped through-air dried fibrous structure.

8. The fibrous structure of claim 1 having a first and a second side and a formulation comprising a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof and a carrier disposed on the first or second side.

9. A tissue product comprising at least one tissue web, the tissue web comprising at least about 0.5 percent, by weight of the fibrous structure, agave fiber and a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof, the product having a basis weight from about 10 to about 60 gsm, a geometric mean tensile (GMT) greater than about 400 g/3" and a sheet bulk greater than about 5.0 cc/g.

10. The tissue product of claim 9 wherein the fibrous structure comprises at least about 10 ppb limonene.

11. The tissue product of claim 9 wherein the fibrous structure comprises from about 10 to about 200 ppb limonene and from about 50 to about 500 ppb 6-Methyl-5-hepten-2-one.

12. The tissue product of claim 9 wherein the fibrous structure comprises from about 1.0 to about 40 percent, by weight of the fibrous structure, agave fiber and from 60 to about 99 percent, by weight of the fibrous structure, wood pulp fibers.

13. The tissue product of claim 9 wherein the tissue web is a creped tissue web.

14. A method of manufacturing a tissue web having a lemon-like odor comprising the steps of:

a. Forming a fiber slurry comprising agave fiber and wood pulp fiber;

b. Forming a tissue web from the fiber slurry, the web having a first and a second side; and

c. Depositing on at least a first side of the web a formulation comprising a volatile agave compound selected from the group consisting of limonene, hexanaldehyde and 6-Methyl-5-hepten-2-one and combinations thereof and a carrier.

15. The method of claim 14 wherein the tissue web comprises at least about 10 ppb limonene.

16. The method of claim 14 wherein the tissue web comprises from about 10 to about 200 ppb limonene and from about 50 to about 500 ppb 6-Methyl-5-hepten-2-one.

17. The method of claim 14 wherein the volatile agave compounds comprise from about 0.0001 to 0.5 percent, by weight of the formulation.

18. The method of claim 14 wherein the carrier is selected from group consisting of water, emollients, fatty acids, fatty alcohols, humectants, thickeners and combinations thereof.

19. The method of claim 14 wherein the carrier is a water and oil emulsion and comprises from about 35 to about 60 percent, by weight of the formulation.

20. The method of claim 14 wherein the tissue web comprises from about 1.0 to about 30 percent, by weight of the tissue web, agave fiber.

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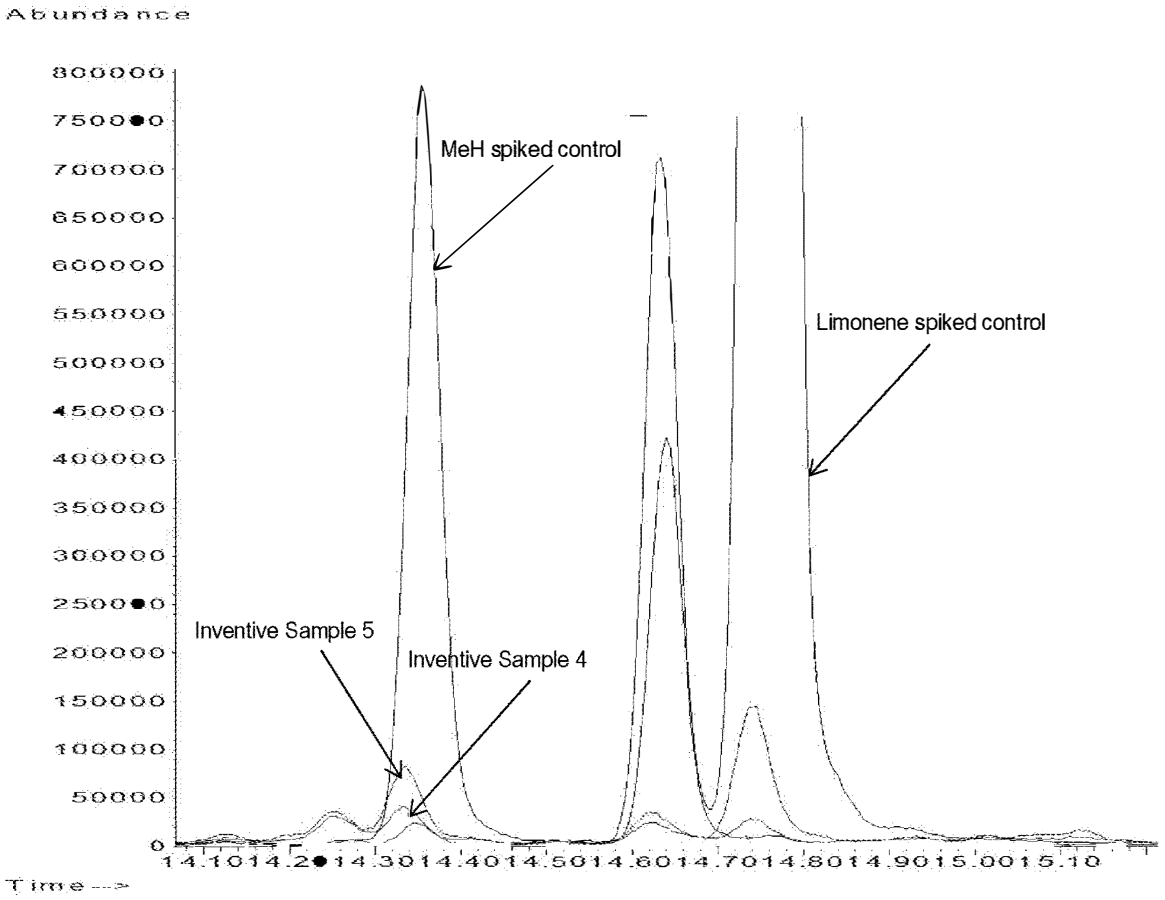

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FIG. 1

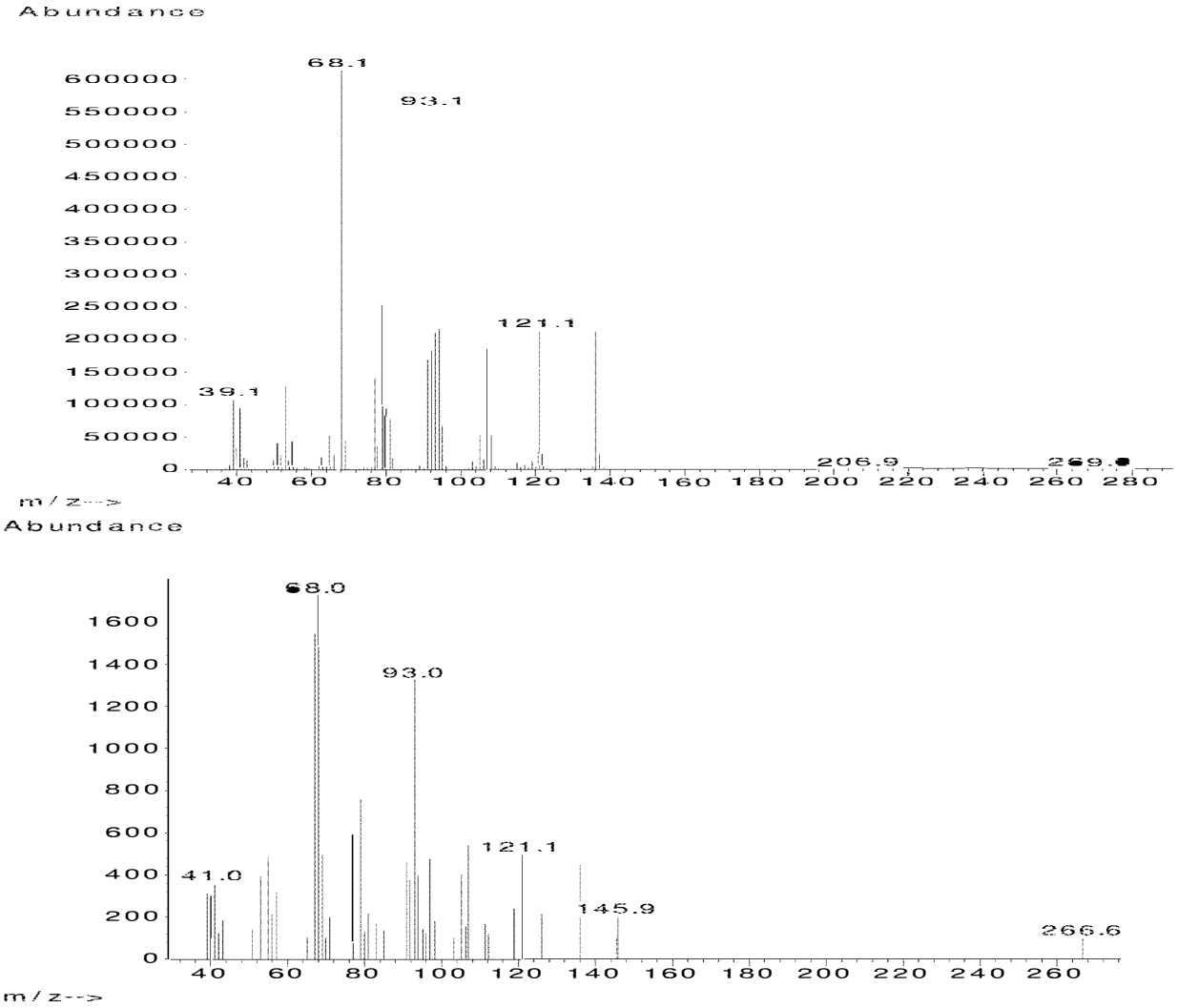

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FIG. 2

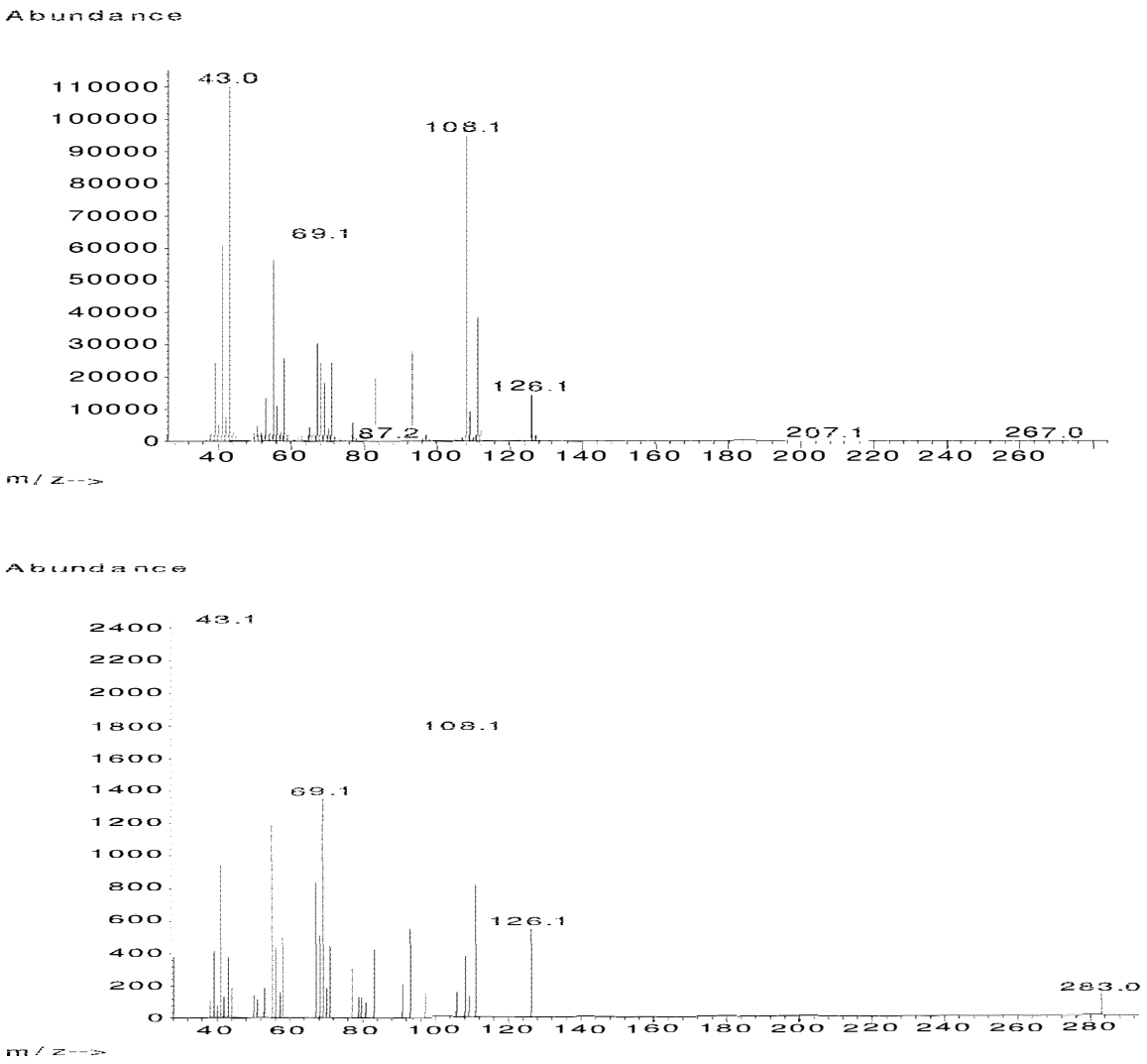

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FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/059097

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21, A47K

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

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

EPODOC/ WPI/ CA/ CABA: Agave, sisal, henequen, agave tequilana, blue agave, agave azul, tissue, paper, limonene, hexanal, hexanaldehyde, 6-methyl-5-hepten-2-one, scent, fragrance and like terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2168894 A1 (FISHER, T. E.) 7 August 1997 See figures, pg 5 - pg 8	1-20
X	JP H07-197400 A (KURESHIA KK) 1 August 1995 See abstract, [0009], [0031]-[0038] and Table 1 of the original non-English language document (a machine translation is enclosed **only** for your reference)	1-4, 6-20
X	IÑIGUEZ-COVARRUBIAS, G. ET AL., Utilization of by-products from the tequila industry. Part 2: potential value of *Agave tequilana* Weber *azul* leaves. *Bioresource Technology*, 4 January 2001, Vol. 77, No. 2, pages 101-108 [Retrieved on 2016-12-09] <DOI: 10.1016/S0960-8524(00)00167-X> See abstract, Table 6, pg 104 right column second paragraph - pg 105 left column fourth paragraph and pg 107 left column second paragraph - right column first paragraph	1-4, 6-20

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

*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09/01/2017 *(day/month/year)*	20/01/2017 *(day/month/year)*

Name and mailing address of the ISA/SG

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Form PCT/ISA/210 (second sheet) (January 2015)

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ESCOTO-GARCÍA, T. ET AL., Fermentative-Chemical and Mechanical Treatment of Agave Bagasse (Agave Tequilana Weber) for its Application in Hand Crafted Paper. *Revista Mexicana de Ingenieria Quimica*, 30 November 2006, Vol. 5, No. Supl. 1, pages 23-27 [Retrieved on 2016-12-09] <DOI: NOT AVAILABLE> See title, abstract and Fig. 2	1-20
X	JAOUADI, M. ET AL., A Study of the Physical and Mechanical Properties of Paper Made from *Agave americana* L. Fibers. *Materials and Manufacturing Processes*, 22 April 2011, Vol. 26, No. 4, pages 567-572 [Retrieved on 2016-12-09] <DOI: 10.1080/10426910903124878> See abstract, pg 568 left column second paragraph - right column fourth paragraph, pg 572 left column first and second paragraphs, Table 7	1-4, 6-20
X	IDARRAGA, G. ET AL., Pulp and Paper from Blue Agave Waste from Tequila Production. *Journal of Agricultural and Food Chemistry*, 4 September 1999, Vol. 47, No. 10, pages 4450-4455 [Retrieved on 2016-12-09] <DOI: 10.1021/JF990045N> See abstract, pg 4451 left column second paragraph - right column first paragraph, Tables 1-3	1-3
A	GHOSH, A. K., Fundamentals of Paper Drying – Theory and Application from Industrial Perspective. *Evaporation, Condensation and Heat transfer*, 12 September 2011, pages 535-582 [Retrieved on 2016-12-21] <DOI: 10.5772/1042> See pg 574-575	6-7
A	CN 104116454 A (SHENZHEN HUANSHENG HOUSEWARE CO LTD) 29 October 2014 See [0006], [0008], [0032], [0035]-[0051] of the original non-English language document (a machine translation is enclosed **only** for your reference)	8, 14-20
A	US 2007/0298995 A1 (EGGERS, M. ET AL.) 27 December 2007 See [0078], [0084], [0101], [0135]	8, 14-20

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA 2168894 A1	07/08/1997	-	
JP H07-197400 A	01/08/1995	-	
CN 104116454 A	29/10/2014	-	
US 2007/0298995 A1	27/12/2007	EP 1872831 A1	02/01/2008
		EP 1875942 A1	09/01/2008
		JP 2008-001700 A	10/01/2008

Supplemental Box
(Classification of Subject Matter)

Int. Cl.
D21H 11/12 (2006.01)
D21H 17/06 (2006.01)
D21F 11/00 (2006.01)
A47K 10/16 (2006.01)
D21H 27/00 (2006.01)
D21H 23/22 (2006.01)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
16255M3-WO-JC		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US2023/017658	6 April 2023 (06-04-2023)	8 April 2022 (08-04-2022)

Applicant

THE PROCTER & GAMBLE COMPANY

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language,** the international search was carried out on the basis of:

[X] the international application in the language in which it was filed

[ ] a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. [ ] This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

c. [ ] With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. [ ] **Certain claims were found unsearchable** (See Box No. II)

3. [ ] **Unity of invention is lacking** (see Box No III)

4. With regard to the **title,**

[X] the text is approved as submitted by the applicant

[ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

[X] the text is approved as submitted by the applicant

[ ] the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings,**

a. the figure of the **drawings** to be published with the abstract is Figure No. 1A

[X] as suggested by the applicant

[ ] as selected by this Authority, because the applicant failed to suggest a figure

[ ] as selected by this Authority, because this figure better characterizes the invention

b. [ ] none of the figures is to be published with the abstract

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/017658

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H11/12 D21H27/00
ADD.

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)
D21H

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/019421 A1 (PROCTER & GAMBLE [US]) 2 February 2017 (2017-02-02) claims 1,2,5 page 17, line 23 - line 24	1-15
X	WO 2014/053947 A1 (KIMBERLY CLARK CO [US]) 10 April 2014 (2014-04-10) claim 1 page 10, line 8 - line 9	1-5

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 2023	20/06/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Ponsaud, Philippe

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2023/017658

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017019421 A1	02-02-2017	CA 2993536 A1	02-02-2017
		EP 3325715 A1	30-05-2018
		US 2017022670 A1	26-01-2017
		WO 2017019421 A1	02-02-2017
WO 2014053947 A1	10-04-2014	AU 2013326171 A1	30-04-2015
		BR 112015007311 A2	04-07-2017
		CA 2885906 A1	10-04-2014
		EP 2904148 A1	12-08-2015
		KR 20150066543 A	16-06-2015
		MX 338654 B	25-04-2016
		US 2014096924 A1	10-04-2014
		US 2016097163 A1	07-04-2016
		WO 2014053947 A1	10-04-2014
		ZA 201502851 B	30-11-2016

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Information on Search Strategy - Pilot phase (see OJ 2015, A86)
The type of information contained in this sheet may change during the pilot for improving the usefulness of this new service.

Application Number
PCT/US2023/017658

TITLE: THE TITLE IS AS PROVIDED ON PAGE 1 OF THE DESCRIPTION

APPLICANT: THE PROCTER & GAMBLE COMPANY

IPC CLASSIFICATION: D21H11/12, D21H27/00

EXAMINER: Ponsaud, Philippe

CONSULTED DATABASES: WPI

CLASSIFICATION SYMBOLS DEFINING EXTENT OF THE SEARCH:

IPC:

CPC:

FI/F-TERMS:

KEYWORDS OR OTHER ELEMENTS FEATURING THE INVENTION:

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2023/017658	06.04.2023	08.04.2022

International Patent Classification (IPC) or both national classification and IPC
INV. D21H11/12 D21H27/00

Applicant
THE PROCTER & GAMBLE COMPANY

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	see form PCT/ISA/210	Ponsaud, Philippe Telephone No. -0

Form PCT/ISA/237 (Cover Sheet) (July 2022)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2023/017658

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a))

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the international application as filed.

   b. ☐ furnished subsequent to the international filing date for the purposes of international search (Rule 13*ter*.1(a)),

   ☐ accompanied by a statement to the effect that the sequence listing does not go beyond the disclosure in the international application as filed.

4. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, this opinion has been established to the extent that a meaningful opinion could be formed without a WIPO Standard ST.26 compliant sequence listing.

5. Additional comments:

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2-15
	No:	Claims	1
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-15
Industrial applicability (IA)	Yes:	Claims	1-15
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Point VIII

1 Claim 1 since the amount of abaca or bamboo fibers is not defined in the claim nor is the nature and amount of the further ingredients that have to be present in order to achieve the technical effect underlying the invention. It is indeed not credible that said technical effect may be achieved for each and any sanitary tissue only defined, as structural features, as comprising non-wood fibers selected from the group consisting of bamboo, abaca and mixtures thereof, i.e. encompassing an infinity of embodiments.

2 Furthermore in claim 1 the TS7 value is merely a result-to-be-achieved which detracts from the claim of the claim since the structural features which allow to achieve this parameter are not defined in the claim.

Point V

3 Reference is made to the following documents:

D1 WO 2017/019421 A1 (PROCTER & GAMBLE [US]) 2 February 2017 (2017-02-02)

D2 WO 2014/053947 A1 (KIMBERLY CLARK CO [US]) 10 April 2014 (2014-04-10)

4 Independent claim 1

Document D1 (see claims 1+2+5 and page 17, lines 23-24) discloses a sanitary tissue paper product comprising non-wood fibers being abaca and the TS7 value of the tissue is less than 7,5.

Thus the subject-matter of present claim 1 is not novel over D1 (Art. 33(2) PCT).

Document D2 (see claim 1) discloses a sanitary tissue paper having a TS value of less than 8. The tissue paper may comprise non-wood fibers (see page 10, lines 8-9). The sole different of present claim 1 over D2 is that the non-wood fibers are selected from abaca and bamboo or mixtures thereof.

There is however no surprising and unexpected technical effect shown in the description for this particular selection. Furthermore there is no mention in claim 1 of the amount of such non-wood fiber in the tissue paper, so that it is not even credible that any technical effect could be obtained, when using these fibers, over the whole scope of the claim.

Thus claim 1 represents an alternative over D2, which is obvious since abaca and bamboo are well known non-wood fibers.

Thus the subject-matter of present claim 1 lacks an inventive step over D2 combined with the common general knowledge (Art. 33(3) PCT).

5 Dependent claims

The remaining dependent claims do not appear to be inventive over D1 or D2 combined with the common general knowledge since they contain only usual features, which are arrived at by the person skilled in the art through routine optimization work. Moreover, in view of the description, no surprising and unexpected technical effect results from these claims when taken in isolation.

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Possible steps after receipt of the international search report (ISR) and written opinion of the International Searching Authority (WO/ISA)

General information

For all international applications, the competent International Searching Authority **(ISA)** will establish an international search report **(ISR)** accompanied by a written opinion of the International Searching Authority **(WO/ISA)**. The **WO/ISA** may be responded to by

- filing informal comments with the **International Bureau of WIPO (IB)** (where no demand for international preliminary examination **(demand)** is filed)
- filing amendments under Art. 19 PCT (this can be done whether or not a **demand** is filed)
- filing amendments under Art. 34 PCT and/or formal observations in response to objections raised in the **WO/ISA** (where a **demand** *is* actually filed)

This document explains these possibilities.

Filing informal comments

After receipt of the **ISR and WO/ISA**, the applicant may file informal comments on the **WO/ISA, directly with the IB** (see International Search and Preliminary Examination Guidelines 2.15). These will be communicated to the designated/elected Offices, together with the International Preliminary Report on Patentability **(IPRP)** at 30 months from the priority date.

Amending claims under Art. 19 PCT

The applicant may file **amended claims** under Art. 19 PCT, **directly with the IB** by the later of the following dates:

- 2 months from the date of mailing of the **ISR** and the **WO/ISA**
- 16 months from the priority date

However, any such amendment received by the **IB** after the expiration of the applicable time limit shall be **considered to have been received on time** by the **IB**, if it reaches it **before** the technical preparations for international publication have been completed (the 15th day prior to the date of publication, see PCT Applicant's Guide, International Phase, 9.013).

For further information, please see Rule 46 PCT as well as form PCT/ISA/220.

Please also note that, when filing amended claims under Art. 19 PCT, such amendments shall be **accompanied by a letter** identifying the amendments made and also the basis for the amendments in the application as originally filed (Rule 46.5(b) PCT). Where a **demand** is filed, failure to comply with this requirement may result in the amendments being ignored in the International Preliminary Examination Report **(IPER)**, see Rule 70.2(c-*bis*) PCT.

Filing a demand for international preliminary examination

In principle, the **WO/ISA** will be considered to be the written opinion of the International Preliminary Examining Authority (**IPEA**). Where the **WO/ISA** issued by the **EPO** as **ISA** gives a positive opinion on the international application and the invention to which it relates, filing a **demand** with the **EPO** as **IPEA** would normally be unnecessary, since a positive IPRP would anyway be established by the IB based on the WO/ISA (see also further below).

If the applicant wishes to file a **demand** (for example, to allow him to argue his case in international preliminary examination with regard to objections raised in a negative **WO/ISA** before the **IPEA** issues an **IPER**), this must be done before expiration of **3 months after the date of mailing of the ISR and WO/ISA** or **22 months after priority date,** whichever expires later (Rule 54*bis* PCT). Amendments under Art. 34 PCT can be filed with the IPEA, normally at the same time as filing the demand (Rule 66.1(b) PCT) or within the time limit set for reply to any written opinion issued during international preliminary examination by the **IPEA**.

If a **demand** is filed at the **EPO** as **IPEA** and no comments/amendments have been received by the time the **EPO** starts drawing up the **IPER** (Rule 66.4*bis* PCT), the **WO/ISA** will be transformed by the **IPEA** into an **IPER** (also called the **IPRP (Chapter II)** which would merely reflect the content of the **WO/ISA** (OJ 10/2011, 532). The **demand** can still be withdrawn (Art. 37 PCT).

Please also note that, when filing amendments under Art. 34 PCT, such amendments shall be accompanied by a letter which identifies the amendments made and also the basis for the amendments in the application as originally filed (Rule 66.8(a) PCT). Failure to comply with this requirement may result in the amendments being ignored in the **IPER (IPRP (Chapter II))**, see Rule 70.2(c-*bis*) PCT.

Filing a request for supplementary international search

The applicant may, with the **IB**, file a request for **supplementary international search** under Rule 45*bis*.1 PCT. The present **ISR** and **WO/ISA** may also be taken into account in the execution of that supplementary international search, provided that these are available to the Authority charged with this task before it starts the supplementary search (Rule 45*bis*.5 PCT).

This kind of request **cannot be filed specifying the ISA** who did the **international search**.

More information on this topic can be found in the **PCT Applicant's Guide**, Chapter 8 (http://www.wipo.int/pct/en/guide/ip08.html).

End of the international phase

Where no **demand** is filed, at the end of the international phase, the **IB** will transform the **WO/ISA** into the IPRP (PCT Chapter I) (Rule 44*bis* PCT), which will then be transmitted together with possible informal comments to the designated Offices. Where a demand is filed, the **WO/ISA** is not transformed into an **IPRP** (**Chapter I**) by the **IB**, but rather the **IPEA** will establish an **IPER**, (the IPER is the same as the IPRP (PCT Chapter II), see Rule 70.15 PCT).

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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 December 2014 (18.12.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/200455 A1

(51) International Patent Classification:
D21H 27/30 (2006.01) *D21H 11/04* (2006.01)
D21H 11/00 (2006.01)

(21) International Application Number:
PCT/US2013/044891

(22) International Filing Date:
10 June 2013 (10.06.2013)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **KIMBERLY-CLARK WORLDWIDE, INC.** [US/US]; 2300 Winchester Road, Neenah, WI 54956 (US).

(72) Inventors: **SHANNON, Thomas, Gerard**; 1604 Meadowbreeze Circle, Neenah, WI 54956 (US). **TIMM, Jeffrey, James**; N8709 County Highway M, Menasha, WI 54952 (US).

(74) Agent: **SULLIVAN, Michael, J.**; Kimberly-Clark Worldwide, Inc., 2300 Winchester Road, Neenah, WI 54956 (US).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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, 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, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

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

WO 2014/200455 A1

(54) **Title**: LAYERED TISSUE STRUCTURES COMPRISING MACROALGAE

(57) **Abstract**: The disclosure provides multi-layered tissue webs, and products incorporating the same, where the webs comprise macroalgae fibers selectively incorporated into one or more layers of the web. More specifically the disclosure provides soft and durable tissue webs comprising from about 0.5 to about 5 percent macroalage fibers, by weight of the web, where the macroalage fibers are selectively incorporated into the air contacting layer of the web. Selectively incorporating macroalgae in this manner increases the strength and durability of the web without negatively affecting stiffness.

LAYERED TISSUE STRUCTURES COMPRISING MACROALGAE

BACKGROUND

Tissue products, such as facial tissues, paper towels, bath tissues, napkins, and other similar products, are designed to include several important properties. For example, the products should have good bulk, a soft feel, and should have good strength and durability. Unfortunately, however, when steps are taken to increase one property of the product, other characteristics of the product are often adversely affected.

To achieve the optimum product properties, tissue products are typically formed, at least in part, from pulps containing wood fibers and often a blend of hardwood and softwood fibers to achieve the desired properties. Typically when attempting to optimize surface softness, as is often the case with tissue products, the papermaker will select the fiber furnish based in part on fiber length, aspect ratio and thickness of the fiber cell wall. Unfortunately, the need for softness is balanced by the need for durability. Durability in tissue products may be defined in terms of tensile strength, burst strength and tear strength. Typically tear strength and burst strength have a positive correlation with tensile strength while tensile strength, and thus durability, and softness are inversely related. Thus the paper maker is continuously challenged with the need to balance the need for softness with a need for durability. Unfortunately, tissue paper durability generally decreases as the average fiber length is reduced. Therefore, simply reducing the pulp average fiber length can result in an undesirable trade-off between product softness and product durability.

Besides durability, long fibers also play an important role in overall tissue product softness. While surface softness in tissue products is an important attribute, a second element in the overall softness of a tissue sheet is stiffness. Stiffness can be measured from the tensile slope of stress – strain tensile curve. Generally, a decrease in tensile slope results in lower stiffness, which typically provides better overall softness. However, at a given tensile strength and slope short fibers will display a greater stiffness than long fibers. While not wishing to be bound by theory, it is believed that this behavior is due to the higher number of hydrogen bonds required to produce a product of a given tensile strength with short fibers than with long fibers. Thus, easily collapsible, low coarseness long fibers, such as those provided by Northern softwood kraft ("NSWK") fibers typically supply the

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best combination of durability and softness in tissue products when those fibers are used in combination with hardwood kraft fibers, such as Eucalyptus hardwood kraft ("EHWK") fibers. While NSWK fibers have a higher coarseness than EHWK fibers, their small cell wall thickness relative to lumen diameter combined with their long length makes them the ideal candidate for optimizing durability and softness in tissue.

Unfortunately, supply of NSWK is under significant pressure both economically and environmentally. As such, prices of NSWK have escalated significantly creating a need to find alternatives to optimize softness and strength in tissue products. Another type of softwood fiber is Southern softwood kraft ("SSWK"), which is widely used in fluff pulp containing absorbent products such as diapers, feminine care absorbent products and incontinence products. Unfortunately while not under the same supply and environmental pressures as NSWK, SSWK fibers are generally poorly suited for making soft tissue products. While having long fiber length, the SSWK fibers have too wide a cell wall width and too narrow a lumen diameter and thus create stiffer, harsher feeling products than NSWK.

The tissue papermaker who is able to obtain pulps having a desirable combination of fiber length and coarseness from fiber blends generally regarded as inferior with respect to average fiber properties may reap significant cost savings and/or product improvements. For example, the papermaker may wish to make a tissue paper of superior strength without incurring the usual degradation in softness which accompanies higher strength. Alternatively, the papermaker may wish a higher degree of paper surface bonding to reduce the release of free fibers without suffering the usual decrease in softness which accompanies greater bonding of surface fibers. As such, a need currently exists for a tissue product formed from a fiber that will improve durability without negatively affecting other important product properties, such as softness.

Outside of softwood kraft pulp fibers very few options exist for papermakers when seeking a satisfactory fiber to provide strength without negatively impacting softness. Thus, there remains a need for alternative papermaking fibers that may deliver softness while maintaining satisfactory strength.

SUMMARY

It has now been discovered that macroalgae fibers, despite having a relatively short average fiber length and high aspect ratios, may be incorporated into a tissue web, and particularly the air contacting, also referred to herein as the non-fabric contacting side, of a multilayered web. Selectively incorporating macroalgae fibers in this manner yields webs having improved strength without a significant increase in stiffness. Surprisingly, these properties are particularly acute when macroalgae fibers are substituted for wood fibers in relatively modest amounts, such as less than about 5 percent, and more preferably less than about 3 percent, such as from about 0.5 to about 3 percent by weight of the web, and when the fabric contacting layer of the web is substantially free from macroalgae fibers.

Accordingly, in certain embodiments, the present disclosure provides a multi-layered tissue web comprising a fabric contacting fibrous layer and a non-fabric contacting fibrous layer, wherein the fabric contacting fibrous layer consists essentially of conventional papermaking fibers and the non-fabric contacting fibrous layer comprises a blend of macroalgae fibers and conventional papermaking fibers. Preferably the fabric contacting layer is substantially free of macroalgae fibers and the tissue web comprises from about 0.5 to about 5 percent by weight macroalgae fibers. In a particularly preferred embodiment the fabric contacting fibrous layer comprises hardwood kraft fibers and the non-fabric contacting fibrous layer comprises macroalgae and softwood kraft fibers.

In yet other embodiments the present disclosure provides a multi-layered tissue web comprising a fabric contacting fibrous layer and a non-fabric contacting fibrous layer, wherein the fabric contacting fibrous layer is substantially free of macroalgae fibers and the non-fabric contacting fibrous layer comprises from about 0.5 to about 5 percent by weight of the web macroalgae fibers, the tissue web having a basis weight greater than about 35 gsm, a geometric mean tensile of at least about 800 g/3" and geometric mean slope of less than about 6 kgf.

In still other embodiments the present disclosure provides a method of forming a macroalgae tissue web comprising the steps of dispersing a dry lap pulp comprising from about 1 to about 30 percent by weight macroalgae to form a first fiber slurry, dispersing a conventional papermaking pulp to form a second fiber slurry, depositing the second fiber slurry onto a forming fabric, depositing the first fiber slurry adjacent to the second fiber slurry to form a wet web, dewatering the wet web to a consistency from about 20 to about

30 percent, and drying the wet web to a consistency of greater than about 90 percent thereby forming a macroalgae tissue web.

DEFINITIONS

As used herein the term "macroalgae fibers" refers to any cellulosic fibrous material derived from red algae such as, for example, *Gelidium elegance*, *Gelidium corneum*, *Gelidium amansii*, *Gelidium robustum*, *Gelidium chilense*, *Gracelaria verrucosa*, *Eucheuma Cottonii*, *Eucheuma Spinosum*, or *Beludul*, or brown algae such as, for example, *Pterocladia capillacea*, *Pterocladia lucia*, *Laminaria japonica*, *Lessonia nigrescens*. Macroalgae fibers generally have an aspect ratio (measured as the average fiber length divided by the average fiber width) of at least about 80.

As used herein the term "red algae fiber" refers to any cellulosic fibrous material derived from Rhodophyta. Particularly preferred red algae fiber includes cellulosic fibrous material derived from *Gelidium amansii*, *Gelidium corneum, Gelidium asperum*, *Gelidium chilense* and *Gelidium robustum*. Red algae fibers generally have an aspect ratio (measured as the average fiber length divided by the average fiber width) of at least about 80.

As used herein the term "geometric mean tensile" (GMT) refers to the square root of the product of the MD tensile strength and CD tensile strength of the web, which are measured as described in the Test Methods section.

As used herein, the term "slope" refers to slope of the line resulting from plotting tensile versus stretch and is an output of the MTS TestWorks™ in the course of determining the tensile strength as described in the Test Methods section. Slope is reported in the units of grams (g) per unit of sample width (inches) and is measured as the gradient of the least-squares line fitted to the load-corrected strain points falling between a specimen-generated force of 70 to 157 grams (0.687 to 1.540 N) divided by the specimen width. Slopes are generally reported herein as having units of grams per 3 inch sample width or g/3".

As used herein, the term "geometric mean slope" (GM Slope) generally refers to the square root of the product of machine direction slope and cross-machine direction slope.

As used herein the term "Machine Direction Durability" generally refers to the ability of the web to resist crack propagation initiated by defects in the web and is calculated from MD Tensile Index (calculated by dividing the MD Tensile Strength by the

basis weight) and MD stretch (output of the MTS TestWorks™ in the course of determining the tensile strength as described in the Test Methods section) according to the formula:

$$Machine\ Direction\ Durability = 0.6\ (MD\ Tensile\ Index^{0.74} + MD\ Stretch^{0.58})$$

As used herein, the term "stiffness index" refers to the quotient of the geometric mean slope (having units of kgf) divided by the geometric mean tensile strength (having units of g/3") multiplied by 1,000.

As used herein the term "average fiber length" refers to the length weighted average length of fibers determined utilizing a Kajaani fiber analyzer model No. FS-100 available from Kajaani Oy Electronics, Kajaani, Finland. According to the test procedure, a pulp sample is treated with a macerating liquid to ensure that no fiber bundles or shives are present. Each pulp sample is disintegrated into hot water and diluted to an approximately 0.001 percent solution. Individual test samples are drawn in approximately 50 to 100 ml portions from the dilute solution when tested using the standard Kajaani fiber analysis test procedure. The weighted average fiber length may be expressed by the following equation:

$$\sum_{x_i=0}^{k} (x_i \times n_i)/n$$

where k = maximum fiber length

x_i = fiber length

n_i = number of fibers having length x_i

n = total number of fibers measured.

As used herein, the term "caliper" is the representative thickness of a single sheet (caliper of tissue products comprising two or more plies is the thickness of a single sheet of tissue product comprising all plies) measured in accordance with TAPPI test method T402 using an EMVECO 200-A Microgage automated micrometer (EMVECO, Inc., Newberg, OR). The micrometer has an anvil diameter of 2.22 inches (56.4 mm) and an anvil pressure of 132 grams per square inch (per 6.45 square centimeters) (2.0 kPa).

As used herein, the term "basis weight" generally refers to the bone dry weight per unit area of a tissue and is generally expressed as grams per square meter (gsm). Basis weight is measured using TAPPI test method T-220.

As used herein, the term "sheet bulk" generally refers to the quotient of the sheet caliper expressed in microns, divided by the dry basis weight, expressed in grams per square meter. The resulting sheet bulk is expressed in cubic centimeters per gram.

As used herein, the term "tissue product" generally refers to various paper products, such as facial tissue, bath tissue, paper towels, napkins, and the like. Normally, the basis weight of a tissue product of the present invention is less than about 80 grams per square meter (gsm), in some embodiments less than about 60 gsm, and in some embodiments, between about 10 to about 60 gsm.

As used herein, the term "layer" refers to a plurality of strata of fibers, chemical treatments, or the like, within a ply.

As used herein, the terms "layered tissue web," "multi-layered tissue web," "multi-layered web," and "multi-layered paper sheet," generally refer to sheets of paper prepared from two or more layers of aqueous papermaking furnish which are preferably comprised of different fiber types. The layers are preferably formed from the deposition of separate streams of dilute fiber slurries, upon one or more endless foraminous screens. If the individual layers are initially formed on separate foraminous screens, the layers are subsequently combined (while wet) to form a layered composite web.

The term "ply" refers to a discrete product element. Individual plies may be arranged in juxtaposition to each other. The term may refer to a plurality of web-like components such as in a multi-ply facial tissue, bath tissue, paper towel, wipe, or napkin.

DETAILED DESCRIPTION

In general, the present disclosure relates to tissue webs, and products produced therefrom, comprising conventional papermaking fibers and macroalgae fibers. It has been discovered that by replacing some of the conventional papermaking fibers in the tissue web with macroalgae fibers, and more specifically conventional fibers disposed in the non-fabric contacting layer of a multi-layer tissue structure, that a stronger and more durable web may be produced without sacrificing softness.

The discovery that macroalgae fibers may be used to form soft, strong tissue webs and more specifically that macroalgae fibers displacing conventional fibers in the non-fabric contacting layer, is particularly surprising provided the relative short length of

macroalgae fibers and their high aspect ratio. Table 1 compares the fiber properties of three different fibers – hardwood, softwood and macroalgae.

TABLE 1

Fiber Type	Average Fiber Length (mm)	Average Fiber Width (μm)	Fiber Length: Fiber Width
G. amansii	0.7	5	140
NSWK Pulp Fiber	2.18	27.6	79
EHWK Pulp Fiber	0.76	19.1	40

For macroalgae pulp fibers, the ratio of length to width (commonly referred to as the "aspect ratio") generally varies between about 120 and about 250, although both length and width vary amongst species. Generally, average fiber lengths for macroalgae fibers range from about 0.3 to about 1.0 mm, while fiber width varies from about 3 to about 7 μm. As shown in Table 1, macroalgae fibers are generally shorter than both EHWK and NSWK fibers, but have significantly greater aspect ratios.

Despite the tendency of macroalgae fibers to have high aspect ratios and short average fiber lengths it has now been surprisingly discovered that they may be a satisfactory replacement for conventional papermaking fibers in tissue webs. In particular, it has been discovered that selectively incorporating macroalgae fibers into the non-fabric contacting layer of a multi-layered tissue structure actually increases tensile strength without negatively effecting stiffness. In fact, in certain instances, the increase in tensile may be accompanied by only a slight increase in geometric mean modulus, resulting in a web having a lower stiffness index. Previously, it was believed that the greatest benefit was achieved when macroalgae fibers were used to replace a portion of the long fiber fraction and more particularly the long fibers disposed in the middle layer of a three layered web. However, it has now been discovered that the beneficial effect on tensile and stiffness is particularly acute when the macroalgae is substituted for convention papermaking fibers in the non-fabric contacting layer of a multi-layered web as illustrated in the tables below.

TABLE 2

	Macroalgae (wt%)	Basis Wt. (gsm)	GMT (g/3″)	MD Tensile Index	GM Slope (kgf)	stiffness index	MD Durability Index
Control	0	33.9	605	23.6	5.52	9.12	9.03
Air Layer	4.5	34.1	873	35.9	6.93	7.94	11.40
Fabric Layer	4.5	34.5	711	31.3	6.97	9.80	10.57

TABLE 3

	Delta GMT	Delta stiffness index	Delta MD Durability Index
Air Layer	44%	-13%	26%
Fabric Layer	18%	7%	17%

The macroalgae fibers are preferably derived from algae from the Division Rhodophyta. More preferably the macroalgae fibers have been subjected to processing to remove hydrocolloids, and more preferably agar, from the cell wall. For example, macroalgae fibers may be processed by extracting heteropolysaccharides as a cell wall component with hot water, followed by freezing, melting and drying. More preferably the macroalgae fibers are prepared using pulping methods known in the art such as those disclosed in US Patent No. 7,622,019, the contents of which are incorporated herein in a manner consistent with the present disclosure. Regardless of the specific method of extraction, in certain embodiments it may be desirable that the macroalgae fibers have been processed such that the resulting fibers have an agar content of less than about 5 percent by weight of the fibers, more preferably less than about 3 percent by weight of the fibers and still more preferably less than about 2 percent by weight of the fibers.

In certain embodiments the pulped macroalgae fibers may be subjected to bleaching. For example, pulped macroalgae fibers may be subjected to a two stage bleaching treatment using a chlorine dioxide in the first stage and hydrogen peroxide in the second stage. In the first stage 5 percent active chlorine dioxide by dry weight of the material may be used to bleach the fiber at pH 3.5 and 80°C for about 60 minutes. In the second stage, 5 percent active hydrogen peroxide by dry weight of the material may be used to bleach the fiber at pH 12 and 80°C for about 60 minutes.

The macroalgae fibers preferably have an average fiber length greater than about 300 μm, such as from about 300 to about 1000 μm and more preferably from about 300 to about 700 μm. The macroalgae fibers preferably have a width greater than about 3 μm, such as from about 3 to about 10 μm, and more preferably from about 5 to about 7 μm. Accordingly, it is preferred that the macroalgae fibers have an aspect ratio greater than about 80, such as from about 100 to about 400 and more preferably from about 150 to about 350.

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The macroalgae pulp fibers may be used as either dry or wet lap pulps. In those embodiments where the macroalgae is used as a dry lap (a pulp having a moisture content less than about 50 percent, more preferably from about 1 to about 15 percent) it is preferred that it is coprocessed with conventional papermaking fibers and more preferably that the pulped macroalgae fibers are not dried prior to processing with conventional papermaking fibers.

In particularly preferred embodiments macroalgae fibers are provided as dry lap pulps, a fibrous web having a basis weight of at least about 150 grams per square meter (gsm) and a moisture content of less than about 30 percent and more preferably less than about 20 percent, such as from about 1 to about 10 percent moisture. The macroalgae pulps are preferably provided as a blend of macroalgae pulp fiber and conventional papermaking fibers, such that the pulp comprises less than about 30 percent macroalgae fibers by weight. The dry lap pulps may be manufactured by blending never-dried macroalgae fibers with conventional papermaking fibers, forming a wet fiber web from the blended fibers and then drying the fiber web to form dry pulp sheets. The resulting pulp sheets surprisingly have improved strength and durability compared to both pulp sheets formed from dried macroalgae fibers and pulp sheets formed from conventional papermaking fibers alone. Further, pulps prepared as described herein are readily dispersible using traditional processing equipment, such as hydropulpers.

Regardless of the species or particular average fiber length, tissue webs of the present disclosure comprise at least about 0.5 percent macroalgae by total weight of the web and more preferably at least about 1 percent and still more preferably from about 2 to about 5 percent. The tissue webs comprising macroalgae may be either blended or layered webs. Where the webs are multi-layered, they may be layered such that one layer is substantially free from macroalgae fibers, while another layer comprises conventional papermaking and macroalgae fibers. It should be understood that, when referring to a layer that is substantially free of macroalgae fibers, negligible amounts of the fibers may be present therein, however, such small amounts often arise from the macroalgae fibers applied to an adjacent layer, and do not typically substantially affect the softness or other physical characteristics of the web.

Conventional papermaking fibers may comprise wood pulp fibers formed by a variety of pulping processes, such as kraft pulp, sulfite pulp, thermomechanical pulp, and

the like. Further, the wood fibers may be any high-average fiber length wood pulp, low-average fiber length wood pulp, or mixtures of the same. One example of suitable high-average length wood pulp fibers include softwood fibers such as, but not limited to, northern softwood, southern softwood, redwood, red cedar, hemlock, pine (e.g., southern pines), spruce (e.g., black spruce), combinations thereof, and the like. One example of suitable low-average length wood pulp fibers include hardwood fibers, such as, but not limited to, eucalyptus, maple, birch, aspen, and the like. In certain instances, eucalyptus fibers may be particularly desired to increase the softness of the web. Eucalyptus fibers can also enhance the brightness, increase the opacity, and change the pore structure of the web to increase its wicking ability. Moreover, if desired, secondary fibers obtained from recycled materials may be used, such as fiber pulp from sources such as, for example, newsprint, reclaimed paperboard, and office waste.

In a particularly preferred embodiment macroalgae fibers are utilized in the tissue web as a replacement for low average fiber length wood fibers such as hardwood fibers and more specifically Eucalyptus kraft fibers. In one particular embodiment, macroalgae fibers are incorporated into a multi-layered web having a middle layer disposed between an air contacting layer (non-fabric contacting layer) and a fabric contacting layer where the air contacting layer comprises a blend of hardwood fibers and macroalgae fibers, the middle layer comprises softwood fibers and the fabric contacting layer comprises hardwood fibers and is substantially free from macroalgae fibers. In such embodiments the macroalgae fiber may be added to the air contacting layer such that the total web comprises about 0.5 percent by total weight of the web macroalgae fibers, such as from about 1 to about 5 percent and more preferably from about 2 to about 3 percent.

In addition to varying the amount of macroalgae within the web, as well as the amount in any given layer, the physical properties of the web may be varied by specifically selecting a particular layer or layers for incorporation of the macroalgae fibers. It has now been discovered that the greatest increase in tensile is achieved by selectively incorporating the macroalgae fibers in a multi-layered web such that the layer comprising macroalgae is not brought into contact with the forming fabric during formation of the web.

In a particularly preferred embodiment, the present disclosure provides a tissue web having enhanced tensile strength without a corresponding increase in stiffness, where the multi-layered tissue web comprises fabric and non-fabric contacting layers, wherein the

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fabric contacting fibrous layer comprises conventional papermaking fibers and is substantially free from macroalgae fibers and the non-fabric contacting fibrous layer comprises conventional papermaking fibers and macroalgae fibers. Preferably the webs have a GMT strengths greater than about 500 g/3", such as from about 500 to about 1500 g/3", and more preferably from about 700 to about 1200 g/3", yet have a stiffness index less than about 10.0, and more preferably less than about 9.0, such as from about 7.0 to about 10.0.

In still other embodiments, the present disclosure provides tissue webs having enhanced bulk, softness and durability. Improved durability, such as increased machine and cross-machine direction stretch (MD Stretch and CD Stretch), and improved softness may be measured as a reduction in the slope of the tensile-strain curve (measured as GM Slope) or the stiffness index. For example, tissue webs prepared as described herein generally have a GM Slope less than about 9.0 kgf, such as from about 6.0 to about 9.0 kgf and more preferably from about 6.5 to about 7.5 kgf. The GM Slopes are achieved at GMT strengths from about 700 to about 1500 g/3", yielding stiffness indexes from about 7.0 to about 10.0.

Similarly, webs may also have MD Stretch from greater than about 12 percent and more preferably greater than about 15 percent, such as from about 15 to about 20 percent, yielding webs having Machine Direction Durability greater than about 10.0, such as from about 10.0 to about 12.0 and more preferably from about 10.5 to about 11.5.

Webs prepared as described herein may be converted into either single or multi-ply rolled tissue products that have improved properties over the prior art. In one embodiment the present disclosure provides a rolled tissue product comprising a spirally wound tissue web having at least two layers wherein the air contacting layer comprising less than about 5 percent macroalgae by weight of the web, such as from about 0.5 to about 4 percent, and wherein the tissue web has a bone dry basis weight greater than about 35 gsm, a sheet bulk greater than about 15 cc/g and a stiffness index less than about 9.0.

The tissue webs may also be incorporated into tissue products that may be either single- or multi-ply, where one or more of the plies may be formed by a multi-layered tissue web having macroalgae fibers selectively incorporated in one of its layers. In one embodiment the tissue product is constructed such that the macroalgae fibers are brought into contact with the user's skin in-use. For example, the tissue product may comprise two multi-layered through-air dried webs wherein each web comprises a fabric contacting

fibrous layer substantially free from macroalgae and a non-fabric contacting fibrous layer comprising macroalgae. The webs are plied together such that the outer surface of the tissue product is formed from the fabric contacting fibrous layers of each web, such that the surface brought into contact with the user's skin in-use comprises macroalgae fibers.

If desired, various chemical compositions may be applied to one or more layers of the multi-layered tissue web to further enhance softness and/or reduce the generation of lint or slough. For example, in some embodiments, a wet strength agent can be utilized to further increase the strength of the tissue product when wet. As used herein, a "wet strength agent" is any material that when added to pulp fibers can provide a resulting web or sheet with a wet geometric tensile strength to dry geometric tensile strength ratio in excess of about 0.1. Typically these materials are termed either "permanent" wet strength agents or "temporary" wet strength agents. As is well known in the art, temporary and permanent wet strength agents may also sometimes function as dry strength agents to enhance the strength of the tissue product when dry.

Wet strength agents may be applied in various amounts depending on the desired characteristics of the web. For instance, in some embodiments, the total amount of wet strength agents added can be between about 1 to about 60 pounds per ton (lbs/T), in some embodiments between about 5 to about 30 lbs/T, and in some embodiments between about 7 to about 13 lbs/T of the dry weight of fibrous material. The wet strength agents can be incorporated into any layer of the multi-layered tissue web.

A chemical debonder can also be applied to soften the web. Specifically, a chemical debonder can reduce the amount of hydrogen bonds within one or more layers of the web, which results in a softer product. Depending on the desired characteristics of the resulting tissue product, the debonder can be utilized in varying amounts. For example, in some embodiments, the debonder can be applied in an amount between about 1 to about 30 lbs/T, in some embodiments between about 3 to about 20 lbs/T, and in some embodiments, between about 6 to about 15 lbs/T of the dry weight of fibrous material. The debonder can be incorporated into any layer of the multi-layered tissue web.

Any material capable of enhancing the soft feel of a web by disrupting hydrogen bonding can generally be used as a debonder in the present invention. In particular, as stated above, it is typically desired that the debonder possess a cationic charge for forming an electrostatic bond with anionic groups present on the pulp. Some examples of suitable

cationic debonders can include, but are not limited to, quaternary ammonium compounds, imidazolinium compounds, bis-imidazolinium compounds, diquaternary ammonium compounds, polyquaternary ammonium compounds, ester-functional quaternary ammonium compounds (e.g., quaternized fatty acid trialkanolamine ester salts), phospholipid derivatives, polydimethylsiloxanes and related cationic and non-ionic silicone compounds, fatty and carboxylic acid derivatives, mono and polysaccharide derivatives, polyhydroxy hydrocarbons, etc. For instance, some suitable debonders are described in US Patent Nos. 5,716,498, 5,730,839, 6,211,139, 5,543,067, and WO/0021918, all of which are incorporated herein in a manner consistent with the present disclosure.

Still other suitable debonders are disclosed in US Patent Nos. 5,529,665 and 5,558,873, both of which are incorporated herein in a manner consistent with the present disclosure. In particular, US Patent No. 5,529,665 discloses the use of various cationic silicone compositions as softening agents.

Tissue webs of the present disclosure can generally be formed by any of a variety of papermaking processes known in the art. Preferably the tissue web is formed by through-air drying and be either creped or uncreped. For example, a papermaking process of the present disclosure can utilize adhesive creping, wet creping, double creping, embossing, wet-pressing, air pressing, through-air drying, creped through-air drying, uncreped through-air drying, as well as other steps in forming the paper web. Some examples of such techniques are disclosed in US Patent Nos. 5,048,589, 5,399,412, 5,129,988 and 5,494,554 all of which are incorporated herein in a manner consistent with the present disclosure. When forming multi-ply tissue products, the separate plies can be made from the same process or from different processes as desired.

For example, in one embodiment, tissue webs may be creped through-air dried webs formed using processes known in the art. To form such webs, an endless traveling forming fabric, suitably supported and driven by rolls, receives the layered papermaking stock issuing from the headbox. A vacuum box is disposed beneath the forming fabric and is adapted to remove water from the fiber furnish to assist in forming a web. From the forming fabric, a formed web is transferred to a second fabric, which may be either a wire or a felt. The fabric is supported for movement around a continuous path by a plurality of guide rolls. A pick up roll designed to facilitate transfer of web from fabric to fabric may be included to transfer the web.

Preferably the formed web is dried by transfer to the surface of a rotatable heated dryer drum, such as a Yankee dryer. The web may be transferred to the Yankee directly from the throughdrying fabric or, preferably, transferred to an impression fabric which is then used to transfer the web to the Yankee dryer. In accordance with the present disclosure, the creping composition of the present disclosure may be applied topically to the tissue web while the web is traveling on the fabric or may be applied to the surface of the dryer drum for transfer onto one side of the tissue web. In this manner, the creping composition is used to adhere the tissue web to the dryer drum. In this embodiment, as the web is carried through a portion of the rotational path of the dryer surface, heat is imparted to the web causing most of the moisture contained within the web to be evaporated. The web is then removed from the dryer drum by a creping blade. The creping web as it is formed further reduces internal bonding within the web and increases softness. Applying the creping composition to the web during creping, on the other hand, may increase the strength of the web.

In another embodiment the formed web is transferred to the surface of the rotatable heated dryer drum, which may be a Yankee dryer. The press roll may, in one embodiment, comprise a suction pressure roll. In order to adhere the web to the surface of the dryer drum, a creping adhesive may be applied to the surface of the dryer drum by a spraying device. The spraying device may emit a creping composition made in accordance with the present disclosure or may emit a conventional creping adhesive. The web is adhered to the surface of the dryer drum and then creped from the drum using the creping blade. If desired, the dryer drum may be associated with a hood. The hood may be used to force air against or through the web.

In other embodiments, once creped from the dryer drum, the web may be adhered to a second dryer drum. The second dryer drum may comprise, for instance, a heated drum surrounded by a hood. The drum may be heated from about 25 to about 200°C, such as from about 100 to about 150°C.

In order to adhere the web to the second dryer drum, a second spray device may emit an adhesive onto the surface of the dryer drum. In accordance with the present disclosure, for instance, the second spray device may emit a creping composition as described above. The creping composition not only assists in adhering the tissue web to the

dryer drum, but also is transferred to the surface of the web as the web is creped from the dryer drum by the creping blade.

Once creped from the second dryer drum, the web may, optionally, be fed around a cooling reel drum and cooled prior to being wound on a reel.

For example, once a fibrous web is formed and dried, in one aspect, the creping composition may be applied to at least one side of the web and the at least one side of the web may then be creped. In general, the creping composition may be applied to only one side of the web and only one side of the web may be creped, the creping composition may be applied to both sides of the web and only one side of the web is creped, or the creping composition may be applied to each side of the web and each side of the web may be creped.

Once creped the tissue web may be pulled through a drying station. The drying station can include any form of a heating unit, such as an oven energized by infra-red heat, microwave energy, hot air, or the like. A drying station may be necessary in some applications to dry the web and/or cure the creping composition. Depending upon the creping composition selected, however, in other applications a drying station may not be needed.

In other embodiments, the base web is formed by an uncreped through-air drying process such as those described, for example, in US Patent Nos. 5,656,132 and 6,017,417, both of which are hereby incorporated by reference herein in a manner consistent with the present disclosure. The uncreped through-air drying process may comprise a twin wire former having a papermaking headbox which injects or deposits a furnish of an aqueous suspension of wood fibers onto a plurality of forming fabrics, such as an outer forming fabric and an inner forming fabric, thereby forming a wet tissue web. The forming process may be any conventional forming process known in the papermaking industry. Such formation processes include, but are not limited to, Fourdriniers, roof formers such as suction breast roll formers, and gap formers such as twin wire formers and crescent formers.

The wet tissue web forms on the inner forming fabric as the inner forming fabric revolves about a forming roll. The inner forming fabric serves to support and carry the newly-formed wet tissue web downstream in the process as the wet tissue web is partially

dewatered to a consistency of about 10 percent based on the dry weight of the fibers. Additional dewatering of the wet tissue web may be carried out by known paper making techniques, such as vacuum suction boxes, while the inner forming fabric supports the wet tissue web. The wet tissue web may be additionally dewatered to a consistency of at least about 20 percent, more specifically between about 20 to about 40 percent, and more specifically about 20 to about 30 percent.

The forming fabric can generally be made from any suitable porous material, such as metal wires or polymeric filaments. For instance, some suitable fabrics can include, but are not limited to, Albany 84M and 94M available from Albany International (Albany, NY) Asten 856, 866, 867, 892, 934, 939, 959, or 937; Asten Synweve Design 274, all of which are available from Asten Forming Fabrics, Inc. (Appleton, WI); and Voith 2164 available from Voith Fabrics (Appleton, WI). The wet web is then transferred from the forming fabric to a transfer fabric while at a solids consistency of between about 10 to about 35 percent and, particularly, between about 20 to about 30 percent. As used herein, a "transfer fabric" is a fabric that is positioned between the forming section and the drying section of the web manufacturing process.

Transfer to the transfer fabric may be carried out with the assistance of positive and/or negative pressure. For example, in one embodiment, a vacuum shoe can apply negative pressure such that the forming fabric and the transfer fabric simultaneously converge and diverge at the leading edge of the vacuum slot. Typically, the vacuum shoe supplies pressure at levels between about 10 to about 25 inches of mercury. As stated above, the vacuum transfer shoe (negative pressure) can be supplemented or replaced by the use of positive pressure from the opposite side of the web to blow the web onto the next fabric. In some embodiments, other vacuum shoes can also be used to assist in drawing the fibrous web onto the surface of the transfer fabric.

Typically, the transfer fabric travels at a slower speed than the forming fabric to enhance the MD and CD stretch of the web, which generally refers to the stretch of a web in its cross (CD) or machine direction (MD) (expressed as percent elongation at sample failure). For example, the relative speed difference between the two fabrics can be from about 1 to about 30 percent, in some embodiments from about 5 to about 20 percent, and in some embodiments, from about 10 to about 15 percent. This is commonly referred to as "rush transfer." During "rush transfer," many of the bonds of the web are believed to be

broken, thereby forcing the sheet to bend and fold into the depressions on the surface of the transfer fabric 8. Such molding to the contours of the surface of the transfer fabric 8 may increase the MD and CD stretch of the web. Rush transfer from one fabric to another can follow the principles taught in any one of the following patents, US Patent Nos. 5,667,636, 5,830,321, 4,440,597, 4,551,199, 4,849,054, all of which are hereby incorporated by reference herein in a manner consistent with the present disclosure. The wet tissue web is then transferred from the transfer fabric to a throughdrying fabric.

While supported by the throughdrying fabric, the wet tissue web is dried to a final consistency of about 94 percent or greater by a throughdryer. The drying process can be any noncompressive drying method which tends to preserve the bulk or thickness of the wet web including, without limitation, throughdrying, infra-red radiation, microwave drying, etc. Because of its commercial availability and practicality, throughdrying is well known and is one commonly used means for noncompressively drying the web for purposes of this invention. Suitable throughdrying fabrics include, without limitation, fabrics with substantially continuous machine direction ridges whereby the ridges are made up of multiple warp strands grouped together, such as those disclosed in US Patent No. 6,998,024. Other suitable throughdrying fabrics include those disclosed in US Patent No. 7,611,607, which is incorporated herein in a manner consistent with the present disclosure, particularly the fabrics denoted as Fred (t1207-77), Jetson (t1207-6) and Jack (t1207-12). The web is preferably dried to final dryness on the throughdrying fabric, without being pressed against the surface of a Yankee dryer, and without subsequent creping.

Additionally, webs prepared according to the present disclosure may be subjected to any suitable post processing including, but not limited to, printing, embossing, calendering, slitting, folding, combining with other fibrous structures, and the like.

TEST METHODS

Tensile

Samples for tensile strength testing are prepared by cutting a 3" (76.2 mm) x 5" (127 mm) long strip in either the machine direction (MD) or cross-machine direction (CD) orientation using a JDC Precision Sample Cutter (Thwing-Albert Instrument Company, Philadelphia, PA, Model No. JDC 3-10, Ser. No. 37333). The instrument used for

measuring tensile strengths is an MTS Systems Sintech 11S, Serial No. 6233. The data acquisition software is MTS TestWorks™ for Windows Ver. 4 (MTS Systems Corp., Research Triangle Park, NC). The load cell is selected from either a 50 Newton or 100 Newton maximum, depending on the strength of the sample being tested, such that the majority of peak load values fall between 10 and 90 percent of the load cell's full scale value. The gauge length between jaws is 2 ± 0.04 inches (50.8 ± 1 mm). The jaws are operated using pneumatic-action and are rubber coated. The minimum grip face width is 3" (76.2 mm), and the approximate height of a jaw is 0.5 inches (12.7 mm). The crosshead speed is 10 ± 0.4 inches/min (254 ± 1 mm/min), and the break sensitivity is set at 65 percent. The sample is placed in the jaws of the instrument, centered both vertically and horizontally. The test is then started and ends when the specimen breaks. The peak load is recorded as either the "MD tensile strength" or the "CD tensile strength" of the specimen depending on the sample being tested. At least six (6) representative specimens are tested for each product, taken "as is," and the arithmetic average of all individual specimen tests is either the MD or CD tensile strength for the product.

EXAMPLES

Commodity pulps were obtained as follows – Eucalyptus kraft pulp ("EHWK") was obtained from Fibria, San Paulo, Brazil, Southern softwood kraft pulp ("SSWK") was obtained from Abitibi Bowater, Mobile, AL, North softwood kraft pulp ("NSWK") was obtained from Northern Pulp Nova Scotia Corporation, Abercrombie, NS, and wet (never-dried) red algae pulp was obtained from Pegasus International, Daejeon, Korea.

Dry lap red algae pulp ("RA") was prepared by blending EHWK with wet red algae pulp and forming a dry lap pulp sheet using a Fourdrinier machine comprising a wire forming section, a suction box, a pair of registered wet press rolls, and three cylindrical air dryers. Each fiber type was weighed individually and dispersed in a pulper for 25 to 30 minutes, yielding a fiber slurry with a consistency of 3 percent, and then returned to a stock tank for use in the formation of the pulp sheet. The entire stock preparation system was heated to 50°C.

The fiber slurries were mixed depending on the desired blend of the dry lap pulp and then pumped to the headbox and deposited onto the forming section of the paper machine under pressure to increase drainage. The resulting fibrous web was pressed to

further remove water using weight of the first press roll, which was adjusted to maximize caliper. The dewatered fibrous web was subjected to drying using a series of dryer cans, the initial dryer can pressure was 100 pounds per square inch (psig) in the first, second, and third section, corresponding to about 177°C. The resulting dry lap pulp sheet had a moisture content of less than about 10 percent and a basis weight of about 230 gsm.

A single ply through-air dried tissue web was made generally in accordance with US Patent No. 5,607,551, which is herein incorporated by reference in a manner consistent with the present disclosure. Initially NSWK was dispersed in a pulper for 30 minutes at 3 percent consistency at about 100°F. The NSWK was then transferred to a dump chest and subsequently diluted to approximately 0.75 percent consistency. EHWK was dispersed in a pulper for 30 minutes at about 3 percent consistency at about 100°F. The EHWK was then transferred to a dump chest and subsequently diluted to about 0.75 percent consistency. Two separate dispersions of red algae (RA) dry lap pulp were prepared depending upon which layer of the tissue web the red algae was to be added to. Dry lap red algae pulps (80 wt% EHWK and 20 wt% red algae) prepared as described above were dispersed in a pulper for 30 minutes at about 3 percent consistency at about 100°F and then transferred to a dump chest and subsequently diluted to about 0.75 percent consistency.

The pulp slurries were subsequently pumped to separate machine chests and further diluted to a consistency of about 0.1 percent. Pulp fibers from each machine chest were sent through separate manifolds in the headbox to create a 3-layered tissue structure. The flow rates of the stock pulp fiber slurries into the flow spreader were adjusted to give a target web basis. The fiber compositions of the layered sheets are described in Table 4 below. The formed web was non-compressively dewatered and rush transferred to a transfer fabric traveling at a speed about 28 percent slower than the forming fabric. The web was then transferred to a throughdrying fabric and dried.

The base sheet webs were converted into various bath tissue rolls. Specifically, base sheet was calendered using one or two conventional polyurethane/steel calenders comprising either a 4 or a 40 P&J polyurethane roll on the air contacting side of the sheet and a standard steel roll on the fabric contacting side. Table 4 shows the process conditions for each of the samples prepared in accordance with the present example. Tables 5 and 6 summarize the physical properties of the finished product.

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TABLE 4

Sample	NBSK Center Layer (wt%)	Air Contacting Layer (wt%)	Fabric Contacting Layer (wt%)	Starch (kg/MT)	Debonder (kg/MT)
Control 1	40	30 EHWK	30 EHWK	0	0
Control 2	40	30 EHWK	30 EHWK	3	0
Control 3	40	30 EHWK	30 EHWK	6	0
18	40	2.25 RA 27.75 EHWK	2.25 RA 27.75 EHWK	0	0
19	40	2.25 RA 27.75 EHWK	2.25 RA 27.75 EHWK	3	0
20	40	4.5 RA 25.5 EHWK	4.5 RA 25.5 EHWK	0	0
21	40	4.5 RA 25.5 EHWK	4.5 RA 25.5 EHWK	0	4
24	40	30 EHWK	9 RA 21 EHWK	0	0
25	40	30 EHWK	9 RA 21 EHWK	2	0
26	40	9 RA 21 EHWK	30 EHWK	2	0
27	40	9 RA 21 EHWK	30 EHWK	2	5
37	40	4.5 RA 25.5 EHWK	30 EHWK	0	0
38	40	30 EHWK	4.5 RA 25.5 EHWK	0	0

TABLE 5

Sample	GMT (g/3")	Basis Wt. (gsm)	Sheet Caliper (μm)	Sheet Bulk (cc/g)	GM Slope (kgf)	stiffness index
Control 1	605	33.9	379	11.2	5.52	9.12
Control 2	855	34.3	392	11.4	6.79	7.94
Control 3	974	33.7	413	12.3	7.94	8.15
18	855	33.2	363	10.9	7.44	8.70
19	1090	33.3	388	11.7	9.28	8.51
20	1055	33.3	391	11.7	10.64	10.09
21	887	33.2	382	11.5	8.42	9.49
24	637	33.9	403	11.9	6.69	10.50
25	817	33.1	430	13.0	6.66	8.15
26	1148	33.6	404	12.0	8.71	7.59
27	687	33.5	392	11.7	6.1	8.88
37	873	34.1	394	11.5	6.93	7.94
38	711	34.5	405	11.7	6.97	9.80

TABLE 6

Sample	MD Tensile (g/3")	MD Tensile Index	MD Stretch (%)	MD Durability Index
Control 1	799.0	23.6	14.35	9.03
Control 2	1126.4	32.8	15.60	10.90
Control 3	1292.6	38.4	16.83	12.00
18	1202.7	36.2	16.25	11.57
19	1515.5	45.5	17.06	13.23
20	1526.7	45.8	16.73	13.25
21	1350.5	40.7	17.07	12.42
24	840.9	24.8	13.94	9.22
25	1120.8	33.9	15.66	11.09
26	1615.6	48.1	16.02	13.54
27	990.8	29.6	14.28	10.16
37	1223.9	35.9	15.26	11.40
38	1079.3	31.3	15.18	10.57

The relative change in the GMT, MD Tensile Index, MD Durability Index and stiffness index, compared to an identical control without macroalgae, is summarized in Table 7 below.

TABLE 7

Sample	RA (wt%)	RA Layer	Delta GMT	Delta stiffness index	Delta MD Durability Index
Control 1	0	-	-	-	-
18	4.5%	Air/Fabric	41%	-5%	28%
37	4.5%	Air	44%	-13%	26%
38	4.5%	Fabric	18%	7%	17%

While tissue webs and products comprising the same have been described in detail with respect to the specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

We claim:

1. A layered tissue web comprising a first air contacting layer and a second fabric contacting layer, wherein the first air contacting layer comprises from about 0.5 to about 5 weight percent macroalgae fibers by weight of the web.

2. The layered tissue web of claim 1 having a stiffness index of less than about 10.

3. The layered tissue web of claims 1 or 2 having an MD Durability Index of greater than about 10.

4. The layered tissue web of any one of the foregoing claims having a basis weight from about 15 to about 45 gsm, a geometric mean tensile index of at least about 30 and geometric mean slope of less than about 10.0 kgf.

5. The layered tissue web of any one of the foregoing claims having a geometric mean tensile from about 700 to about 1200 g/3" and a geometric mean slope from about 6.0 to about 9.0 kgf.

6. The layered tissue web of any one of the foregoing claims having a basis weight from about 30 to about 40 gsm.

7. The layered tissue web of any one of the foregoing claims wherein the second fabric contacting layer is substantially free of macroalgae fibers.

8. The layered tissue web of any one of the foregoing claims wherein the first air contacting layer comprise from about 1.0 to about 4.0 weight percent macroalgae fibers by weight of the web.

9. The layered tissue web of any one of the foregoing claims wherein the macroalgae fibers are red algae pulp fibers derived from *Gelidium elegance*, *Gelidium corneum*, *Gelidium amansii*, *Gelidium robustum*, *Gelidium chilense*, *Gracelaria verrucosa*, *Eucheuma Cottonii*, *Eucheuma Spinosum*, or *Beludul*.

10. A layered tissue web comprising an air contacting layer comprising conventional papermaking fibers and from about 0.5 to about 5 weight percent macroalgae fibers by weight of the web, a middle layer comprising conventional papermaking fibers

and a fabric contacting layer comprising conventional papermaking fibers, wherein the fabric contacting layer is substantially free of macroalgae fibers.

11. The layered tissue web of claim 10 wherein the middle layer is substantially free of macroalgae fibers.

12. The layered tissue web of claims 10 or 11 wherein the fabric contacting layer comprises hardwood fibers, the middle layer comprises softwood fibers and the air contacting layer comprises macroalgae and hardwood fibers.

13. The layered tissue web of any one of claims 10 through 12 having a basis weight greater than about 30 gsm, a geometric mean tensile greater than about 1000 g/3" and a stiffness index less than about 9.0.

14. The layered tissue web of any one of claims 10 through 12 having a basis weight from about 15 to about 40 gsm, a geometric mean tensile index of at least about 30 and a geometric mean slope of less than about 10 kgf.

15. The layered tissue web of claim 10 having a stiffness index of less than about 10.0.

16. The layered tissue web of any one of claims 10 through 15 having an MD Durability Index of greater than about 10.

17. A method of forming a layered tissue web comprising the steps of:

a. dispersing a macroalgae dry lap pulp to form a first fiber slurry;

b. dispersing a conventional papermaking pulp to form a second fiber slurry;

c. depositing the first and second fiber slurries onto a forming fabric such that the second fiber slurry contacts the forming fabric and the first fiber slurry contacts the air to form a wet web;

d. dewatering the wet web to a consistency of from about 20 to about 30 percent; and

e. drying the wet web to a consistency of greater than about 90 percent thereby forming a dried macroalgae tissue web.

18. The method of claim 17 wherein the macroalgae dry lap pulp has a moisture content of less than about 10 percent and wherein the macroalgae dry lap pulp comprises from about 1 to about 30 percent by weight of the dry lap pulp macroalgae pulp fibers and from about 99 to about 70 percent by weight of the dry lap pulp conventional papermaking fibers.

19. The method of claim 17 further comprising the steps of transferring the dewatered web from the forming fabric to a transfer fabric traveling at a speed from about 10 to about 40 percent slower than the forming fabric; and transferring the web to a throughdrying fabric.

20. The method of claim 17 wherein the drying step comprises transferring the dewatered web to the surface of a Yankee dryer and further comprising the step of creping the dried macroalgae tissue web from the surface of the Yankee dryer.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/044891

A. CLASSIFICATION OF SUBJECT MATTER

D21H 27/30(2006.01)i, D21H 11/00(2006.01)i, D21H 11/04(2006.01)i

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)
D21H 27/30; D21H 11/12; D21H 19/10; D21H 11/00; D21H 21/14; D21H 21/16; D01C 1/00; A61K 7/00; D21H 11/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:tissue, macroalgae, multi-layer tissue, papermaking fiber, macroalgae fiber

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 8298374 B2 (SHANNON, THOMAS GERARD et al.) 30 October 2012 See columns 2 and 7; abstract.	1-3,10-12,15,17-20
A	JP 04-202893 A (MITSUBISHI HEAVY IND. LTD.) 23 July 1992 See the whole document.	1-3,10-12,15,17-20
A	WO 00-38625 A2 (KIMBERLY-CLARK WORLDWIDE, INC.) 06 July 2000 See See the whole document.	1-3,10-12,15,17-20
A	US 6332952 B1 (HSU, JAY CHIEHLUNG et al.) 25 December 2001 See the whole document.	1-3,10-12,15,17-20
A	US 7972474 B2 (UNDERHILL, RICHARD et al.) 05 July 2011 See the whole document.	1-3,10-12,15,17-20

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"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
"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
"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
"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
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 March 2014 (14.03.2014)	**14 March 2014 (14.03.2014)**

Name and mailing address of the ISA/KR
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Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/044891

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-9,13,14,16
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2013/044891

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 8298374 B2	30/10/2012	US 2011-0303375 A1	15/12/2011
		WO 2011-154855 A2	15/12/2011
		WO 2011-154855 A3	12/04/2012
JP 04-202893A	23/07/1992	None	
WO 00-38625 A2	06/07/2000	AR 022161 A1	04/09/2002
		AR 022163 A1	04/09/2002
		AR 023078 A1	04/09/2002
		AU 2000-17300 A	31/07/2000
		AU 2000-21700 A	31/07/2000
		AU 2000-87400 A	31/07/2000
		AU 764723 B2	28/08/2003
		AU 764723 C	20/05/2004
		AU 769563 B2	29/01/2004
		AU 773120 B2	20/05/2004
		AU 773120 C	14/04/2005
		BR 9916592 A	22/01/2002
		BR 9916642 A	22/01/2002
		BR 9916694 A	11/12/2001
		CN 1211070 C	20/07/2005
		CN 1335764 A	13/02/2002
		CN 1344153 A	10/04/2002
		CN 1344154 A	10/04/2002
		CO 5111023 A1	26/12/2001
		CO 5150154 A1	29/04/2002
		CO 5150202 A1	29/04/2002
		DE 69925637 D1	07/07/2005
		DE 69925637 T2	11/05/2006
		DE 69927288 D1	20/10/2005
		DE 69927288 T2	13/07/2006
		DE 69927288 T3	30/12/2010
		DE 69928690 D1	05/01/2006
		DE 69928690 T2	24/08/2006
		EP 1140009 A2	10/10/2001
		EP 1140009 B1	14/09/2005
		EP 1140009 B2	18/08/2010
		EP 1140010 A2	10/10/2001
		EP 1140010 B1	30/11/2005
		EP 1143927 A2	17/10/2001
		EP 1143927 B1	01/06/2005
		JP 2002-533365 A	08/10/2002
		JP 2002-533366 A	08/10/2002
		JP 2004-512853 A	30/04/2004
		RU 2239409 C2	10/11/2004
		RU 2244565 C2	20/01/2005
		TW 446554 B	21/07/2001
		TW I241196 B	11/10/2005
		TW I247610 B	21/01/2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 6485733 B1	26/11/2002
		US 6517848 B1	11/02/2003
		US 6521240 B1	18/02/2003
		US 6521241 B1	18/02/2003
		US 6521242 B1	18/02/2003
		US 6551607 B1	22/04/2003
		WO 00-38625 A3	16/11/2000
		WO 00-38626 A2	06/07/2000
		WO 00-38626 A3	02/11/2000
		WO 00-38747 A2	06/07/2000
		WO 00-38747 A3	12/10/2000
US 6332952 B1	25/12/2001	AR 019173 A1	26/12/2001
		AU 2000-84899 A	17/01/2000
		AU 747675 B2	16/05/2002
		CA 2335111 A1	06/01/2000
		CA 2335111 C	04/01/2011
		CO 5080812 A1	25/09/2001
		DE 69936652 D1	06/09/2007
		DE 69936652 T2	21/05/2008
		EP 1102896 A1	30/05/2001
		EP 1102896 B1	25/07/2007
		ES 2286888 T3	01/12/2007
		JP 2002-519533 A	02/07/2002
		PE 09632000 A1	27/09/2000
		TW 574457 B	01/02/2004
		WO 00-00698 A1	06/01/2000
US 7972474 B2	05/07/2011	AU 2007-325441 A1	21/06/2007
		AU 325441 B2	10/02/2011
		BR PI0619777 A2	18/10/2011
		CA 2630867 A1	21/06/2007
		EP 1960596 A1	27/08/2008
		KR 10-2008-0075869 A	19/08/2008
		RU 2008128116 A	20/01/2010
		RU 2393284 C2	27/06/2010
		US 2007-0131366 A1	14/06/2007
		WO 2007-070124 A1	21/06/2007

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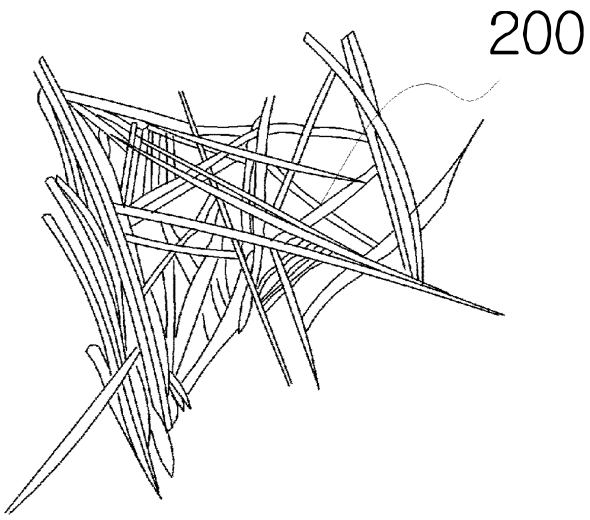
(74) Agent: **KIM, Sung-Gyu**; 4th Fl. Jangan Bldg., 827-3 Yok-sam-dong, Kangnam-gu, Seoul 135-080 (KR).

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— *with international search report*

(54) Title: MANUFACTURING METHOD OF BAMBOO CHIP FOR MANUFACTURING THE SOLUBILITY PULP AND THEREOF



(57) Abstract: There are provided a method for manufacturing a bamboo chip for a soluble pulp and a bamboo chip manufactured therefrom, the bamboo capable of improving their productivity and obtaining high-quality products, as well as manufacturing the soluble pulps economically and environment-friendly. The present invention provides a method for manufacturing bamboo chips including steps of: softening bamboo stems and giving bulkiness in a process of manufacturing bamboo chips by pressing and crushing the bamboo, which has compact and structural characteristics in nature, with a convex roller to tear the bamboo stems into pieces in a longitudinal direction, and simultaneously cutting the bamboo stems into bamboo chips having desired lengths; removing a large amount of unnecessary substances, such as lignin, thin- wall tissues, joints, silicified barks and the like, in celluloses in the above-mentioned process so as to facilitate easy penetration of chemical agents and effectively remove lignin and hemicellulose in a process for extracting a pulp; and pressing and bending the bamboo chips into certain shapes to package the bamboo chips, and transporting the bamboo chips to a container or a bulk carrier in an economic manner.

WO 2008/044860 A1

Description

MANUFACTURING METHOD OF BAMBOO CHIP FOR MANUFACTURING THE SOLUBILITY PULP AND THEREOF

Technical Field

[1] The present invention relates to a method for manufacturing a bamboo chip and a bamboo chip manufactured therefrom, and more particularly to a method for manufacturing a bamboo chip capable of improving their productivity and obtaining high-quality products, as well as manufacturing a soluble pulps economically and environment-friendly, and a bamboo chip manufactured therefrom.

Background Art

[2] Generally, natural bamboo fibers has been directly developed as a non-woven fiber without undergoing the dissolution process. Also, pulps for paper are used as raw materials for tissue papers and sanitary products (other products such as packaging papers, toilet papers, cosmetic papers, hygienic bands, diapers, etc.), and soluble pulps are used as raw materials for synthetic fibers, cellophanes, plastics, various cellulose-based derivatives (for example, viscose rayon, rayon stable, etc.).

[3] Therefore, the present invention is to provide a method capable of improving their productivity and obtaining high-quality products, as well as manufacturing the above-mentioned various pulps economically and environment-friendly.

[4] Generally, needle-leaf trees, broad-leaved trees, other woods are used as raw pulp materials, and the increasing use of the wood pulp increases the felling of woods since the wood pulp is obtained from wood chips.

[5] Global environments have been abruptly destroyed and damaged owing to this merciless felling of woods, resulting in serious problems to the global environments such as the destruction of an ozone layer, the abnormal weathers, etc. Therefore, the world regulates the damages to the forests and consume a large amount of the cost for prevention of the forests, which leads to the increase in the cost of the wood chips.

[6] Accordingly, in order to solve the above problems, there have been many ardent attempts to produce a raw material including non-wood materials other than the woods, produce a high-quality soluble pulp from the raw material and manufacture various products with the soluble pulp.

[7] Among them, there have been many ardent attempts to use a bamboo, which may grow within a short period and be used as a raw pulp material, to obtain a natural fiber, a pulp for paper, a soluble pulp, and manufacture various papers or fiber products from the above raw materials, and patents regarding the raw materials have been also published home and abroad

[8] Reviewing the use of a bamboo as described in the patents published home and abroad, bamboo leaves or foreign substance are removed from a bamboo; the remaining bamboo is cut into pieces having a length and width of about 20 to 30mm and a thickness of about 2 to 3mm to obtain bamboo chips 300 as shown in FIG. 4; the bamboo chip 300 is treated with chemical agents at high temperature in a cooking process to soften and pulp the bamboo chips, the pulped products are subject to a dedusting process, a selection process, a washing and concentration process and a bleaching process to manufacture desired paper products.

[9] For the processes, the cooking process for adding various chemical agents to bamboo chips and treating the bamboo chips at high temperature is important.

[10] When the various chemical agents are added to the bamboo chips and the bamboo chips are treated at high temperature in the case of the cooking process, how quickly and easily the chemical agents used to pulp the bamboo chips are penetrated into the bamboo is important to facilitate its delignification. And, for the soluble pulp, it is important to remove hemicellulose, which is used to improve a yield and quality of a pulp by increasing a content of alpha-cellulose.

[11] However, for the pulp for paper, some of hemicellulose remaining in a pulp is used to increase a yield and quality of a pulp.

[12] However, the bamboo has many bamboo joints, thin-wall tissues and silicified barks since fragmented bamboo chips that have been used up to now are generally prepared by simply cutting bamboo into a certain length and size. Therefore, chemical agents are not easily penetrated into the bamboo in the cooking process since its hard and compact structural characteristics, which leads to the insufficient cooking operations. Therefore, the yield and quality of the pulp obtained in the cooking process may be reduced.

[13] In order to solve the problem, there are provided methods of increasing amount of the added cooking agents, increasing a cooking temperature, or extending a cooking time so as to improve conditions where chemical agent for cooking a bamboo is penetrated into bamboo chips. However, the addition of excessive cooking agents results in the environmental pollution, and the increase in temperature and the extension of process time leads to the increased energy consumption, and also cause damages to alpha-cellulose.

[14] In addition, the production cost may be increased since a huge investment for facilities is required for its mass productions, and it is difficult to extract a good quality of alpha-cellulose in the process of manufacturing bamboo chips since unnecessary parts, for example bamboo joints, lignin, thin-wall tissues, silicified barks and the like, are introduced into the cooking process.

[15] Also, the transportation cost is high in transporting the bamboos by a container

since the fragmented bamboo chips are difficult to stack, store and package for thier transportation, and it is also difficult to invest the cost for additional facilities for the transportation by bulk carriers and make a contract for the use of the bulk carriers. Furthermore, it is also difficult to produce uniform products due to the growth of fungi and bacteria, as well as to store the bamboo.

Disclosure of Invention

Technical Problem

[16] Accordingly, the present invention is designed to solve the above problems, and therefore it is an object of the present invention to provide a method for manufacturing bamboo chips capable of obtaining various pulps and also reducing the production cost with the reduction of the distribution cost even when amounts of cooking agents and process time as well as a cooking temperature are lowered in the process of manufacturing a bamboo natural fiber, a soluble pulp and a pulp for paper from the bamboo chips.

Technical Solution

[17] In order to accomplish the above object, one embodiment of the present invention provides a method for manufacturing bamboo chips including steps of: softening bamboo stems and giving bulkiness in a process of manufacturing bamboo chips by removing bamboo branches, leaves and bamboo joints from a bamboo having compact and structural characteristics in nature, pressing and crushing the bamboo with a convex roller to tear the bamboo stems into pieces in a longitudinal direction, and simultaneously cutting the bamboo stems into bamboo chips having desired lengths; removing a large amount of unnecessary substances, such as lignin, thin-wall tissues, joints, silicified barks and the like, in celluloses in the above-mentioned process so as to facilitate easy penetration of chemical agents and effectively remove lignin and hemicellulose in a process for extracting a pulp; and pressing and bending the bamboo chips into certain shapes to package the bamboo chips, and transporting the bamboo chips to a container and a bulk carrier in an economic manner.

Advantageous Effects

[18] In order to use bamboos to manufacture various pulps, the bamboos are manufactured into chip shapes to facilitate pulping the bamboos, the bamboos have advantages in the pulping process by crushing and tearing the bamboos into pieces in a longitudinal direction using a convex roller and a rotary cutter without manufacturing the bamboos into fragments in the art, and simultaneously giving bulkiness. Also, the bamboo chips may be easily transported to a container and a bulk carrier since the bamboo chips may be bended into a certain size to package the bamboo chips, thereby reducing the distribution cost

[19]

Brief Description of the Drawings

[20] FIG. 1 is a diagram showing a bamboo used to manufacture bamboo chips according to the present invention.

[21] FIG. 2 is a diagram showing the bamboo chips according to one embodiment of the present invention.

[22] FIG. 3 is a diagram showing the bamboo chips according to another embodiment of the present invention.

[23] FIG. 4 is a diagram showing conventional bamboo chips.

[24]

Best Mode for Carrying Out the Invention

[25] Hereinafter, preferred embodiment of the present invention will be described in detail with reference to the accompanying drawings. First, parts have the same reference numerals if the parts are functionally identical, or similar to each other in the accompanying drawings.

[26] FIG. 1 is a diagram showing a bamboo 100 used in the present invention, and FIGS. 2 and 3 are diagrams showing a bamboo chip 200 manufactured from the bamboo 100 according to one exemplary embodiment of the present invention.

[27] According to the present invention, the schematic process includes steps of felling bamboos in a mountainous district, removing bamboo branches and leaves form the bamboos, transporting the bamboos to a mill for manufacturing bamboo chips, removing bamboo joints from the transported bamboos, and introducing the bamboos into a process for manufacturing bamboo chips.

[28] The manufacturing ot the bamboo chips includes steps of transferring bamboos, cutting the transferred bamboos while crushing the bamboos in a longitudinal direction, separating dusts and other foreign substances that are generated in the crushing and cutting process, selecting and collecting the crushed and cut bamboo chips, pressing the collected bamboo chips, bending the bamboo chips, followed by undergoing the stacking, storing and transportation processes.

[29] Hereinafter, the present invention will be described in more detail with reference to the accompanying drawings.

[30] In the process for manufacturing bamboo chips, various devices may be provided in the bamboo supply unit, but the bamboos are supplied through a conventional conveyor.

[31] The bamboos supplied through the conveyor are passed through pressing parts in which convex rollers are installed in double row, and the cylindrical bamboos are pressed and crushed into pieces having a width of 1 to 3 mm in a longitudinal direction

while passing through a plurality of convex rollers in the pressing parts, thereby giving bulkiness. Then, the bamboos, which have been tore once in a longitudinal direction while passing through the pressing parts in which convex rollers are installed, are cut into pieces having a length of about 20 to 40 mm while passing through rotary cutters composed of a plurality of cutting blades, to thereby obtain bamboo chips 200 as shown in FIGS. 2 or 3.

[32] As described above, the cylindrical bamboo 100 is pulverized into pieces while passing through convex rollers and rotary cutters, and cellulose-free bamboo joints of the bamboos and hemicellulose and lignin in the bamboos are pulverized into dusts. The generated dusts are inhaled with a fan and separated into a cyclone, and the separated by-products are used for desired applications.

[33] Also, a hard bark layer containing a large amount of good and desirable cellulose is tore into pieces in a longitudinal direction while being partially damaged by the convex rollers, and simultaneously bulkiness is given to the tore bamboos, which leads to the easy penetration of chemical agent in an agent-treating process.

[34] The bamboo chips prepared thus are transferred through a conveyor to a screen that is arranged in a selection part. For the bamboo chips transferred to the screen, unnecessary foreign substances such as small bamboo chips or dusts fall down through the vibrating screen, that are later used for other applications. Then, the good bamboo chips remaining on the screen are selected for use. The selected good bamboo chips are collected through the conveyor, pressed and bended into a desired size. The bended products are transferred into a conventional pulping process.

[35] For the bamboo chip 200 of the present invention prepared thus, a structure of the bamboo chip 200, unlike the conventional fragmented chip 300, has bulkiness since a hard bark layer is tore into thin and long pieces in the process of crushing and cutting cylindrical bamboos in a longitudinal direction using the rotary cutters and the pressing parts in which the convex rollers are installed, thereby to crush and remove most of cellulose-free bamboo joints or inner woody parts containing a large content of hemicellulose and to allow a bark layer with high availability to remains at the same time, and the remaining bark layer are also tore into pieces and damaged by the convex rollers. Therefore, a medicinal fluid is easily penetrated into the bamboo chips in the agent-treating process for manufacturing a soluble pulp.

[36] As described above, the bamboo chip 200 according to the present invention is prepared by cutting bamboos into thin pieces having a length of 1 to 3 mm in a longitudinal direction while damaging the bamboos, and therefore the most of unnecessary bamboo joints or inner woody parts are removed in this process, which leads to the easy penetration of the chemical agents the bamboo chips in the later processes. As a result, the method according to the present invention is environment-friendly and

its cost may be reduced since it is possible to shorten a cooking time and lower a cooking temperature, as well as to reduce an amount of cooking agents, and a large content of good alpha-cellulose may be produced to obtain a soluble pulp having excellent quality, thereby obtaining a high quality of natural fibers, pulps for paper and soluble pulps.

[37] In addition, the bamboo chips prepared according to the method of the present invention is easy to stack and store since the bamboo chips may be pressed, bended into a certain size, and then packaged, and the distribution cost may be reduced since a larger amount of the bamboo chips may be stacked in the container for its transportation.

[38] The following Table 1 lists the results obtained by comparing the conventional fragmented chip 300 with the bamboo chip 100 according to the present invention.

[39] Table 1

Comparison of bamboo chips of the present invention and conventional fragmented bamboo chips

	Inventive bamboo chips	Conventional fragmented bamboo chips	Comparison
Amount of added Agent	Low	High	20 to 30%
Removal of foreign substances	High	Low	Different by 20%
Cooking time	Short	Long	Shortened by 15%
Yield	High	Low	Higher by 15% or more
Production rate	Large amount/ bamboo	Small amount/bamboo	High facility investment
Cost for waste disposal	Low	High	Lower by 35%
Alpha-cellulose	High	Low	Higher by 2 to 3%
Transport of Products	Possible	Impossible	Stacking standard in container
Distribution cost of Products	Low	High	

[40] As listed in the Table 1, the bamboo chip 200 according to the present invention may be useful to reduce an amount of the used chemical agents since the bamboo chip

200 has a good penetration of medicinal fluids for a pulping process when compared to the conventional bamboo chip 300, to increase a yield and improve productivity as well as shorten a cooking time since the unnecessary foreign substances are effectively removed in the process of manufacturing a bamboo chip, to obtain a high quality of natural fiber and pulp since the bamboo chip 200 has a high content of alpha-cellulose, and to reduce the distribution cost since it is possible to transport the bamboo chips into a container and a bulk carrier after the bamboo chips are pressed and bended.

[41] The description proposed herein is just an exemplary embodiment for the purpose of illustrations only, not intended to limit the scope of the invention, so it should be understood that other equivalents and modifications could be made thereto without departing from the spirit and scope of the invention as apparent to those skilled in the art. Therefore, it should be understood that the present invention might be not defined within the scope of which is described in detailed description but within the scope of which is defined in the claims and their equivalents.

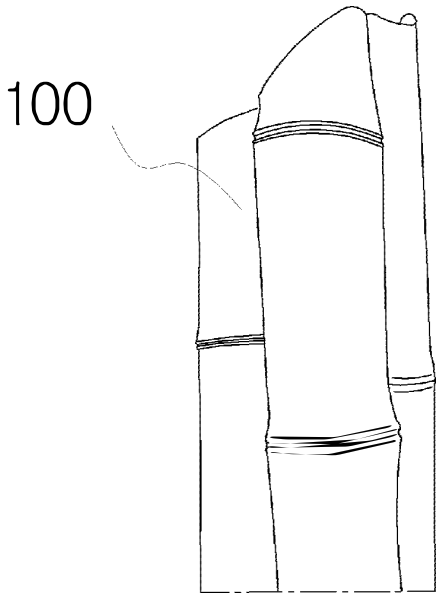
Claims

[1] A method for manufacturing bamboo chip to obtain a soluble pulp, comprising:
cutting a bamboo into pieces having a length of 20 to 40 mm using a cutter, and simultaneously tearing bamboo into pieces having a width of 1 to 3 mm while crushing the bamboo in a longitudinal direction using a plurality of convex rollers so as to give bulkiness;
transferring the crushed and cut bamboo chips to a screen to remove foreign substances; and
pressing and bending the foreign substance-free bamboo chips.

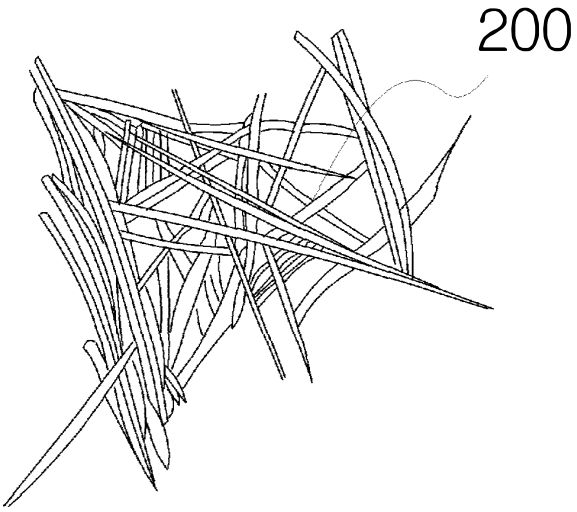
[2] The bamboo chip for manufacturing a soluble pulp, wherein a bamboo from which bamboo joints are removed is cut into bamboo chips having a width of 1 to 3 mm to give bulkiness, and the bamboo chips have a length of 20 to 40 mm, and are pressed and bended.

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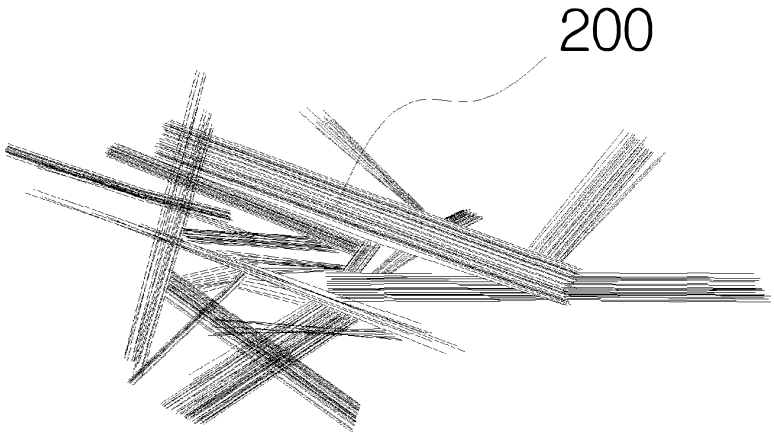
[Fig. 1]



[Fig. 2]



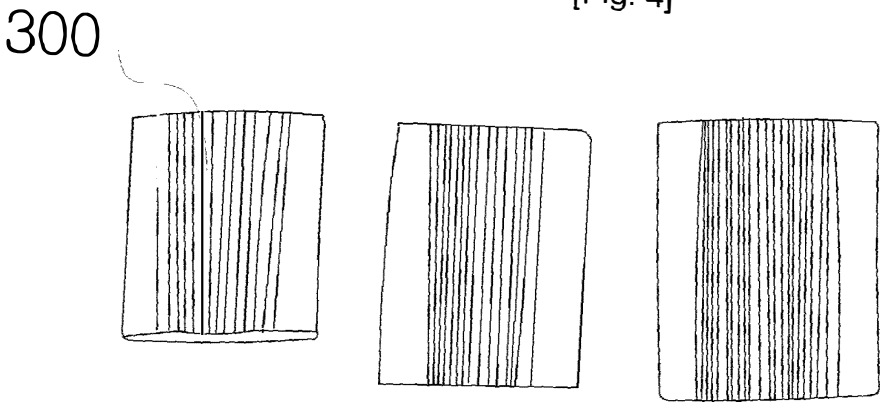
[Fig. 3]



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[Fig. 4]



INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

D21C 3/00(2006.01)i

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 8 D21B 1/14, D21C 1/02, D21C 3/26, D21H 5/14

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKIPASS (KIPO internal) Key words: "bamboo chip, cutting and tearing, bulkiness, solubility, and similar terms"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	D1: US05198074 A (Eduardo J. Villavicencio & Jose B. Dos Santos) Mar. 30, 1993 - See column 3 line 59 to column 4 line 17.	1, 2
A	D2: US04455195 A (Homan B. Kinsley) Jun 19, 1984 - See column 3 line 14 to column 4 line 24.	1, 2

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

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US05198074A	30.03.1993	BR9201155A	01.06.1993
US04455195A	19.06.1984	BR8304917A	22.11.1983
		CA1192072A1	20.08.1985
		EP97716A1	11.01.1984
		EP97716B1	13.09.1989
		FI81131B	31.05.1990
		FI81131C	10.09.1990
		FI833154A	05.09.1983
		IT1159952A	04.03.1987
		JP2004716B4	30.01.1990
		NO833139A	01.09.1983
		WO8302469A1	21.07.1983

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(54) Title: POROUS WEB MATERIAL

(57) Abstract

A fibrous, porous web material of the non-heat seal type having a basis weight of 9 to 18 g m^{-2} and comprises a first layer and a second layer juxtaposed thereto wherein the second layer has a smaller pore size than the first layer. The paper is useful for producing beverage infusion bags (e.g. teabags) from which there is minimal passage of fine particles from the bags into their packaging.

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POROUS WEB MATERIAL

The present invention relates to a fibrous, porous web material of the non-heat seal type intended for use particularly, but not exclusively, for the production of infusion sachets for brewing beverages such as tea, coffee and the like.

Infusion sachets for brewing beverages (e.g. so called teabags and coffee bags) are generally produced from either "heat seal" or "non-heat seal" fibrous porous web material (hereinafter also referred to as paper for convenience). Heat seal paper generally comprises two layers. One of these two layers includes fusible polymeric fibres which allow two layers of the paper to be heat sealed together in the production of infusion bags. The other layer is present as an insulation layer to prevent polymer (in the other layer) sticking to heated dies during conversion of the paper to produce an infusion sachet. In contrast, a non-heat seal paper (which normally has a basis weight in the range of 9 to 18 g m^{-2} and typically about 12.3 g m^{-2}) is generally comprised of a single layer comprised of vegetable fibres which does not incorporate fusible polymeric fibres. Thus, as its name suggests, non-heat seal paper cannot be heat sealed to itself. Infusion bags are produced from such paper by crimping or otherwise mechanically securing two layers of the paper together.

There is however a problem in some areas with conventional non-heat seal papers for use in the production of teabags in that fine tea dust (resulting from interaction of tea leaves during processing thereof) or fine particles of tea have a tendency to pass thorough the paper to the outside of the teabag. Since teabags are generally packaged in boxes or other types of "outer" packaging, the fine tea particles or dust are "loose" in the packaging and this is undesirable from the aesthetic viewpoint.

One possibility for overcoming this problem would be to increase the percentage of finer fibres (preferably hardwood fibres) in the stock from which the single ply paper is produced. This would result in a paper with smaller pores thus reducing the amount of fine tea or tea dust which can pass through the paper.

The increase of hardwood fibres or other short fibres in the single layer to achieve the required pore size distribution would, however, affect overall paper strength to the extent that the paper would not have sufficient strength for manufacture into infusion bags. A further disadvantage which would be associated with the use of hardwood fibres in the layer would be the incidence of pin-hole generation through air entrainment.

A further disadvantage of conventional non-heat sealpaper is that it is difficult to provide a pattern in the paper using conventional methods. The patterns which are desired are those which can readily be produced in papers of the "heat seal" type. Such patterns may comprise a matrix of perforations which are formed through the web and which are intended to allow the passage of water therethrough. Alternatively the pattern may be either a logo or other marking indicating the manufacture of either the paper or infusion sachets prepared therefrom.

Such perforations are generally formed in heat seal paper by one of two methods. Firstly the perforations may be formed by a pattern of projections (known as knuckles) on the wire on which the fibrous suspension (used for producing the paper) is produced during the "wet laying" operation. Secondly the pattern may be formed in the web by fluid jets, e.g. using a PERFOJET apparatus.

Non-heat seal paper is generally comprised of a single layer (as indicated above) and typically has a basis weight of 12.3 g m^{-2} The patterning methods discussed above cannot generally be used for such non-heat seal paper. Thus, if the paper is formed on a wire provided with knuckles, the paper cannot be easily released from the wire. This is believed to be due to the fact that the cellulosic fibres of the paper are more cohesive because of their greater contact with the wire and their wetness (and as such are therefore more difficult to release) than the cylindrical synthetic fibres in heat seal paper. If a liquid jet is used to pattern such a non-heat seal paper, the resultant material is too "open" as the jet would 'strike through' the single layer and would allow beverage precursor material (e.g. tea leaves) to pass through the paper.

It is therefore an object of the present invention to obviate or mitigate the above mentioned disadvantages.

According to the first aspect of the present invention there is provided a fibrous, porous web material of the non-heat seal type having a basis weight of 9 to 18 g m^{-2} and comprising a first layer and a second layer juxtaposed thereto wherein the second layer has a smaller pore size then the first layer.

According to the second aspect of the present invention there is provided a beverage infusion bag comprising a beverage precursor material enclosed within a sachet formed of a material in accordance with the first aspect of the invention.

In the web material of the first aspect of the invention, the second layer has a smaller pore size than the first layer. The material is such that it is capable of preventing or inhibiting passage therethrough of fine particles of a beverage precursor material (e.g. tea leaves) and such that it has the required strength for conversion to beverage infusion bags. The invention thus provides a non-heat seal paper which may be converted to tea bags from which there is minimal passage of fine particles from bags into their packaging.

Obviously the reduction in porosity as provided by the second layer is not so high as to prevent passage of water through the material during infusion of the beverage.

The material of the invention also has the advantage that it may be patterned by means of a fluid jet, as detailed more fully below.

The material of the invention preferably has a basis weight of 9 to 15 g m^{-2}, more preferably 9 to 14 g m^{-2}, even more preferably 11 to 13 g m^{-2}, and most preferably 12 to 13 g m^{-2}. Typically the basis weight will be 12.3 to 12.4 g m^{-2}.

The material of the invention may be produced in accordance with a third aspect of the invention by wet laying the first layer and, whilst draining water therefrom, laying the second layer on top of the first layer. This "two stage" production method has an advantage in that any voids in the first layer caused by air-entrainment will be filled (as a result of drainage through the voids) by the fibres of the second layer. Thus the size of the voids is reduced, contributing to the overall

reduced porosity of the web. There is the further advantage of the "two stage" process in that for a material of a particular basis weight it allows an increased speed of production as compared to the production of a single layer material of the same basis weight.

The second layer may be produced in a number of ways to ensure that it has a pore size lower than the first layer. In a preferred embodiment of the invention, the second layer is produced from fibres (e.g. hardwood fibres) which are shorter and finer than the fibres (e.g. vegetable fibres) of the first layer. Alternatively, it is possible for the second layer to comprise fibres which are coarser than those of the first layer and to be used in an amount such as to provide a highly tortuous path along which a particle would need to pass to traverse the second layer. It is this highly tortuous path which provides the required small pore size.

As indicated, it is preferred that the majority of the fibres from which the second layer is formed have a mean cross-sectional size and/or length less than those of the first layer.

Preferably the fibres in the second layer provide 10 to 50% by weight of the total weight of the web material. In a preferred material in accordance with the invention, the first layer comprises vegetable fibres and the second layer comprises hardwood fibres.

The hardwood fibres of the second layer may for example comprise 10% to 50%, preferably 20% to 40%, by weight of the total weight of the web material. The hardwood fibres preferably have a length of 0.4mm to 2.5mm and may for example have a mean length of about 0.8mm. The fibre width may be 10 to 25 microns with a mean of about 14 microns. Hardwood fibres are finer and shorter than softwood fibres. Examples of hardwood fibres which may be used include birch, beech and eucalypt. If desired, the second layer may comprise of Softwood, Sisal and/or Jute or man made fibres as part of the fibre components of the layer.

Although it is preferred that the second layer comprises hardwood fibres, it is possible for the second layer to be comprised of other fibre types.

Preferably the vegetable fibres of the first layer provide 50% to 90%, more preferably 50% to 70%, by weight of the web material. These fibres will generally have a length of 0.8mm to 9mm and may for example have a mean length of about 4.3mm. A suitable vegetable fibre is Manila (Abaca).

If desired, the first layer may comprise Sisal and/or Jute as part of the vegetable fibre component of the layer. It may also be possible to produce a similar material with man made fibres, although the preferred way would be as described above.

If desired, a proportion of the vegetable fibres of the first layer may be replaced by softwood fibres. Preferably the amount of softwood fibres does not exceed 75% by weight of the first layer. Softwood fibres are long, flat ribbon-like fibres which are readily distinguished by a person skilled in the art from vegetable fibres and hardwood fibres. The softwood fibres may have a length of 0.8mm to 5mm and a width of 12 to 60 microns. Typical means of these values are 3.8mm and 29 microns respectively. The softwood fibres may for example be obtained from spruce, pine, cedar, western hemlock, fir or redwood.

It is preferred that the web material of the invention has a thickness in the range of 30- 100μm more typically in the region of 40 - 60μm.

It should be appreciated that the invention also covers papers comprising three or more layers. Thus, it is possible in accordance with the invention to produce a paper having a central layer comprised of softwood fibres sandwiched between an outer layer comprised of Manila fibres and another outer layer comprised of hardwood fibres. The layer comprised of hardwood fibres would have the smallest pore size whereas the layer comprised of Manila fibres may have a larger pore size than the layer comprised of softwood fibres or vice versa. This construction may be modified so that the layer comprised of Manila fibres is the central layer and the layer comprised of softwood fibres forms an outer layer.

As indicated above, the material in accordance with the invention may be patterned by means of fluid jets during the paper forming step on the papermaking fabric or wire.

If the material comprises only two layers and the fibres of the second layer are shorter and finer than those of the first layer then the pattern is formed in the second layer of the material, i.e. that layer having the smaller pores. This is an important feature since the shorter fibres (of the second layer) provide good pattern definition because of their lower cohesiveness and greater ease of movement than the longer fibres of the first layer which provide strength during processing.

The ability to provide patterns in non-heat seal papers is an important aspect of the present invention in its own right and therefore in accordance with a fourth aspect of the invention there is provided a method of producing a patterned paper of the non-heat seal type comprising wet laying a first fibrous layer and subsequently a second layer thereon, and forming a pattern in the wet laid web during the paper forming step whilst the web is on the papermaking fabric or wire by means of fluid jets.

The fluid jets are preferably liquid jets, e.g. water jets. The pattern may be formed whilst the paper is on the wire by means of a patterning station which is comprised of a rotary hollow cylinder having perforations (defining the required pattern) in the wall thereof and means for directing a fluid radially outwardly through the perforations in the cylinder to form the pattern in the web. The liquid pressure is preferably 1-8 bar, more preferably 3-4 bar. The pattern may be formed using a PERFOJET apparatus.

A method of producing a web material in accordance with the invention will be described with reference to the accompanying drawing.

The web material is formed from two fibrous stocks. One stock (for forming the first layer) comprises vegetable fibres (and optionally other fibre types, e.g. softwood fibres) and the other stock (for forming the second layer) comprises hardwood fibres (and optionally other fibre types).

Typically the process for production of this paper is as follows:-

As shown in the drawing, the stock for forming the first layer 1 is laid onto a continuously moving paper forming fabric 2 from a head box 3. Water is withdrawn as shown by the arrows 4 and the second layer 5 is subsequently laid down from a further head box 6.

A pattern is formed at a patterning station 7 comprised of a rotary perforated cylinder 8 within which is located a spray-head 9 for providing liquid (preferably water) jets, which are directed through the perforations in cylinder 8. It is these perforations which provide the desired pattern. A suction box 10 serves to remove water from the web.

The liquid jet pressure is preferably 3-4 bars which causes perforations to be formed in the layer 2. There is no substantial perforation of layer 1.

Layer 5 is the one having the smaller pore size and is formed from shorter fibres than used for layer I.

The web may be passed around steam heat drying cylinders (not shown) or other drying means (e.g. gas heated through dryers) and may be subjected to further impregnation with additive at a size press (not shown). Wet or dry strength agents may be added either in the head box or the size press.

Other machine configurations could also be used.

Papers having the three layer construction may be produced using an apparatus of the type illustrated in the drawing modified by the inclusion of a third head box.

The invention is illustrated by the following non-limiting Example.

Example

A paper having a basis weight of 12.3 g m^{-2} was prepared using the procedure shown in the drawing by wet laying a first (base) layer of vegetable fibres combined with softwood and a second (top) layer of hardwood fibres which comprised 25% by weight of the total weight of the material.

Tests were conducted on the material obtained to determine how effective it was at preventing the percolation therethrough of fine sand. The sand dust percolation was determined as the percent by weight of a sample of sand having a particle size in the range 106-150 μm which would pass through the paper in a standard test which involves vibrating a horizontally disposed sample of the paper on which the sand is located.

As a result of the test, less than 10% of the sand was found to have passed through the papers. This compares with a value of 35-50% obtained using a conventional non-heat seal paper sold in the industry.

Thus the material of the invention is superior to prior art materials for use in producing beverage infusion bags (e.g. tea bags) to prevent dust therein passing outwardly through the paper.

CLAIMS

1. A fibrous, porous web material of the non-heat seal type having a basis weight of 9 to 18 g m^{-2} and comprising a first layer and a second layer juxtaposed thereto wherein the second layer has a smaller pore size than the first layer.

2. A method as claimed in claim 1 having a basis weight of 9 to 15 g m^{-2}.

3. A material as claimed in claim 2 having a basis weight of 9 to 14 g m^{-2}.

4. A material as claimed in claim 3 having a basis weight of 11 to 13 g m^{-2}.

5. A material as claimed in claim 4 having a basis weight of 12 to 13 g m^{-2}.

6. A material as claimed in any one of claims 1 to 5 wherein the majority of the fibres of the second layer are finer than the majority of the fibres of the first layer.

7. A material as claimed in any one of claims 1 to 5 wherein the first layer comprises vegetable fibres.

8. A material as claimed in claim 7 wherein the first layer comprises vegetable fibres in an amount to provide 50% to 90% by weight of the web material.

9. A material as claimed in claim 8 wherein the vegetable fibres of the first layer provide 50% to 70% by weight of the web material.

10. A material as claimed in any one of claims 7 to 9 wherein the vegetable fibres have a length of 0.8mm to 9mm.

11. A material as claimed in any one of claims 7 to 10 wherein the vegetable fibre is Manila.

12. A material as claimed in any one of claims 7 to 11 wherein the first layer also incorporates softwood fibres.

13. A material as claimed in claim 12 wherein the softwood fibres have a length of 0.8mm to 6mm.

14. A material as claimed in claim 12 or 13 wherein the softwood fibres are of spruce, pine, cedar, western hemlock, fir or redwood.

15. A material as claimed in any one of claims 1 to 14 wherein the second layer comprises hardwood fibres.

16. A material as claimed in claim 15 wherein the hardwood fibres have a length of 0.4mm to 2.5mm.

17. A material as claimed in claim 15 or 16 wherein the hardwood fibres are of birch, beech or eucalypt.

18. A material as claimed in any one of claims 15 to 17 wherein the hardwood fibres of the second layer comprise 10% to 50% by weight of the total weight of the web material.

19. A material as claimed in claim 18 wherein the hardwood fibres of the second layer comprise 20% to 40% by weight of the total weight of the web material.

20. A material as claimed in any one of claims 1 to 19 which comprises three or more layers.

21. A material as claimed in any one of claims 1 to 20 having a thickness of less than 100 μm.

22. A material as claimed in any one of claims 1 to 21 wherein a layer of the material has a pattern formed therein by means of fluid jets.

23. A material as claimed in claim 22 comprised of two layers and wherein the pattern is formed in the layer having the smaller pore size.

24. A material as claimed in claim 23 comprised of three or more layers and wherein the pattern is formed in either of the outer layers.

25. A beverage infusion bag comprising a beverage precursor material enclosed within a sachet formed of a material as claimed in any one of claims 1 to 23.

26. A method of producing a material as claimed in any one of claims 1 to 22 wherein the layers are successively wet-laid onto a paper -forming fabric or wire.

27. A method as claimed in claim 26 additionally comprising the step of forming a pattern in one of the layers by means of fluid jets.

28. A method of producing a patterned paper of the non-heat seal type comprising wet laying a first fibrous layer and subsequently a second layer thereon, and forming a pattern in the wet laid web during the paper forming step whilst the web is on the papermaking fabric or wire by means of fluid jets.

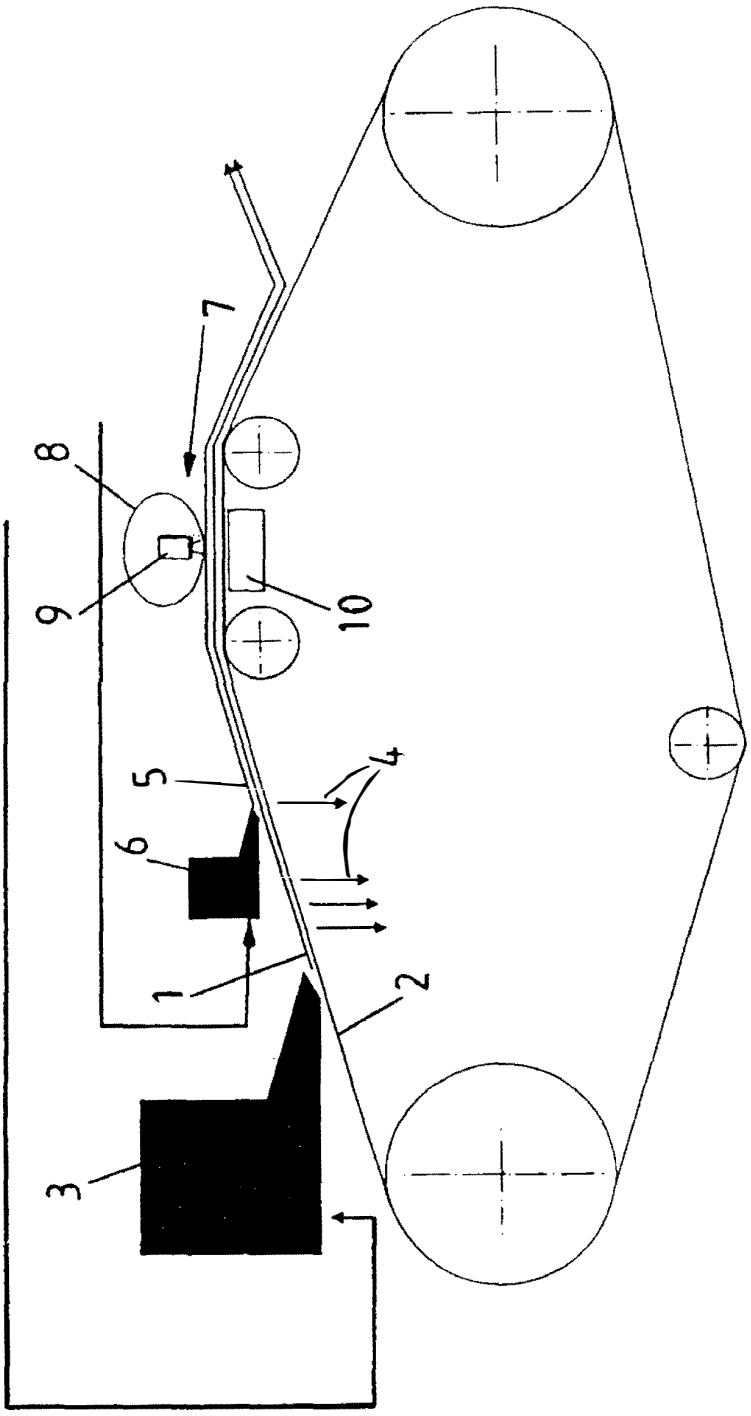
29. A method as claimed in claim 27 or 28 wherein the fluid is liquid.

30. A method as claimed in claim 29 wherein the liquid pressure is 1 to 8 bars.

31. A method as claimed in claim 30 wherein the liquid pressure is 3 to 4 bars.

32. A method as claimed in any one of claims 27 to 31 wherein the pattern is formed whilst the paper is on the wire by means of a patterning station which is comprised of a rotary hollow cylinder having perforations defining the require pattern in the wall thereof and means for directing a fluid radially outwardly through the perforations in the cylinder to form the pattern in the web.

1–1



INTERNATIONAL SEARCH REPORT

Interna' ·l Application No
PCT/GB 96/01839

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B7/02 B32B29/00 D21H27/38 D21H27/08 B65D81/00

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 6 B32B D21H B65D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,2 157 656 (RALPH N. DOBLE) 9 May 1939 see page 1, column 1, line 33 - column 2, line 2 see page 2, column 1, line 67 - column 2, line 18	1
A	EP,A,0 656 224 (PAPCEL PAPIER UND CELLULOSE TE) 7 June 1995 see column 1, line 1 - line 7; figure 1 see column 2, line 1 - line 15 see column 3, line 5 - line 20 see column 3, line 52 - column 4, line 4 see column 4, line 40 - line 50	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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

"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

"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

"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 November 1996	10. 12. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Pamies Olle, S

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

...rmation on patent family members

Internat...l Application No
PCT/GB 96/01839

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-2157656	09-05-39	NONE	
EP-A-0656224	07-06-95	DE-U- 9318405	27-01-94
		ES-T- 2074408	16-09-95
		JP-A- 7213832	15-08-95

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
16255M4-WO-JC		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US2023/017659	6 April 2023 (06-04-2023)	8 April 2022 (08-04-2022)
Applicant		
THE PROCTER & GAMBLE COMPANY		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language,** the international search was carried out on the basis of:
      [X] the international application in the language in which it was filed
      [ ] a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. [ ] This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   c. [ ] With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. [ ] **Certain claims were found unsearchable** (See Box No. II)

3. [ ] **Unity of invention is lacking** (see Box No III)

4. With regard to the **title,**
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings,**
   a. the figure of the **drawings** to be published with the abstract is Figure No. 1A
      [X] as suggested by the applicant
      [ ] as selected by this Authority, because the applicant failed to suggest a figure
      [ ] as selected by this Authority, because this figure better characterizes the invention
   b. [ ] none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/017659

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H27/30 D21H27/38
ADD.

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)
D21H

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/041986 A2 (KIMBERLY CLARK CO [US]; SHANNON THOMAS GERARD [US]) 28 March 2013 (2013-03-28) claim 9 page 11, line 15 - line 19	1-15
X	WO 97/04956 A1 (CROMPTON J R PLC [GB]; GBUR IVAN [GB] ET AL.) 13 February 1997 (1997-02-13) claims 1,8,15	1-15
X	WO 2016/173641 A1 (SCA HYGIENE PROD AB [SE]) 3 November 2016 (2016-11-03) claim 7	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 June 2023	21/06/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Ponsaud, Philippe

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2023/017659

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013041986 A2	28-03-2013	AU 2012311164 A1	06-03-2014
		BR 112014005592 A2	21-03-2017
		CA 2847064 A1	28-03-2013
		CN 103814173 A	21-05-2014
		CO 6910179 A2	31-03-2014
		EP 2758593 A2	30-07-2014
		KR 20140068073 A	05-06-2014
		MX 337233 B	18-02-2016
		TW 201319358 A	16-05-2013
		US 2013071678 A1	21-03-2013
		US 2013299107 A1	14-11-2013
		US 2014284010 A1	25-09-2014
		US 2016069029 A1	10-03-2016
		WO 2013041986 A2	28-03-2013
WO 9704956 A1	13-02-1997	AU 6624796 A	26-02-1997
		DE 69607757 T2	31-08-2000
		EP 0842043 A1	20-05-1998
		US 6139883 A	31-10-2000
		WO 9704956 A1	13-02-1997
WO 2016173641 A1	03-11-2016	AU 2015393147 A1	09-11-2017
		CN 107532385 A	02-01-2018
		CO 2017010865 A2	16-01-2018
		EC SP17078850 A	28-02-2018
		EP 3289139 A1	07-03-2018
		HK 1246833 A1	14-09-2018
		MA 41084 A1	30-11-2018
		RU 2670867 C1	25-10-2018
		SG 11201708100W A	29-11-2017
		TN 2017000446 A1	12-04-2019
		US 2018127920 A1	10-05-2018
		WO 2016173641 A1	03-11-2016

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Information on Search Strategy - Pilot phase (see OJ 2015, A86)
The type of information contained in this sheet may change during the pilot for improving the usefulness of this new service.

Application Number
PCT/US2023/017659

TITLE: THE TITLE IS AS PROVIDED ON PAGE 1 OF THE DESCRIPTION

APPLICANT: THE PROCTER & GAMBLE COMPANY

IPC CLASSIFICATION: D21H27/30, D21H27/38

EXAMINER: Ponsaud, Philippe

CONSULTED DATABASES: WPI

CLASSIFICATION SYMBOLS DEFINING EXTENT OF THE SEARCH:

IPC:

CPC: D21H27/30, D21H27/38

FI/F-TERMS:

KEYWORDS OR OTHER ELEMENTS FEATURING THE INVENTION:

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2023/017659	06.04.2023	08.04.2022

International Patent Classification (IPC) or both national classification and IPC
INV. D21H27/30 D21H27/38

Applicant
THE PROCTER & GAMBLE COMPANY

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	see form PCT/ISA/210	Ponsaud, Philippe Telephone No. -0

Form PCT/ISA/237 (Cover Sheet) (July 2022)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2023/017659

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a))

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the international application as filed.

   b. ☐ furnished subsequent to the international filing date for the purposes of international search (Rule 13*ter*.1(a)),

   ☐ accompanied by a statement to the effect that the sequence listing does not go beyond the disclosure in the international application as filed.

4. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, this opinion has been established to the extent that a meaningful opinion could be formed without a WIPO Standard ST.26 compliant sequence listing.

5. Additional comments:

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2, 3, 5-9, 11-15
	No:	Claims	1, 4, 10
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-15
Industrial applicability (IA)	Yes:	Claims	1-15
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Point VIII

1 The subject-matter of claim 1 is not clear since the fibrous composition of each layer is not defined with sufficient details so that it is not credible that any surprising and unexpected technical effect would arise for any embodiments falling within the scope of present claim 1, which is extremely broad. Thus claim 1 lacks essential features (Art. 6 PCT).

Point V

2 Reference is made to the following documents:

D1 WO 2013/041986 A2 (KIMBERLY CLARK CO [US]; SHANNON THOMAS GERARD [US]) 28 March 2013 (2013-03-28)

D2 WO 97/04956 A1 (CROMPTON J R PLC [GB]; GBUR IVAN [GB] ET AL.) 13 February 1997 (1997-02-13)

D3 WO 2016/173641 A1 (SCA HYGIENE PROD AB [SE]) 3 November 2016 (2016-11-03)

3 Independent product claim 1

Document D1 (see claim 9) discloses a multi-layer through air dried tissue product, wherein the first layer comprises wood pulp fibers and the second layer comprises at least 50% by weight of bamboo fibers. Page 11, lines 15-19 of D1 discloses that the seocnd layer comprises 50 to 100% by weight of bamboo fibers.

Document D2 (see claims 1+8+15) discloses also the subject-matter of present claim 1.

Document D3 (see claim 7) also discloses the subject-matter of present claim 1.

Thus the subject-matter of claim 1 is not novel over D1, D2 and D3 (Art. 33(2) PCT).

4 Dependent claims

Dependent claims 4 and 10 are not novel over D1 (see claim 9 of D1).

The remaining dependent claims do not appear to be inventive over any of D1, D2 or D3 combined with the common general knowledge since they contain only usual features, which are arrived at by the person skilled in the art through routine optimization work. Moreover, in view of the description, no surprising and unexpected technical effect results from these claims when taken in isolation.

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PGR2026-00078

Possible steps after receipt of the international search report (ISR) and written opinion of the International Searching Authority (WO/ISA)

General information

For all international applications, the competent International Searching Authority **(ISA)** will establish an international search report **(ISR)** accompanied by a written opinion of the International Searching Authority **(WO/ISA)**. The **WO/ISA** may be responded to by

- filing informal comments with the **International Bureau of WIPO (IB)** (where no demand for international preliminary examination **(demand)** is filed)
- filing amendments under Art. 19 PCT (this can be done whether or not a **demand** is filed)
- filing amendments under Art. 34 PCT and/or formal observations in response to objections raised in the **WO/ISA** (where a **demand** *is* actually filed)

This document explains these possibilities.

Filing informal comments

After receipt of the **ISR and WO/ISA**, the applicant may file informal comments on the **WO/ISA, directly with the IB** (see International Search and Preliminary Examination Guidelines 2.15). These will be communicated to the designated/elected Offices, together with the International Preliminary Report on Patentability **(IPRP)** at 30 months from the priority date.

Amending claims under Art. 19 PCT

The applicant may file **amended claims** under Art. 19 PCT, **directly with the IB** by the later of the following dates:

- 2 months from the date of mailing of the **ISR** and the **WO/ISA**
- 16 months from the priority date

However, any such amendment received by the **IB** after the expiration of the applicable time limit shall be **considered to have been received on time** by the **IB**, if it reaches it **before** the technical preparations for international publication have been completed (the 15th day prior to the date of publication, see PCT Applicant's Guide, International Phase, 9.013).

For further information, please see Rule 46 PCT as well as form PCT/ISA/220.

Please also note that, when filing amended claims under Art. 19 PCT, such amendments shall be **accompanied by a letter** identifying the amendments made and also the basis for the amendments in the application as originally filed (Rule 46.5(b) PCT). Where a **demand** is filed, failure to comply with this requirement may result in the amendments being ignored in the International Preliminary Examination Report **(IPER)**, see Rule 70.2(c-*bis*) PCT.

Filing a demand for international preliminary examination

In principle, the **WO/ISA** will be considered to be the written opinion of the International Preliminary Examining Authority (**IPEA**). Where the **WO/ISA** issued by the **EPO** as **ISA** gives a positive opinion on the international application and the invention to which it relates, filing a **demand** with the **EPO** as **IPEA** would normally be unnecessary, since a positive IPRP would anyway be established by the IB based on the WO/ISA (see also further below).

If the applicant wishes to file a **demand** (for example, to allow him to argue his case in international preliminary examination with regard to objections raised in a negative **WO/ISA** before the **IPEA** issues an **IPER**), this must be done before expiration of **3 months after the date of mailing of the ISR and WO/ISA** or **22 months after priority date,** whichever expires later (Rule 54*bis* PCT). Amendments under Art. 34 PCT can be filed with the IPEA, normally at the same time as filing the demand (Rule 66.1(b) PCT) or within the time limit set for reply to any written opinion issued during international preliminary examination by the **IPEA**.

If a **demand** is filed at the **EPO** as **IPEA** and no comments/amendments have been received by the time the **EPO** starts drawing up the **IPER** (Rule 66.4*bis* PCT), the **WO/ISA** will be transformed by the **IPEA** into an **IPER** (also called the **IPRP (Chapter II)** which would merely reflect the content of the **WO/ISA** (OJ 10/2011, 532). The **demand** can still be withdrawn (Art. 37 PCT).

Please also note that, when filing amendments under Art. 34 PCT, such amendments shall be accompanied by a letter which identifies the amendments made and also the basis for the amendments in the application as originally filed (Rule 66.8(a) PCT). Failure to comply with this requirement may result in the amendments being ignored in the **IPER (IPRP (Chapter II))**, see Rule 70.2(c-*bis*) PCT.

Filing a request for supplementary international search

The applicant may, with the **IB**, file a request for **supplementary international search** under Rule 45*bis*.1 PCT. The present **ISR** and **WO/ISA** may also be taken into account in the execution of that supplementary international search, provided that these are available to the Authority charged with this task before it starts the supplementary search (Rule 45*bis*.5 PCT).

This kind of request **cannot be filed specifying the ISA** who did the **international search**.

More information on this topic can be found in the **PCT Applicant's Guide**, Chapter 8 (http://www.wipo.int/pct/en/guide/ip08.html).

End of the international phase

Where no **demand** is filed, at the end of the international phase, the **IB** will transform the **WO/ISA** into the IPRP (PCT Chapter I) (Rule 44*bis* PCT), which will then be transmitted together with possible informal comments to the designated Offices. Where a demand is filed, the **WO/ISA** is not transformed into an **IPRP** (**Chapter I**) by the **IB**, but rather the **IPEA** will establish an **IPER**, (the IPER is the same as the IPRP (PCT Chapter II), see Rule 70.15 PCT).

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(54) Title: LATHER-FORMING TISSUE PAPER PRODUCT

(57) Abstract: The present invention relates to a disposable tissue paper product which feels dry to the touch and comprises a lathering surfactant in a form capable of forming lather upon contact with water, wherein said tissue paper product is obtainable by applying said lathering surfactant or a composition containing the lathering surfactant to one or more plies of dry tissue paper web, the lathering surfactant is present in an amount of 0.01 to 6 g/m^2, and, if a composition containing the lathering surfactant is applied, the total amount of non-volatile components of said composition does not exceed 20 wt.-% of the dry weight of said one or more tissue paper plies, a process for its manufacture and its use in cleaning hard surfaces.

LATHER-FORMING TISSUE PAPER PRODUCT

The present invention concerns a dry tissue paper product, in particular a dry tissue paper product capable of producing lather, a process for its manufacture, a method for cleaning a hard surface using the same and its use for cleaning hard surfaces.

TECHNICAL BACKGROUND

Aqueous-based cleansers for hard surfaces such as windows, mirrors and reflecting surfaces are well known in the art. US 4,343,725 discloses for instance such a cleanser comprising a mixture of water-soluble nonionic polyoxyethylene glycol polymer and at least one water-soluble surface active compound. It is taught that a diluted solution of these cleansers can be applied on glass surfaces by means of a sponge or cloth, or can be sprayed directly on the surface by means of a spray pump and be wiped off immediately with a chamois, a rubber squeegee, a wipe, a cloth or a paper towel. This is a rather cumbersome procedure and it would be desirable to provide an efficient cleansing system where dilution and dosage steps are omitted or simplified and the carrier of the cleansing composition itself could act as wipe.

Wet wipes are equally known in the art. Commercially available wet wipes intended for personal care typically comprise nonwoven substrates on the basis of synthetic fibers which are impregnated with cleansing, cosmetic or dermatologic compositions. Wet wipes of this type are also disclosed in WO 03/000219 A1, EP 1 222 915 A2, EP 1 210 928 A1, EP 0 058 633 A1 and US 4,448,704. US 6,730,621 B2 discloses a wet wipe belonging to the same product category and being referred to as “disposable substantially damp cleansing article”. The cleansing article is discussed in connection with personal cleansing and conditioning products and has a cleansing composition impregnated onto a flexible

substrate such as a nonwoven cloth. The impregnated compositions include lathering surfactants and water. WO 03/054132 A1 relates to an oil-absorbing cleaning tissue (dry or wet) having a polymer-surfactant complex, where the term "tissue" includes however numerous non-paper materials. Moreover, this document does neither relate to dry tissue paper wipes nor is it taught that the surfactant develops lather. CN 1073492 A also discloses a wet paper article for cleaning hard surfaces, though in view of the polishing effect to be achieved the liquid composition contains wax as essential component. Wet wipes are also disclosed in JP 1168999 A, US 6,750,160 B1, EP 0 099 209 A and EP 0 799 568 A1 while the latter two documents emphasize the disinfectant character of the cleaning composition impregnated therein. US 2002/0029984 A1 discloses a wet toilet seat wipe comprising a disinfectant cleaning solution comprising a quick-drying alcohol.

One major disadvantage of wet wipes resides in the need to provide a moisture tight package. Otherwise, the wet wipe would dry out and loose its effectiveness. Moreover, due to their content of synthetic fibers, nonwoven substrates typically used in wet wipes are not or only slowly biodegradable, and they show inferior flushability and disintegration, *e.g.* when disposed into a toilet or a sewage system. Nonwovens based on synthetic fibers moreover render it more difficult to provide the wipe in the form of rolls where the single sheets are separated by perforations or in the form of folded sheets since synthetic fibers show a much higher resistance to folding, cutting or perforation steps. In addition, nonwovens are much more expensive than tissue paper products.

Nonwovens and other thermoplastic non-paper layers are also used in the wipes of US 4,600,620, US 2003/0104750 A1 and US 2003/0104966 which all mention that the wipe can be used for cleaning hard surfaces. Some wipes for cleaning hard surfaces (e.g. US 2005/0129897, US 2002/0132747) also include abrasive

materials or layers which are typically made from a web of thermoplastic fibers.

The aforementioned drawbacks also apply to nonwoven substrates based on synthetic fibers as used in dry wipes for personal care. WO 99/013861 discloses for instance a disposable, singe use personal care cleansing and conditioning article comprising

A) a water-insoluble substrate, wherein at least a first portion is wet extensible and at least a second portion is less wet extensible than said first portion, and

B) at least one lathering surfactant added onto or impregnated into said substrate.

A similar substantially dry cleansing article with a lathering surfactant is described in WO 99/12519. A lathering surfactant is also mentioned in US 2002/0013109 which discloses a two-ply disposable article comprising a nonwoven ply. There exists also a series of patent applications in the name of Procter & Gamble including WO 96/14835 relating to a water-insoluble carrier for a solid emulsion comprising a continuous lipid phase with a high melting waxy material deposited onto the wipe substrate. The material is intended to be sufficiently brittle so as to be easily disrupted by low shear contact (for instance during wiping of the skin) to readily release an internal skin conditioning phase. Yet it is stated in the art (US 6,391,835 B1) that the continuous external lipid phase is neither sufficiently robust for processing and handling nor sufficiently releasable under cleaning conditions.

US 6,391,835 B1 discloses a disposable substantially dry cleansing article having a lathering surfactant and a C6-C12 alkyl diol impregnated into flexible substrate. As examples for the insoluble substrate, this document mentions nonwoven

substrates, woven substrates, hydro-entangled substrates and air entangled substrates. This article is referred to as personal cleansing and conditioning product which should gently cleanse the skin or hair, cause little or no irritation and not leave the skin or hair overly dry after frequent use.

A similar disposable substantially dry foamable product and its use in personal cleansing and conditioning of skin or hair is disclosed in US 6,491,937 B1.

US 5,213,884 relates to a tissue suitable for use in the disinfection of hard surfaces, etc. wherein the tissue plies are bound together with an adhesive polymer mixed with solid particles comprising a chlorine release agent. Although the use of surfactant in combination with the chlorine release agent is mentioned in this document, it is not taught to apply the same in a form and an amount entailing lather formation.

US 2004/0031107 A1 relates to a cleaning material for dry cleaning hard surfaces and textile products in the form of a planar-like structure with host substances such as cyclodextrins applied wherein said host substances may contain and release one or more active components such as surfactants. This document does not relate to tissue paper subtrates. Moreover, the use of host substances makes the manufacture of this cleaning material complicated and expensive which is to be avoided in line with the present invention.

FR 2 538 238 A discloses a cleaning sheet or web comprising a substrate impregnated with a mixture of surface active agent and fatty component and/or polyol in an amount that the substrate remains dry. This cleaning sheet does not require water for cleaning hard surfaces, apparently due to the use of relatively high polyol/surfactant ratios in the impregnating composition. According to example 1, the

impregnated serviette contained 37.4 wt.-% of the cleaning composition which is undesirably high for economic reasons. Moreover, since water is not required for cleaning, nothing is said about the capability of the surfactants to form lather.

DE 20 2004 003 519 U1 describes in very general terms a dry paper product containing washing, cleaning, personal hygiene or disinfecting compositions.

In view of this prior art it is one object of the present invention to provide an economic tissue paper product suitable for efficiently wiping hard surfaces such as furniture, kitchen appliance, windows etc.

One further object of the present invention resides in providing a disposable and degradable tissue paper product which has an excellent shelf life.

One further object of the present invention involves providing a tissue paper product showing sufficient mechanical strength during wiping, preferably with as little substrate material as possible. Moreover, it would be desirable that the tissue paper product shows at least sufficient bulk and thickness values, even if a cleaning composition has been added thereto.

One further technical object of the invention is to provide a tissue paper product that does not require moisture tight packaging or wrapping materials.

It is one further technical object to provide such a tissue paper product having an excellent cleaning effect.

According to one further technical object, the tissue paper product should be made from a material that can be dispensed in a roll of single sheets separated by perforations; or in the form of folded sheets or stacked sheets.

It is moreover one technical object of the present invention to provide a process for the manufacture of such tissue paper products, their use for cleaning hard surfaces and a cleaning process utilizing these wipes.

Further objects will become apparent from the following detailed description of the invention.

BRIEF SUMMARY OF THE INVENTION

The present invention relates to a disposable tissue paper product which feels dry to the touch and comprises a lathering surfactant in a form capable of forming lather upon contact with water, wherein

said tissue paper product is obtainable by applying said lathering surfactant or a composition containing said lathering surfactant to one or more plies of dry tissue paper web,

the lathering surfactant is present in an amount of 0.01 to 6 g/m^2, and,

if a composition containing the lathering surfactant is applied, the total amount of non-volatile components of said composition does not exceed 20 wt.-% of the dry weight of said one or more tissue paper plies.

The present invention also relates to a process for the manufacture of a disposable tissue paper product as defined above comprising the step of applying a lathering surfactant or a composition containing the same to at least one surface of one or more plies of a dry tissue paper web and a process for the manufacture of a disposable tissue paper product which feels dry to the touch and comprises a lathering surfactant, said process comprising the step of applying an aqueous composition comprising a lathering surfactant to a moving tissue paper web by means of a slot die.

Further, the present invention pertains to the use of the aforementioned tissue paper product for cleaning a hard surface and a process for cleaning a hard surface comprising the steps of wetting this tissue paper product with water and wiping over the hard surface.

DESCRIPTION OF THE FIGURES

Figure 1 shows one embodiment of an application process according to the invention wherein a liquid composition comprising a lathering surfactant is applied by means of slot die device (2) onto tissue web (1).

Figure 2 shows slot die (9), application lip (10), valve section (11) and adjustable rack (12) of a slot die device usable in the present invention.

Figure 3 shows various process parameters regarding the application of a liquid composition comprising a lathering surfactant onto tissue web (1) by means of slot die device (2).

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a disposable tissue paper product which feels dry to the touch and comprises a lathering surfactant in a form capable of forming lather (to be understood as synonymous to "foam") upon contact with water. The lather is typically formed during the wiping movement which involves the mechanical agitation of lathering surfactant and water in the presence of air. The lather formation contributes to the excellent cleaning effect achieved with the present invention. The term "in a form capable of forming lather" means that the lathering surfactant is accessible for water added to the tissue paper product. This may not be the case if the lathering surfactant is enclosed by materials having a barrier function, for

instance a continuous oil phase in W/O emulsions. How this accessibility can be achieved is known in the art.

To achieve the dry feel the water content of this tissue paper product should preferably not exceed 15 wt.-%. More preferred water contents are 12 wt.-% or less, more preferably 10 wt.-% or less, in particular 9 wt.-% or less, or 8 wt.-% or less. The water content is preferably measured according to the industrial standard DIN 54540-9.

The term “tissue paper product” is used for products made from (raw) tissue paper webs. Based on the underlying compatibility of production processes (wet laying of fiber mixtures), “tissue” production is counted among the papermaking techniques. The production of tissue is distinguished from the paper production by its lower basis weight and its much higher tensile energy absorption index.

The tensile energy absorption index is arrived at from the tensile energy absorption in which the tensile energy absorption is related to the test sample volume before inspection (length, width, thickness of sample between the clamps before tensile load). Paper and tissue paper also differ in general with regard to the modulus of elasticity that characterizes the stress-strain properties of these planar products as a material parameter.

A tissue's high tensile energy absorption index results from the outer or inner creping. The former is produced by compression of the paper web adhering to a dry cylinder as a result of the action of a creping doctor blade. The inner creping results from a difference in speed between two wires ("fabrics"). This causes the still moist, plastically deformable paper web to be internally broken up by compression and shearing, thereby rendering it more stretchable under load than an uncreped paper. A high tensile energy absorption index can also be achieved by forming the dry or wet tissue into or imparting to the dry or wet tissue

a 3D structure through the wires themselves. Most of the functional properties typical of tissue and tissue products result from the high tensile energy absorption index (see DIN EN 12625-4).

In line with the common understanding of the art, the term "tissue paper product" thus does not extend to multi-ply products that comprise plies not made from tissue paper, in particular plies from synthetic materials such as nonwoven plies. This ensures the enhanced degradability of the tissue paper product of the present invention.

The tissue paper product of the invention preferably has two or more tissue paper plies, more preferably 2 to 6 plies, for instance 3 or 4 plies. Each ply may be constituted by one, two or more layers. These layers can for instance differ in their fiber composition (long fibers, short fibers, origin of the fibers, etc.) or in the chemical treatment to which the corresponding fibers were subjected (softener, strength agents, etc.). These layers can be generated by supplying different slurries of papermaking fibers to multi-layered headboxes.

The one ply raw tissue paper used in the present invention preferably has a basis weight of 10 to 75 g/m^2, more preferably 14 to 30 g/m^2, in particular 15 to 25 g/m^2. The total basis weight of the one or more tissue webs prior to treatment with lathering surfactant preferably does not exceed 100 g/m^2, and is more preferably 20 to 80 g/m^2, in particular 25 to 75 g/m^2, for instance 30 to 70 g/m^2, or 35 to 60 g/m^2. The treatment with the lathering surfactant leads to an increase in thickness of the final product, *e.g.* of 10 to 30%, preferably 15 to 25%, and most preferably about 20% in relation to the total thickness of the one or more tissue webs prior to the treatment.

Among the plies constituting the tissue paper product, one or more plies, preferably all plies were subjected to a through

air drying (TAD) step, as explained below in further detail in connection with tissue paper manufacture.

For multiply products it is preferred that two or more plies, in particular all plies are joined with each other through mechanical ply bonding means (*e.g.*, embossing) and/or chemical ply bonding means. The structured surface resulting from embossing steps may have a positive impact on the cleaning efficiency. In the alternative, the plies of the multiply product do not adhere to each other.

The tissue paper product of the invention, and therefore also the individual plies thereof, contain as main fibrous component cellulosic fibers. To ensure the necessary flushability and/or degradability, the weight content of non-degradable, in particular synthetic fiber types should be kept as low as possible and preferably does not exceed the values of 20 wt.-% or 10 wt.-% with increasing preference. In one preferred embodiment of the invention, the fiber mixture(s) used for wet laying the raw tissue web of one or more, in particular all tissue plies consists solely of cellulosic fibers.

The cellulosic fibres to be used may be of regenerated type (e.g. Lyocell), although the use of other types of pulps is preferred. The pulps employed can be a primary fibrous material or a secondary fibrous material (recycled pulps). The pulp can stem from lignin-free or low lignin sources, such as cotton linters, esparto (alfa) grass, bagasse (e.g. cereal straw, rice straw, bamboo, or hemp), hemp fibres or flax. Preferably the pulp is produced from ligno-cellulosic material, such as softwood (which typically originates from conifers) or hardwood (typically from deciduous trees).

It is possible to use "chemical pulps" or "mechanical pulps", whereby the use of chemical pulps is preferred.

"Chemical pulps" are, according to DIN 6730, fibrous materials obtained from plant raw materials of which most non-cellulosic components have been removed by chemical pulping without substantial mechanical post treatment. "Mechanical pulp" is the general term for fibrous material made of wood entirely or almost entirely by mechanical means, optionally at increased temperatures. Mechanical pulp can be sub-divided into the purely mechanical pulps (groundwood pulp and refined mechanical pulp) as well as mechanical pulps subjected to chemical pre-treatment, such as chemo-mechanical pulp (CMP), or chemo-thermo mechanical pulp (CTMP).

In the present invention it is preferred to use chemical pulps as derived from sulfite or sulfate (Kraft) processes. These pulps can be derived from softwood or hardwood species as exemplified above.

In terms of bleaching the pulp, it is preferred to use chlorine-free bleaching steps in view of the production of environmentally sound products and process steps.

The above described cellulosic fiber materials could be used unrefined or refined (beaten). In the case of refining, a freeness level of about 17 to 35 °SR (according to DIN-ISO 5267/1, March 19, 1999)is normally applied to the long fiber fraction of the cellulose furnish and depending on the desired strength level of the final tissue web.

To enhance wet strength one or more plies, in particular all plies of the tissue paper product are preferably treated with a wet strength agent.

The wet strength agent is preferably added to the cellulosic fibers, for instance to a slurry of papermaking fibers conducted to the headbox, in such an amount, in terms of active substance, that 0.01 to 5 wt.-%, more preferably 0.01 to 3 wt.-%, in particular 0.5 to 2 wt.-%, based on the total amount of untreated cellulosic fibers are retained. If not

stated otherwise, the amount of untreated cellulosic fibers refers to the dry weight thereof, as measured according to EN 20638:1993.

The wet strength agent is preferably a cationic polymer containing cationic groups, such as positively charged quaternary nitrogen atoms. The wet strength agent can be selected from, but is not limited to urea-formaldehyde resins, melamine-formaldehyde resins, polyvinylamine, polyureide-formaldehyde resins, glyoxal-acrylamide resins and cationic materials obtained by the reaction of polyalkylene polyamines with polysaccharides such as starch and various natural gums, as well as 3-hydroxyazetidinium ion-containing resins, which are obtained by reacting nitrogen-containing polymers with epichlorohydrine. The above materials are mentioned in US 3,998,690 where also references for their disclosure are found.

The most preferred type of cationic polymer is 3-hydroxy azetidinium ion-containing resins. They include, but are not limited to, neutral or alkaline-curing thermosetting wet strength resins which can be selected from polyaminoamide-epichlorohydrine resins, polyamine-epichlorohydrine resins and aminopolymer-epichlorohydrine resins. In this context, explicit reference is made to a more detailed description of these wet strength agents in the section from column 2, line 43 to column 3, line 23 of US 5,316,623. Examples of these are the well known Kymene ® resins available from Hercules Inc. or EKA XP 4016 available from Eka Chemicals.

One or more, in particular all plies of the tissue paper product may also comprise a dry strength agent which is preferably added to the papermaking fibers in such an amount that 0.01 to 3 wt.-%, more preferably 0.1 to 2 wt.-%, based on the total amount of untreated cellusic fibers (dry weight according to EN 20638:1993) is retained by the fibers.

The dry strength agent is preferably a water-soluble anionic polymer. The water soluble anionic polymer is preferably selected from polycarboxylic acids and anhydrides such as starch-based polymers, (meth)acrylic acid-derived polymers and copolymers, maleic-anhydride-derived copolymers, vinyl copolymers of carboxylic acids and cellulose-based polymers. These can be further exemplified by polyacrylates, polymethacrylates, maleic anhydride-vinyl acetate polymers, polyvinylmethylether-maleic anhydride copolymers, methacrylic acid-acryl amide copolymers, isopropenyl acetate-maleic anhydride copolymers, itaconic acid-vinylacetate colpoymers, alpha-methyl styrene-maleic anhydride copolymers, styrene-maleic anhydride copolymers, methyl methacrylate-maleic anhydride copolymers, acrylic acid-styrene copolymers, carboxymethyl cellulose, succinic half esters of cellulose, graft polymerised polyacrylate-polyssacharide copolymers, succinic half esters of starch and oxidation products of the above-listed polyssacharides.

Preferably starch-based polymers, vinyl copolymers of carboxylic acids and cellulose-based polymers are used. Among these, the use of carboxyalkylated polysaccharides, in particular carboxyalkylated cellulose is most preferred.

The water-soluble carboxyalkylated polysaccharides include carboxymethyl cellulose (CMC), carboxymethyl hydroxycellulose (CMHEC), carboxymethyl hydroxypropylcellulose (CMHPC), carboxymethylguar (CMG), carboxymethylated locust bean gum, carboxymethyl starch and the like, and their alkali metal salts or ammonium salts.

Surprisingly, it was found that the incorporation of a lathering surfactant into a tissue paper product maintains the wet tensile strength while it improves the haptic properties (surface softness), thickness and compressibility which properties generally contribute to consumer acceptance.

The lathering surfactant to be used in the present invention is not subject to any particular limitations. By a "lathering surfactant" is meant a surfactant, which when combined with water and mechanically agitated generates a foam or lather. Not all surfactants show this property. Suitable lathering surfactants are known in the art and described for instance in "McCutcheon's, Detergents and Emulsifiers, North American edition (1986)", published by allured Publishing Corporation; "McCutcheon's, Functional materials, North American Editor (1992)", US 3,929,678, WO 99/013861, US 6,391,835 other documents cited under "technical background", and the "Handbook of Industrial Surfactants" (Third Edition 2000) compiled by Michael and Irene Ash, Synapse Information Resources, Inc.

The tissue paper product of the invention comprises preferably 0.01 to 6 g/m^2, more preferably 0.01 to 3 g/m^2, even more preferably 0.05 to 1 g/m^2 of one or more lathering surfactants. If a composition containing the lathering surfactant is applied, the total amount of non-volatile components of said composition preferably does not exceed 20 wt.-% of the raw tissue paper ply or plies (dry weight of ply or plies according to EN 20638:1993). More preferred upper limits are 15 wt.-% and 10 weight%, for instance also 8, 7, 6, 5, 4 or 3 wt.-%. "Non-volatile" components of the composition are those (e.g. lathering surfactant or water-binding agent) which cannot be removed under the drying conditions described in EN 20638:1993.

The lathering surfactant may be cationic but is preferably selected from anionic lathering surfactants, amphoteric lathering surfactants, nonionic lathering surfactants and mixtures thereof.

Among the anionic lathering surfactant useful herein are the following non-limiting examples which include the classes of:

(a1) Alkyl benzene sulfonates in which the alkyl group contains from 9 to 15 carbon atoms, preferably 11 to 14 carbon atoms in straight chain or branched chain configuration. One embodiment is a linear alkyl benzene sulfonate containing about 12 carbon atoms in the alkyl chain. Another preferred example is a linear alkyl benzene sulfonate wherein the alkyl represents a mixture of C10 and C13 alkyl which is one component in Lumorol® 4339 (Zschimmer & Schwarz, Germany).

(a2) Alkyl sufonates obtained by sulfating an alcohol having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms. The alkyl sulfates have the formula $ROSO_3^-M^+$ where R is the C_{8-22} alkyl group and M is a mono- and/or divalent cation.

(a3) Paraffin sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, in the alkyl moiety . These surfactants are commercially available as Hostapur SAS from Hoechst Celanese.

(a4) Olefin sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms. Most preferred is sodium C_{14}-C_{16} olefin sulfonate, available as Bioterge AS 40®.

(a5) Alkyl ether sulfates derived from an alcohol having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, ethoxylated with less than 30, preferably less than 12 (e.g. 1 to 4 on average) moles of ethylene oxide. One embodiment is sodium lauryl ether sulfate formed from 2 moles average ethoxylation, commercially available as Standopol ES-2®. One preferred embodiment are sodium (C10-C16)alkyl ether sulfates with preferably 1 to 4 moles of ethylene oxide on average which are present as one ingredient in Spülflott® (Tillmann GmbH) and Lumorol® 4339 and K5240 (Zschimmer & Schwarz, Germany).

(a6) Alkyl glyceryl ether sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, in the alkyl moiety.

(a7) Fatty acid ester sulfonates of the formula: $R^1CH(SO_3^-M^+)CO_2R^2$ where R^1 is straight or branched alkyl from about C_8 to C_{18}, preferably C_{12} to C_{16}, and R^2 is straight or branched alkyl from about C_1 to C_6, preferably primarily C_1, and M+ represents a mono- or divalent cation.

(a8) Secondary alcohol sulfates having 6 to 18, preferably 8 to 16 carbon atoms.

(a9) Fatty acyl isethionates having form 10 to 22 carbon atoms, with sodium cocoyl isethionate being preferred.

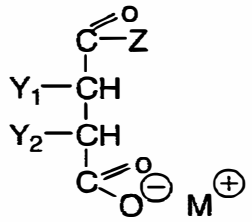
(a10) Dialkyl sulfosuccinates wherein the alkyl groups range from 3 to 20 carbon atoms each.

(a11) Alkanoyl sarcosinates corresponding to the formula $RCON(CH_3)CH_2CH_2CO_2M$ wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms and M is a water-soluble cation such as ammonium, sodium, potassium and trialkanolammonium. Most preferred is sodium lauroyl sarcosinate.

(a12) Alkyl lactylates wherein the alkyl groups range from 8 to 12 carbon atoms, with sodium lauroyl lactylate sold as Pationic 138 C® available from the Patterson Chemical Company as the most preferred.

(a13) Taurates having from 8 to 16 carbon atoms, with cocoyl methyl taurate being preferred.

(a14) Sulfosuccinates having a twofold negative charge (and either one counterion carrying the charge +2 or two counterions carrying the charge +1), in particular monoalkyl or monoacyl sulfosuccinates, preferably disodiummonoalkyl or monoacylsulfosuccinates wherein the alkyl group has from 8 to 20 carbon atoms. According to one preferred embodiment these sulfosuccinates have the following formula (1)



wherein Y_1 is hydrogen and Y_2 is $SO_3^-M^+$, or preferably Y_1 is $SO_3^-M^+$ and Y_2 is hydrogen; M^+ is the counterion, preferably sodium and Z comprises at least one alk(en)yl, alkanoyl or alkenoyl group which is bound to the terminating carbon atom of the sulfosuccinate chain by a linker preferably selected from -O-, -NH-, -O-$(CH_2CH_2$-O-$)_n$ wherein n is 0 or 1-12, i.e. (poly)alkylenoxy obtained by ethoxylating with not more than 12, preferably 1 to 4 on average moles of ethylene oxide, ethanol amide (MEA), monoisopropanol amide (MIPA) and diethanol amide (DEA). The alk(en)yl, alkanoyl or alkenoyl group may be branched or linear, preferably the latter, and has preferably from 8 to 20, more preferably 10 to 18, even more preferably 12 to 16 carbon atoms. According to one more preferred embodiment, Z = X-$(CH_2CH_2$-O$)_n$-R wherein X is -O- or -NH- and n is 0 or 1 to 4 on average and R represents an alkenyl or preferably alkyl group having from 8 to 20, preferably 10 to 18, even more preferably 12 to 16 carbon atoms.

Non-limiting commercially available examples for this class of anionic surfactants (in their INCI nomenclature) are disodium cetearyl sulfosuccinamate, disodium cetearyl sulfosuccinate, disodium cocamido DEA-sulfosuccinate, disodium cocamido MIPA-sulfosuccinate, disodium cocamido PEG-3 sulfosuccinate, disodium cocoyl sulfosuccinamate, disodium cocoyl sulfosuccinate, disodium C12-15 pareth sulfosuccinate, disodium deceth-6 sulfosuccinate, disodium dodecyloxy propyl sulfosuccinamate, disodium isodecyl sulfosuccinate, disodium lauramido DEA-sulfosuccinate, disodium lauramido MEA-sulfosuccinate, disodium laureth sulfosuccinate (one ingredient of Lumorol® K5240), disodium lauryl

sulfosuccinate, disodium myristamido MEA-sulfosuccinate, disodium nonoxynol-10 sulfosuccinate, disodium oleamido MEA-sulfosuccinate, disodium oleamido MIPA-sulfosuccinate, disodium oleth-3 sulfosuccinate, disodium N-oleyl sulfosuccinamate, disodium oleyl sulfosuccinate, disodium stearyl sulfosuccinamate, disodium tallow sulfosuccinamate and disodium undecylenamido MEA-sulfosuccinate.

Where this is not yet explicitly indicated it is preferred that the positive counterion(s) present in the anionic surfactants according to item (1) to (14) are (an) ammonium or alkali metal ion(s), such as potassium and in particular sodium ion(s).

In addition, reference can be made to the description of anionic lathering surfactants in EP 1 011 630 B1 (based on WO 99/013861), specifically par. [0124] to [0134] said passage being incorporated by reference.

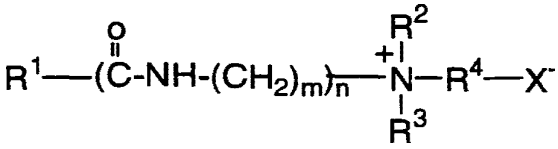
Amphoteric lathering surfactants useful for the present invention include aliphatic secondary and tertiary amines, preferably wherein the nitrogen is in a cationic state, in which the aliphatic radicals can be straight or branched chain and wherein one of the radicals contains an ionisable water solubilizing group such as carboxy, sulphonate, sulphate, phosphate or phosphonate. Illustrative substances are cocamidopropyl betaine (one component of Lumorol® K 5240), cocamphoacetate, cocamphodiacetate, cocamphopropionate, cocamphodioproprionate, cocamidopropyl PG-dimonium chloride phosphate, coco dimethyl carboxymethyl betaine, cetyl dimethyl betaine and combination thereof.

As regards non-limiting examples of amphoteric lathering surfactants reference is also made to the description found in par. [0141] to [0150] of EP 1 011 630 B1 which is also incorporated by reference.

Nonlimiting examples of amphoteric or zwitterionic surfactants are those selected from the group consisting of betaines, sultaines, hydroxysultaines, alkyliminoacetates, iminodialkanoates, aminoalkanoates, and mixtures thereof.

Examples of betaines include the higher alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, cetyl dimethyl betaine (available as Lonzaine 16SP from Lonza Corp.), lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine, coco dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis (2-hydroxyethyl) sulfopropyl betaine, amido-betaines and amidosulfobetaines (wherein the $RCONH(CH_2)_3$ radical is attached to the nitrogen atom of the betaine), oleyl betaine (available as amphoteric Velvetex OLB-50 from Henkel), and cocamidopropyl betaine (available as Velvetex BK-35 and BA-35 from Henkel).

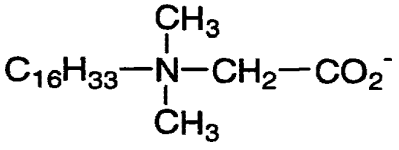
Examples of sultaines and hydroxysultaines include materials such as cocamidopropyl hydroxysultaine (available as Mirataine CBS from Rhone-Poulenc). Preferred for use herein are amphoteric surfactants having the following formula (2):



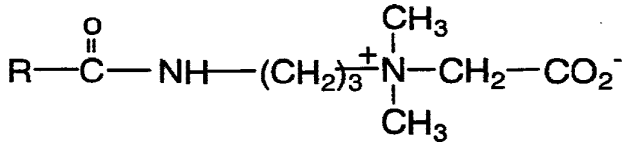
wherein R^1 is unsubstituted, saturated or unsaturated, straight or branched chain alkyl having from 9 to 22 carbon atoms. Preferred R^1 has from 11 to 18 carbon atoms; more preferably from 12 to 18 carbon atoms; more preferably still from 14 to 18 carbon atoms; m is an integer from 1 to 3, more preferably from 2 to 3, and more preferably 3; n is either 0 or 1, preferably 1; R^2 and R^3 are independently selected from the groups consisting of alkyl having from 1 to 3 carbon

atoms, unsubstituted or mono-substituted with hydroxy, preferred R^2 and R^3 are CH_3; X is selected from the groups consisting of CO_2, SO_3 and SO_4; R^4 is selected from the group consisting of saturated or unsaturated, straight or branched chain alkyl, unsubstituted or monosubstituted with hydroxy, having 1 to 5 carbon atoms. When X is CO_2, R^4 preferably has 1 or 3 carbon atoms, more preferably 1 carbon atom. When X is SO_3 or SO_4, R^4 preferably has from 2 to 4 carbon atoms, more preferably 3 carbon atoms. Examples of amphoteric surfactants of the present invention include the following compounds:

Cetyl dimethyl betaine (this material also has the CTFA designation cetyl betaine)

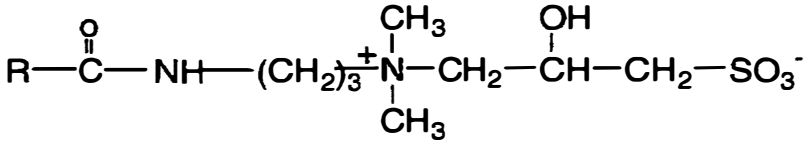


Cocamidopropylbetaine



wherein R has from 9 to 13 carbon atoms

Cocamidopropyl hydroxyl sultaine



wherein R has from 9 to 13 carbon atoms.

Examples of other useful amphoteric surfactants are alkyliminoacetates, and iminodialkanoates and amino-alkanoates of the formulas $RN[(CH_2)_m-CO_2M]_2$ and $RNH(CH_2)_m-CO_2M$ wherein m is from 1 to 4, R is a C_8-C_{22} alkyl or alkenyl, and M is H, alkali metal, alkaline earth metal,

ammonium, or alkanolammonium. Also included are imidazolinium and ammonium derivatives. Specific examples of suitable amphoteric surfactants include sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091 and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378. Other examples of useful amphoterics include amphoteric phosphates, such as coamido-propyl PG-dimonium chloride phosphate (commercially available as Monaquat PTC, from Mona Corp.). Also useful are amphoacetates such as disodium lauroamphodiacetate, sodium lauroamphoacetate, and mixtures thereof.

The nonionic surfactant is preferably selected from amine oxides, alkylglucosides, alkylpolyglucosides, polyhydroxy fatty acid amides, alkoxylated mono- and di-fatty acid esters, alkoxylated fatty alcohols, alkoxylated alkylphenols, fatty acid monoglycerides, polyoxyethylene sorbitan, lathering sucrose esters (e.g. sorbitan mono-and di fatty acids), and mixtures thereof as well as N-(hydroxyalkyl)-fatty acid amides and mixtures of these with any of the above nonionic surfactants

(n1) Amine oxides preferably correspond to the general formula (1)

$$R^1R^2R^3NO \quad (1)$$

wherein R^1 is an alkyl, alkenyl or monohydroxy alkyl radical of from 8 to 22, in particular 12 to 18 carbon atoms, wherein said alkyl, alkenyl or monohydroxy alkyl may be linked to 0 to 10 ethylene oxide moieties, and/or 0 to 1 glyceryl moiety, and R^2 and R^3 are aliphatic groups containing from about 1 to 3 carbon atoms and from 0 to 1 hydroxy group, e.g. methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl. The amine oxide may also represent a mixture wherein for instance

R^1 differs in the number of carbon atoms. This is frequently the case if the alkyl, alkenyl or monohydroxy alkyl is derived from natural fatty acid mixtures such as occurring in coconut (cocamine oxide).

Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyldimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide. According to one embodiment, the amine oxide lathering surfactant is alkyl dimethyl amine oxide, in particular coco dimethyl amine oxide.

(n2) Alkylglucosides and alkylpolyglucosides are useful herein, and can be broadly defined as condensation products of long chain alcohols, e.g. C8-30 alcohols, with sugars or starches or sugar or starch polymers, i.e., glycosides or polyglycosides. These compounds can be represented by the formula (S)n-O-R wherein S is a sugar moiety such as glucose, fructose, mannose, and galactose; n is an integer of from 1 to 1000, and R is a C8-30 alkyl group. Examples of long chain alcohols from which the alkyl group can be derived include decyl alcohol, cetyl alcohol, stearyl alcohol, lauryl alcohol, myristyl alcohol, oleyl alcohol, and the like. Preferred examples of these surfactants include those wherein S is a glucose moiety, R is a C8-20 alkyl group, and n is an integer of from 1 to 9. Commercially available examples of these surfactants include decyl polyglucoside (available as APG 325 CS from Henkel) and lauryl polyglucoside (available as APG 600CS and 625 CS from Henkel). Also useful are sucrose ester surfactants such as sucrose cocoate and sucrose laurate.

(n3) Other useful nonionic surfactants include polyhydroxy fatty acid amide surfactants, more specific examples of which

include glucosamides, corresponding to the structural formula (2).

$$R^5\text{-}C(=O)\text{-}N(R^4)\text{-}Z \quad (2)$$

wherein: R^4 is H, C1-C4 alkyl, 2-hydroxyethyl, 2-hydroxypropyl, preferably C1-C4 alkyl, more preferably methyl or ethyl, most preferably methyl; R^5 is C5-C31 alkyl or alkenyl, preferably C7-C19 alkyl or alkenyl, more preferably C9-C17 alkyl or alkenyl, most preferably C11-C15 alkyl or alkenyl; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably is a sugar moiety selected from the group consisting of glucose, fructose, maltose, lactose, galactose, mannose, xylose, and mixtures thereof. An especially preferred surfactant corresponding to the above structure is coconut alkyl N-methyl glucoside amide (i.e., wherein the R^5CO-moiety is derived from coconut oil fatty acids). Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent No. 2,965,576, to E.R. Wilson, issued December 20, 1960, U.S. Patent No. 2,703,798, to A.M. Schwartz, issued March 8, 1955; and U.S. Patent No. 1,985,424, to Piggot, issued December 25, 1934.

(n4) Preferred alkoxylated mono- and di- fatty acid esters include the condensation products of 1 to 100 mol (e.g. 2 to 50 mol) of ethylene oxide or propylene oxide with 1 mol (monoester) or 2 mol (diester) of fatty acids having preferably from 8 to 20 carbon atoms. Mono- and di- fatty acid esters of ethylene glycol (condensation product of 1 mol ethylenoxide) include for instance ethylene glycol distearate.

(n5) Alkoxylated fatty alcohols preferably include the condensation products of C10-C20 fatty alcohols with from 1 or 2 to 100 mol, in particular 2 to 12 mol of ethylene oxide or propylene oxide. The fatty alcohol may be branched or linear and has preferably from 10 to 16 carbon atoms. Examples for commercially available foam-building alkoxylated fatty alcohols include the following (INCI nomenclature): C10-C12 pareth-5, C12-14 pareth-7, isodeceth-6, isoundeceth-3, isoundeceth-6, isoundeceth-9, isoundeceth-12, laureth-2, trideceth-8, trideceth-15, C12-16 pareth with various average ethoxylation degrees (-1,-2,-3,-5,-6,-7,-8 or -11), C14-16 pareth-7, steareth-200, trideceth, trideth-10, isodeceth-11, trideceth-11, oleth-25.

(n6) Alkoxylated alkylphenols are preferably obtained by condensing C2-C10 alkylphenols with from 2 to 20 mols of alkylene oxides such as ethylene oxide or propylene oxide.

(n7) Preferred fatty acid monoglycerides are obtained by esterifying one hydroxyl group of glycerol with one fatty acid having preferably from 8 to 20 carbon atoms.

(n8) Preferred polyoxyethylene sorbitan surfactants include polyoxyethylene residues derived from 2 to 100 mol of ethylene oxide and are for instance commercially available as Polysorbate® 80 and Tween® 80.

(n9) Lathering sucrose esters are preferably derived from sucrose and a fatty acid having preferably 8 to 22, in particular 12 to 18 C atoms, such as sucrose cocoate or sucrose laurate.

(n10) N-(hydroxylalkyl)-fatty acid amides can be obtained by the amidation reaction of a fatty acid and an amino alcohol component. The amino alcohol component preferably represents an amino alcohol having a primary or secondary amine group, one or two hydroxy groups and two, three or four carbon atoms. Preferred embodiments of this amino alcohol component

are monoethanol amine (MEA), diethanol amine (DEA) or monoisopropanol amine (MIPA). The fatty acid component may be saturated or unsaturated, for instance monounsatured. The fatty acid component preferably has 10 to 20 carbon atoms, for instance 12 to 18 carbon atoms. The fatty acid component may be linear or branched. Linear saturated fatty acids are preferred. Commercially available examples of foam building surfactants belonging to this class are (in their INCI nomenclature) isosteramide DEA, lauramide MEA, lauramide MIPA, myristamide MEA, lauramide DEA, oleamide MIPA, palm kernel amide MEA, myristamide MEA, palm kernel amide DEA, cocamide DEA, myristamide DEA and cocamide DEA.

It is preferred to apply the lathering surfactant(s) and optionally other components mentioned hereinafter as aqueous solution to the tissue web. Such aqueous solutions are commercially available, for instance Spülflott® "Standard" (available from Tillmann GmbH, Germany) or Lumorol® 4339 or Lumorol® K 5240 available from Zschimmer & Scharz, Germany. The content of active substances in these commercially available surfactant solutions can vary considerably. In general, suitable aqueous solutions have a content of active substances (total surfactants) in the order of 5 to 80, in particular 15 to 70 wt-%. To optimize application of the respective surfactant solution the same can be diluted or concentrated.

According to the present invention, the following commercially available foam-building surfactants (in their INCI nomenclature) can be used:

Ammonium deceth sulfate, ammonium nonoxynol-6 sulfate, Cocamide MIPA, Coco-betaine, Cocodihydroxyethylamine oxide, Coco hydroxyethyl PEG-imidazolinium chloride phosphate, Coco oleamidopropyl betaine, Cycloneopentyl, cyclo (dimethylaminoethyl) pyrophosphato zirconate, dimesyl salt, DEA-myreth sulfate, Di (butyl, methyl pyrophosphato) ethylene titanate di (dioctyl, hydrogen phosphite), Dicyclo

(dioctyl) pyrophosphato dioctyl titanate, Dicyclo (dioctyl) pyrophosphato titanate, Di (dioctylphosphato) ethylene titanate, Di (dioctylpyrophosphato) ethylene titanate, Disodium caproamphodiacetate, Disodium caproamphodipropionate, Isopropanolamine lauryl sulfate, Isopropyl titanium triisostearate, Isostearamido-propyl morpholine lactate, Lauramidopropylamine oxide, Lauroampho PEG-glycinate phosphate, Lauroyl chloride, Minkamidopropylamine oxide, N-Octyl pyrrolidone, PEG-6 cocamide MEA; PEG-5 lauramide, PEG-10-PPG-10 glyceryl stearate, PEG 20-PPG-10 glyceryl stearate, PEG-80 sorbitan laurate, Potassium lauryl sulfate, Sesamdiopropyl dimethylamine lactate, Sodium C9-14 alkyl sulfate, Sodium coco-glucoside tartate, Sodium cocomonoglyceride sulfate, Sodium C12-15 pareth-3-sulfate, Sodium isodecyl sulfate, Sodium lauramido DEA-sulfosuccinate, Sodium laureth-5 carboxylate, Sodium lauroamphoacetate, Sodium lauroyl methylaminopropionate, Sodium lauryl sulfoacetate, Sodium methyl myristoyl taurate, Sodium nonoxynol-6 sulfate, Sodium oleoamphohydroxypropylsulfonate, Sodium oleoamphopropionate, Sodium N-oleoyl sarcosinate, Sodium tallamphopropionate, Sodium trideceth-3 carboxylate, Sodium trideceth-6 carboxylate, Sodium triacylbenzene sulfonate, Stearamidopropylamine oxide, Tallowamidopropyl hydroxyl-sultaine, Tetra (2,dialkyloxymethyl)-1 butoxy titanium di (ditridecyl)phosphite, Wheat germamidopropylamine oxide, Sodium C12-C15 alkyl sulfate, Oleoyl sarcosine, Stearoyl sarcosine, Coco propionate, Disodium tallow aminodipropionate, DEA-lauryl sulfate, Undecylenoyl collagen amino acids, Disodium oleamido MIPA-sulfosuccinate, Canolamidopropyl betaine, Cocaminobutyric acid, Cocodimethylammonium-3-sulfopropylbetaine, Cocoiminiodipropionate, Cocoyl sarcosine, DEA-lauryl sulfate, Mixed isopropanolamines lauryl sulfate, Myristoyl sarcosine, Octoxynol-50, Oleamide MIPA, Oleoyl sarcosine, Sodium caproyl lactylate, Sodium cocoamphoacetate, Sodium cocamphohydroxypropyl sulfonate, Sodium cocaamphopropionate, Sodium cocoyl isethionate, Sodium deceth sulfate, Sodium

laureth-12 sulfate, Sodium lauryl phosphate, Sodium methyl cocoyl taurate, Sodium methyl oleoyl taurate, Sodium myristoyl sarcosinate, Sodium myristyl sulfate, Sodiumm nonoxynol-4-sulfate, Steapyrium chloride, Stearamide, Stearoyl sarcosine, TEA-lauryl sulfate, Trideceth-3 carboxylic acid, Sodium lauroyl sarcosinate, Sodium methyl cocoyl taurate, Sodium cocoyl isetionate, C12-C14 alkyl dimethyl betaine, Cocoamidopropyl hydroxysultaine, Cocamidopropyl sulfobetaine, Cocodimethylammonium-3-sulfopropylbetaine, Hydrolyzed wheat protein, Lauryl betaine, Lauryl hydroxysultaine, PEG-3 cocamide MEA, Stearamide, Disodium cocoamphodipropionate, Lauramidopropyl betaine, Sodium nonoxynol-4 sulfate, Sodium trideceth sulfate, isostearamidopropyl betaine, Ammonium lauryl sulfate, Oleoyl sarcosine, Sodium caproamphoacetate, Sodium cocoamphopropionate, Sodium nonoxynol-4 sulfate, TEA-lauryl sulfate, Sodium/TEA-lauroyl hydrolyzed collagen amino acids, TEA-lauroyl keratin amino acids, Oleyl betaine, Ammonium decyl sulfate, Ammonium lauryl sulfate, Ammonium 2-ethylhexanol sulfate, TEA-dodecylbenzenesulfonate, Sodium laureth sulfate, Babassuamidopropylamine oxide, Babassuamidopropyl betaine, Caparamide DEA, Disodium lauroamphodiacetate, Minkamidopropyl betaine, PEG-3 cocamide, PEG-6 lauramide, Sesamidopropyl betaine, Wheat germamidopropyl betaine, Cocamine oxide, Myristamine oxide, Sodioum lauryl sulfate, Lauryl betaine, Sodium lauroyl sarcosinate, Almondamidopropalkonium chloride, Babassamidopropalkonium chloride, Babassamidopropyl dimethylamine lactate, Bisisostearamidopropyl ethoxyethyl dimonium chloride, Capryloyl hydrolyzed collagen, Oleamidopropyl betaine, Olivamidopropalkonium chloride, Palmitoyl collagen amino acids, Sodium cocoyl hydrolyzed soy protein, Stearamidopropyl cetearyl dimonium tosylate, Sucrose ricinoleate, Wheat germamidopropalkonium chloride, Cocoyl sarcosine, Sodium nonoxynol-4 sulfate, Deceth-4 phosphate, Myristamine oxide, Palmitamine oxide, Sodium cocoamphohydroxypropyl sulfonate, Sodium lauroyl sarcosinate, DEA laurate sulfate, Oleoyl sarcosine, Potassium

dihydroxyethyl cocoamine oxide phosphate, Sodium cocoamphopropionate, Sodium α sulfomethyl cocoate, Sodium myristyl sulfate, Stearoyl sarcosine, Bisisostearamidopropyl ethoxyethyl dimonium chloride, C12-14 alkyl dimethyl betaine, Lapyrium chloride, Laurly/myristyl betaine, Oleamine oxide, Sodium cocoamphohydroxypropyl sulfonate, Sodium lauroyl sarcosinate, Sodium methyl oleoyl taurate, Steapyrium chloride, Cocoyl sarcosine, DEA-laureth sulfate, Oleoyl sarcosine, Sodium cocoamphoacetate, Sodium cocoamphopropionate, Sodium C12-15 pareth sulfate, Myristoyl sarcosine, TEA-lauryl sulfate, Myristamine oxide, Cocaminobutyric acid, Sodium oleyl sulfosuccinamate, C12-14 alkyl dimethyl betaine, Ammonium lauryl sulfate, Canolamidopropyl betaine, Cocamidopropyl betaine, Sodium/magnesium laureth sulfate, Sodium caproamphoacetate, Trisodium lauroampho PG-acetate phosphate chloride, Sodium laureth sulfosuccinate, Sodium lauryl sulfosuccinate, Ammonium lauryl sulfate, Ammonium/TEA lauryl sulfate, Cocamidopropyl hydroxysultaine, Cocamidopropyl sulfobetaine, Disodium cocamphodiacetate, Distearyldimonium chloride, Lapyrium chloride, Lauryl/myristyl betaine, Linoleamidopropyl betaine, Milk lipid amiodpropylamine oxide, Mixed isopropanolamines myristate, Oleyl betaine, Palmitamine oxide, PPG-1 hydroxyethyl caprylamide, PPG-2 hydroxyethyl cocamide, hydroxyethyl linoleamide, Quaternium-76 hydrolyzed collagen, Silicone quaternium-2, Sodium C12-15 alkoxypropyl iminodipropionate, Sodium C12-15 alkyl sulfate, Sodium C14-16 olefin sulfonate, Sodium decylbenzene sulfonate, Sodium laureth-13 acetate, Sodium/magnesium laureth sulfate, Sodium methyl cocoyl taurate, Sodium trideceth sulfate, Soyamidopropylamine oxide, Soyamidopropyl betaine, TEA-ammonium lauryl sulfate, TEA-cocoyl hydrolyzed collagen, Sodium lauroyl oat aminoacids, Ammonium lauryl sulfate, Cocoyl sarcosine, DEA-lauryl sulfate, Disodium cocoamphodiacetate, Magnesium lauryl sulfate, Sodium lauroyl sarcosinate, Sodium methyl cocoyl taurate, Cocoyl sarcosine, Sodium myristoyl sarcosinate, Sodium nonoxynol-4 sulfate, C12-14 alkyl dimethyl betaine, Canolamidopropyl betaine,

Cocamidopropyl betaine, Cocamidopropyl sulfobetaine, cocamine oxide, DEA-laureth sulfate, Disodium cocamido DEA-sulfosuccinate, Disodium cocoamphodipropionate, Isostearamidopropyl betaine, Lauramidopropyl betaine, Lauramidopropyl dimethyl betaine, Lauryl betaine, Magnesium lauryl sulfate, Myristamidopropyl dimethylamine dimethicone copolyol phosphate, Myristamine oxide, Sodium C12-15 alkoxypropyl iminodipropionate, Sodium cocoyl isethionate, Sodium lauroyl sarcosinate, Sodium myristoyl sarcosinate, Sodium/TEA-lauroyl hydrolyzed collagen amino acids, TEA-lauroyl keratin amino acids, TEA-lauryl sulfate, Capryloyl hydrolyzed collagen, Undecylenoyl collagen amino acids, Bisisostearamidopropyl ethoxyethyl dimonium chloride, Capryloyl hydrolyzed collagen, Dipalmitoyl hydroxyproline, Oleamidopropyl betaine, Olivamidopropyl betaine, Palmitoyl collagen amino acids, Sodium cocoyl hydrolyzed soy protein, Undecylenoyl collagen amino acids, Disodium cocoamphodipropionate, Capryloyl hydrolyzed collagen, Palmitoyl collagen amino acids, Sodium stearyl sulfosuccinamate, Undecylenoyl collagen amino acids, Sodium cocoyl hydrolyzed collagen, Cocamidopropyl PG-dimonium chloride phosphate, TEA-cocoyl hydrolyzed soy protein, Cocamidopropyl PG-dimonium chloride phosphate, Myristamidopropyl dimethylamine dimethicone copolyol phosphate, Sodium stearyl sulfosuccinamate, Lauramine oxide, Sodium lauroyl sarcosinate, Disodium nonoxynol-10 sulfosuccinate, Ammonium decyl sulfate, Cocodimethylammonium-3-sulfopropylbetaine, Cocoyl sarcosine, Isohexylpropylamine, Lauryl betaine, Oleamidopropyl betaine, Oleoyl sarcosine, Sodium cocoamphoacetate, Sodium C12-15 pareth sulfate, Sodium triaceth sulfate, Stearoyl sarcosine, Magnesium lauryl sulfate, TEA-lauryl sulfate, Sodium methyl lauroyl taurate, Sodium methyl palmitoyl taurate, Sodium methyl stearoyl taurate, Lauramine oxide, C13-15 dimethyl amine oxide, Dihydroxyethyl tallowamine oxide, Almondamidopropyl betaine, Lauroyl sarcosine, Cocamidopropylamine oxide, Palmitoyl collagen amino acids, Undecylenoyl collagen amino acids, Dihydroxyethyl cocamine oxide,

TEA-lauryl sulfate, Ammonium decyl sulfate, Disodium lauraminodipropionate, Myristamine oxide, Lauramidopropyl dimethyl betaine, Linoleamidopropyl betaine, Canolamidopropyl betaine, TEA-lauroyl keratin amino acids.

The term "aqueous" means that water is the main solvent (per volume) of the lathering surfactant, but does not exclude the presence of water-miscible solvents, such as aliphatic alcohols (in this respect polyols are not counted among the solvents). It is however preferred that water is the only solvent.

It is neither necessary nor preferred that the lathering surfactant is present as polymer-surfactant complex as described for instance in WO 03/054132.

The tissue product of the present invention may also comprise a water-binding agent, in particular a polyhydric alcohol. Typical polyhydric alcohols include glycerol, polyalkyleneglycols and alkylene polyols and their derivatives, including propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol (for instance those having an average molecular weight of 200 to 2.000.000) and derivative thereof, sorbitol, hydroxypropyl sorbitol, hexylglycol, 1,3-butylene glycol, 1,2,6-hexantriol, ethoxylated glycerol, propoxylated glycerol and mixtures thereof.

According to one embodiment of the present invention, the lathering surfactant (e.g. of nonionic, anionic or amphoteric type) or a mixture thereof is combined with a water-binding agent selected from C5-C12 alkyl diols such as propylene glycol, hexylene glycol, octylene glycol, decylene diol and dodecylene diol. However, according to another embodiment, the above C5-C12 alkyl diol is not used.

Whatever type of water-binding agent is employed, the weight ratio of water-binding agent(s) to lathering surfactant(s)

preferably ranges from 1/2 to 1/10, more preferably from 1/1 to 1/8, and is for instance 1/2 to 1/6 or 1/2.5 to 1/4.

According to one further embodiment of the present invention, the composition comprising the lathering surfactant or a mixture of lathering surfactants comprises at least one alkoxylated fatty acid partial glyceride. The fatty acid glyceride comprises, preferably as main component by weight, mono- and/or diglycerides of a fatty acid (mixture) having preferably from 10 to 20, in particular 12 to 18 carbon atoms, as occurring in a fatty acid mixture derived from coconut. This partial glyceride is alkoxylated, preferably ethoxylated with preferably 1 to 100, in particular 2 to 12 mol ethyleneoxide. One commercially available surfactant of this type is PEG-9 cocoglyceride as used in Lumorol® K 5240 (Zschimmer & Schwarz, Germany)

A perfume may also be added to the tissue paper product of the invention, for instance by incorporating the same into the aqueous surfactant composition to be applied.

The tissue paper product of the invention preferably comprises a mixture of anionic and amphoteric lathering surfactants or a mixture of anionic and nonionic lathering surfcactants. In the first mixture the total content of anionic lathering surfactants and the total content of amphoteric lathering surfactants, respectively, may each be at least 5, for instance at least 10, at least 15, at least 20, at least 25 or at least 30 parts by weight based on the entire mixture of lathering surfactants, for instance based on the entire mixture of anionic and amphoteric lathering surfactants, if no other lathering surfactants are present. In the second mixture the total content of anionic lathering surfactants and the total content of nonionic lathering surfactants, respectively, may each be at least 5, for instance at least 10, at least 15, at least 20, at least 25 or at least 30 parts by weight based on the entire mixture of lathering surfactants, for instance based on the entire

mixture of anionic and nonionic lathering surfactants, if no other lathering surfactants are present. If other surfactants are present, these weight ratios preferably also apply to the entire mixture of surfactants.

In the above mixtures (anionic/amphoteric or anionic/nonionic) at least one anionic lathering surfactant can be selected from the above classes (a1) to (a14), at least one nonionic lathering surfactant can be selected from the above classes (n1) to (n10) and at least one amphoteric surfactant can be selected from betaines, sultaines, hydroxysultaines, alkyliminoacetates, iminodialkanolates, aminoalkanoates as described above. The anionic, amphoteric or nonionic lathering surfactant may also be selected from the above-identified commercially available surfactant types.

According to one preferred embodiment (A), the aqueous composition comprising a lathering surfactant comprises a mixture of

- at least one (e.g. 1, 2, 3) anionic lathering surfactant, preferably belonging to one of the above classes (a1), (a2), (a3), (a4), (a5), (a6), (a7), (a8), (a9), (a10), (a11), (a12), (a13), (a14), or mixtures thereof, for instance one or more of the above-identified commercially available surfactants, more preferably (a5) an alkylether sulfate, in particular (C10-C16) alkyl ethoxylate sulphuric acid, sodium salt, and

- at least one (e.g. 1, 2, 3) amphoteric lathering surfactant, preferably one selected from betaines, sultaines, hydroxysultaines, alkyliminoacetates, iminodialkanoates, aminoalkanoates, and mixtures thereof, for instance one or more of the above-identified commercially available surfactants, in particular one combining a tertiary amine in a cationic state and a carboxy group, such as occurring in

betaines, more preferably a surfactant of formula (2), in particular cocamidopropyl betaine.

In this embodiment (A) the anionic lathering surfactant(s) is preferably present in a higher weight ratio than the amphoteric lathering surfactant(s). Preferably, the amount of anionic lathering surfactant(s) is at least 25 to 75 parts by weight and that of the amphoteric lathering surfactant(s) less than 25 parts by weight based on the entire mixture of lathering surfactants, preferably based on the entire mixture of surfactants, if applicable. The amphoteric lathering surfactant(s) is preferably added in an amount corresponding to at least 1, for instance at least 2, at least 5, at least 10, at least 15 or at least 20 parts by weight based on the entire mixture of lathering surfactants, preferably based on the entire mixture of surfactants, if applicable. According to this embodiment, the aqueous mixture comprising a lathering surfactant may also comprise an inorganic or organic acid, such as citric acid. An aqueous surfactant solution of this type is commercially available under the trade name Spülflott® from Tillmann GmbH, Germany.

According to one further preferred embodiment (B), the aqueous solution comprising a lathering surfactant comprises a mixture of

- at least one (e.g. 1, 2, 3) anionic lathering surfactant, preferably belonging to one of the above classes (a1), (a2), (a3), (a4), (a5), (a6), (a7), (a8), (a9), (a10), (a11), (a12), (a13), (a14), or mixtures thereof, for instance one or more of the above-identified commercially available surfactants, in particular (a1) an alkylbenzene sulfonate such as the sodium salt of a C10-C13 alkyl benzene sulfonate and/or (a5) an alkyl ether sulfate, and

- at least one (e.g. 1, 2, 3) nonionic lathering surfactant, preferably belonging to one of the above

classes (n1), (n2), (n3), (n4), (n5), (n6), (n7), (n8), (n9), (n10), or mixtures thereof, for instance one or more of the above-identified commercially available surfactants, in particular (n5) a fatty alcohol ethoxylate and/or (n10) a N-hydroxy alkyl-fatty acid amide such as fatty acid diethanol amide (DEA).

In this embodiment the total content of anionic and nonionic lathering surfactants, respectively, is each at least 5, for instance at least 10, at least 15, at least 20, at least 25, at least 30 parts by weight based on the entire mixture of lathering surfactants, preferably based on the entire mixture of surfactants, if applicable. One commercially available aqueous surfactant solution of this type is Lumorol® 4339 which is available from Zschimmer & Schwarz, Germany.

According to further preferred embodiment (C), the aqueous solution comprising a lathering surfactant comprises a mixture of

- at least two (e.g. 2, 3, 4) anionic lathering surfactants, preferably belonging to at least two of the above classes (a1), (a2), (a3), (a4), (a5), (a6), (a7), (a8), (a9), (a10), (a11), (a12), (a13), (a14), for instance two of the above-identified commercially available surfactants, in particular (a5) alkyl ether sulfate such as sodium laureth sulfate and/or (a14) a sulfosuccinate having a twofold negative charge, in particular one of formula (1) such as disodium laureth sulfosuccinate, and

- at least one (e.g. 1, 2, 3) amphoteric lathering surfactant, preferably one selected from betaines, sultaines, hydroxysultaines, alkyliminoacetates, iminodialkanoates, aminoalkanoates, and mixtures thereof, for instance one or more of the above-identified commercially available surfactants, in particular one combining a tertiary amine being in a

cationic state and a carboxylate as in betaine surfactants, more preferably a surfactant of formula (2), most preferably cocamidopropylbetaine.

In this embodiment the weight ratio of anionic lathering surfactants and amphoteric lathering surfactant(s), respectively, is each at least 5, for instance at least 10, at least 15, at least 20, at least 25, at least 30 weight parts based on the entire mixture of lathering surfactants preferably based on the entire mixture of surfactants, if applicable. A commercially available aqueous surfactant solution of this type is Lumorol® K5240 available from Zschimmer % Schwarz, Germany. Lumorol® K5240 also contains PEG-9 cocoglyceride.

The tissue paper product of the present invention is obtainable by applying the lathering surfactant or a composition containing the same to one or more plies of a dry raw tissue paper web.

The term "dry tissue web" relates to a raw tissue web as obtained after the final drying step as normally effected at the Yankee cylinder or any other drying means, *e.g.* TAD. Even "dry" tissue webs have a residual water content which, as a rule, does not exceed 10 wt.-%. More preferably the residual water content is less than 8 wt.-%, in particular less than 6 wt.-%, for instance less than 5 wt.-% as measured according to EN20638:1993. Therefore, it is permissible to equate in this context the terms "dry" and "substantially dry". It is to be noted that the equilibrium residual water content at ambient conditions is about 7 wt.-%.

The dry web addition method leading to the tissue paper product of the invention is to be distinguished from wet web addition methods as disclosed for instance in US 4,940,513. The addition of lathering surfactant to a wet web leads to a very homogenous distribution throughout the tissue thickness

and a relatively strong binding between surfactant and fiber surface which is further enhanced in the subsequent drying step. The same incidentally applies to the addition of surfactants to the slurry of papermaking fibers fed to the headbox. Therefore, a dry web addition method as used in the present invention is believed to be more efficient regarding the foaming and cleansing effect of the surfactant used.

The above-described residual water contents may increase slightly if the lathering surfactant is applied as aqueous solution. To ensure that the tissue paper product still feels dry to the touch, the tissue paper product may therefore be subjected to a drying step. However, the drying step is optional and it may be unnecessary to subject the tissue paper product to drying. In-line drying can be achieved by known drying means such as radiant heat sources (e.g. IR), microwave devices, hot air blowers and heated rollers. Off-line convection ovens, microwave ovens or forced air ovens can be used for instance.

There are no specific restrictions as to where the lathering surfactant is present in the tissue paper product of the present invention and how it is distributed over its surface and/or throughout its thickness. The lathering surfactant may be present only on one side of the tissue paper product or on both sides, or it may be present in between the plies constituting the tissue paper product. According to one embodiment of the present invention, the lathering surfactant is present as continuous coating on one or both sides of the tissue paper product. According to a further embodiment, the lathering surfactant penetrates in the tissue paper product, partially or fully, after having been applied to one or both surfaces thereof. According to one further embodiment, the lathering surfactant is not applied, or not solely applied to one or two outer surfaces, but also to an intermediate ply as existing for instance in tissue paper products having three or more plies. According to one further embodiment the lathering surfactant is present in solid (*e.g.* powdery) form

between at least one outer surface, or between both outer surfaces, and at least one intermediate ply as occurring in tissue paper products having three or more plies.

According to one preferred embodiment, the lathering surfactant is present discontinuously on one or two surfaces of the product, preferably in the form of discrete deposits. The term "deposits" is not restricted to coatings solely located at and immobilized at the surface of the outer tissue plies. This term covers simultaneously those cases where the lathering surfactant is applied discontinuously to discrete areas and then partially or fully impregnates the tissue in a direction perpendicular to its surface. Simultaneously the lathering surfactant may also spread horizontally from the limited area where it was applied. According to the embodiment described in this paragraph, the surface coverage may for instance range from 10 to 90%, for instance from 20 to 80% or from 30 to 70%.

There are also no specific limitations regarding the geometry of the discrete deposits. While the later-described slot die application technique is particularly suitable to generate thin stripes having a length of 0.3 mm to 2 cm, any other pattern can be used to achieve the effect of the present invention including circles, squares, other polygons, rectangular shapes, continuous straight and wavy lines, grids, etc.

If the lathering composition applied to the tissue paper product contains other components than the lathering surfactant, for instance water-binding diol, the same are preferably applied in admixture with the lathering surfactant as described above. Nonetheless, the lathering surfactant and the other component may also be added separately.

Basically, the tissue paper product of the present invention can be marketed in any conceivable form and size. Some embodiments where cleaning can be most effectively conducted

are however preferred. These include endless rolls mounted on a dispenser having a cutting blade enabling the user to cut off single sheets having an appropriate size for the intended use. According to one preferred embodiment, the tissue paper product of the present invention is converted in a manner similar as household towels, that is to rolls where single sheets are separated by perforations. According to one further preferred embodiment, single sheets are pre-cut to size, optionally folded and typically combined to piles of several sheets which can be wrapped by a plastic film or packaged in a paper or plastic box. One side of this box may encompass a removable lid portion, which is for instance surrounded by a predetermined breaking line. Thereby, the user can take out individual sheets from the box without the need of fully opening the same. Moreover, the sheets can be folded in such a manner that removing the upper sheet will entrain the adjacent lower sheet until the same appears in the opening and is ready to hand. One further embodiment involves a continuous web of sheets separated by perforations. Said web would be folded along the perforation thereby resulting in a zigzag conformation. The tissue paper product according to the invention may be provided in the form of rolls, piles, stacks, bricks, or any other shape of folded (*i.e.* single-folded or multifolded) or unfolded sheets. For instance, the tissue paper product may be a glove which optionally comprises a polymeric carrier material.

The tissue paper product of the invention may be offered for sale in a special dispenser. If the tissue paper product of the invention is in the form of a roll, it may or may not contain a core, or it may be solid. The color of the tissue paper product of the invention may be white or any arbitrary color, including pictures and/or texts. For instance, the surface of the product can be printed with a text and/or drawing explaining the cleaning concept of the present invention.

In respect of the above-described embodiments it is preferred, but not necessary that single sheets of the tissue paper product have a greater size than sheets of tissue paper products used for personal care including hankies, personal care wipes or toilet paper sheets. Generally, the sheet size may vary largely and may be in the range from 25 cm^2 to 2500 cm^2. Preferably, the sheet size is greater than 200 cm^2, more preferably greater than 350 cm^2, still more preferably greater than 400 cm^2, most preferably greater than 500 cm^2. Even greater sizes, for instance up to 800 cm^2 and above are also conceivable, although a typical range will be from 550 to 700 cm^2.

The disposable tissue paper product of the invention may contain additional ingredients such as perfumes, scenting agents, antibacterial agents and antimould agents.

The present invention also relates to a process for the manufacture of a disposable tissue paper product as described above and below, said process comprising the step of applying a lathering surfactant or a composition containing the same to at least one surface of one or more plies of a dry tissue paper web. In this process it is preferred to apply a liquid composition comprising a lathering surfactant to a moving tissue paper web by means of a slot die.

The present invention also relates to a process for the manufacture of a disposable tissue paper product which feels dry to the touch and comprises a lathering surfactant, said process comprising the step of applying a liquid composition comprising a lathering surfactant to a moving tissue paper web by means of a slot die. In this process, the moving tissue paper web can be a wet web, but is preferably a dry web as described in the present specification and the claims.

In both processes, the liquid composition and the final product preferably have the characteristics described in the present specification and the claims. In the above processes

of manufacturing the tissue paper product of the invention, the liquid composition may be an aqueous composition or a solvent-based composition. Preferably it is an aqueous composition, more preferably an aqueous solution of the lathering surfactant, optionally containing further components or ingredients *e.g.* those identified above. The solvent of the composition is not particularly limited in kind, as long as this can dissolve the lathering surfactant in a sufficient amount but it is preferably a volatile solvent that can easily be removed by drying, such as acetone, methanol, ethanol, and isopropanol. Moreover, in either process, in place of a slot die, another non-spraying equipment can be used for applying the liquid composition.

Preferred embodiments of these processes are described in the following and in the claims. One embodiment is shown in figure 1. The dry tissue paper web (1) is led from master roll (5) through optional control section (box) before it is conducted between backup roll (application roll) (3) and slot die device (2). By means of slot die device (2), a liquid composition comprising a lathering surfactant is discontinuously applied to one side of tissue web (1). Application roll (6) (optional) makes it possible to coat the other side of tissue web (1) by means of a second slot die device (not shown). After each coating step it can be preferred to subject the tissue web to a drying step by means of dryer (4) or (4') to reduce its water or solvent content. Non-limiting examples of known drying means include the use of radiant heat sources (e.g. IR), microwave devices, hot air blowers, and heated rollers. Drying also helps to reduce the contamination of subsequent idler rolls (8) or (8'). The tissue paper web comprising the lathering surfactant is finally wound on master roll (7).

Figure 2 shows the application lip (10) and the valve section (11) of the slot die (9). One or more valves of the valve section (11) are arranged to regulate the distribution of the coating fluid which is to be conducted to the application lip

(10). The coating amount is in general terms controlled by the speed of gear pumps. The adjustable rack (12) is used to arrange the slot die (9) in an optimal application position in order to get the best possible coating fluid transfer to the substrate.

Slot die devices are typically used in the textile industry for applying hot melts to textile webs. The present inventors have surprisingly found that slot die devices are very suitable for applying liquid compositions comprising a lathering surfactant since hardly any foaming or other undesired phenomena such as lint deposition are observed.

There are no specific limitations regarding the slot die device to be used. Preferably a porous coat® application system available from Nordson Co., such as BC62 porous coat® applicator is used. The porous coat® system uses an extrusion die design that incorporates a series of hydraulic compartments which are fed by dedicated positive displacement gear pumps. This arrangement allows the system to apply a wide variety of uniform but typically discontinuous coatings over a broad range of coat weights and patterns. The coating widths can be altered easily by opening or closing the flow valves on either side of the die. Pump speeds are adjusted automatically to maintain consistent add-on rates. The system can be employed for off-roll coating which tends to achieve surface coatings and against-the-roll coating which typically leads to a deeper penetration. Details of a preferred mode used in the present invention will be given later.

One document describing porous coat® technology in further detail is US 5,750,444 in the name of Nordson Co. Considering the adaptation of coating fluid and substrate necessary for the present invention, the porous coat® system thus can be described as an apparatus for applying an aqueous composition of a lathering surfactant to a tissue paper web, said apparatus comprising a slot extruder die having a die outlet and means to meter an aqueous solution of a lathering

surfactant in quantities sufficient to produce a discontinuous random pattern of said composition from the die slot outlet, means for running a tissue paper web past and in close vicinity to or in contact with said die outlet for receiving a coating thereon of said aqueous solution of a lathering surfactant.

Preferably, the apparatus includes a plurality of independent selectively controlled land areas feeding said fine slot extruder die outlet, at least one of said segments preferably including a plurality of independent selectively controlled, recessed land areas.

One example of a random pattern that can be generated with the porous coat® technology is shown in figure 1 of US 5,750,444.

Other slot die devices and application conditions as disclosed in a series of US patents in the name of Nordson Co. may also be used under the proviso that adaptations in view of the use of a liquid solution of lathering surfactant as coating fluid and tissue paper as substrate may become necessary. This series of US patents includes US 5,423,935; US 5,429,840; US 5,685,911; US 5,418,009; US 5,524,828 and US 5,683,036. US 5,423,935 teaches for instance an apparatus and methods for producing intermittent, discrete patterns of coating material where the patterns have sharp, square leading and training edges, as well as side edges.

In the present invention, a slot die applicator, in particular one implementing the porous coat® technology is preferably used under the conditions shown in figure 3. Figure 3 shows how the slot die applicator is preferably positioned in respect of application roll (3) and tissue web (1). Preferably, a small distance of from 0.05 to 5 mm is adjusted between the application lip (10) of slot die device (2) and application roll (3). More preferably, this distance is from 0.2 to 1.5 mm. The distance is shown as Δ_2 in figure 3.

Moreover, the application lip (10) can be positioned above and below a horizontal line going through the centre of application roll (3) without adversely affecting the coating result. This leeway is shown as Δ_1 in figure 3 and preferably ranges from 25 mm above to 25 mm below the roll centre.

Moreover, it was found that it is not necessary to mount the slot die applicator in vertical position. Good coating results are also achieved if the slot die applicator is tilted by a head angle α of from -10° to +15°.

Similarly, it is not necessary to feed the incoming tissue web (1) to application roll (3) in a perfectly vertical position. The incoming web angle β was found to be preferably -15° to +15°.

A discontinuous coating of lathering surfactant (and other optional ingredients) can also be achieved by applying the liquid composition comprising the lathering surfactant with the non-impact printing technique disclosed in US 2004/0131842 or other suitable techniques. In the alternative, the discontinuous application of the lathering surfactant is accomplished by an intermittent supply of the liquid composition onto the tissue paper web, the frequency of the supply being synchronized with the movement of the tissue paper web. This way, a desired pattern of the lathering surfactant can be created on the tissue paper web.

The aqueous composition to be applied to the tissue web preferably comprises of from 0.5 to 60 wt.-% of one or more lathering surfactants and optionally from 0.5 to 50 wt.-% of water binding agent, preferably one or more polyhydric alcohols. More preferably, the lathering surfactant content is from 5 to 50 wt.-%, in particular 10 to 40 wt.-%, for instance 15 to 35 wt.-%. More preferred contents of water-binding agent range from 2 to 40 and 5 to 30 wt.-% (for instance 7 to 20 or 10 to 15 wt.-%).

The aqueous composition may also contain other minor components, for instance dyes, perfume or fragrance, for instance those disclosed in par. [0074] of US 2004/0031107, or antimicrobial agents, for instance those described in par. [0060] to [0065] of US 2004/0031107. Dyes are preferably water-soluble and can be used for purely aesthetic reasons to make visible a pattern of deposits of lathering surfactant, but also to indicate to the user which surface of the tissue paper product carries the lathering surfactant. These minor components are preferably employed in amounts of not more than 5, in particular not more than 1 wt.-%. The excellent cleaning effect of the paper tissue product of the invention can however be achieved without antimicrobial agents. The aqueous composition preferably does not contain any hydrophobic oils or waxes as used for instance in polishing wipes since these may counteract the cleaning effect.

The aqueous composition preferably has a viscosity ranging from 0.01 to 0.15 Pa x sec at a temperature of 23°C (using a Haake rheometer of type Rheostress 1 equipped with a measuring madrel (cone mandrel) C35/2°). Depending on the viscosity of the surfactant-containing fluid at the application temperature a suitable application temperature can be selected. Aqueous solutions of lathering surfactant with an optional content of water-binding agent are preferably applied at room temperature or temperatures close thereto, for instance at 10 to 30°C, typically 15 to 25°C.

The above aqueous composition is preferably applied to at least one side of single- or multi-ply tissue web in an amount of 0.1 to 5 g/m^2, more preferably 0.3 to 3 g/m^2, in particular 0.5 to 2 g/m^2.

The tissue paper web to be treated with a lathering surfactant can be made in line with methods known in the art. Such methods comprise the following process steps.

a. providing a paper making slurry,

b. forming that includes the headbox and the wire section,

c. optionally the press section (which is not required for TAD processes)

d. the drying portion (TAD (through air drying) and/or conventional drying on the Yankee cylinder) which also usually includes the crepe process essential for tissues having an "outer" creping,

e. optionally the monitoring and winding area.

Paper can be formed by placing the fibres, in an oriented or random manner, on one or between two continuously revolving wires of a paper making machine while simultaneously removing the main quantity of water of dilution until dry-solids contents of usually between 8 and 35 % are obtained.

Once the furnish is deposited on one or between two forming wires, or between a wire and a felt, the formed fibre-network is referred to as a web. The web is for example dewatered by centrifugal, pressing and vacuum forces. Also application of thermal energy in order to enhance dewatering could be used. Typically but not limiting, the web is transferred to a pressing felt, where the web is pressed, followed by drying at elevated temperature. Other transportation means, such as coarse fabrics or wires could be used as well. The particular techniques and typical equipment for making webs according to the process just described are well known to those skilled in the art. In a typical process, a low consistency pulp furnish is provided in a pressurized headbox. The headbox has an opening slice for delivering a thin deposit of pulp furnish onto the forming wire to form a wet web. The web is then typically dewatered to a fibre consistency of between about 8% and about 35% (total web weight basis) by vacuum

dewatering and further dewatered by pressing operations wherein the web is subjected to pressure developed by opposing mechanical members, for example, cylindrical rolls.

Drying the formed primary fibrous web occurs in one or more steps by mechanical and thermal means until a final dry-solids content of usually about 93 to 98 %. In the case of tissue making, this stage is followed by the crepe process which crucially influences the properties of the finished tissue product in conventional processes. The conventional dry crepe process ("outer creping") involves creping on a usually 4.5 to 6 m diameter drying cylinder, the so-called Yankee cylinder, by means of a creping doctor blade with the aforementioned final dry-solids content of the raw tissue paper (wet creping can be used if lower demands are made of the tissue quality). The creped, finally dry raw tissue paper (raw tissue) is then available for further processing into the tissue paper product according to the invention.

Instead of the conventional tissue making process described above, the invention gives preference to the use of a modified technique in which an improvement in specific volume is achieved by a special kind of drying within process section (c) and in this way an improvement in the bulk softness of the thus made tissue paper is achieved. This process, which exists in a variety of subtypes, is termed the TAD (through air drying) technique. It is characterized by the fact that the "primary" fibrous web that leaves the sheet making stage is pre-dried to a dry-solids content of e.g. about 60 to 80% before final contact drying on the Yankee cylinder by blowing hot air through the fibrous web. Lower dry-solid contents of 30 to 60 % before the Yankee dryer are also feasible. The fibrous web is supported by an air-permeable wire or belt and during its transport is guided over the surface of an air-permeable rotating cylinder drum. The additional application of mechanical pressing by increased wire tension could be used in order to increase drying efficiency. Structuring the supporting wire or belt

makes it possible to produce any pattern of compressed zones broken up by deformation in the moist state, resulting in increased mean specific volumes and consequently leading to an increase in bulk softness without decisively decreasing the strength of the fibrous web. Such a pattern is fixed in the area of the TAD-cylinder. Thereafter the pattern is further imprinted between the TAD-fabric and the Yankee-cylinder. The TAD process may also be used to provide the tissue paper product of the invention with watermarks.

Creping ("inner creping") may be conducted also during transfer of the paper sheet from the forming wire directly to the TAD-fabric or via a transfer fabric. For this creping the forming fabric runs faster than the following fabric receiving the sheet (rush transfer). For example, when applying the TAD technique for the production of raw tissue and the usual double-screen sheet formation in c-wrap configuration, for example, the so-called inner sheet-forming screen can thus be operated at a speed that is up to 40% faster than that of the next fabric or that of the subsequent felt, the initially formed and already pre-drained paper web being transferred to the next TAD fabric. This causes the still moist and as a result plastically deformable paper web to be internally broken up by compression and shearing, thereby rendering it more stretchable under load than a paper that has undergone neither "inner" nor outer creping. This transfer of still plastically deformable paper web at a differential speed that simultaneously takes effect may also be brought about in other embodiments between a transfer fabric and the so-called TAD imprinting fabric or between two transfer fabrics.

Another possible influence on the softness and strength of the raw tissue lies in the production of a layering in which the primary fibrous web to be formed is built up by a specially constructed headbox in the form of physically different layers of fibrous material, these layers being jointly supplied as a pulp strand to the sheet making stage.

When processing ("converting") the raw fibrous web or raw tissue paper into the final product, the following procedural steps are normally used individually or in combination: cutting to size (longitudinally and/or cross cutting), producing a plurality of plies, producing chemical and/or mechanical (e.g. by embossing) ply adhesion, volumetric and structural embossing, folding, imprinting, perforating, smoothing, stacking, rolling up.

To produce multi-ply tissue paper products, such as towels or kitchen towels, an intermediate step preferably occurs with so-called doubling in which the raw tissue in the finished product's desired number of plies is usually gathered on a common multiply master roll.

The processing step from the raw tissue that has already been optionally wound up in several plies to the finished tissue product occurs in processing machines which include operations such as repeated smoothing of the tissue, edge embossing, to an extent combined with full area and/or local application of adhesive to produce ply adhesion of the individual plies (raw tissue) to be combined together, as well as longitudinal cut, folding, cross cut, placement and bringing together a plurality of individual tissues and their packaging as well as bringing them together to form larger surrounding packaging or bundles. The individual paper ply webs can also be pre-embossed (micro and macroembossing) and then combined in a roll gap according to the foot-to-foot, foot-to-ground or nested methods. Decor embossing or spot embossing is also possible.

These converting techniques are known in the art.

In accordance with the present invention it is preferred to apply the lathering surfactant to the tissue paper web within the converting line (in-line). However, the lathering

surfactant can likewise be applied in a separate production step (off-line).

The present invention also relates to the use of a tissue paper product which feels dry to the touch and comprises a lathering surfactant for cleaning hard surfaces. For the purpose of the present specification, a "hard surface" is intended to mean any surface commonly referred to as hard other than the human skin. The tissue paper product used for this purpose preferably shows the characteristics stated before and in the appended claims. The tissue paper product of the invention is suitable to clean all different types of hard surfaces for instance furniture, kitchen appliance, wall material (e.g. tiles), floor material, doors, electric appliance, reflecting surfaces (e.g. mirror, window), bathtubs, sinks, toilets, dishes, outer and inner areas of a car, bicycles, motorbikes, lab equipment, shoes, glasses etc. As will be appreciated, the application field of the tissue paper product of the invention is manifold, and it can for example be used at home, in hospitals, restaurants and public toilets.

The present invention also relates to a process for cleaning a hard surface, preferably the aforementioned ones, said process comprising the steps of wetting the tissue paper product of the present invention with water and wiping over the hard surface.

Examples

The following test methods were used to evaluate the tissue papers produced. The test samples were conditioned over 12 hours at 50% relative humidity and 23 °C prior to testing.

3.1. Basis weight

The basis weight was determined according to DIN EN 12625-6.

3.2. Thickness

The measurement is made by a precision micrometer (precision 0.001mm) according to a modified method based on EN 12625, part 3. For this purpose, the distance created by a sample between a fixed reference plate and a parallel pressure foot is measured. The diameter of the pressure foot is 35.7 ± 0.1 mm (10.0 cm^2 nominal area). The pressure applied is 2.0 kPa ± 0.1 kPa. The pressure foot is movable at a speed rate of 2.0 ± 0.2 mm/s.

A usable apparatus is a thickness meter type L & W 51D20 (available from Lorentzen & Wettre, US).

The paper to be measured, i.e. two sheets of a single-ply or multi-ply paper are cut into pieces having a diameter in accordance with the standard EN 12625, part 3, *i.e.* a diameter of above 80 mm, (*e.g.*, pieces of sizes of 10 x 10 cm) and conditioned in an atmosphere of 23°C, 50 % RH (Relative Humidity) for at least 18 hours.

During measurement the sheets are placed beneath the pressure plate which is then lowered. The thickness value for the sheet is then read off 5 sec after the pressure value has stabilised. The thickness measurement is then repeated four times with further samples treated in the same manner.

The mean value of the 5 values obtained is taken as thickness of the two sheets measured.

3.3. Wet tensile strength in N/m (MD or CD)

The wet strength was determined according to prEN ISO/FDIS 12625-5:2001(E) Tissue Paper and Tissue Products, Part 5: determination of wet tensile strength (CEN TC 172).

To ensure that the wet strength of the samples has fully developed, the samples to be tested were always artificially aged before conducting the tensile test. Aging was effected by heating the samples in an air-circulating drying cabinet to (105 ±2) °C for a period of 15 min.

3.4. Freeness value

The freeness value (in °SR) was measured according to DIN-ISO 5267/1 of March 1999 corresponding to EN-ISO 5267/1 of July 2000.

3.5. Dry weight.

The dry weight was determined according to DIN EN 20638 Pulp: determination of the dry-solids content (ISO 638: 1978); German version EN 20638:1993.

Hereinafter weight proportions ("Kg/t") always refer to the amount of treated cellulosic fibres (dry weight).

Reference example

A tissue paper web was manufactured in a TAD paper machine from 100% Celest pulp (manufactured by SCA Östrand) having a freeness value of about 21°SR to which a wet strength agent (type Giluton 1100/37 N, distributed by BK Giulini of Ludwigshafen, Germany) had been added in an amount of 12 kg/t active content.

A three-ply tissue web was produced by overlaying three of these TAD tissue paper webs having each a basis weight of about 20 g/m^2 followed by an embossing and gluing step in a conventional embossing station to join the webs under formation of so-called nested embossments. A PVA (polyvinyl alcohol) glue was used as an adhesive.

In a converting line the three-ply web was perforated, cut to size and wound to a roll of tissue paper of household towel grade wherein the individual sheets had a size of 24.6 x 26.1 cm, a basis weight of 60.5 g/m^2, a thickness of 753.0 µm, a wet tensile strength (MD) of 322.0 N/m and a wet tensile strength (CD) of 174.8 N/m.

Example 1

By means of an application station as shown in figure 3, 1.0 g/m^2 Lumorol® K 5240 (aqueous solution of sodium laureth sulfate, disodium laureth sulfosuccinate, cocoamidopropylbetain, PEG-9 cocoglycerides, active content about 66 wt.-%, water content 34 wt-%, available from Zschimmer & Schwarz) was applied to one side of the three ply web described in reference example 1.

The slot die applicator used was BC62 porous coat® from Nordson Co., US. The application parameters shown in figure 3 were as follows. Δ_1 = 10 mm (below the roll), Δ_2 = 1,0 mm, α = 12°, β = 10°. The production speed was 200 m/min.

The resulting tissue paper product was evaluated in the same manner as reference example and had the characteristics shown hereinafter in table 1.

Table 1

	Ref. Example	Example 1
Coating amount (g/m^2)	---	1.00
Thickness (µm)	753	770
Wet tensile strength (MD) (N/m)	322.0	308.1
Wet tensile strength (CD) (N/m)	174.8	198.5

These results indicate that the application of relatively minor amounts of lathering surfactants based on Lumorol® K 5240 surprisingly may contribute in a positive fashion to thickness while wet tensile strength is essentially maintained or even slightly improved.

Example 2

Example 1 was repeated with the sole difference that instead of 1.0g of Lumorol® K 5240, 1.0g of Lumorol® K 4339 from Zschimmer & Schwarz was applied onto the three-ply tissue paper. Lumorol® K 4339 is based on an aqueous solution of sodium C_{10}-C_{13} alkyl benzene sulfonate, fatty alcohol ether sulfate, fatty alcohol ethoxylate and fatty acid diethanolamide (active content about 51 wt-% , water content about 49 wt.-%).

Example 3

Example 1 was repeated with the sole difference that instead of 1.0g of Lumorol® K 5240, 3.0 g of Spülflott® from Tillmann GmbH was applied onto the three-ply tissue paper. Spülflott® is an aqueous solution of sodium C_{10}-C_{16}-alkylethoxylate sulfuric acid, cocoamidopropylbetain and citric acid with an active content of approximately 20 wt-%.

Example 4

Moreover, the cleaning efficiency of a tissue paper products being coated with a cleaning substance according to Examples 1 to 3 was evaluated in the following cleansing tests.

The surface of a mirror having a size of 400 × 500 mm was evenly coated with a thin layer of sunflower oil using an amount of 5 to 10 ml of the oil.

Tests A_1, A_2 and A_3 (for Examples 1, 2 and 3) : Then sufficient water was added to the coated side of the tissue

paper product to fully wet the same. This side was drawn under slight pressure by hand slowly and evenly over one part of the mirror surface.

Tests B_1, B_2 and B_3 (for Examples 1, 2 and 3): Tests A_1, A_2 and A_3 were repeated with the sole difference that the tissue paper web was doubled before another part of the mirror surface was cleaned in the same manner as in Tests A_1, A_2 and A_3.

Tests C_1, C_2 and C_3 (for Examples 1, 2 and 3): Sufficient water was added to the uncoated side of the tissue paper product to fully wet the same. This side was used for cleaning another part of the mirror surface in the same manner as in Tests A_1, A_2 and A_3.

Test R: Sufficient water was added to one side of an uncoated tissue paper product similar to the one described in the Reference Example to fully wet the same. This product was used for cleaning one further part of the mirror surface in the same manner as in Tests A_1, A_2 and A_3.

The cleaning efficiency was visually evaluated. Tests A_1, A_2 and A_3, B_1, B_2 and B_3 and C_1, C_2 and C_3 showed a much greater cleaning effect than Test R where remainders of the oil were clearly visible. Moreover, tests A_1, A_2 and A_3 and B_1, B_2 and B_3 produced hardly any streaks.

C L A I M S

1. A disposable tissue paper product which feels dry to the touch and comprises a lathering surfactant in a form capable of forming lather upon contact with water, wherein

said tissue paper product is obtainable by applying said lathering surfactant or a composition containing the lathering surfactant to one or more plies of dry tissue paper web,

the lathering surfactant is present in an amount of 0,01 to 6 g/m^2, and,

if a composition containing the lathering surfactant is applied, the total amount of non-volatile components of said composition does not exceed 20 wt.-% of the dry weight of said one or more tissue paper plies.

2. Tissue paper product according to claim 1 which has two or more tissue paper plies.

3. Tissue paper product according to claim 1 or 2 wherein each of said one or more plies has a total basis weight of 10 to 75 g/m^2.

4. Tissue paper product according to any of claims 1 to 3 wherein said one or more plies were subjected to a through air drying (TAD) step.

5. Tissue paper product according to any of claims 2 to 4 wherein two or more plies are joined with each other through mechanical or chemical means, and optionally the application of adhesive between said plies.

6. Tissue paper product according to any of claims 1 to 5 wherein said one or more plies comprise a wet strength agent.

7. Tissue paper product according to any of claims 1 to 6 wherein one or more lathering surfactants are present in an amount of 0,01 to 3 g/m^2.

8. Tissue paper product according to any of claims 1 to 7 wherein the lathering surfactant is selected from anionic lathering surfactants, amphoteric lathering surfactants, non-ionic lathering surfactants and mixtures thereof.

9. Tissue paper product according to claim 8 wherein the lathering surfactant is a non-ionic surfactant which is selected from amine oxides, alkylglucosides, alkylpolyglucosides, polyhydroxy fatty acid amides, alkoxylated mono- and di-fatty acid esters, alkoxylated fatty alcohols, alkoxylated alkylphenols, fatty acid monoglycerides, polyoxyethylene sorbitan, lathering sucrose esters and mixtures thereof.

10. Tissue paper product according to claim 9 wherein the lathering non-ionic surfactant is an amine oxide surfactant.

11. Tissue paper product according to any of claims 1 to 10 wherein the tissue product also comprises a water-binding agent, in particular a polyhydric alcohol.

12. Tissue paper product according to claim 11 wherein the weight ratio of water-binding agent(s)/lathering surfactant(s) is from 1/2 to 1/10.

13. Tissue paper product according to any of claims 1 to 12 wherein said tissue product is obtainable by applying an aqueous composition comprising the lathering surfactant,

preferably one as defined in any of claims 8 to 10 and optionally a water-binding agent as defined in Claim 11.

14. Tissue paper product according to any of claims 1 to 13 wherein the lathering surfactant is present discontinuously on at least one surface of the product, preferably in the form of discrete deposits.

15. Tissue paper product according to any of claims 1 to 14 wherein the water content is less than 10 wt.-%.

16. Tissue paper product according to any of claims 1 to 15 provided in the form of rolls, piles, stacks or bricks of folded or unfolded sheets.

17. Tissue paper product according to any of claims 1, 2, 3, 4, 5, 6, 7, 8, 14, 15 and 16 which comprises a mixture of anionic and amphoteric lathering surfactants.

18. Tissue paper according to claim 17 obtainable by applying an aqueous solution (A) comprising a mixture of at least one anionic lathering surfactant and at least one amphoteric lathering surfactant.

19. Tissue paper product according to claim 18 wherein the anionic surfactant is selected from alkyl ether sulfates and the amphoteric surfactant is selected from betaines.

20. Tissue paper according to claim 17 obtainable by applying an aqueous solution (C) comprising a mixture of at least two anionic lathering surfactants and at least one amphoteric lathering surfactant.

21. Tissue paper product according to claim 20 wherein one anionic surfactant is selected from alkyl ether sulfates, the other one from sulfosuccinates having a twofold negative charge and the amphoteric surfactant is selected from betaines.

22. Tissue paper product according to any of claims 1, 2, 3, 4, 5, 6, 7, 8, 14, 15 and 16 which comprises a mixture of anionic and nonionic lathering surfactants.

23. Tissue paper according to claim 21 obtainable by applying an aqueous solution (B) comprising a mixture of at least one anionic lathering surfactant and at least one nonionic lathering surfactant.

24. Tissue paper product according to claim 23 wherein the anionic surfactant is selected from alkylbenzene sulfates, alkyl ether sulfates and mixtures thereof and the amphoteric surfactant is selected from fatty alcohol ethoxylates, N-hydroxy alkyl fatty acid amides and mixtures thereof.

25. Process for the manufacture of a disposable tissue paper product as defined in any of claims 1 to 24 comprising the step of applying a lathering surfactant or a composition containing the same to at least one surface of one or more plies of a dry tissue paper web.

26. Process according to claim 25 wherein a liquid composition comprising a lathering surfactant is applied to a moving tissue paper web (1) by means of an application device (2) comprising a slot die (9).

27. Process for the manufacture of a disposable tissue paper product which feels dry to the touch and comprises a lathering surfactant, said process comprising the step of applying a liquid composition comprising a lathering surfactant to a moving tissue paper web (1) by means of an application device (2) comprising a slot die (9).

28. Process according to any of claims 25 to 27 wherein the lathering surfactant is applied discontinuously, preferably in the form of discrete deposits.

29. Process according to claim 26 or 27, wherein the liquid composition is an aqueous composition.

30. Process according to claim 29 wherein the aqueous composition comprises from 0,5 to 60 wt.-% of lathering surfactant and optionally from 0,5 to 50 wt.-% of water-binding agent, preferably polyhydric alcohol.

31. Process according to claim 29 or 30 wherein the aqueous composition has a viscosity of from 0.01 to 0.15 Pa·s at a temperature of 23°C.

32. Process according to any of claims 26 to 31 wherein a drying device (4, 4') is provided downstream of the application device (2) comprising a slot die (9).

33. Use of a tissue paper product as defined in any of claims 1 to 24 for cleaning hard surfaces.

34. Use according to claim 33 wherein the hard surfaces are selected from furniture, kitchen appliance, wall material, floor material, doors, electric appliance, reflecting surfaces, bathtubs, sinks, toilets, dishes, outer and inner areas of a car, bicycles, motorbikes and lab equipment.

35. Process for cleaning a hard surface comprising the steps of wetting the tissue paper product of any of claims 1 to 24 with water and wiping over the hard surface.

Figure 1

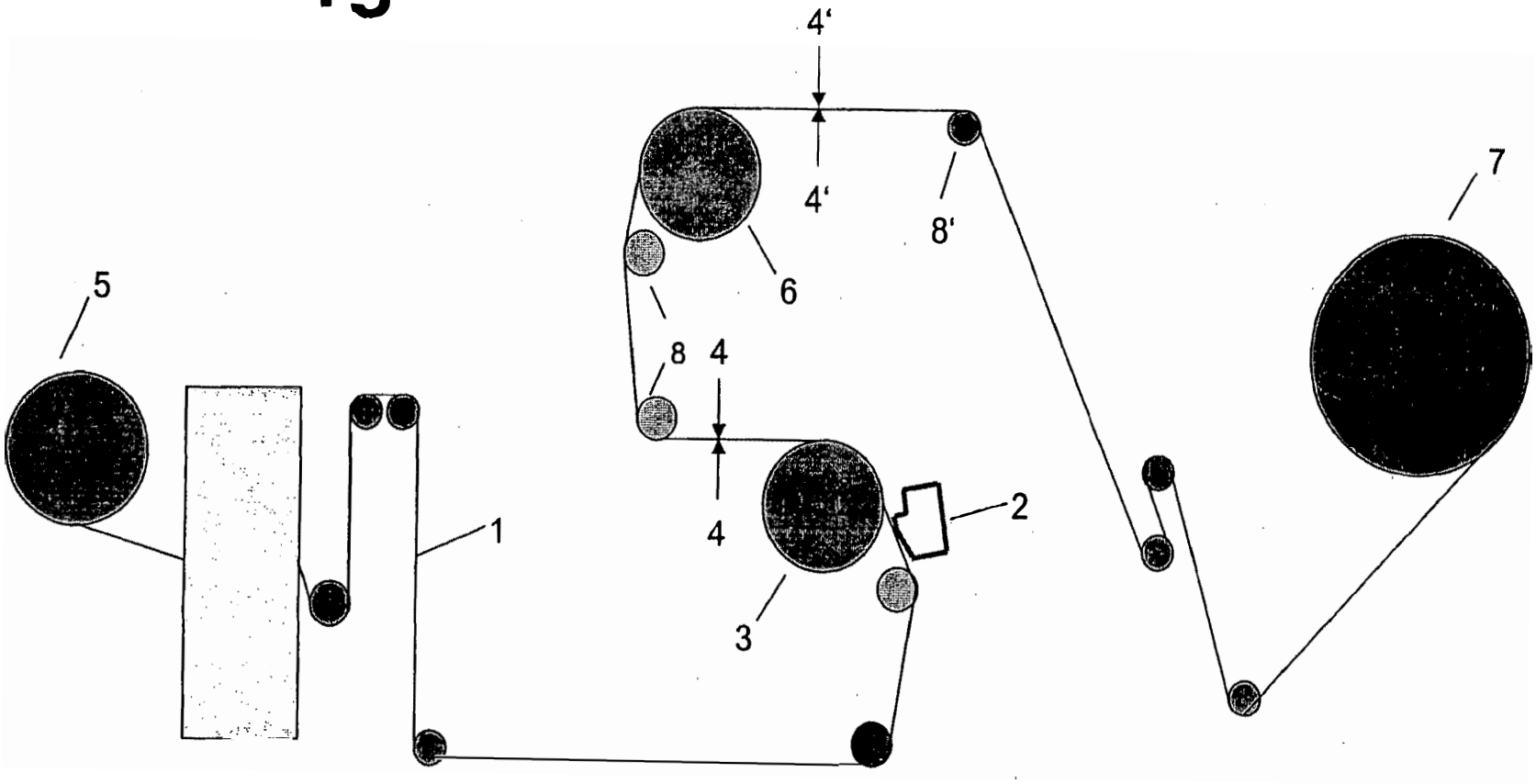


Figure 2

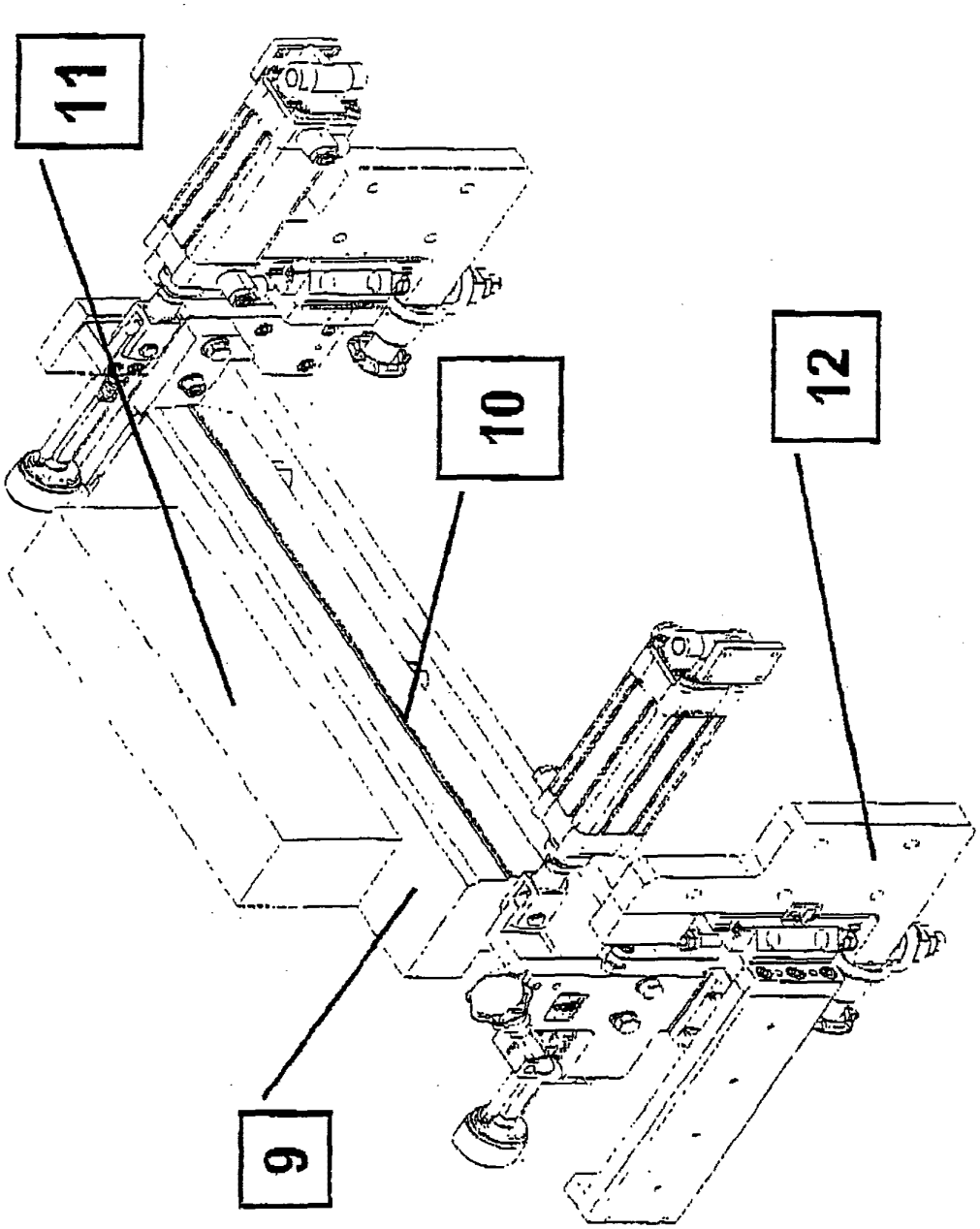
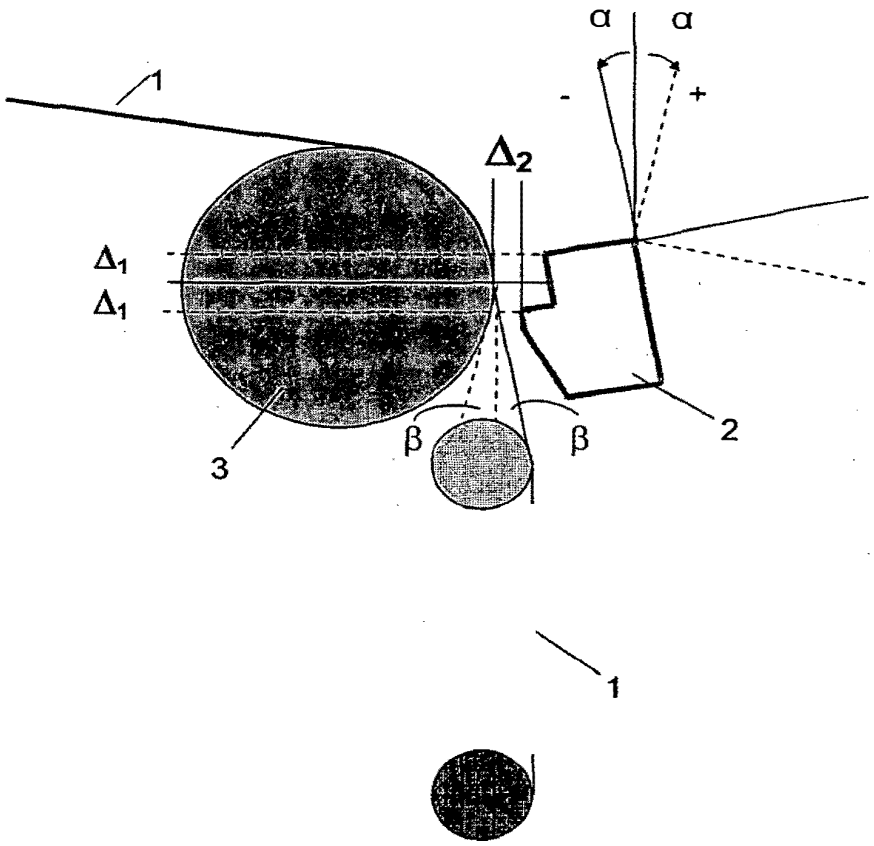


Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/002771

A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 03/054132 A (HENKEL KGAA [DE]; GLUESEN BIRGIT [DE]; ZIGANKE KERSTIN [DE]; RYBINSKI) 3 July 2003 (2003-07-03) cited in the application abstract	1,25,27, 33,35
Y	WO 99/13861 A (PROCTER & GAMBLE [US]) 25 March 1999 (1999-03-25) cited in the application abstract claim 2	1,25,27, 33,35

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

"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

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"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

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"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.

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03054132 A	03-07-2003	AU 2002361047 A1	09-07-2003
		DE 10162811 A1	10-07-2003
WO 9913861 A	25-03-1999	AT 226064 T	15-11-2002
		AU 735421 B2	05-07-2001
		AU 8745598 A	05-04-1999
		BR 9811789 A	05-09-2000
		CA 2302561 A1	25-03-1999
		CN 1277548 A	20-12-2000
		DE 69808790 D1	21-11-2002
		DE 69808790 T2	14-08-2003
		EP 1011630 A1	28-06-2000
		ES 2186199 T3	01-05-2003
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		JP 2006008693 A	12-01-2006

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Published:

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(54) **Title**: HIGH BULK HESPERALOE TISSUE

(57) **Abstract**: The invention relates to tissue products comprising hesperaloe fibers and methods of producing the same. Preferably the hesperaloe fibers are high yield hesperaloe pulp fibers, which have demonstrated the ability to replace substantially all of the long fiber fraction of the papermaking furnish without negatively effecting important tissue product properties such as CD Stretch, CD Durability and bulk. Thus, the tissue product may comprise greater than about 90 weight percent hesperaloe fiber and more preferably greater than about 95 weight percent.

HIGH BULK HESPERALOE TISSUE

BACKGROUND OF THE DISCLOSURE

Tissue products, such as facial tissues, paper towels, bath tissues, napkins, and other similar products, are designed to include several important properties. For example, the products should have good bulk, a soft feel, and should have good strength and durability. Unfortunately, however, when steps are taken to increase one property of the product, other characteristics of the product are often adversely affected.

To achieve the optimum product properties, tissue products are typically formed, at least in part, from pulps containing wood fibers and often a blend of hardwood and softwood fibers to achieve the desired properties. Typically when attempting to optimize surface softness, as is often the case with tissue products, the papermaker will select the fiber furnish based in part on the coarseness of pulp fibers. Pulps having fibers with low coarseness are desirable because tissue paper made from fibers having a low coarseness can be made softer than similar tissue paper made from fibers having a high coarseness. To optimize surface softness even further, premium tissue products usually comprise layered structures where the low coarseness fibers are directed to the outside layer of the tissue sheet with the inner layer of the sheet comprising longer, coarser fibers.

Unfortunately, the need for softness is balanced by the need for durability. Durability in tissue products can be defined in terms of tensile strength, tensile energy absorption (TEA), burst strength and tear strength. Typically tear, burst and TEA will show a positive correlation with tensile strength while tensile strength, and thus durability, and softness are inversely related. Thus the paper maker is continuously challenged with the need to balance the need for softness with a need for durability. Unfortunately, tissue paper durability generally decreases as the fiber length is reduced. Therefore, simply reducing the pulp fiber length can result in an undesirable trade-off between product surface softness and product durability.

Besides durability long fibers also play an important role in overall tissue product softness. While surface softness in tissue products is an important attribute, a second element in the overall softness of a tissue sheet is stiffness. Stiffness can be measured from the tensile slope of stress – strain tensile curve. The lower the slope the lower the stiffness and the better overall softness the product will display. Stiffness and tensile strength are positively correlated, however at a given tensile strength shorter fibers will display a greater stiffness than long fibers. While not wishing to be bound by theory, it is believed that this behavior is due to the higher number of hydrogen bonds required to produce a product of a given tensile strength with short fibers than with long fibers. Thus, easily

collapsible, low coarseness long fibers, such as those provided by northern softwood kraft (NSWK) fibers typically supply the best combination of durability and softness in tissue products when those fibers are used in combination with hardwood Kraft fibers such as Eucalyptus hardwood Kraft fibers. While Northern Softwood Kraft Fibers have a higher coarseness than Eucalyptus fibers their small cell wall thickness relative to lumen diameter combined with their long length makes them the ideal candidate for optimizing durability and softness in tissue.

Unfortunately supply of NSWK is under significant pressure both economically and environmentally. As such, prices of NSWK have escalated significantly creating a need to find alternatives to optimize softness and strength in tissue products. Alternatives, however, are limited. For example, southern softwood kraft (SSWK) may only be used in limited amounts in the manufacture of tissue products because its high coarseness results in stiffer, harsher feeling products than NSWK. Thus, there remains a need for an alternative to NSWK for the manufacture of premium tissue products, which must be both soft and strong.

SUMMARY OF THE DISCLOSURE

The present inventors have successfully used hesperaloe fibers to produce a tissue having satisfactory softness, strength and bulk. To produce the instant tissue products the inventors have successfully moderated the changes in strength and stiffness typically associated with substituting conventional wood papermaking fibers, such as NSWK, with hesperaloe fibers. Not only have the inventors succeeded in moderating changes to strength and stiffness they have done so without negatively effecting bulk. As such, the tissue products of the present invention have properties comparable to or better than those produced using conventional wood papermaking fibers, and more particularly softwood fibers, and still more particularly NSWK fibers. Accordingly, in certain preferred embodiments, the invention provides tissue products in which hesperaloe fibers replace at least about 95 percent of the NSWK, more preferably at least about 98 percent and still more preferably all NSWK without negatively effecting the tissue products strength, stiffness and bulk.

In still other embodiments the present invention provides a tissue product comprising at least about 90 weight percent hesperaloe fiber, the tissue product having a CD Stretch greater than about 15 percent and sheet bulk greater than about 15 cc/g.

In yet another embodiment the present invention provides a tissue product greater than about 90 weight percent hesperaloe fiber and substantially free from long average fiber length kraft fibers, such as NSWK and SSWK, the tissue product having a sheet bulk greater than about 15 cc/g, a Stiffness Index less than about 5.0 and a CD Durability greater than about 8.0.

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In another embodiment the present invention provides a tissue product comprising at least one through-air dried tissue web, the web comprising at least about 90 weight percent hesperaloe fiber, the tissue product having a CD Stretch greater than about 14 percent, a CD Durability greater than about 8.0 and a Stiffness Index less than about 5.0.

In other embodiments the present invention provides a single-ply tissue web having a CD stretch greater than about 12 percent, such as from about 12 to about 18 percent, and a CD tensile strength from greater than about 1,000 g/3", such as from about 1,000 to about 2,500 g/3", the tissue web comprising at least about 90 weight percent high yield hesperaloe pulp fibers.

In still other embodiments the present invention provides a method of making a tissue web comprising the steps of: (a) forming an aqueous suspension of high yield hesperaloe pulp fibers (b) depositing an aqueous suspension of high yield hesperaloe pulp fibers onto a forming fabric traveling at a first rate of speed to form a wet web; (c) dewatering the web to a consistency of about 20 percent or greater; (d) transferring the web to a throughdrying fabric; and (e) throughdrying the web, wherein the web comprises at least about 90 weight percent high yield hesperaloe pulp fibers.

DEFINITIONS

As used herein, a "tissue product" generally refers to various paper products, such as facial tissue, bath tissue, paper towels, napkins, and the like. Normally, the basis weight of a tissue product of the present invention is less than about 80 grams per square meter (gsm), in some embodiments less than about 60 gsm, and in some embodiments from about 10 to about 60 gsm and more preferably from about 20 to about 50 gsm.

As used herein, the term "layer" refers to a plurality of strata of fibers, chemical treatments, or the like within a ply.

As used herein, the terms "layered tissue web," "multi-layered tissue web," "multi-layered web," and "multi-layered paper sheet," generally refer to sheets of paper prepared from two or more layers of aqueous papermaking furnish which are preferably comprised of different fiber types. The layers are preferably formed from the deposition of separate streams of dilute fiber slurries, upon one or more endless foraminous screens. If the individual layers are initially formed on separate foraminous screens, the layers are subsequently combined (while wet) to form a layered composite web.

The term "ply" refers to a discrete product element. Individual plies may be arranged in juxtaposition to each other. The term may refer to a plurality of web-like components such as in a multi-ply facial tissue, bath tissue, paper towel, wipe, or napkin.

As used herein, the term "basis weight" generally refers to the bone dry weight per unit area of a tissue and is generally expressed as grams per square meter (gsm). Basis weight is measured using TAPPI test method T-220.

As used herein, the term "CD Durability" refers the cross-machine direction tensile energy absorption (expressed in g•cm/cm^2) at a given cross-machine direction tensile strength (having units of grams per three inches) as defined by the equation:

$$CD\ Durability = \frac{CD\ TEA\ (\mathrm{g} \bullet \mathrm{cm/cm2})}{CD\ Tensile\ (g/3")}\ x\ 1{,}000$$

While the CD Durability may vary tissue products prepared according to the present disclosure generally have a CD Durability greater than about 8.0, more preferably greater than about 9.0 and still more preferably greater than about 10.0.

As used herein, the term "caliper" is the representative thickness of a single sheet (caliper of tissue products comprising two or more plies is the thickness of a single sheet of tissue product comprising all plies) measured in accordance with TAPPI test method T402 using an EMVECO 200-A Microgage automated micrometer (EMVECO, Inc., Newberg, OR). The micrometer has an anvil diameter of 2.22 inches (56.4 mm) and an anvil pressure of 132 grams per square inch (per 6.45 square centimeters) (2.0 kPa).

As used herein, the term "sheet bulk" refers to the quotient of the caliper (µm) divided by the bone dry basis weight (gsm). The resulting sheet bulk is expressed in cubic centimeters per gram (cc/g). Tissue products prepared according to the present invention generally have a sheet bulk greater than about 12 cc/g, more preferably greater than about 14 cc/g and still more preferably greater than about 16 cc/g.

As used herein, the term "fiber length" refers to the length weighted average length of fibers determined utilizing a Kajaani fiber analyzer model No. FS-100 available from Kajaani Oy Electronics, Kajaani, Finland. According to the test procedure, a pulp sample is treated with a macerating liquid to ensure that no fiber bundles or shives are present. Each pulp sample is disintegrated into hot water and diluted to an approximately 0.001 percent solution. Individual test samples are drawn in approximately 50 to 100 ml portions from the dilute solution when tested using the standard Kajaani fiber analysis test procedure. The weighted average fiber length may be expressed by the following equation:

$$\sum_{x_i=0}^{k} (x_i \times n_i)/n$$

where k = maximum fiber length

x_i = fiber length

n_i = number of fibers having length x_i

n = total number of fibers measured.

As used herein, the term "hesperaloe fiber" refers to a fiber derived from a plant of the genus *Hesperaloe* of the family Asparagaceae including, for example, *Hesperaloe funifera*. The fibers are generally processed into a pulp for use in the manufacture of tissue products according to the present invention. Preferably the pulping process is a high yield pulping process. The high yield hesperaloe pulp fibers generally have a lignin content, measured as Klason lignin, from about 10 to about 15 weight percent. The terms "hesperaloe fiber" and "high yield hesperaloe pulp fiber" may be used interchangeably herein when referring to non-wood fibers incorporated into tissue products, one skilled in the art will appreciate however that when incorporating non-wood fibers into tissue products it is preferred that the fibers be processed, such as by high yield pulping.

As used herein, the term "slope" refers to slope of the line resulting from plotting tensile versus stretch and is an output of the MTS TestWorks™ in the course of determining the tensile strength as described in the Test Methods section herein. Slope is reported in the units of grams (g) per unit of sample width (inches) and is measured as the gradient of the least-squares line fitted to the load-corrected strain points falling between a specimen-generated force of 70 to 157 grams (0.687 to 1.540 N) divided by the specimen width. Slopes are generally reported herein as having units of kilograms per sample width, such as kg/3".

As used herein, the term "geometric mean slope" (GM Slope) generally refers to the square root of the product of machine direction slope and cross-machine direction slope. GM Slope generally is expressed in units of kg.

As used herein, the term "geometric mean stretch" (GM Stretch) generally refers to the square root of the product of machine direction slope and cross-machine direction stretch. GM Stretch generally is expressed as a percentage.

As used herein, the terms "geometric mean tensile" and "GMT" refer to the square root of the product of the machine direction tensile strength and the cross-machine direction tensile strength of the web.

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As used herein, the term "Stiffness Index" refers to the quotient of the geometric mean tensile slope, defined as the square root of the product of the MD and CD slopes (having units of kg), divided by the geometric mean tensile strength (having units of grams per three inches).

$$Stiffness\ Index = \frac{\sqrt{MD\ Tensile\ Slope\ (kg) x\ CD\ Tensile\ Slope(kg)}}{GMT\ (g/3")}\ x\ 1{,}000$$

While the Stiffness Index may vary tissue products prepared according to the present disclosure generally have a Stiffness Index less than about 5.0.

DETAILED DESCRIPTION OF THE DISLOSURE

Generally the skilled tissue maker is concerned with balancing various tissue properties such as bulk, softness, stiffness and strength. For example, the tissue maker often desires to increase bulk without stiffening the tissue product or reducing softness, while at the same time maintaining a given tensile strength. Previous attempts to manufacture tissue using hesperaloe fibers have not successfully balanced these important tissue properties. For example, previous attempts have generally resulted in reduced bulk with dramatic increases in tensile and stiffness. Despite the failings of the prior art, the present inventors have now succeeded in moderating the changes in strength and stiffness without negatively effecting bulk when manufacturing a tissue product comprising hesperaloe fibers.

Not only were previous attempts to balance bulk, strength, stiffness and softness unsuccessful, the resulting tissue products were not suitable for use as premium bath tissue because the strengths and modulus were excessively high. For example, when compared to Northern® Bathroom Tissue the inventive code of US 5,320,710 had 11 percent lower bulk, 23 percent greater modulus and 148 percent greater stiffness (measured as the modulus divided by the tensile strength). The present inventors have overcome these failings to provide a tissue product that is comparable or better than commercially available bath tissue products.

Without being bound by any particular theory, the high degree of strength and stiffness observed previously in tissue products may be attributed in-part to the morphology of hesperaloe fiber when prepared by chemical pulping, which has a relatively long fiber length, high aspect ratio and high ratio of fiber length to cell wall thickness. A comparison of fiber morphology, as reported in the literature for, hesperaloe kraft pulp fibers, conventional NSWK and SSWK is provided in Table 1, below.

TABLE 1

Fiber	Fiber Length (mm)	Average Fiber Width (μm)	Cell Wall Thickness (μm)	Aspect Ratio	Fiber Length : Cell Wall Thickness
H. Funifera kraft pulp	3.4	16.5	3.5	206	971
NSWK	3.5	36	6	97	583
SSWK	4.0	43	7	93	571

Despite the foregoing properties of hesperaloe kraft pulp fibers and the tendency of such pulps to produce overly strong and stiff tissue products, the present inventors have discovered that hesperaloe fibers processed by high yield pulping means, such as mechanical pulping, may be a suitable replacement for high fiber length wood fibers without decreasing bulk, significantly altering tensile, increasing stiffness or reducing softness. Processing of hesperaloe fibers by high yield pulping means generally yields a fiber having a slightly shorter fiber length and higher coarseness compared to hesperaloe chemical pulp fibers.

Not only have the present inventors discovered that hesperaloe may replace high fiber length wood fibers, such as NSWK, but also that the resulting tissue products have physical properties comparable to or better than those produced using NSWK fibers. Accordingly, in certain embodiments, hesperaloe fibers may replace at least about 95 percent of the NSWK in the tissue product, more preferably at least about 98 percent and still more preferably all NSWK without negatively effecting the tissue products softness and durability.

In addition to replacing substantially all of the long fiber fraction of the papermaking furnish, in certain embodiments, substantially the entire furnish may comprise hesperaloe fiber. Accordingly, in certain embodiments the tissue product may comprise greater than about 90 weight percent hesperaloe fiber and more preferably greater than about 95 weight percent. Surprisingly, forming a tissue product using a furnish consisting essentially of hesperaloe fiber improves the moldability of the nescient tissue web, enables the use of higher vacuum levels and improves the cross-machine direction properties, stiffness and bulk of the finished product. The improvements in these important tissue properties is illustrated in the table below, which compares a tissue product comprising a furnish of 40 weight percent hesperaloe and 60 weight percent EHWK and a product comprising 100 weight percent hesperaloe with a control comprising 40 weight percent NSWK and 60 weight percent EHWK. All of the products had a basis weight of about 38 gsm and comprised a single-ply through-air dried web manufactured using similar conditions.

TABLE 2

Hesperaloe Fiber (wt%)	Delta Sheet Bulk	Delta CD Stretch	Delta Stiffness Index	Delta CD Durability
40	5%	22%	-15%	20%
100	14%	85%	-47%	54%

The improved properties are further illustrated in the table below which compares the change in various tissue product properties relative to comparable tissue products comprising NSWK. All tissues shown in Table 3 are single-ply products having a basis weight of about 30 grams per square meter (gsm) and comprising either 40 weight percent NSWK and 60 weight percent EHWK or 100 weight percent hesperaloe fiber.

TABLE 3

	NSWK	High Yield Hesperaloe Fiber	Delta (%)
Sheet Bulk (cc/g)	24.5	28.06	14.5
CD Stretch (%)	8.31	15.53	86.9
CD TEA	2.87	16.84	487
CD Durability	6.5	10.0	53.8
Stiffness Index	6.35	3.32	-47.7
GM Stretch	12	17.8	48.7

As illustrated in Table 3, forming a tissue product from a furnish comprising a high percentage of hesperaloe fiber, such as greater than about 90 weight percent, yields a product having a high degree of CD Stretch. Accordingly, in one embodiment tissue products of the present invention have a CD Stretch greater than about 12 percent, more preferably greater than about 14 percent and still more preferably greater than about 15 percent, such as from about 12 to about 18 percent. Provided these relatively high degrees of CD Stretch, the tissue products also have relatively high degrees of GM Stretch, such as greater than about 15 percent, more preferably greater than about 17 percent and still more preferably greater than about 19 percent.

In addition to having improved stretch properties, the tissue products also have improved bulk. As such, the tissue products generally have a sheet bulk greater than about 15 cc/g, more preferably greater than about 20 cc/g, still more preferably greater than about 24 cc/g and even more preferably greater than about 28 cc/g.

In other embodiments the tissue products have low stiffness, measured as Stiffness Index, and a relatively high degree of CD Durability. As such, the products are generally soft, yet extremely durable. Accordingly, the tissue products may have a CD Durability greater than about 8.0, more preferably greater than about 10.0 and still more preferably greater than about 12.0. The tissue

products may also have a Stiffness Index less than about 5.0, more preferably less than about 4.5 and still more preferably less than about 4.0.

In other embodiments the present invention provides a tissue product comprising at least about 90 percent, by weight of the tissue product, high yield hesperaloe pulp fiber, the tissue product having a CD Stretch greater than about 12 percent, a CD Durability greater than about 8.0 and a sheet bulk greater than about 12 cc/g. In still other embodiments the present disclosure provides a tissue product having a CD Stretch greater than about 12 percent, more preferably greater than about 14 percent and still more preferably greater than about 15 percent, and a Stiffness Index less than about 5.0 and comprising from about 90 to about 100 percent, by weight of the tissue product, high yield hesperaloe pulp fiber.

In other embodiments the tissue products have a Stiffness Index less than about 5.0 and a CD Durability greater than about 8.0, such as from about 8.0 to about 12.0. In one particularly preferred embodiment the tissue product comprises a through-air dried web comprising at least about 95 weight percent hesperaloe fiber, the tissue product having a CD Durability Index greater than about 8.0 and a Stiffness Index less than about 5.0.

In still other embodiments the present invention provides tissue products having improved stretch and high sheet bulk such as a tissue product have a CD Stretch greater than 12 percent, a geometric mean stretch (GM Stretch) greater than about 15 percent and a sheet bulk greater than about 20 cc/g. The foregoing tissue products generally comprise at least about 90 weight percent hesperaloe fiber and in a particularly preferred embodiment are substantially free from softwood kraft fibers and particularly NSWK.

The tissue webs may be incorporated into tissue products that may be either single- or multi-ply, where one or more of the plies may be formed by a multi-layered tissue web having hesperaloe fibers selectively incorporated in one of its layers. In one embodiment the tissue product is constructed such that the hesperaloe fibers are not brought into contact with the user's skin in-use. For example, the tissue product may comprise two multi-layered through-air dried webs wherein each web comprises a first fibrous layer substantially free from hesperaloe fibers and a second fibrous layer comprising hesperaloe fibers. The webs are plied together such that the outer surface of the tissue product is formed from the first fibrous layer of each web and the second fibrous layer comprising the hesperaloe fibers is brought into contact with the user's skin in-use.

Generally hesperaloe fibers useful in the present invention are derived from non-woody plants in the genus Hesperaloe in the family Agavaceae. Suitable species within the genus Hesperaloe

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include, for example *H. funifera*, *H. nocturna*, *H. parviflova*, and *H. changii*, as well as combinations thereof.

In certain embodiments the hesperaloe fibers are processed by a high yield pulping process, such as mechanically treating the fibers. High yield pulping processes include, for example, mechanical pulp (MP), refiner mechanical pulp (RMP), pressurized refiner mechanical pulp (PRMP), thermomechanical pulp (TMP), high-temperature TMP (HT-TMP) RTS-TMP, thermopulp, groundwood pulp (GW), stone groundwood pulp (SGW), pressure groundwood pulp (PGW), super pressure groundwood pulp (PGW-S), thermo groundwood pulp (TGW), thermo stone groundwood pulp (TSGW) or any modifications and combinations thereof. Processing of hesperaloe fibers using a high yield pulping process generally results in a pulp having a yield of at least about 85 percent, more preferably at least about 90 percent and still more preferably at least about 95 percent.

The high yield pulping process may comprise heating the hesperaloe fiber above ambient temperatures, such as from about to 100 to about 200ºC and more preferably from about 120 to about 190ºC while subjecting the fiber to mechanical forces. In other embodiments a caustic or oxidizing agent may be introduced to the process to facilitate fiber separation. For example, in one embodiment a 3-8 percent solution of NaOH may be added to the fiber during mechanical treatment. Although a caustic or oxidizing agent may be added during processing, it is generally preferred that the hesperaloe fiber is not pretreated with a chemical agent prior to processing. For example, high yield hesperaloe pulps are generally prepared without pretreatment of the fiber with an aqueous solution of sodium sulfite or the like, which is commonly employed in the manufacture of chemi-mechanical wood pulps.

Generally the high yield pulping process removes from about 1 to about 3 weight percent of the lignin from the hesperaloe fiber. As such high yield hesperaloe pulp useful in the present invention generally has a lignin content less than about 15 weight percent, preferably less than about 13 weight percent and still more preferably less than about 11 weight percent, such as from about 10 to about 15 weight percent.

In a particularly preferred embodiment hesperaloe fibers are utilized in the tissue web as a replacement for high fiber length wood fibers such as softwood fibers and more specifically NSWK or Southern softwood kraft (SSWK). In one particular embodiment the hesperaloe fibers are substituted for NSWK such that the total amount of NSWK, by weight of the tissue product, is less than about 10 percent and more preferably less than about 5 percent. In other embodiments it may be desirable to replace all of the NSWK with hesperaloe fibers such that the tissue product is substantially free from NSWK. In other embodiments hesperaloe fibers may be blended with SSWK fibers such that the total

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amount of SSWK, by weight of the tissue product, is less than about 10 percent and more preferably less than about 5 percent.

If desired, various chemical compositions may be applied to one or more layers of the multi-layered tissue web to further enhance softness and/or reduce the generation of lint or slough. For example, in some embodiments, a wet strength agent can be utilized, to further increase the strength of the tissue product. As used herein, a "wet strength agent" is any material that, when added to pulp fibers can provide a resulting web or sheet with a wet geometric tensile strength to dry geometric tensile strength ratio in excess of about 0.1. Typically these materials are termed either "permanent" wet strength agents or "temporary" wet strength agents. As is well known in the art, temporary and permanent wet strength agents may also sometimes function as dry strength agents to enhance the strength of the tissue product when dry.

Wet strength agents may be applied in various amounts, depending on the desired characteristics of the web. For instance, in some embodiments, the total amount of wet strength agents added can be between about 1 to about 60 pounds per ton (lbs/T), in some embodiments, between about 5 to about 30 lbs/T, and in some embodiments, between about 7 to about 13 lbs/T of the dry weight of fibrous material. The wet strength agents can be incorporated into any layer of the multi-layered tissue web.

A chemical debonder can also be applied to soften the web. Specifically, a chemical debonder can reduce the amount of hydrogen bonds within one or more layers of the web, which results in a softer product. Depending on the desired characteristics of the resulting tissue product, the debonder can be utilized in varying amounts. For example, in some embodiments, the debonder can be applied in an amount between about 1 to about 30 lbs/T, in some embodiments between about 3 to about 20 lbs/T, and in some embodiments, between about 6 to about 15 lbs/T of the dry weight of fibrous material. The debonder can be incorporated into any layer of the multi-layered tissue web.

Any material capable of enhancing the soft feel of a web by disrupting hydrogen bonding can generally be used as a debonder in the present invention. In particular, as stated above, it is typically desired that the debonder possess a cationic charge for forming an electrostatic bond with anionic groups present on the pulp. Some examples of suitable cationic debonders can include, but are not limited to, quaternary ammonium compounds, imidazolinium compounds, bis-imidazolinium compounds, diquatemary ammonium compounds, polyquaternary ammonium compounds, ester-functional quaternary ammonium compounds (e.g., quaternized fatty acid trialkanolamine ester salts), phospholipid derivatives, polydimethylsiloxanes and related cationic and non-ionic silicone compounds, fatty and carboxylic acid derivatives, mono and polysaccharide derivatives, polyhydroxy

hydrocarbons, etc. For instance, some suitable debonders are described in US Patent Nos. 5,716,498, 5,730,839, 6,211,139, 5,543,067, and WO/0021918, all of which are incorporated herein in a manner consistent with the present disclosure.

Still other suitable debonders are disclosed in US Patent Nos. 5,529,665 and 5,558,873, both of which are incorporated herein in a manner consistent with the present disclosure. In particular, US Patent No. 5,529,665 discloses the use of various cationic silicone compositions as softening agents.

Tissue webs useful in forming tissue products of the present invention can generally be formed by any of a variety of papermaking processes known in the art. For example, a papermaking process of the present disclosure can utilize adhesive creping, wet creping, double creping, embossing, wet-pressing, air pressing, through-air drying, creped through-air drying, uncreped through-air drying, as well as other steps in forming the paper web. Examples of papermaking processes and techniques useful in forming tissue webs according to the present invention include, for example, those disclosed in US Patent Nos. 5,048,589, 5,399,412, 5,129,988 and 5,494,554 all of which are incorporated herein in a manner consistent with the present disclosure. In one embodiment the tissue web is formed by through-air drying and be either creped or uncreped. When forming multi-ply tissue products, the separate plies can be made from the same process or from different processes as desired.

TEST METHODS

Sheet Bulk

Sheet Bulk is calculated as the quotient of the dry sheet caliper (µm) divided by the basis weight (gsm). Dry sheet caliper is the measurement of the thickness of a single tissue sheet measured in accordance with TAPPI test methods T402 and T411 om-89. The micrometer used for carrying out T411 om-89 is an Emveco 200-A Tissue Caliper Tester (Emveco, Inc., Newberg, OR). The micrometer has a load of 2 kilo-Pascals, a pressure foot area of 2500 square millimeters, a pressure foot diameter of 56.42 millimeters, a dwell time of 3 seconds and a lowering rate of 0.8 millimeters per second.

Tensile

Tensile testing was done in accordance with TAPPI test method T-576 “Tensile properties of towel and tissue products (using constant rate of elongation)” wherein the testing is conducted on a tensile testing machine maintaining a constant rate of elongation and the width of each specimen tested is 3 inches. More specifically, samples for dry tensile strength testing were prepared by cutting a

3 ± 0.05 inch (76.2 ± 1.3 mm) wide strip in either the machine direction (MD) or cross-machine direction (CD) orientation using a JDC Precision Sample Cutter (Thwing-Albert Instrument Company, Philadelphia, PA, Model No. JDC 3-10, Serial No. 37333) or equivalent. The instrument used for measuring tensile strengths was an MTS Systems Sintech 11S, Serial No. 6233. The data acquisition software was an MTS TestWorks® for Windows Ver. 3.10 (MTS Systems Corp., Research Triangle Park, NC). The load cell was selected from either a 50 Newton or 100 Newton maximum, depending on the strength of the sample being tested, such that the majority of peak load values fall between 10 to 90 percent of the load cell's full scale value. The gauge length between jaws was 4 ± 0.04 inches (101.6 ± 1 mm) for facial tissue and towels and 2 ± 0.02 inches (50.8 ± 0.5 mm) for bath tissue. The crosshead speed was 10 ± 0.4 inches/min (254 ± 1 mm/min), and the break sensitivity was set at 65 percent. The sample was placed in the jaws of the instrument, centered both vertically and horizontally. The test was then started and ended when the specimen broke. The peak load was recorded as either the "MD tensile strength" or the "CD tensile strength" of the specimen depending on direction of the sample being tested. Ten representative specimens were tested for each product or sheet and the arithmetic average of all individual specimen tests was recorded as the appropriate MD or CD tensile strength the product or sheet in units of grams of force per 3 inches of sample. The geometric mean tensile (GMT) strength was calculated and is expressed as grams-force per 3 inches of sample width. Tensile energy absorbed (TEA) and slope are also calculated by the tensile tester. TEA is reported in units of gm cm/cm^2. Slope is recorded in units of kg. Both TEA and Slope are directional dependent and thus MD and CD directions are measured independently. Geometric mean TEA and geometric mean slope are defined as the square root of the product of the representative MD and CD values for the given property.

Multi-ply products were tested as multi-ply products and results represent the tensile strength of the total product. For example, a 2-ply product was tested as a 2-ply product and recorded as such. A basesheet intended to be used for a two ply product was tested as two plies and the tensile recorded as such. Alternatively, a single ply may be tested and the result multiplied by the number of plies in the final product to get the tensile strength.

EXAMPLE

Single-ply uncreped through-air dried (UCTAD) tissue webs were made generally in accordance with US Patent No. 5,607,551. The tissue webs and resulting tissue products were formed from various fiber furnishes including, Eucalyptus Hardwood Kraft (EHWK) pulp, NSWK pulp, and high yield hesperaloe pulp (HYH).

The EHWK furnish was prepared by dispersing about 120 pounds (oven dry basis) EHWK pulp in a pulper for 30 minutes at a consistency of about 3 percent. The fiber was then transferred to a machine chest and diluted to a consistency of 1 percent.

The NSWK furnish was prepared by dispersing about 50 pounds (oven dry basis) of NSWK pulp in a pulper for 30 minutes at a consistency of about 3 percent. The fiber was then transferred to a machine chest and diluted to a consistency of 1 percent.

The HYH was prepared by dispersing about 50 pounds (oven dry basis) HYH pulp in a pulper for 30 minutes at a consistency of about 3 percent. The fiber was then transferred to a machine chest and diluted to a consistency of 1 percent. HYH was produced by processing *H. Funifera* using a three stage non-wood pulping process commercially available from Taizen America (Macon, GA). The hesperaloe was not refined. The hesperaloe had an average fiber length of about 1.85 mm and a fiber coarseness of about 5.47 mg/100 m.

The stock solutions were pumped to a 3-layer headbox after dilution to 0.75 percent consistency to form a three layered tissue web. Layered tissue structures were produced as indicated in Table 4, below. The relative weight percentage of the layers was 30% / 40% / 30%.

TABLE 4

Sample	Furnish Layering	Redibond 2038 A (kg/ton)/Layer	Refining (min)	Vacuum (Inches Hg)
Control 1	EHWK/NSWK/EHWK	3/All	1	4
Control 2	EHWK/HYH/EHWK	0	-	4
Inventive 1	HYH/HYH/HYH	0	-	4
Inventive 2	HYH/HYH/HYH	0	-	9
Inventive 3	HYH/HYH/HYH	0	-	12

The formed web was non-compressively dewatered and rush transferred to a transfer fabric traveling at a speed about 28 percent slower than the forming fabric. The transfer vacuum at the transfer to the TAD fabric was varied as indicated in Table 4. The web was then transferred to a T-1205-2 TAD fabric (commercially available from Voith Fabrics, Appleton, WI and previously disclosed in US Patent No. 8,500,955, the contents of which are incorporated herein in a manner consistent with the present disclosure). The web was then dried and wound into a parent roll. The effect of hesperaloe fibers on various tissue properties, including tensile, durability and softness, is summarized in the tables below.

TABLE 5

Sample	Basis Weight (gsm)	Sheet Bulk (cc/g)	GMT (g/3")	GM Slope (kg)	CD Tensile (g/3")	CD TEA (g•cm/cm^2)	CD Stretch (%)
Control 1	29.6	24.5	576	3.60	440	2.87	8.3
Control 2	29.1	25.8	1152	6.10	800	6.29	10.1
Inventive 1	29.5	26.9	2306	9.06	1665	15.53	12.5
Inventive 2	28.8	27.2	2482	9.05	1576	17.83	12.3
Inventive 3	30.5	28.1	2583	8.58	1670	16.84	15.4

TABLE 6

Sample	Stiffness Index	GM Stretch (%)	CD Durability
Control 1	6.26	12.0	6.5
Control 2	5.30	13.9	7.9
Inventive 1	3.93	15.8	9.3
Inventive 2	3.64	15.8	11.3
Inventive 2	3.32	16.4	10.1

While tissue webs, and tissue products comprising the same, have been described in detail with respect to the specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto and the foregoing embodiments:

In a first embodiment the present invention provides a tissue product comprising at least about 90 weight percent high yield hesperaloe pulp fibers, the tissue product having a CD Durability greater than about 8.0 and a sheet bulk greater than about 15 cc/g.

In a second embodiment the present invention provides the tissue product of the first embodiment having a CD Stretch greater than about 12 percent, more preferably greater than about 14 percent and still more preferably greater than about 15 percent.

In a third embodiment the present invention provides the tissue product of the first or the second embodiments having a CD Durability from about 8.0 to about 12.0.

In a fourth embodiment the present invention provides the tissue product of any one of the first through the third embodiments having GM Stretch greater than about 15 percent, more preferably greater than about 17 percent and still more preferably greater than about 18 percent.

In a fifth embodiment the present invention provides the tissue product of any one of the first through the fourth embodiments having a Stiffness Index less than about 5.0 and more preferably less than about 4.5 and still more preferably less than about 4.0.

In a sixth embodiment the present invention provides the tissue product of any one of the first through the fifth embodiments having a bulk greater than about 15 cc/g and more preferably greater than about 20 cc/g and still more preferably greater than about 25 cc/g.

In a seventh embodiment the present invention provides the tissue product of any one of the first through the sixth embodiments wherein the tissue product is substantially free from softwood kraft pulp fibers.

In an eighth embodiment the present invention provides the tissue product of any one of the first through the seventh embodiments comprising from about 95 to about 98 weight percent high yield hesperaloe pulp fibers.

In a ninth embodiment the present invention provides the tissue product of any one of the first through the eighth embodiments wherein the high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.

In a tenth embodiment the present invention provides the tissue product of any one of the first through the ninth embodiments wherein the tissue product is substantially free from NSWK fibers.

In an eleventh embodiment the present invention provides the tissue product of any one of the first through the tenth embodiments wherein the tissue product comprises at least one through-air dried ply.

In a twelfth embodiment the present invention provides the tissue product of any one of the first through the eleventh embodiments wherein the tissue product comprises a single-ply uncreped through-air dried tissue web.

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WHAT IS CLAIMED IS:

1. A tissue product comprising at least about 90 weight percent high yield hesperaloe pulp fibers, the tissue product having a CD Durability greater than about 8.0 and a sheet bulk greater than about 15 cc/g.

2. The tissue product of claim 1 having a CD Stretch greater than about 12 percent.

3. The tissue product of claim 1 having a CD Durability from about 8.0 to about 12.0.

4. The tissue product of claim 1 having a GM Stretch greater than about 15 percent.

5. The tissue product of claim 1 having a Stiffness Index less than about 5.0.

6. The tissue product of claim 1 wherein the sheet bulk is from about 20 to about 30 cc/g.

7. The tissue product of claim 1 wherein the tissue product is substantially free from softwood kraft pulp fibers.

8. The tissue product of claim 1 wherein the tissue product comprises from about 95 to about 98 weight percent high yield hesperaloe pulp fibers.

9. The tissue product of claim 1 wherein the high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.

10. The tissue product of claim 1 wherein the tissue product comprises at least one through-air dried ply.

11. The tissue product of claim 1 wherein the tissue product comprises a single-ply uncreped through-air dried tissue web.

12. A single-ply tissue web having a percent CD stretch greater than about 12 percent and a CD tensile strength from greater than about 1,000 g/3", the tissue web comprising at least about 90 weight percent high yield hesperaloe pulp fibers.

13. The single-ply tissue web of claim 12 having a CD TEA greater than about 15.0 g•cm/cm^2.

14. The single-ply tissue web of claim 12 having a CD Durability greater than about 8.0.

15. The single-ply tissue web of claim 12 having a basis weight from about 20 to about 60 gsm and a sheet bulk greater than about 15 cc/g.

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16. The single-ply tissue web of claim 12 wherein the tissue web is a through-air dried web.

17. The single-ply tissue web of claim 12 wherein the tissue web is an uncreped through-air dried web.

18. A method of making a tissue web comprising the steps of: (a) forming an aqueous suspension of high yield hesperaloe pulp fibers (b) depositing an aqueous suspension of high yield hesperaloe pulp fibers onto a forming fabric traveling at a first rate of speed to form a wet web; (c) dewatering the web to a consistency of about 20 percent or greater; (d) transferring the web to a throughdrying fabric; and (e) throughdrying the web, wherein the web comprises at least about 90 weight percent high yield hesperaloe pulp fibers.

19. The method of claim 18 further comprising the step of rush transferring the dewatered web to a transfer fabric, the transfer fabric traveling at a rate of speed from about 1 to about 30 percent slower than the speed of the forming fabric.

20. The method of claim 18 wherein the throughdried web is uncreped.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/033181

A. CLASSIFICATION OF SUBJECT MATTER

A47K 10/16(2006.01)i

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)
A47K 10/16; D21H 27/38; D21H 11/12; D21H 27/00; B65H 18/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: tissue, hesperaloe, durability, bulk, stretch, web, throughdry, and tensile

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013-0068867 A1 (HERMANS et al.) 21 March 2013 See paragraphs [0018], [0023], [0040]-[0042], [0064]; claims 1, 4-10, 15, 20 and table 5.	1-20
Y	US 5320710 A (REEVES et al.) 14 June 1994 See column 2, lines 54-68; claims 1-2 and figure 2.	1-20
A	US 2014-0284010 A1 (KIMBERLY-CLARK WORLDWIDE, INC.) 25 September 2014 See paragraphs [0027], [0081], [0089] and claims 1, 10-11.	1-20
A	US 2005-0236122 A1 (MULLALLY et al.) 27 October 2005 See paragraphs [0013], [0016], [0089] and claims 1, 9, 26.	1-20
A	US 2013-0199741 A1 (STAGE et al.) 08 August 2013 See claims 1-6 and table 8.	1-20

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

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Date of the actual completion of the international search	Date of mailing of the international search report
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013-0068867 A1	21/03/2013	AU 2012-311166 A1	13/03/2014
		CN 103827392 A	28/05/2014
		EP 2758598 A2	30/07/2014
		KR 10-2014-0068072 A	05/06/2014
		MX 2014002696 A	14/04/2014
		US 2014-0027077 A1	30/01/2014
		US 8574399 B2	05/11/2013
		US 8852398 B2	07/10/2014
		WO 2013-041988 A2	28/03/2013
		WO 2013-041988 A3	13/06/2013
US 05320710 A	14/06/1994	None	
US 2014-0284010 A1	25/09/2014	AU 2012-311164 A1	06/03/2014
		AU 2012-311164 B2	22/01/2015
		CA 2847064 A1	28/03/2013
		CN 103814173 A	21/05/2014
		CO 6910179 A2	31/03/2014
		EP 2758593 A2	30/07/2014
		EP 2758593 A4	29/04/2015
		KR 10-1497884 B1	02/03/2015
		KR 10-2014-0068073 A	05/06/2014
		MX 2014002400 A	05/06/2014
		TW 201319358 A	16/05/2013
		US 2013-0071678 A1	21/03/2013
		US 2013-0299107 A1	14/11/2013
		US 8524374 B2	03/09/2013
		US 8778505 B2	15/07/2014
		WO 2013-041986 A2	28/03/2013
		WO 2013-041986 A3	23/05/2013
US 2005-0236122 A1	27/10/2005	AU 2006-262860 A1	04/01/2007
		AU 2006-262860 A8	28/02/2008
		AU 2006-262860 B2	06/01/2011
		CA 2547672 A1	28/07/2005
		CA 2547672 C	13/03/2012
		EP 1699977 A1	13/09/2006
		EP 1920109 A1	14/05/2008
		KR 10-1254833 B1	15/04/2013
		KR 10-2008-0024140 A	17/03/2008
		MX 2007016282 A	07/03/2008
		US 2005-0133175 A1	23/06/2005
		US 2005-0136222 A1	23/06/2005
		US 2008-0035288 A1	14/02/2008
		US 7294229 B2	13/11/2007
		US 7300543 B2	27/11/2007
		US 7726349 B2	01/06/2010
		WO 2005-068720 A1	28/07/2005
		WO 2007-001576 A1	04/01/2007

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013-0199741 A1	08/08/2013	AU 2013-217357 A1	21/08/2014
		AU 2013-217357 B2	28/05/2015
		CN 104093903 A	08/10/2014
		EP 2812488 A1	17/12/2014
		EP 2812488 A4	09/09/2015
		KR 10-2014-0131348 A	12/11/2014
		MX 2014009286 A	27/08/2014
		US 2015-0101774 A1	16/04/2015
		US 8940376 B2	27/01/2015
		WO 2013-118014 A1	15/08/2013

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(54) **Title**: TISSUE PRODUCT COMPRISING BAMBOO

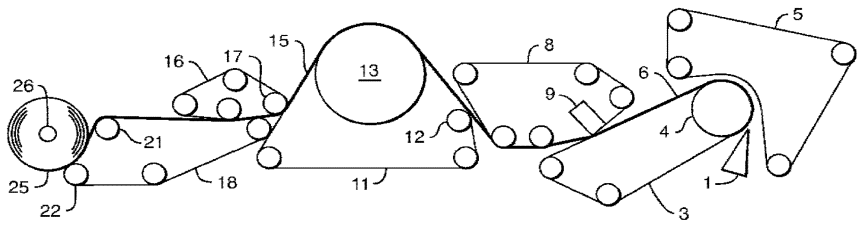


FIG. 1

(57) **Abstract**: The disclosure provides tissue webs, and products incorporating the same, where the webs comprise wood and bamboo fibers. More specifically the disclosure provides soft and durable through-air dried tissue webs comprising at least about 10 percent bamboo fiber by weight of the web. In the through-air dried tissue webs of the present disclosure, bamboo typically replaces high average fiber length wood fibers, which increases the bulk of the through-air dried web without negatively effecting softness or durability.

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TISSUE PRODUCT COMPRISING BAMBOO

FIELD OF THE INVENTION

This disclosure relates to soft and durable through-air dried tissue webs, and tissue products comprising the same, wherein the tissue webs comprise wood and bamboo fibers. It has been discovered that replacing high average fiber length wood fibers with bamboo fibers in a through-air dried web increases sheet bulk without negatively effecting durability or stiffness.

BACKGROUND

Tissue products, such as facial tissues, paper towels, bath tissues, napkins, and other similar products, are designed to include several important properties. For example, the products should have good bulk, a soft feel, and should have good strength and durability. Unfortunately, however, when steps are taken to increase one property of the product, other characteristics of the product are often adversely affected.

Tissue products are made via one of two primary tissue manufacturing processes: conventional wet press (CWP) and through-air drying (TAD). In CWP, the tissue is formed on a forming fabric from either a suction breast roll or twin wire former and the embryonic web is transferred to a papermaking felt and dewatered by pressing with one or two pressure roll nips against the surface of a large steam heated cylinder called a Yankee dryer. The pressing process also assists in transfer of the sheet to the Yankee dryer surface. An adhesive solution is sprayed on the dryer surface prior to the sheet transfer in order to provide good bonding between the sheet and the dryer surface. The sheet is removed from the Yankee surface by a doctor blade in the creping process. In the TAD process, the sheet is formed on a forming fabric and transferred to one or more other fabrics as it is dewatered to a consistency of 25 percent or higher. After the initial dewatering the sheet is dried while in contact with the fabric by blowing hot air through the fabric until the consistency is 40 percent or higher. In conventional through-air dried processes, the through-air dried web is adhered to a Yankee dryer and creped. A roll may be present at the point of transfer to assist in the transfer of the web from the drying fabric to the Yankee dryer but absent the presence of high pressure used to dewater the web in the CWP process. Alternatively TAD tissue may be prepared without creping where foreshortening of the web occurs with a

differential velocity transfer of the wet laid web from the forming fabric to a substantially slower moving, open mesh transfer fabric. Thereafter the web is dried while preventing macroscopic rearrangement of the fibers in the plane of the web. The web is then dried on a fabric in the through-air dryer to a consistency of 90 percent or higher and wound. No Yankee dryer is used in the uncreped through-air dried (UCTAD) process. Through-air dried tissue products are typically associated with higher quality tier tissue products than conventional wet pressed products due to their higher bulk and greater absorption capacity.

To achieve the optimum product properties, tissue products are typically formed, at least in part, from pulps containing wood fibers and often a blend of hardwood and softwood fibers to achieve the desired properties. Typically when attempting to optimize surface softness, as is often the case with tissue products, the papermaker will select the fiber furnish based in part on the coarseness of pulp fibers. Pulps having fibers with low coarseness are desirable because tissue paper made from fibers having a low coarseness can be made softer than similar tissue paper made from fibers having a high coarseness. To optimize surface softness even further, premium tissue products usually comprise layered structures where the low coarseness fibers are directed to the outside layer of the tissue sheet with the inner layer of the sheet comprising longer, coarser fibers.

Unfortunately, the need for softness is balanced by the need for durability. Durability in tissue products can be defined in terms of tensile strength, tensile energy absorption (TEA), burst strength and tear strength. Typically tear, burst and TEA will show a positive correlation with tensile strength while tensile strength, and thus durability, and softness are inversely related. Thus the paper maker is continuously challenged with the need to balance the need for softness with a need for durability. Unfortunately, tissue paper durability generally decreases as the average fiber length is reduced. Therefore, simply reducing the pulp average fiber length can result in an undesirable trade-off between product surface softness and product durability.

Besides durability long fibers also play an important role in overall tissue product softness. While surface softness in tissue products is an important attribute, a second element in the overall softness of a tissue sheet is stiffness. Stiffness can be measured from the tensile slope of stress – strain tensile curve. The lower the slope the lower the stiffness and the better overall softness the product will display. Stiffness and tensile strength are positively correlated, however at a given tensile strength shorter fibers will display a

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greater stiffness than long fibers. While not wishing to be bound by theory, it is believed that this behavior is due to the higher number of hydrogen bonds required to produce a product of a given tensile strength with short fibers than with long fibers. Thus, easily collapsible, low coarseness long fibers, such as those provided by Northern Softwood Kraft (NSWK) fibers typically supply the best combination of durability and softness in tissue products when those fibers are used in combination with hardwood Kraft fibers such as Eucalyptus hardwood Kraft fibers. While Northern Softwood Kraft Fibers have a higher coarseness than Eucalyptus fibers their small cell wall thickness relative to lumen diameter combined with their long length makes them the ideal candidate for optimizing durability and softness in tissue.

Unfortunately, supply of NSWK is under significant pressure both economically and environmentally. As such, prices of NSWK fibers have escalated significantly creating a need to find alternatives to optimize softness and strength in tissue products. Another type of softwood fiber is Southern Softwood Kraft (SSWK) widely used in fluff pulp containing absorbent products such as diapers, feminine care absorbent products and incontinence products. Unfortunately while not under the same supply and environmental pressures as NSWK, fibers from SSWK are too coarse for tissue products and are unsuitable for making soft tissue products. While having long fiber length, the SSWK fibers have too wide a cell wall width and too narrow a lumen diameter and thus create stiffer, harsher feeling products than NSWK.

The tissue papermaker who is able to obtain pulps having a desirable combination of fiber length and coarseness from fiber blends generally regarded as inferior with respect to average fiber properties may reap significant cost savings and/or product improvements. For example, the papermaker may wish to make a tissue paper of superior strength without incurring the usual degradation in softness which accompanies higher strength. Alternatively, the papermaker may wish a higher degree of paper surface bonding to reduce the release of free fibers without suffering the usual decrease in softness which accompanies greater bonding of surface fibers. As such, a need currently exists for a tissue product formed from a fiber that will improve durability without negatively affecting other important product properties, such as softness.

Outside of Northern and Southern softwood pulp fibers very few options exist for papermakers when selecting long fibers. Bamboo fibers have been used in paper for many

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years primarily in India and China. Long and short fiber bamboo species are reported. Bamboo fibers have been used to replace wood fibers in blended, conventional wet pressed tissue products in India and China. Unfortunately commercially available bamboo pulps comprise a mixture of species of bamboos including long and short fibers. Length weighted average fiber lengths are significantly shorter than northern and southern softwood pulp fibers. In addition, the bamboo pulps contain a high portion of primary fines in the form of parenchyma cells. It is well known that the presence of high levels of fines in tissue products create a decrease in surface softness and an increase in stiffness of tissue sheets. Thus, tissue sheets comprising high amounts of bamboo fibers tend to be less soft than those comprising wood fibers. Moreover, given the relatively short fiber length and high level of primary fines, bamboo pulp fibers would not be predicted to provide good durability or softness properties to premium tissue products when specifically replacing wood pulp fibers. Generally, bamboo fibers have coarseness and fines that are too high to replace hardwood fibers and an average fiber length that is too short and cell walls that are too thick to replace softwood fibers.

SUMMARY

It has now been unexpectedly discovered that bamboo fibers, despite having relatively short fiber length, thick cell walls and a narrow lumen may be incorporated into a through-air dried tissue web, and particularly the non-skin contacting layer of a multi layered web, to yield a tissue web having improved bulk without a significant increase in stiffness or decrease in durability. These properties are particularly acute when bamboo fibers are substituted for high average fiber length wood fibers, such as softwood fibers and more specifically Northern Softwood Kraft (NSWK). Accordingly, in certain preferred embodiments, bamboo fibers may replace at least about 50 percent of the NSWK in the web and more preferably at least about 75 percent of the NWSK, such that bamboo fiber comprises at least about 10 percent and more preferably at least about 20 percent by weight of the web. Moreover, it has been discovered that softness levels may be further improved by disposing the bamboo fibers within the fibrous tissue web such that the bamboo fibers are not brought into contact with a user's skin in-use, such as in the middle layer of a three layered structure. Furthermore, it has been discovered that through-air dried webs comprising bamboo fibers have an unexpected increase in bulk. The improved durability

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and bulk are observed for several species of bamboo, including both tropical and temperate timber bamboo.

Accordingly, the present disclosure provides, in one embodiment, a through-air dried tissue web comprising bamboo fiber, wherein the bamboo fiber comprises at least about 10 percent by weight of the tissue web. If desired, the bamboo pulp fibers may have an average fiber length greater than about 1 mm, such as from about 1.1 to about 2.5 mm and more preferably from about 1.2 to about 2 mm.

In another embodiment, the present disclosure provides a through-air dried tissue web comprising bamboo fiber wherein the bamboo fiber has replaced a significant portion of the long fiber, particularly NSWK fiber such that the amount of NSWK fiber in the web is less than about 20 percent of the total web such as from about 0 to about 15 percent and more preferably from about 0 to about 10 percent of the total weight of the web.

In other embodiments, the present disclosure provides a multi-layered through air dried tissue web comprising two or more layers including a first layer and a second layer, wherein a greater weight percent of bamboo fiber is present in the second layer than in the first layer. In certain preferred embodiments the first layer comprises hardwood fibers and the second layer comprises bamboo and softwood fibers, wherein the weight ratio of bamboo fiber to softwood fiber is greater than 1:1.

In still other embodiments the disclosure provides a multi-layered tissue web comprising a first fibrous layer and a second fibrous layer, wherein the first fibrous layer comprises wood fibers and the second fibrous layer comprises bamboo fiber, wherein bamboo fibers comprise from about 75 to about 100 percent by weight of the second layer.

In other embodiments the disclosure provides a through-air dried tissue product comprising bamboo fibers, wherein the bamboo fibers are selected from the group consisting of temperate running bamboos including but not limited to *Phyllostachys heterocycla pubescens*, *Phyllostachys nigra variant Henon*, *Phyllostachys vivax* and *Phyllostachys Bambusoides,* and mixtures thereof.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of one embodiment of a process for forming an uncreped through-air dried tissue web for use in the present disclosure.

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DEFINITIONS

It should be noted that, when employed in the present disclosure, the terms "comprises," "comprising," and other derivatives from the root term "comprise" are intended to be open-ended terms that specify the presence of any stated features, elements, integers, steps, or components, and are not intended to preclude the presence or addition of one or more other features, elements, integers, steps, components, or groups thereof.

As used herein, the term "Tear Index" refers to the quotient of the geometric mean tear strength (typically expressed in grams) divided by the geometric mean tensile strength (typically expressed in grams per 3 inches) multiplied by 1,000 where the geometric mean tear index is defined as the square root of the product of the machine directional tear strength and the cross directional tear strength.

$$Tear\ Index = \frac{\sqrt{MD\ Tear\ x\ CD\ Tear}}{GMT}\ x\ 1{,}000$$

While tear index may vary depending on the composition of the tissue web, as well as the basis weight of the web, webs prepared according to the present disclosure generally have a Tear Index greater than about 5, more preferably greater than about 6 and still more preferably greater than about 7 such as from about 7 to about 20.

As used herein, the term "Burst Index" refers to the quotient of the dry burst peak load (also referred to as the dry burst strength and typically expressed gram feet) divided by the geometric mean tensile strength multiplied by 10.

$$Burst\ Index = \frac{Dry\ Burst\ Strength}{GMT}\ x\ 10$$

While Burst Index may vary depending on the composition of the tissue web, as well as the basis weight of the web, webs prepared according to the present disclosure generally have a burst index greater than 3, more preferably greater than about 4 and still more preferably greater than about 5.

As used herein, the terms "geometric mean tensile" and "GMT" refer to the square root of the product of the machine direction tensile strength and the cross-machine direction tensile strength of the web. As used herein, tensile strength refers to geometric mean tensile strength as would be apparent to one skilled in the art unless otherwise stated.

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As used herein, the terms "geometric mean tensile energy index" and "TEA Index" refer to the square root of the product of the MD and CD tensile energy absorption ("MD TEA" and "CD TEA," typically expressed in g•cm/cm^2) divided by the GMT strength multiplied by 1,000.

$$TEA\ Index = \frac{\sqrt{MD\ TEA\ x\ CD\ TEA}}{GMT}\ x\ 1{,}000$$

While the TEA Index may vary depending on the composition of the tissue web, as well as the basis weight of the web, webs prepared according to the present disclosure generally have a TEA Index greater than about 6, more preferably greater than about 7 and still more preferably greater than about 8, such as from about 8 to about 20.

As used herein, the term "Durability Index" refers to the sum of the tear index, burst index and TEA Index and is an indication of the durability of the product at a given tensile strength.

$$Durability\ Index = Tear\ Index + Burst\ Index + TEA\ Index$$

While the Durability Index may vary depending on the composition of the tissue web, as well as the basis weight of the web, webs prepared according to the present disclosure generally have a Durability Index values of about 15 or greater, more preferably about 18 or greater and still more preferably about 20 or greater such as from about 20 to about 50.

As used herein, the term "Stiffness Index" refers to the quotient of the geometric mean tensile slope, defined as the square root of the product of the MD and CD tensile slopes, divided by the geometric mean tensile strength.

$$Stiffness\ Index = \frac{\sqrt{MD\ Tensile\ Slope\ x\ CD\ Tensile\ Slope}}{GMT}\ x\ 1{,}000$$

While the Stiffness Index may vary depending on the composition of the tissue web, as well as the basis weight of the web, webs prepared according to the present disclosure generally have a Stiffness Index values of less than about 16, more preferably less than about 15 and still more preferably less than about 14 such as from about 5 to about 14.

As used herein, the term "average fiber length" refers to the length weighted average length of fibers determined utilizing a Kajaani fiber analyzer model No. FS-100 available from Kajaani Oy Electronics, Kajaani, Finland. According to the test procedure, a pulp sample is treated with a macerating liquid to ensure that no fiber bundles or shives are

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present. Each pulp sample is disintegrated into hot water and diluted to an approximately 0.001 percent solution. Individual test samples are drawn in approximately 50 to 100 ml portions from the dilute solution when tested using the standard Kajaani fiber analysis test procedure. The weighted average fiber length may be expressed by the following equation:

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$$\sum_{x_i=0}^{k} (x_i \times n_i)/n$$

where k = maximum fiber length

x_i = fiber length

n_i = number of fibers having length x_i

n = total number of fibers measured.

As used herein, a "tissue product" generally refers to various paper products, such as facial tissue, bath tissue, paper towels, napkins, and the like. Normally, the basis weight of a tissue product of the present invention is less than about 80 grams per square meter (gsm), in some embodiments less than about 60 gsm, and in some embodiments, between about 10 to about 60 gsm.

Tissue products are further differentiated from other paper products in terms of their bulk. The bulk of the tissue and towel products of the present invention is calculated as the quotient of the caliper (hereinafter defined), expressed in microns, divided by the basis weight, expressed in grams per square meter. The resulting bulk is expressed as cubic centimeters per gram. In certain embodiments tissue products may have a bulk greater than about 5 cm^3/g and still more preferably greater than about 7 cm^3/g, such as from about 7 to about 15 cm^3/g. Tissue webs prepared according to the present disclosure may have higher bulk than the tissue products incorporating the same webs. For example, tissue webs may have a bulk greater than about 7 cm^3/g, such as greater than about 10 cm^3/g, such as from about 12 to about 24 cm^3/g.

As used herein, the term "layer" refers to a plurality of strata of fibers, chemical treatments, or the like within a ply.

As used herein, the terms "layered tissue web," "multi-layered tissue web," "multi-layered web," and "multi-layered paper sheet," generally refer to sheets of paper prepared from two or more layers of aqueous papermaking furnish which are preferably comprised of different fiber types. The layers are preferably formed from the deposition of separate streams of dilute fiber slurries, upon one or more endless foraminous screens. If the individual layers are initially formed on separate foraminous screens, the layers are subsequently combined (while wet) to form a layered composite web.

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The term "ply" refers to a discrete product element. Individual plies may be arranged in juxtaposition to each other. The term may refer to a plurality of web-like components such as in a multi-ply facial tissue, bath tissue, paper towel, wipe, or napkin.

DETAILED DESCRIPTION

In general, the present disclosure relates to a through-air dried tissue product comprising a tissue web that has been formed from wood and bamboo fibers. It has been discovered that by replacing some of the wood fibers with bamboo fibers that a bulkier and more durable web may be produced without sacrificing softness.

Table 1 compares hardwood (Eucalyptus pulp fiber, Aracruz Cellulose, Brazil) softwood (NSWK pulp fiber, Northern Pulp, Canada) and kraft pulps prepared from three different bamboo species, *Phyllostachys edulis*, *Bambusa vulgaris* and *Phyllostachys nigra variant Henon*.

TABLE 1

Fiber Type	Average Fiber Length (mm)	Average Fiber Width (μm)	Fiber Length: Fiber Width	Coarseness (mg/100 m)
Phyllostachys edulis	1.23	8.4	146	10.53
Bambusa vulgaris	2.09	10.9	192	10.37
Phyllostachys nigra variant Henon	1.65	9.0	184	10.85
NSWK Pulp Fiber	2.18	27.6	79	14.83
Eucalyptus Pulp Fiber	0.76	19.1	40	8.95

For bamboo pulp fibers, the ratio of length to width (commonly referred to as the "aspect ratio") generally varies between about 150 and about 200, although both length and width vary amongst species. Generally average fiber lengths for bamboo pulp fibers range from about 2 mm for *B. vlgaris* to about 1.2 mm for *Phyllostachys edulis*. As shown in Table 1, bamboo pulp fibers are generally greater in length than Eucalyptus fibers, but shorter than NSWK fibers. However, bamboo pulp fibers tend to have greater aspect ratios and higher coarseness than Eucalyptus fibers. Additionally, bamboo pulp fibers tend to have relatively slender lumens and thick cell walls, yielding Runkel Ratios (ratio of twice the cell wall thickness to the diameter of the lumen) greater than 1. For example, the reported Runkel Ratios for *Phyllostachys nigra variant Henon* and *Bambusa vulgaris* are 2.17 and 3.20 respectively. Fibers having Runkel Ratios greater than 1 are commonly considered poor

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candidates for use in tissue because the thick cell walls produce stiff webs having poor tensile strength and low bulk.

Despite the tendency of bamboo pulp fibers to have relatively thicker cell walls, higher Runkel Ratios, higher aspect ratios and shorter average fiber lengths compared to softwood fibers it has now been surprisingly discovered that they may replace softwood fibers in a through-air dried tissue web without decreasing durability and bulk or increasing stiffness. Even more surprising is that substitution of bamboo fibers for softwood fibers actually increases bulk without negatively affecting durability and stiffness.

Accordingly, in a preferred embodiment the disclosure provides a tissue web and more preferably a through-air dried tissue web and still more preferably a multi-layered through-air dried web comprising bamboo, wherein the bamboo fibers comprise at least about 10 percent of the total weight of the web. In a particularly preferred embodiment, the tissue web comprises a multi-layered through-air dried web wherein bamboo fiber is selectively disposed in only one of the layers such that the bamboo fiber is not brought into contact with the user's skin in-use. For example, in one embodiment the tissue web may comprise a two layered web wherein the first layer consists essentially of wood fibers and is substantially free of bamboo fibers and the second layer comprises bamboo fibers, wherein the bamboo fibers comprises at least about 50 percent by weight of the second layer, such as from about 50 to about 100 percent by weight of the second layer. It should be understood that, when referring to a layer that is substantially free of bamboo fibers, negligible amounts of the fibers may be present therein, however, such small amounts often arise from the bamboo fibers applied to an adjacent layer, and do not typically substantially affect the softness or other physical characteristics of the web.

The tissue webs may be incorporated into tissue products that may be either single or multi-ply, where one or more of the plies may be formed by a multi-layered tissue web having bamboo fibers selectively incorporated in one of its layers. A particularly preferred embodiment tissue product is constructed such that the bamboo fibers are not brought into contact with the user's skin in-use. For example, the tissue product may comprise two multi-layered through-air dried webs wherein each web comprises a first fibrous layer substantially free from bamboo and a second fibrous layer comprising bamboo. The webs are plied together such that the outer surface of the tissue product is formed from the first

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fibrous layers of each web, such that the surface brought into contact with the user's skin in-use is substantially free of bamboo fibers.

Generally, the bamboo fibers incorporated in the webs of the present disclosure are fibrous materials derived from any bamboo species. The bamboo fiber species may be selected from the group consisting of *Acidosasa sp., Ampleocalamus sp., Arundinaria sp., Bambusa sp., Bashania sp., Borinda sp., Brachystachyum sp., Cephalostachyum sp., Chimonobambusa sp., Chusquea sp., Dendrocalamus sp., Dinochloa sp., Drepanostachyum sp., Eremitis sp., Fargesia sp., Gaoligongshania sp., Gelidocalamus sp., Gigantochloa sp., Guadua sp., Hibanobambusa sp., Himalayacalamus sp., Indocalamus sp., Indosasa sp., Lithachne sp., Melocanna sp., Menstruocalamus sp., Nastus sp., Neohouzeaua sp., Neomicrocalamus sp., Ochlandra sp., Oligostachyum sp., Olmeca sp., Otatea sp., Oxytenanthera sp., Phyllostachys sp., Pleioblastus sp., Pseudosasa sp., Raddia sp., Rhipidocladum sp., Sasa sp., Sasaella sp., Sasamorpha sp., Schizostachyum sp., Semiarundinaria sp., Shibatea sp., Sinobambusa sp., Thamnocalamus sp., Thyrsostachys sp., Yushania sp.* and mixtures thereof.

In some embodiments, the bamboo fiber is from temperate bamboos of the Phyllostachys species, for example *Phyllostachys heterocycla pubescens*, also known as Moso Bamboo. However, it is to be understood that the compositions disclosed herein are not limited to containing any one bamboo fiber and may comprise a plurality of fibers of different species. For example, the composition may comprise a bamboo from a *Phyllostachys heterocycla pubescens* and a bamboo from a different species such as, for example, *Phyllostachys bambusoides*.

Bamboo fiber for use in the webs and products of the present disclosure may be produced by any appropriate methods known in the art. Preferably the bamboo fibers are pulped bamboo fibers, produced by chemical processing of crushed bamboo stalk. The chemical processing may comprise treating the crushed bamboo stalk with an appropriate alkaline solution. The skilled artisan will be capable of selecting an appropriate alkaline solution. Bamboo fiber may also be produced by mechanical processing of crushed bamboo stalk, which may involve enzymatic digestion of the crushed bamboo stalk.

Although bamboo fiber may be produced by any appropriate methods known in the art, the preferred method for manufacturing the bamboo pulp is as a chemical pulping method such as, but not limited to, kraft, sulfite or soda/AQ pulping techniques.

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Preferably the bamboo fibers are bamboo pulp fibers and have an average fiber length of at least about 1 mm. When blends of fibers from various bamboo species are employed, it is noted that blends may comprise two or more species of bamboo, preferably three or more, such that the average fiber length is at least about 1.2 mm and more preferably at least about 1.5 mm, such as from about 1.2 to about 2 mm.

Regardless of the species or particular average fiber length, at least one layer of a multi-layered web comprises bamboo fiber. The multi-layered web may also contain wood fibers and may be layered such that one layer comprises wood fibers, which optionally is substantially free from bamboo fibers, while another layer comprises wood and bamboo fibers. The wood fibers may include fibers formed by a variety of pulping processes, such as kraft pulp, sulfite pulp, thermomechanical pulp, and the like. Further, the wood fibers may be any high-average fiber length wood pulp, low-average fiber length wood pulp, or mixtures of the same. One example of suitable high-average length wood pulp fibers include softwood fibers such as, but not limited to, northern softwood, southern softwood, redwood, red cedar, hemlock, pine (e.g., southern pines), spruce (e.g., black spruce), combinations thereof, and the like. One example of suitable low-average length wood pulp fibers include hardwood fibers, such as, but not limited to, eucalyptus, maple, birch, aspen, and the like. In certain instances, eucalyptus fibers may be particularly desired to increase the softness of the web. Eucalyptus fibers can also enhance the brightness, increase the opacity, and change the pore structure of the web to increase its wicking ability. Moreover, if desired, secondary fibers obtained from recycled materials may be used, such as fiber pulp from sources such as, for example, newsprint, reclaimed paperboard, and office waste.

In a particularly preferred embodiment bamboo fibers are utilized in the tissue web as a replacement for high average fiber length wood fibers such as softwood fibers and more specifically NSWK. In one particular embodiment, the bamboo fibers are derived from *Phyllostachys pubescens* and replace NSWK such that the total amount of NSWK, by weight of the web, is less than about 10 percent. In other embodiments it may be desirable to replace all of the wood fiber in a given layer such that the layer consists essentially of bamboo fiber.

In certain embodiments it may be desirable to have particular combinations of bamboo and wood pulp fibers within a given layer to provide desired characteristics. For

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example, it may be desirable to combine bamboo and wood fibers having different average fiber lengths, coarseness, cell wall thickness, or other characteristics, in certain layers.

Just as the amount of bamboo within any given layer may be varied, the ratio of bamboo fibers to total fiber in the web may generally vary depending on the desired properties of the tissue product. For instance, the use of a thicker bamboo layer typically results in a tissue product with higher durability but lower softness. Additionally, the use of a large amount of bamboo fibers may negatively impact sheet formation and may increase the cost of manufacture. Likewise, the use of very low amounts of bamboo fibers, i.e., less than about 10 percent of the total weight of the web, typically results in a tissue product having little discernable difference compared to tissue products manufactured without bamboo. Thus, in certain embodiments, tissue webs prepared according to the present disclosure comprise bamboo fibers in an amount from about 10 to about 80 percent by weight of the web, preferably from about from about 15 to about 60 percent and more preferably from about 25 to about 50 percent.

As noted previously, in a preferred embodiment bamboo fibers are introduced to the web as a replacement for softwood fibers, accordingly in such preferred embodiments the amount of softwood fibers in the web may range from about 0 to about 20 percent by weight of the total web, more preferably from 0 to about 10 percent and most preferably less than about 5 percent by weight of the total web. In one preferred embodiment the amount of softwood fiber in the web is less than 1 percent by weight of the total web.

In addition to varying the amount of bamboo within the web, as well as the amount in any given layer, the physical properties of the web may be varied by specifically selecting particular layer(s) for incorporation of the bamboo fibers. It has now been discovered that the greatest increase in softness without adverse effects on tensile strength or other sheet properties is achieved by selectively incorporating the bamboo fibers in a multi-layered web such that the layer comprising bamboo is not brought into contact with the user's skin in-use. Further, if desired, the increase in cost often encountered with bamboo fibers can be reduced by restricting application of the bamboo fibers to only a single layer of the web. For instance, in one embodiment, a three-layered tissue web can be formed in which only the middle layer contains bamboo fibers, while the outer layers are substantially free of bamboo fibers.

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Accordingly, in a preferred embodiment the tissue web is a multi-layered web comprising a first fibrous layer and a second fibrous layer, wherein the first fibrous layer comprises wood fibers and the second fibrous layer comprises bamboo fibers, wherein the amount of bamboo fibers is from about 50 to about 100 percent by weight of the second layer. In certain embodiments the second fibrous layer may comprise a blend of wood and bamboo fibers, and more preferably a blend of bamboo and softwood fibers wherein the amount of bamboo fibers is from about 50 to about 90 percent by weight of the second layer and still more preferably from about 80 to about 95 percent by weight of the second layer. In a particularly preferred embodiment the first fibrous layer comprises hardwood fiber.

In other embodiments the present disclosure provides a two-ply tissue product. In a particularly preferred embodiment, the tissue product contains an upper multi-layered tissue web and a lower multi-layered tissue web that are plied together using well-known techniques. The multi-layered webs comprise at least a first and a second layer, wherein bamboo fibers are selectively incorporated in only one of the layers, such that when the webs are plied together the layers containing the bamboo fibers are not brought into contact with the user's skin in-use. For example, the two-ply tissue product may comprise a first and second tissue web, wherein the tissue webs each comprise a first and second layer. The first layer of each tissue web comprises wood fibers and is substantially free of bamboo fibers, while the second layer of each tissue web comprises bamboo fibers. When the tissue webs are plied together to form the tissue product the second layers of each web are arranged in a facing relationship such that the bamboo fibers are not brought into contact with the user's skin in-use.

If desired, various chemical compositions may be applied to one or more layers of the multi-layered tissue web to further enhance softness and/or reduce the generation of lint or slough. For example, in some embodiments, a wet strength agent can be utilized, to further increase the strength of the tissue product. As used herein, a "wet strength agent" is any material that, when added to pulp fibers can provide a resulting web or sheet with a wet geometric tensile strength to dry geometric tensile strength ratio in excess of about 0.1. Typically these materials are termed either "permanent" wet strength agents or "temporary" wet strength agents. As is well known in the art, temporary and permanent wet

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strength agents may also sometimes function as dry strength agents to enhance the strength of the tissue product when dry.

Wet strength agents may be applied in various amounts, depending on the desired characteristics of the web. For instance, in some embodiments, the total amount of wet strength agents added can be between about 1 to about 60 pound per ton (lb/T), in some embodiments, between about 5 to about 30 lb/T, and in some embodiments, between about 7 to about 13 lb/T of the dry weight of fibrous material. The wet strength agents can be incorporated into any layer of the multi-layered tissue web.

A chemical debonder can also be applied to soften the web. Specifically, a chemical debonder can reduce the amount of hydrogen bonds within one or more layers of the web, which results in a softer product. Depending on the desired characteristics of the resulting tissue product, the debonder can be utilized in varying amounts. For example, in some embodiments, the debonder can be applied in an amount between about 1 to about 30 lb/T, in some embodiments between about 3 to about 20 lb/T, and in some embodiments, between about 6 to about 15 lb/T of the dry weight of fibrous material. The debonder can be incorporated into any layer of the multi-layered tissue web.

Any material capable of enhancing the soft feel of a web by disrupting hydrogen bonding can generally be used as a debonder in the present invention. In particular, as stated above, it is typically desired that the debonder possess a cationic charge for forming an electrostatic bond with anionic groups present on the pulp. Some examples of suitable cationic debonders can include, but are not limited to, quaternary ammonium compounds, imidazolinium compounds, bis-imidazolinium compounds, diquaternary ammonium compounds, polyquaternary ammonium compounds, ester-functional quaternary ammonium compounds (e.g., quaternized fatty acid trialkanolamine ester salts), phospholipid derivatives, polydimethylsiloxanes and related cationic and non-ionic silicone compounds, fatty and carboxylic acid derivatives, mono and polysaccharide derivatives, polyhydroxy hydrocarbons, etc. For instance, some suitable debonders are described in US Patent Nos. 5,716,498, 5,730,839, 6,211,139, 5,543,067, and WO/0021918, all which are incorporated herein in a manner consistent with the present disclosure.

Still other suitable debonders are disclosed in US Patent Nos. 5,529,665 and 5,558,873, both of which are incorporated herein in a manner consistent with the present

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disclosure. In particular, US Patent No. 5,529,665 discloses the use of various cationic silicone compositions as softening agents.

Tissue webs of the present disclosure can generally be formed by any of a variety of papermaking processes known in the art. Preferably the tissue web is formed by through-air drying and be either creped or uncreped. For example, a papermaking process of the present disclosure can utilize adhesive creping, wet creping, double creping, embossing, wet-pressing, air pressing, through-air drying, creped through-air drying, uncreped through-air drying, as well as other steps in forming the paper web. Some examples of such techniques are disclosed in US Patent Nos. 5,048,589, 5,399,412, 5,129,988 and 5,494,554 all of which are incorporated herein in a manner consistent with the present disclosure. When forming multi-ply tissue products, the separate plies can be made from the same process or from different processes as desired.

For example, in one embodiment, tissue webs may be creped through-air dried webs formed using processes known in the art. To form such webs, an endless traveling forming fabric, suitably supported and driven by rolls, receives the layered papermaking stock issuing from headbox. A vacuum box is disposed beneath the forming fabric and is adapted to remove water from the fiber furnish to assist in forming a web. From the forming fabric, a formed web is transferred to a second fabric, which may be either a wire or a felt. The fabric is supported for movement around a continuous path by a plurality of guide rolls. A pick up roll designed to facilitate transfer of web from fabric to fabric may be included to transfer the web.

Preferably the formed web is dried by transfer to the surface of a rotatable heated dryer drum, such as a Yankee dryer. The web may be transferred to the Yankee directly from the throughdrying fabric, or preferably, transferred to an impression fabric which is then used to transfer the web to the Yankee dryer. In accordance with the present disclosure, the creping composition of the present disclosure may be applied topically to the tissue web while the web is traveling on the fabric or may be applied to the surface of the dryer drum for transfer onto one side of the tissue web. In this manner, the creping composition is used to adhere the tissue web to the dryer drum. In this embodiment, as the web is carried through a portion of the rotational path of the dryer surface, heat is imparted to the web causing most of the moisture contained within the web to be evaporated. The web is then removed from the dryer drum by a creping blade. The creping web as it is

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formed further reduces internal bonding within the web and increases softness. Applying the creping composition to the web during creping, on the other hand, may increase the strength of the web.

In another embodiment the formed web is transferred to the surface of the rotatable heated dryer drum, which may be a Yankee dryer. The press roll may, in one embodiment, comprise a suction pressure roll. In order to adhere the web to the surface of the dryer drum, a creping adhesive may be applied to the surface of the dryer drum by a spraying device. The spraying device may emit a creping composition made in accordance with the present disclosure or may emit a conventional creping adhesive. The web is adhered to the surface of the dryer drum and then creped from the drum using the creping blade. If desired, the dryer drum may be associated with a hood. The hood may be used to force air against or through the web.

In other embodiments, once creped from the dryer drum, the web may be adhered to a second dryer drum. The second dryer drum may comprise, for instance, a heated drum surrounded by a hood. The drum may be heated from about 25 to about 200°C, such as from about 100 to about 150°C.

In order to adhere the web to the second dryer drum, a second spray device may emit an adhesive onto the surface of the dryer drum. In accordance with the present disclosure, for instance, the second spray device may emit a creping composition as described above. The creping composition not only assists in adhering the tissue web to the dryer drum, but also is transferred to the surface of the web as the web is creped from the dryer drum by the creping blade.

Once creped from the second dryer drum, the web may, optionally, be fed around a cooling reel drum and cooled prior to being wound on a reel.

For example, once a fibrous web is formed and dried, in one aspect, the creping composition may be applied to at least one side of the web and the at least one side of the web may then be creped. In general, the creping composition may be applied to only one side of the web and only one side of the web may be creped, the creping composition may be applied to both sides of the web and only one side of the web is creped, or the creping composition may be applied to each side of the web and each side of the web may be creped.

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Once creped the tissue web may be pulled through a drying station. The drying station can include any form of a heating unit, such as an oven energized by infra-red heat, microwave energy, hot air or the like. A drying station may be necessary in some applications to dry the web and/or cure the creping composition. Depending upon the creping composition selected, however, in other applications a drying station may not be needed.

In other embodiments, the base web is formed by an uncreped through-air drying process. Referring to FIG. 1, a process of carrying out using the present disclosure will be described in greater detail. The process shown depicts an uncreped throughdried process, but it will be recognized that any known papermaking method or tissue making method can be used in conjunction with the nonwoven tissue making fabrics of the present disclosure. Related uncreped through-air dried tissue processes are described for example, in US Patent Nos. 5,656,132 and 6,017,417, both of which are hereby incorporated by reference herein in a manner consistent with the present disclosure.

In FIG. 1, a twin wire former having a papermaking headbox 10 injects or deposits a furnish of an aqueous suspension of papermaking fibers onto a plurality of forming fabrics, such as the outer forming fabric 5 and the inner forming fabric 3, thereby forming a wet tissue web 6. The forming process of the present disclosure may be any conventional forming process known in the papermaking industry. Such formation processes include, but are not limited to, Fourdriniers, roof formers such as suction breast roll formers, and gap formers such as twin wire formers and crescent formers.

The wet tissue web 6 forms on the inner forming fabric 3 as the inner forming fabric 3 revolves about a forming roll 4. The inner forming fabric 3 serves to support and carry the newly-formed wet tissue web 6 downstream in the process as the wet tissue web 6 is partially dewatered to a consistency of about 10 percent based on the dry weight of the fibers. Additional dewatering of the wet tissue web 6 may be carried out by known paper making techniques, such as vacuum suction boxes, while the inner forming fabric 3 supports the wet tissue web 6. The wet tissue web 6 may be additionally dewatered to a consistency of at least about 20 percent, more specifically between about 20 to about 40 percent, and more specifically about 20 to about 30 percent.

The forming fabric 3 can generally be made from any suitable porous material, such as metal wires or polymeric filaments. For instance, some suitable fabrics can include, but

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are not limited to, Albany 84M and 94M available from Albany International (Albany, NY) Asten 856, 866, 867, 892, 934, 939, 959, or 937; Asten Synweve Design 274, all of which are available from Asten Forming Fabrics, Inc. (Appleton, WI); and Voith 2164 available from Voith Fabrics (Appleton, WI). Forming fabrics or felts comprising nonwoven base layers may also be useful, including those of Scapa Corporation made with extruded polyurethane foam such as the Spectra Series.

The wet web 6 is then transferred from the forming fabric 3 to a transfer fabric 8 while at a solids consistency of between about 10 to about 35 percent, and particularly, between about 20 to about 30 percent. As used herein, a "transfer fabric" is a fabric that is positioned between the forming section and the drying section of the web manufacturing process.

Transfer to the transfer fabric 8 may be carried out with the assistance of positive and/or negative pressure. For example, in one embodiment, a vacuum shoe 9 can apply negative pressure such that the forming fabric 3 and the transfer fabric 8 simultaneously converge and diverge at the leading edge of the vacuum slot. Typically, the vacuum shoe 9 supplies pressure at levels between about 10 to about 25 inches of mercury. As stated above, the vacuum transfer shoe 9 (negative pressure) can be supplemented or replaced by the use of positive pressure from the opposite side of the web to blow the web onto the next fabric. In some embodiments, other vacuum shoes can also be used to assist in drawing the fibrous web 6 onto the surface of the transfer fabric 8.

Typically, the transfer fabric 8 travels at a slower speed than the forming fabric 3 to enhance the MD and CD stretch of the web, which generally refers to the stretch of a web in its cross (CD) or machine direction (MD) (expressed as percent elongation at sample failure). For example, the relative speed difference between the two fabrics can be from about 1 to about 30 percent, in some embodiments from about 5 to about 20 percent, and in some embodiments, from about 10 to about 15 percent. This is commonly referred to as "rush transfer". During "rush transfer", many of the bonds of the web are believed to be broken, thereby forcing the sheet to bend and fold into the depressions on the surface of the transfer fabric 8. Such molding to the contours of the surface of the transfer fabric 8 may increase the MD and CD stretch of the web. Rush transfer from one fabric to another can follow the principles taught in any one of the following patents, US Patent Nos. 5,667,636,

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5,830,321, 4,440,597, 4,551,199, 4,849,054, all of which are hereby incorporated by reference herein in a manner consistent with the present disclosure.

The wet tissue web 6 is then transferred from the transfer fabric 8 to a throughdrying fabric 11. Typically, the transfer fabric 8 travels at approximately the same speed as the throughdrying fabric 11. However, it has now been discovered that a second rush transfer may be performed as the web is transferred from the transfer fabric 8 to a throughdrying fabric 11. This rush transfer is referred to herein as occurring at the second position and is achieved by operating the throughdrying fabric 11 at a slower speed than the transfer fabric 8. By performing rush transfer at two distinct locations, i.e., the first and the second positions, a tissue product having increased CD stretch may be produced.

In addition to rush transferring the wet tissue web from the transfer fabric 8 to the throughdrying fabric 11, the wet tissue web 6 may be macroscopically rearranged to conform to the surface of the throughdrying fabric 11 with the aid of a vacuum transfer roll 12 or a vacuum transfer shoe like the vacuum shoe 9. If desired, the throughdrying fabric 11 can be run at a speed slower than the speed of the transfer fabric 8 to further enhance MD stretch of the resulting absorbent tissue product. The transfer may be carried out with vacuum assistance to ensure conformation of the wet tissue web 6 to the topography of the throughdrying fabric 11.

While supported by the throughdrying fabric 11, the wet tissue web 6 is dried to a final consistency of about 94 percent or greater by a throughdryer 13. The web 15 then passes through the winding nip between the reel drum 22 and the reel 23 and is wound into a roll of tissue 25 for subsequent converting, such as slitting cutting, folding, and packaging.

The web is transferred to the throughdrying fabric for final drying preferably with the assistance of vacuum to ensure macroscopic rearrangement of the web to give the desired bulk and appearance. The use of separate transfer and throughdrying fabrics can offer various advantages since it allows the two fabrics to be designed specifically to address key product requirements independently. For example, the transfer fabrics are generally optimized to allow efficient conversion of high rush transfer levels to high MD stretch while throughdrying fabrics are designed to deliver bulk and CD stretch. It is therefore useful to have moderately coarse and moderately three-dimensional transfer fabrics and throughdrying fabrics which are quite coarse and three dimensional in the

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optimized configuration. The result is that a relatively smooth sheet leaves the transfer section and then is macroscopically rearranged (with vacuum assist) to give the high bulk, high CD stretch surface topology of the throughdrying fabric. Sheet topology is completely changed from transfer to throughdrying fabric and fibers are macroscopically rearranged, including significant fiber-fiber movement.

The drying process can be any noncompressive drying method which tends to preserve the bulk or thickness of the wet web including, without limitation, throughdrying, infra-red radiation, microwave drying, etc. Because of its commercial availability and practicality, throughdrying is well known and is one commonly used means for noncompressively drying the web for purposes of this invention. Suitable throughdrying fabrics include, without limitation, fabrics with substantially continuous machine direction ridges whereby the ridges are made up of multiple warp strands grouped together, such as those disclosed in US Patent No. 6,998,024. Other suitable throughdrying fabrics include those disclosed in US Patent No. 7,611,607, which is incorporated herein in a manner consistent with the present disclosure, particularly the fabrics denoted as Fred (t1207-77), Jeston (t1207-6) and Jack (t1207-12). The web is preferably dried to final dryness on the throughdrying fabric, without being pressed against the surface of a Yankee dryer, and without subsequent creping.

Once the wet tissue web 6 has been non-compressively dried, thereby forming the dried tissue web 15, it is possible to crepe the dried tissue web 15 by transferring the dried tissue web 15 to a Yankee dryer prior to reeling, or using alternative foreshortening methods such as microcreping as disclosed in US Patent No. 4,919,877.

In the wound product, it is often advantageous to wind the product with the softest side facing the consumer, and hence the shearing process to increase the softness of this side is preferred. However, it is also possible to treat the air side of the web rather than the fabric side, and in these embodiments, it would be possible to increase the air-side softness to a level higher than that of the fabric side.

The process of the present disclosure is well suited to forming multi-ply tissue products. The multi-ply tissue products can contain two plies, three plies, or a greater number of plies. In one particular embodiment, a two-ply rolled tissue product is formed according to the present disclosure in which both plies are manufactured using the same papermaking process, such as, for example, uncreped through-air dried. However, in other

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embodiments, the plies may be formed by two different processes. Generally, prior to being wound in a roll, the first ply and the second ply are attached together. Any suitable manner for laminating the webs together may be used. For example, the process includes a crimping device that causes the plies to mechanically attach together through fiber entanglement. In an alternative embodiment, however, an adhesive may be used in order to attach the plies together.

Additionally, webs prepared according to the present disclosure may be subjected to any suitable post processing including, but not limited to, printing, embossing, calendaring, slitting, folding, combining with other fibrous structures, and the like.

By combining bamboo fibers in a tissue web in this manner, the disclosure provides tissue webs having surprising characteristics. For example, through-air dried tissue webs comprising bamboo have improved bulk, without a loss of durability or softness. Table 2 below shows a comparison of through-air dried and conventional wet pressed control webs comprising hardwood and softwood fibers with comparable webs wherein the softwood fiber has been replaced with either bamboo or hardwood Eucalyptus fiber, respectively. As shown in Table 2, the addition of bamboo to the web results in an increase in sheet bulk without negatively effecting durability or softness. However, this effect is only observed for through-air dried tissue webs. When the web is manufactured using conventional wet pressed techniques the bulk actually decreases, while durability and softness are negatively affected. Similarly, replacement of the softwood fiber with hardwood fiber, while resulting in an increase in bulk, causes a decrease in both durability and softness.

TABLE 2

Control	Bamboo			Eucalyptus		
	Delta Bulk	Delta Durability Index	Delta Stiffness Index	Delta Bulk	Delta Durability Index	Delta Stiffness Index
TAD Web	7.7%	-0.8%	12.7%	7.9%	-14.8%	30.1%
CWP Web	-10.9%	-20.6%	31.4%	-7.0%	-30.5%	30.3%

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TEST METHODS

Sheet Bulk

Sheet Bulk is calculated as the quotient of the dry sheet caliper expressed in microns, divided by the dry basis weight, expressed in grams per square meter. The resulting Sheet Bulk is expressed in cubic centimeters per gram. More specifically, the Sheet Bulk is the representative thickness of a single tissue sheet measured in accordance with TAPPI test methods T402 "Standard Conditioning and Testing Atmosphere For Paper, Board, Pulp Handsheets and Related Products" and T411 om-89 "Thickness (caliper) of Paper, Paperboard, and Combined Board." The micrometer used for carrying out T411 om-89 is an Emveco 200-A Tissue Caliper Tester (Emveco, Inc., Newberg, OR). The micrometer has a load of 2 kilo-Pascals, a pressure foot area of 2500 square millimeters, a pressure foot diameter of 56.42 millimeters, a dwell time of 3 seconds and a lowering rate of 0.8 millimeters per second.

Tear

Tear testing was carried out in accordance with TAPPI test method T-414 "Internal Tearing Resistance of Paper (Elmendorf-type method)" using a falling pendulum instrument such as Lorentzen & Wettre Model SE 009. Tear strength is directional and MD and CD tear are measured independently.

More particularly, a rectangular test specimen of the sample to be tested is cut out of the tissue product or tissue basesheet such that the test specimen measures 63 mm ± 0.15 mm (2.5 inches ± 0.006") in the direction to be tested (such as the MD or CD direction) and between 73 and 114 millimeters (2.9 and 4.6 inches) in the other direction. The specimen edges must be cut parallel and perpendicular to the testing direction (not skewed). Any suitable cutting device, capable of the proscribed precision and accuracy, can be used. The test specimen should be taken from areas of the sample that are free of folds, wrinkles, crimp lines, perforations or any other distortions that would make the test specimen abnormal from the rest of the material.

The number of plies or sheets to test is determined based on the number of plies or sheets required for the test results to fall between 20 to 80 percent on the linear range scale of the tear tester and more preferably between 20 to 60 percent of the linear range scale of the tear tester. The sample preferably should be cut no closer than 6 mm (0.25 inch) from

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the edge of the material from which the specimens will be cut. When testing requires more than one sheet or ply the sheets are placed facing in the same direction.

The test specimen is then placed between the clamps of the falling pendulum apparatus with the edge of the specimen aligned with the front edge of the clamp. The clamps are closed and a 20-millimeter slit is cut into the leading edge of the specimen usually by a cutting knife attached to the instrument. For example, on the Lorentzen & Wettre Model SE 009 the slit is created by pushing down on the cutting knife lever until it reaches its stop. The slit should be clean with no tears or nicks as this slit will serve to start the tear during the subsequent test.

The pendulum is released and the tear value, which is the force required to completely tear the test specimen, is recorded. The test is repeated a total of ten times for each sample and the average of the ten readings reported as the tear strength. Tear strength is reported in units of grams of force (gf). The average tear value is the tear strength for the direction (MD or CD) tested. The "geometric mean tear strength" is the square root of the product of the average MD tear strength and the average CD tear strength. The Lorentzen & Wettre Model SE 009 has a setting for the number of plies tested. Some testers may need to have the reported tear strength multiplied by a factor to give a per ply tear strength. For basesheets intended to be multiple ply products, the tear results are reported as the tear of the multiple ply product and not the single ply basesheet. This is done by multiplying the single ply basesheet tear value by the number of plies in the finished product. Similarly, multiple ply finished product data for tear is presented as the tear strength for the finished product sheet and not the individual plies. A variety of means can be used to calculate but in general will be done by inputting the number of sheets to be tested rather than number of plies to be tested into the measuring device. For example, two sheets would be two 1-ply sheets for 1-ply product and two 2-ply sheets (4-plies) for 2-ply products.

Tensile

Tensile testing was done in accordance with TAPPI test method T-576 "Tensile properties of towel and tissue products (using constant rate of elongation)" wherein the testing is conducted on a tensile testing machine maintaining a constant rate of elongation and the width of each specimen tested is 3 inches. More specifically, samples for dry tensile strength testing were prepared by cutting a 3 inches ± 0.05" (76.2 mm ± 1.3 mm)

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wide strip in either the machine direction (MD) or cross-machine direction (CD) orientation using a JDC Precision Sample Cutter (Thwing-Albert Instrument Company, Philadelphia, PA, Model No. JDC 3-10, Serial No. 37333) or equivalent. The instrument used for measuring tensile strengths was an MTS Systems Sintech 11S, Serial No. 6233. The data acquisition software was an MTS TestWorks® for Windows Ver. 3.10 (MTS Systems Corp., Research Triangle Park, NC). The load cell was selected from either a 50 Newton or 100 Newton maximum, depending on the strength of the sample being tested, such that the majority of peak load values fall between 10 to 90 percent of the load cell's full scale value. The gauge length between jaws was 4 ± 0.04 inches (101.6 ± 1 mm) for facial tissue and towels and 2 ± 0.02 inches (50.8 ± 0.5 mm) for bath tissue. The crosshead speed was 10 ± 0.4 inches/min (254 ± 1 mm/min), and the break sensitivity was set at 65 percent. The sample was placed in the jaws of the instrument, centered both vertically and horizontally. The test was then started and ended when the specimen broke. The peak load was recorded as either the "MD tensile strength" or the "CD tensile strength" of the specimen depending on direction of the sample being tested. Ten representative specimens were tested for each product or sheet and the arithmetic average of all individual specimen tests was recorded as the appropriate MD or CD tensile strength the product or sheet in units of grams of force per 3 inches of sample. The geometric mean tensile (GMT) strength was calculated and is expressed as grams-force per 3 inches of sample width. Tensile energy absorbed (TEA) and slope are also calculated by the tensile tester. TEA is reported in units of gm cm/cm^2. Slope is recorded in units of kg. Both TEA and Slope are directional dependent and thus MD and CD directions are measured independently. Geometric mean TEA and geometric mean slope are defined as the square root of the product of the representative MD and CD values for the given property.

Multi-ply products were tested as multi-ply products and results represent the tensile strength of the total product. For example, a 2-ply product was tested as a 2-ply product and recorded as such. A basesheet intended to be used for a two ply product was tested as two plies and the tensile recorded as such. Alternatively, a single ply may be tested and the result multiplied by the number of plies in the final product to get the tensile strength.

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Burst Strength

Burst strength herein is a measure of the ability of a fibrous structure to absorb energy, when subjected to deformation normal to the plane of the fibrous structure. Burst strength may be measured in general accordance with ASTM D-6548 with the exception that the testing is done on a Constant-Rate-of-Extension (MTS Systems Corporation, Eden Prairie, MN) tensile tester with a computer-based data acquisition and frame control system, where the load cell is positioned above the specimen clamp such that the penetration member is lowered into the test specimen causing it to rupture. The arrangement of the load cell and the specimen is opposite that illustrated in FIG. 1 of ASTM D-6548. The penetration assembly consists of a semi spherical anodized aluminum penetration member having a diameter of 1.588 ± 0.005 cm affixed to an adjustable rod having a ball end socket. The test specimen is secured in a specimen clamp consisting of upper and lower concentric rings of aluminum between which the sample is held firmly by mechanical clamping during testing. The specimen clamping rings has an internal diameter of 8.89 ± 0.03 cm.

The tensile tester is set up such that the crosshead speed is 15.2 cm/min, the probe separation is 104 mm, the break sensitivity is 60 percent and the slack compensation is 10 gf and the instrument is calibrated according to the manufacturer's instructions.

Samples are conditioned under TAPPI conditions and cut into 127 x 127 mm ± 5 mm squares. For each test a total of 3 sheets of product are combined. The sheets are stacked on top of one another in a manner such that the machine direction of the sheets is aligned. Where samples comprise multiple plies, the plies are not separated for testing. In each instance the test sample comprises 3 sheets of product. For example, if the product is a 2-ply tissue product, 3 sheets of product, totaling 6 plies are tested. If the product is a single ply tissue product, then 3 sheets of product totaling 3 plies are tested.

Prior to testing the height of the probe is adjusted as necessary by inserting the burst fixture into the bottom of the tensile tester and lowering the probe until it was positioned approximately 12.7 mm above the alignment plate. The length of the probe is then adjusted until it rests in the recessed area of the alignment plate when lowered.

It is recommended to use a load cell in which the majority of the peak load results fall between 10 and 90% of the capacity of the load cell. To determine the most appropriate

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load cell for testing, samples are initially tested to determine peak load. If peak load is < 450 gf a 10 Newton load cell is used, if peak load is > 450 gf a 50 Newton load cell is used.

Once the apparatus is set-up and a load cell selected, samples are tested by inserting the sample into the specimen clamp and clamping the test sample in place. The test sequence is then activated, causing the penetration assembly to be lowered at the rate and distance specified above. Upon rupture of the test specimen by the penetration assembly the measured resistance to penetration force is displayed and recorded. The specimen clamp is then released to remove the sample and ready the apparatus for the next test.

The peak load (gf) and energy to peak (g-cm) are recorded and the process repeated for all remaining specimens. A minimum of five specimens are tested per sample and the peak load average of five tests is reported as the Dry Burst Strength.

EXAMPLES

Example 1: Conventional Wet Pressed Tissue Comprising Bamboo

Sample codes were made using a wet pressed process utilizing a Crescent Former. Accordingly, single ply bath and two ply facial tissue products were produced and tested according to the same tests described in the Test Methods section. The following tissue manufacturing process was used to produce the sample codes.

Initially, northern softwood kraft ("NSWK") pulp was dispersed in a pulper for 30 minutes at 3 percent consistency at about 100° F. In certain instances, as indicated in the tables below, NSWK pulp was refined at 1.5 to 5.0 hp-days/metric ton. The NSWK pulp was then transferred to a dump chest and subsequently diluted to approximately 0.75 percent consistency. Once diluted, in certain instances Kymene® 920A and/or Hercobond® 1366 (both available from Ashland, Covington, KY) was added to the NSWK. When utilized in a multi-layered tissue web, NSWK fibers were added to the middle layer of the 3-layered tissue web.

Aracruz ECF, a eucalyptus hardwood kraft ("EHWK") pulp (Aracruz, Rio de Janeiro, RJ, Brazil) was dispersed in a pulper for 30 minutes at about 3 percent consistency at about 100° F. The EHWK pulp was then transferred to a dump chest and subsequently diluted to about 0.75 percent consistency. The EHWK pulp fibers were used in the two outer layers of the 3-layered tissue structure.

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Commercial bleached bamboo pulps were obtained from Guizhou Chitianhua Paper Co., Ltd., Guizhou, China (herein after "Chinese Bamboo") and Phoenix Pulp and Paper PCL, Khon - Kaen, Thailand (hereinafter "Thai Bamboo"). The Chinese Bamboo was a mixture of 3 species of tropical bamboo *Neosinocalamus affinis*, *Bambusa rigida*, and *Bambusa pervariabilis*×*Dendrocalamopsis Daii*. The Chinese Bamboo was pulped by a TCF sulfate process. The Thai Bamboo was an ECF Bleached Kraft pulp consisting of a mixture of four tropical bamboo species: *Bambusa Bluemeana*, *Bambusa Tulda*, *Bambusa Nana* and *Dendrocalmus Asper*.

Moso Bamboo pulp fibers were prepared from chipped green Moso bamboo poles by a Kraft pulp process using Na_2S and NaOH for digestion followed by oxygen delignification and bleaching with chlorine dioxide. After bleaching the pulp was dried to 30 to 50 percent consistency on a belt press to form a never dried crumb pulp. Never dried pulp was converted to dry lap pulp having a basis weight of around 250 g/m^2 by slurrying 350 oven dried basis pounds of bamboo crumb pulp in 1400 gallons of water in a hydrapulper at about 125°F. The slurry was pulped for about 20 minutes to give 3 percent consistency bamboo pulp slurry. The slurry was passed to a headbox and deposited on a Fourdinier forming belt moving at about 90 feet per minute and dewatered. Minimal pressing was done in the water removal process using only the roll weights in the wet press section of the machine. The dewatered pulp sheet was then passed over three stacks of calendar dryers, dried and rolled on 4-inch cores. Steam pressures in the calendar stacks were controlled to provide a dry lap pulp having between 6 and 8 percent moisture.

Bamboo or NSWK pulp fibers were dispersed in a pulper for 25 minutes at 3 percent consistency at about 100° F. In certain instances, as indicated in the tables below, the bamboo pulp was refined at 1.5 to 5.0 hp-days/metric ton. The bamboo or NSWK pulp was then transferred to a dump chest and subsequently diluted to approximately 0.75 percent consistency. Once diluted, in certain instances Kymene® 920A and/or Hercobond® 1366 were added to the NSWK. When utilized in a multi-layered tissue web, bamboo and NSWK fibers were added to the middle layer of the 3-layered tissue web.

Similarly Bleached Eucalyptus Hardwood Kraft pulp fibers obtained from Fibria, S.A., were dispersed in a pulper for 25 minutes at 3 percent consistency at 100°F. The Eucalyptus pulp slurry was then transferred to a dump chest and subsequently diluted to approximately 0.75 percent consistency. Once diluted, in certain instances Kymene®

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920A, Hercobond® 1366, were added to the NSWK. When utilized in a multi-layered tissue web, bamboo and NSWK fibers were added to the middle layer of the 3-layered tissue web.

In certain instances the pulp fibers from the machine chests were pumped to the headbox at a consistency of about 0.1 percent. Pulp fibers from each machine chest were sent through separate manifolds in the headbox to create a 3-layered tissue structure. The flow rates of the stock pulp fiber slurries into the flow spreader were adjusted to give a target web basis. In those instances where a layer structure was produced, flow of stock pulp fiber slurries was controlled to provide a layer split of about 30 to about 35 percent by total weight of the tissue web EHWK fibers on both outer layers and 30 to about 40 percent NSWK or bamboo pulp fibers in the center layer. The fibers were deposited onto a felt in using a Crescent Former.

In other instances a blended web was produced by weighing out the appropriate amount of the first pulp fiber into the pulper and dispersing for 30 minutes at 3 percent consistency at about 100° F. In some instances the pulp was refined at 1.5 to 5.0 hp-days/metric ton. The first pulp slurry was then transferred equally to three dump chests. The amount of the second pulp fiber was then weighed into the pulper and dispersed and refined in similar fashion if so required. The second pulp slurry was then transferred equally to the three dump chests. The three dump chests now contained a blended mix of the fibers. The dump chests were subsequently diluted to approximately 0.75 percent consistency. Once diluted, in certain instances Kymene® 920A and/or Hercobond® 1366 were added to the blended furnishes in the dump chests. The blended slurries were then diluted to approximately 0.1 percent consistency before being pumped to a 3-layer headbox such that all 3-layer splits were evenly distributed. Alternatively, when no refining was required, the pulps could be blended together in the pulper per the procedure proscribed and then the blended slurry transferred from the pulper to the machine chests.

The wet sheet, about 10 to 20 percent consistency, was adhered to a Yankee dryer, traveling at about 80 to 120 fpm through a nip via a pressure roll.

The consistency of the wet sheet after the pressure roll nip (post-pressure roll consistency or PPRC) was approximately 40 percent. A spray boom situated underneath the Yankee dryer sprayed a creping composition at a pressure of 60 psi at a rate of approximately 0.25 g solids / m^2 of product. The creping composition comprised 0.16

percent by weight of polyvinyl alcohol (PVOH), (Celvol™ 523 available from Celanese Chemicals, Calvert City, KY), 0.013 percent by weight PAE resin (Kymene™ 6500 available from Ashland, Covington, KY) and 0.0013 percent by weight of Resozol™ 2008 (Ashland, Covington, KY).

The sheet was dried to about 98 to 99 percent consistency as it traveled on the Yankee dryer and to the creping blade. The creping blade subsequently scraped the tissue sheet and a portion of the creping composition off the Yankee dryer. The creped tissue basesheet was then wound onto a core traveling at about 50 to about 100 fpm into soft rolls for converting.

To produce the 2-ply facial tissue products (Sample Nos. 1-4), two soft rolls of the creped tissue were then rewound, calendared, and plied together so that both creped sides were on the outside of the 2-ply structure. Mechanical crimping on the edges of the structure held the plies together. The plied sheet was then slit on the edges to a standard width of approximately 8.5 inches and folded, and cut to facial tissue length. Tissue samples were conditioned and tested.

Samples produced according to the present example are summarized in Table 3, below.

TABLE 3

Sample	Single Ply Basis Weight (gsm)	Web Structure	Plies	NSWK (wt %)	EHWK (wt %)	Bamboo (wt %)
1	15.1	Layered	2	30	70	0
2	15.1	Layered	2	40	60	0
3	15.1	Layered	2	0	70	30
4	15.1	Layered	2	0	60	40
5	16.7	Blended	1	40	60	0
6	16.7	Blended	1	40	60	0
7	16.7	Blended	1	0	100	0
8	16.7	Blended	1	0	100	0
9	16.7	Blended	1	0	60	40
10	16.7	Blended	1	0	60	40

Example 2: Uncreped Through-air Dried Tissue Comprising Bamboo

A single ply through-air dried tissue web was made generally in accordance with US Patent No. 5,607,551, which is herein incorporated by reference in a manner consistent with the present disclosure.

More specifically, from about 60 to about 100 pounds (oven dry basis) of Aracruz ECF, a eucalyptus hardwood kraft ("EHWK") pulp (Aracruz, Rio de Janeiro, RJ, Brazil) was dispersed in a pulper at 100°F for 25 minutes at a consistency of 3 percent before being transferred in equal parts to two machine chests and diluted to a consistency of 1 percent. When used, Hercobond 1366 was weighed out and diluted to a 1 percent actives solution with water prior to being added to the machine chest. The fiber slurry and chemical was allowed to mix for five minutes prior to the stock solution being sent to the headbox.

Forty pounds (oven dry basis) of northern softwood kraft fiber ("NSWK") (or bamboo pulp when used) were dispersed in a pulper at 100°F for 25 minutes at a consistency of 3 percent before being transferred to a second machine chest and diluted to 1 percent consistency. The softwood fibers may be refined after pulping and prior to transfer to the machine chest as noted in examples.

To produce a layered tissue web, prior to forming each stock was further diluted to approximately 0.1 percent consistency and transferred to a 3-layer headbox in such a manner as to provide a layered sheet. The fiber composition of the layered sheets are described in the table below. Generally, the outer layers comprised EHWK and the inner layer comprised NSWK, bamboo fibers or a mixture of both.

Blended tissue webs were produced as described above.

The formed web was non-compressively dewatered and rush transferred to a transfer fabric traveling at a speed about 25 percent slower than the forming fabric. The web was then transferred to a throughdrying fabric and dried. Samples 11-15 were converted into rolled products to produce single ply bath tissue products. Samples were produced as described in Table 4, below.

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TABLE 4

Sample	Basis Weight (gsm)	Web Structure	Basesheet or Finished Product	Plies	NSWK (wt%)	EHWK (wt%)	Bamboo (wt%)
11	27.1	Layered	Finished	1	35	65	0
12	27.1	Layered	Finished	1	25	65	10
13	27.1	Layered	Finished	1	10	65	25
14	27.1	Layered	Finished	1	0	65	35
15	27.1	NA	Finished	1	0	0	100
16	27.1	NA	Finished	1	0	100	0
17	36.5	NA	Basesheet	1	0	100	0
18	36.5	Layered	Basesheet	1	0	60	40
19	36.5	Layered	Basesheet	1	40	60	0
20	36.5	NA	Basesheet	1	0	100	0
21	36.5	Layered	Basesheet	1	0	50	50
22	36.5	Layered	Basesheet	1	0	60	40
23	36.5	Layered	Basesheet	1	40	60	0
24	36.5	Layered	Basesheet	1	40	60	0
25	36.5	Layered	Basesheet	1	0	60	40

Example 3: Uncreped Through-air Dried Towels Comprising Bamboo

A single ply uncreped through-air dried (UCTAD) tissue web was made generally in accordance with US Patent No. 5,607,551.

More specifically, from about 50 to about 90 pounds (oven dry basis) of Aracruz ECF, a EHWK pulp (Aracruz, Rio de Janeiro, RJ, Brazil) was dispersed in a pulper for 25 minutes with from about 10 to about 50 pounds of bleached chemi-thermo mechanical pulp ("BCTMP") at a consistency of 3 percent before being transferred in equal parts to three machine chests and diluted to a consistency of 1 percent.

Forty pounds (oven dry basis) of NSWK pulp (or bamboo pulp when used) was dispersed in a pulper for 25 minutes at a consistency of 3 percent and refined at between 1 and 5 horsepower tons/day before being transferred in equal parts to the three machine chests containing the EHWK and BCTMP fibers. The machine chests were then diluted to a consistency of 1 percent. Kymene 920A was added to each machine chest at the rate of 1 percent dry actives to oven dried basis of total pulp. The stock solutions were then passed in equal amounts to a 3-layer headbox after dilution to 0.75 percent consistency to form a blended sheet.

The formed web was non-compressively dewatered and rush transferred to a transfer fabric traveling at a speed about 25 percent slower than the forming fabric. The

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web was then transferred to a throughdrying fabric, dried and calendared. Samples were produced as described in Table 5, below.

TABLE 5

Sample	Single Ply Basis Weight (gsm)	Web Structure	Plies	Bamboo (wt%)	NSWK (wt%)	EHWK (wt %)	BCTMP (wt%)
26	39.0	Blended	1	0	50	25	25
27	39.0	Blended	1	70	0	5	25

Web Strength and Bulk

The effect of bamboo on various tissue strength and durability properties was explored by preparing samples using several levels of bamboo. Table 6 summarizes the physical properties of basesheets prepared as described above. Table 7 summarizes the physical properties of finished produce prepared as described above.

TABLE 6

Sample	Single Ply Basis Weight (gsm)	Plies	Bamboo Total Web (wt%)	Bulk (cm^3/g)	GMT (g/3")	TEA Index	CD TEA ($g \cdot cm/cm^2$)
1	15.1	2	0	9.5	924	10.3	3.6
2	15.1	2	0	11.3	1235	10.2	4.9
3	15.1	2	30	9.0	1158	9.3	3.9
4	15.1	2	40	8.9	1116	10.1	4.8
5	16.7	1	0	9.7	1061	15.0	6.6
6	16.7	1	0	10.4	656	15.8	4.3
7	16.7	1	0	9.3	728	12.7	3.8
8	16.7	1	0	9.3	1024	12.4	5.2
9	16.7	1	40	9.1	1158	11.2	5.5
10	16.7	1	40	9.2	758	12.6	4.3
11	27.1	1	0	9.4	625	8.5	3.3
12	27.1	1	10	9.8	769	8.9	4.2
13	27.1	1	25	10.9	557	8.5	3.2
14	27.1	1	35	10.1	662	9.3	4.2
15	27.1	1	100	10.3	954	10.1	6.5
16	27.1	1	0	9.8	857	8.1	5.0
17	36.5	1	0	21.2	1160	11.2	8.8
18	36.5	1	40	21.9	1089	13.3	10.1
19	36.5	1	0	20.4	1051	12.0	8.9
20	36.5	1	0	22.1	1056	12.0	8.7
21	36.5	1	50	21.5	968	13.3	10.5
22	36.5	1	40	21.0	1167	13.6	13.7
23	36.5	1	0	19.8	1160	13.4	9.6
24	36.5	1	0	20.5	1248	14.7	11.3

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Sample	Single Ply Basis Weight (gsm)	Plies	Bamboo Total Web (wt%)	Bulk (cm^3/g)	GMT (g/3")	TEA Index	CD TEA ($g \cdot cm/cm^2$)
25	36.5	1	40	22.0	1136	13.0	10.2
26	39.0	1	0	20.8	2738	10.9	17.7
27	39.0	1	70	22.6	1616	10.1	12.5

The relative change in bulk (Delta Bulk %), compared to a control to an identical control containing NBSK in place of bamboo, is summarized in the table below.

TABLE 7

Sample	Basis Weight (gsm)	Web Structure	Plies	Method of Manufacture	Bamboo Total Web (wt%)	Bulk (cm^3/g)	Delta Bulk (%)
3	15.1	Layered	2	CWP	30	9.0	-4.5%
4	15.1	Layered	2	CWP	40	8.9	-21.4%
9	16.7	Blended	1	CWP	40	9.1	-6.2%
10	16.7	Blended	1	CWP	40	9.2	-11.7%
12	27.1	Layered	1	UCTAD	10	9.8	3.5%
13	27.1	Layered	1	UCTAD	25	10.9	15.1%
14	27.1	Layered	1	UCTAD	35	10.1	7.1%
15	27.1	Blended	1	UCTAD	100	10.3	9.4%
18	36.5	Layered	1	UCTAD	40	21.9	7.6%
21	36.5	Layered	1	UCTAD	50	21.5	8.6%
22	36.5	Layered	1	UCTAD	40	21.0	5.9%
25	36.5	Layered	1	UCTAD	40	22.0	7.3%
27	39.0	Blended	1	UCTAD	70	22.6	8.7%

Web Softness and Durability

The effect of bamboo on the durability (Durability Index) and softness (Stiffness Index) of the tissue web was explored by preparing samples using several levels of bamboo, the results of which are summarized below.

TABLE 8

Sample	Basis Weight (gsm)	Web Structure	Plies	Bamboo Total Web (wt%)	Tear Index	Stiffness Index	Durability Index
1	15.1	Layered	2	0	10.3	9.4	24.3
2	15.1	Layered	2	0	10.2	10.0	23.2
3	15.1	Layered	2	30	9.3	12.7	19.8
4	15.1	Layered	2	40	10.1	13.0	21.2
5	16.7	Blended	1	0	15.0	9.1	30.2
6	16.7	Blended	1	0	15.8	8.4	33.1

Sample	Basis Weight (gsm)	Web Structure	Plies	Bamboo Total Web (wt%)	Tear Index	Stiffness Index	Durability Index
7	16.7	Blended	1	0	12.7	8.6	23.5
8	16.7	Blended	1	0	12.4	9.3	20.5
9	16.7	Blended	1	40	11.2	10.2	20.6
10	16.7	Blended	1	40	12.6	13.3	27.3
11	27.1	Layered	1	0	8.49	10.9	25.6
12	27.1	Layered	1	10	8.92	10.1	25.8
13	27.1	Layered	1	25	8.46	11.4	23.9
14	27.1	Layered	1	35	9.34	11.3	23.9
15	27.1	Blended	1	100	10.08	11.6	28
16	27.1	Blended	1	0	8.1	11.6	20.5
17	36.5	NA	1	0	11.2	6.0	27.1
18	36.5	Layered	1	40	13.3	5.3	33.5
19	36.5	Layered	1	0	12.0	4.9	31.9
20	36.5	NA	1	0	12.0	6.6	29.2
21	36.5	Layered	1	50	13.3	5.3	34.9
22	36.5	Layered	1	40	13.6	5.8	33.6
23	36.5	Layered	1	0	13.4	4.8	34.2
24	36.5	Layered	1	0	14.7	4.9	37.4
25	36.5	Layered	1	40	13.0	5.5	33.9
26	39.0	Blended	1	0	10.9	4.7	31.8
27	39.0	Blended	1	70	10.1	7.5	31.6

The relative change in the Durability Index and Stiffness Index, compared to an identical control containing NBSK in place of bamboo, is summarized in the table below.

TABLE 9

Sample	Single Ply Basis Weight (gsm)	Web Structure	Plies	Method of Manufacture	Bamboo Total Web (wt%)	Delta Durability Index (%)	Delta Stiffness Index (%)
3	15.1	Layered	2	CWP	30	-20.1%	32.6%
4	15.1	Layered	2	CWP	40	-12.9%	30.2%
9	16.7	Blended	1	CWP	40	-31.7%	31.6%
10	16.7	Blended	1	CWP	40	-17.6%	43.0%
12	27.1	Layered	1	UCTAD	10	0.6%	0.4%
13	27.1	Layered	1	UCTAD	25	-6.5%	-2.2%
14	27.1	Layered	1	UCTAD	35	-6.7%	10.4%
15	27.1	Blended	1	UCTAD	100	9.2%	9.9%
18	36.5	Layered	1	UCTAD	40	5.1%	7.1%

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21	36.5	Layered	1	UCTAD	50	2.0%	11.1%
22	36.5	Layered	1	UCTAD	40	-1.6%	20.4%
25	36.5	Layered	1	UCTAD	40	-9.3%	12.2%
27	39.0	Blended	1	UCTAD	70	-0.4%	61.4%

While tissue webs and products comprising the same have been described in detail with respect to the specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

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We claim:

1. A through-air dried tissue web comprising bamboo fibers, wherein the bamboo fibers comprise from about 10 to about 75 percent by weight of the through-air dried tissue web.

2. The through-air dried tissue web of claim 1 wherein the bamboo fibers have an average fiber length from about 1 to about 2 mm.

3. The through-air dried tissue web of claim 1 wherein the bamboo fiber is derived from a bamboo species selected from the group consisting of *Phyllostachys heterocycla pubescens*, *Phyllostachys nigra variant Heno*, *Phyllostachys vivax* and *Phyllostachys bambusoides*.

4. The through-air dried tissue web of claim 1 wherein the through-air dried web comprises less than about 10 percent softwood fibers by weight of the through-air dried web.

5. The through-air dried tissue web of claim 1 having a Durability Index greater than about 20.

6. The through-air dried tissue web of claim 1 having a Stiffness Index less than about 7.

7. The through-air dried tissue web of claim 1 having a Bulk greater than about 10 cubic centimeters per gram.

8. The through-air dried tissue web of claim 1 wherein the through-air dried web is uncreped.

9. A layered through-air dried tissue web, the web comprising a first fibrous layer and a second fibrous layer, the first fibrous layer comprising wood fibers and the second layer comprising bamboo fibers, wherein the first fibrous layer is substantially free of bamboo fibers and wherein the bamboo fibers comprise at least about 10 percent of the total weight of the through-air dried web.

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10. The layered through-air dried tissue web of claim 9 wherein the first fibrous layer consists essentially of hardwood fibers and the second fibrous layer comprises bamboo and softwood fibers, wherein the amount of softwood fiber in the second fibrous layer is less than about 10 percent by weight of the layer.

11. The layered through-air dried tissue web of claim 9 wherein the first fibrous layer comprises at least about 75 percent hardwood fibers by weight of the first fibrous layer and the second layer comprises at least about 50 percent bamboo fibers by weight of the second fibrous layer.

12. The layered through-air dried tissue web of claim 9 wherein the through-air dried web comprises less than about 10 percent softwood fibers by weight of the through-air dried web.

13. The layered through-air dried tissue web of claim 9 having a Durability Index greater than about 20.

14. The layered through-air dried tissue web of claim 9 having a Stiffness Index less than about 7.

15. The layered through-air dried tissue web of claim 9 having a Bulk greater than about 10 cubic centimeters per gram.

16. A tissue product comprising a first through-air dried tissue web having from about 10 percent to about 75 percent bamboo fibers by weight of the through-air dried tissue web.

17. The tissue product of claim 16 further comprising a second tissue web plied to the first through-air dried tissue web.

18. The product of claim 16 having a Durability Index greater than about 20.

19. The multi-ply tissue product of claim 16 having a Stiffness Index less than about 13.

20. The multi-ply tissue product of claim 16 having a Bulk greater than about 10 cubic centimeters per gram.

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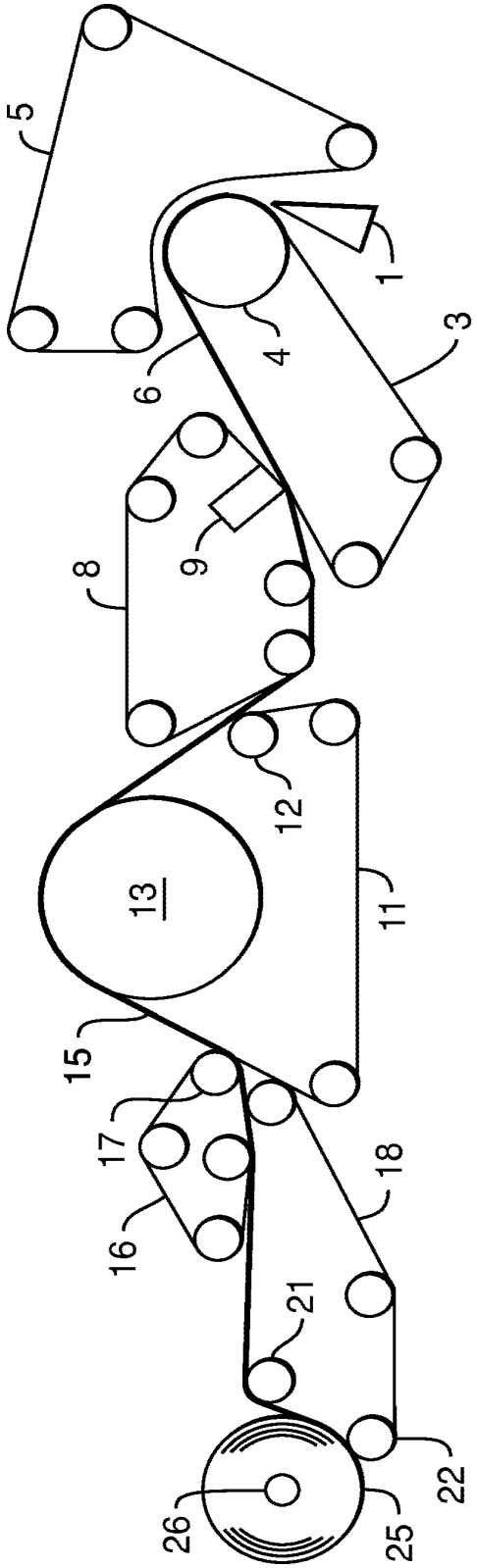


FIG. 1

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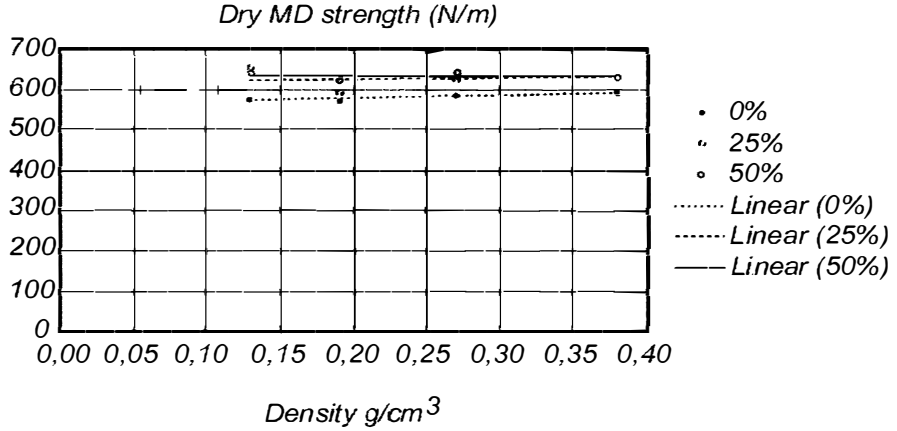


Fig. 1A

(57) Abstract: A stack of tissue paper product, wherein the tissue paper product is forming panels having a length, and a width perpendicular to said length, said panels being piled on top of each other to form a stack height, said tissue paper product comprising at least one non-wood tissue ply, the non-wood tissue ply comprising non-wood pulp fibres being present in an amount of at least 10% by dry weight of the of the non-wood tissue ply, the stack having a density of at least 0.12 g/cm3.

[Continued on next page]

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STACK OF A TISSUE PAPER PRODUCT COMPRISING NON-WOOD FIBRES

TECHNICAL FIELD

The present disclosure relates to a stack of a tissue paper product comprising an amount of non-wood fibres.

BACKGROUND

Tissue paper materials find extensive use in modern society. Toilet paper, and paper towels such as hand towels or household (kitchen) towels, facial tissues, tissue handkerchiefs, napkins, and industrial wipes are staple items of commerce. These products are typically made from papermaking pulp comprising wood fibres, such as hardwood and softwood fibres.

In the following, a “tissue paper product” relates to an absorbent paper product based on cellulose wadding which is also called tissue paper material or tissue paper base-sheet in this field of technology.

Tissue paper material is defined as a soft absorbent paper material having a low basis weight, of for example 8 to 45 g/m^2, preferably 10 to 35 g/m^2 per ply. The total basis weight of multi-ply tissue paper products may preferably be up to a maximum of 110 g/m^2, more preferably to a maximum of 80 g/m^2. Its density is typically below 0.6 g/cm^3, preferably below 0.30 g/cm^3 and more preferably in the range of 0.02 g/cm^3 and 0.20 g/cm^3. The production of tissue paper material is distinguished from conventional paper production, e.g. printing paper production, by its relatively low basis weight and relatively high tensile energy absorption index (see ISO 12625-4). Conventional paper and tissue paper also differ in general with regard to the modulus of elasticity that characterises the stress/strain properties of these generally planar products as a material parameter.

The fibres contained in the tissue paper are mainly cellulosic fibres, such as pulp fibres from chemical pulp (e.g. Kraft or sulphite), or mechanical pulp (e.g. ground wood, thermo mechanical pulp, chemo-mechanical pulp and/or chemo- thermo-mechanical pulp /CTMP). Pulps derived from both deciduous (hardwood) and coniferous (softwood) can be used. Fibres may also come from non-wood plants e.g. cereal, bamboo, jute, or sisal. The fibres or a portion of the fibres may be recycled fibres, which may belong to any or all of the above categories. The fibres can be treated with additives, e.g. fillers, softeners, such as, but not limited to, quaternary ammonium compounds and binders, conventional dry-

strength agents, temporary wet strength agents or wet-strength agents, in order to facilitate the original paper making or to adjust the properties thereof.

Tissue paper products in particular for use as hygiene- or wiping products primarily include all kinds of tissue paper materials including dry-creped tissue paper material, wet-creped tissue paper material, NTT(flat), TAD-paper material (Through Air Drying), tissue paper material based on structured or textured technologies such as ATMOS, NTT (textured), UCTAD, eTAD, QRT, PrimeLineTEX etc. and cellulose or pulp-wadding, or combinations, laminates or mixtures thereof. Typical properties of these hygiene- and wiping products include the ability to absorb tensile stress energy, their drapability, good textile-like flexibility, properties which are frequently referred to as bulk softness, a high surface softness and a high specific volume with a perceptible thickness. A liquid absorbency as high as possible and, depending on the application, a suitable wet and dry strength as well as an appealable visual appearance of the outer product's surfaces are desired. These properties, among others, allow these hygiene and wiping products to be used, for example, as cleaning wipes such as windscreen cleaning wipes, industrial wipes, kitchen paper or the like; as sanitary products such as for example bathroom tissue, handkerchiefs, household towels, towels and the like; as cosmetic wipes such as for example facials and as serviettes or napkins, just to mention some of the products that can be used. Furthermore, the hygiene- and wiping products can be dry, moist, wet, printed or pre-treated in any manner. In addition, the hygiene- and wiping products may be folded, interleaved or individually placed, stacked or rolled, connected or not, in any suitable manner.

The products described above can be used for personal and household use as well as commercial and industrial use. They are adapted to absorb fluids, remove dust, and for other cleaning purposes.

If tissue paper material is to be made out of pulp, the process essentially comprises a forming step that includes a headbox- and a forming wire section, and a drying section, e.g. including through air drying or conventional drying on a Yankee cylinder. The production process can also include a crepe process for tissue paper and, finally, typically a monitoring and winding area.

Tissue paper material can be formed by placing the fibres, in an oriented or random manner, on one or between two endless continuously rotating wires or felts of a paper making machine while simultaneously removing water.

Further dewatering and drying the formed primary fibrous web occur in one or more steps by mechanical and thermal means until a final dry-solid content of usually about 90 to 99% has been reached.

In case of creped tissue paper material making, this stage is followed by the crepe process which influences the properties of the finished tissue paper product in conventional processes. The conventional dry crepe process involves creping on a usually 3.0 to 6.5 m diameter drying cylinder, the so-called Yankee cylinder, by means of a crepe doctor blade with the aforementioned final dry-solids content of the raw tissue paper. Wet creping can be used as well, if lower demands are made of the tissue quality. The creped, finally dry raw tissue paper material, the so-called base tissue, is then available for further processing into the tissue paper product.

Instead of the conventional tissue making process described above, the use of a modified technique is possible in which an improvement in specific volume is achieved by a special kind of drying which leads to an improvement in the e.g. caliper, bulk, softness, etc. of the tissue paper material. This process, which exists in a variety of subtypes, is herein generally termed the structured tissue technique. Examples of structured tissue techniques are TAD ATMOS®, NTT(textured), UCTAD, eTAD, QRT, PrimeLineTex etc.

The processing step from the tissue paper material to the finished tissue paper product occurs in processing machines (converting machines) which include operations such as unwinding the tissue paper material (base tissue), calendering of the tissue, laminating, printing or embossing.

Several plies may be combined together by a combining operation of a chemical nature (e.g. by adhesive bonding), or of a mechanical nature (e.g. by knurling or so-called edge-embossing), or a combination of both. Examples of such process steps for combining plies together will be described in more detail in the below.

Further, the processing to finished tissue paper product may involve e.g. longitudinal cut, folding, cross cut etc. Moreover, individual tissue paper products may be positioned and brought together to form stacks, which may be individually packaged. Such processing steps may also include application of substances like scents, lotions, softeners or other chemical additives.

When several plies are combined together using adhesive bonding, a film of adhesive is deposited over some or all of the surface of at least one of the plies, then the adhesive-treated surface is placed in contact with the surface of at least one other ply.

When several plies are combined together using mechanical bonding, the plies may be combined by knurling, by compression, by edge-embossing, union embossing and/or ultrasonic.

Mechanical and adhesive bonding may also be combined to combine several plies together to form a multi-ply product.

Embossing is to change the shape of a sheet from flat to shaped, so that there are areas that are raised and/or recessed from the rest of the surface. It therefore constitutes a deformation of the previously relatively flat sheet, and results in a ply having a particular relief. The thickness of the ply or of the multiple plies is in most cases increased after embossing compared with its initial thickness.

An embossing process is carried out between an embossing roll and an anvil roll. The embossing roll can have protrusions or depressions on its circumferential surface leading to embossed protrusions/depressions in the paper web. Anvil rolls may be softer than the corresponding embossing roll and may consist of rubber, such as natural rubber, or plastic materials, paper or steel. If the anvil roll is made of a softer material like rubber, a contact area/nip can be formed between the embossing roll (e.g. steel roll) and the anvil roll by the deformation of the softer roll.

By embossing, a pattern can be applied to a tissue paper fulfilling a decorative and/or functional purpose.

A functional purpose may be to improve the properties of the hygiene paper product, that is, the embossment may improve the product thickness, absorbency, bulk, softness etc.

A functional purpose may also be to provide a joint to another ply in a multi-ply product.

Tissue paper products display a number of physical properties which are of importance for their use for example as toilet paper, hand towels, kitchen towels, facial tissues, handkerchiefs, napkins, wipe or the like. Examples of such properties are their strength, softness, and absorbency (primarily for aqueous systems). These physical properties are generally tuned for addressing common consumer demand in view of the intended use of the tissue paper product.

For example, tissue paper products need to retain their strength at least for a time period of use e.g. for wiping liquids or moisture.

At the same time, there are requirements regarding tactile properties such as softness as tissue paper products may be intended to come in intimate contact with the body and skin. Accordingly, it is desired that tissue paper products shall exhibit sufficient softness in order to ensure consumer's comfort.

However, some of the desired physical properties of tissue paper products are generally conflicting properties. One example is strength and softness. Often, as strength in a tissue paper product rises, the softness declines.

Hence, it is desired to provide a tissue paper product providing a good balance between required properties. For example, it is desired to provide a tissue paper product achieving a satisfactory balance between softness and strength.

Further, there is a desire to reduce the consumption of wood fibre to produce tissue paper products. This desire is advocated by e.g. rising costs for wood fibre, concerns involving sustainable forest management, and other environmental reasons such as carbon foot print.

To this end, attempts have been made to replace some or all of the wood fibre in tissue paper products with for example recycled fibres and/or with non-wood fibres. However, since the fibre content in the pulp will naturally impact the above-mentioned physical properties of the resulting tissue paper material, the replacement of virgin wood fibres with other fibres in the pulp is not uncomplicated.

This applies not only to the product of tissue paper materials per se, but also the converting, handling and/or storage of the tissue paper products. When subject to procedures which may involve e.g. folding, compressing or loading the tissue paper products, tissue paper products comprising non-wood fibre and/or recycled fibres have been found to behave differently than conventional products using virgin wood fibre. To fulfil the need for replacing some or all of the wood fibre in tissue paper products with for example recycled fibres and/or with non-wood fibres, it is therefore necessary to find

solutions for the tissue paper products handling and storage, ensuring the function of the tissue paper products also after e.g. packaging.

Thus, there is a need for improvement and/or alternatives for tissue paper products in view of one or more of the above-mentioned desires.

SUMMARY

An object of the present invention is to fulfill said need for improvement and/or alternatives.

To this end, it is proposed herein to use non-wood cellulose pulp fibres in tissue paper materials and tissue paper products.

The non-wood cellulose pulp fibres may be chemical pulp fibres.

Optionally, the non-wood cellulose pulp fibres may be never-dried fibres. “Never-dried” means herein that the fibres have not been subject to drying before use in the tissue making process. It is believed that the non-wood cellulose pulp fibres being never-dried may contribute to the non-wood cellulose pulp fibres being suitable for use in tissue paper materials and tissue paper products.

Optionally, the non-wood cellulose pulp fibres contain at least 15% hemicellulose. It is believed that such a hemicellulose content may contribute to the non-wood cellulose pulp fibres being suitable for use in tissue paper materials and tissue paper products.

Optionally, the non-wood cellulose pulp fibres contain no more than 15 % lignin. For example, the non-wood cellulose pulp fibres may contain no more than 12 % lignin. In yet another example, the non-wood cellulose pulp fibres may contain no more than 10% lignin. It is believed that such a lignin content may contribute to the non-wood cellulose pulp fibres being suitable for use in tissue paper materials and tissue paper products.

For example, the non-wood cellulose pulp fibres may contain at least 15% hemicellulose and no more than 15 % lignin, such as no more than 12 % lignin or no more than 10% lignin.

Optionally, the non-wood cellulose pulp fibres are pre-treated, to obtain the desired amounts of lignin and/or hemicellulose.

Further, the non-wood cellulose pulp fibres may have a relatively low average fibre length.

Optionally, the non-wood cellulose pulp fibres have an average fibre length of less than 1700 µm.

Optionally, the non-wood cellulose pulp fibres have an average fibre length of less than 1200 µm.

Optionally, the non-wood cellulose pulp fibres have an average fibre length of less than 1000 µm.

Optionally, the non-wood cellulose pulp fibres have an average fibre length of less than 900 µm.

Further, it is believed that the non-wood cellulose pulp fibres having a relatively high breaking length may contribute to the non-wood cellulose pulp fibres being suitable for use in tissue paper materials and tissue paper products. The breaking length is the initial breaking length of the non-wood cellulose pulp fibres as measured on the non-wood cellulose pulp fibres after the pulping process.

Optionally, the non-wood cellulose fibres have a breaking length of more than 3000 m.

For example, the non-wood cellulose fibres may have a breaking length of more than 3000 m and an average fibre length of less than 1700 µm, such as less than 1200 µm or less than 900 µm.

Also, it is believed that the non-wood cellulose pulp fibres having a relatively high ratio between breaking length and average fibre length may contribute to the non-wood cellulose pulp fibres being suitable for use in tissue paper materials and tissue paper products.

Optionally, the non-wood cellulose fibres have a breaking length/average fibre length of more than 3.7.

Optionally, the non-wood cellulose fibres have a breaking length/average fibre length ratio of more than 4.0.

Optionally, the non-wood cellulose fibres have a breaking length/average fibre length ratio of more than 4.5.

For example, the non-wood cellulose fibres may have a breaking length/average fibre length ratio of more than 5 such as more than 5.5.

For example, the non-wood cellulose fibres may have a breaking length/average fibre length ratio of more than 3.7 such as more than 4 and an average fibre length of less than 1700 µm, such as less than 1200 µm, less than 1000 µm, or less than 900 µm.

For comparison, it may be mentioned that different types of conventional hardwood and softwood pulps display lower breaking length/average fibre length ratios than those suggested in the above for the non-wood cellulose fibres. This applies also to examples of never-dried hardwood and softwood pulps. Average ratios as calculated for different types of hardwood and softwood pulps are indicated in the table in the below.

Type of pulps	Average ratio
BEK	2.4
BHK	2.0
BSK	1.0
BSS	0.6
NBHK	2.3
NBSK	1.2
Never-dried HW	0.9
Never-dried SW	1.0

(BEK – Bleached Eucalyptus Pulp, BHK – Bleached Hardwood Kraft, BSK – Bleached Softwood Kraft, BSS – Bleached Softwood Sulfite, Northern Bleached Hardwood Kraft, Northern Bleached Softwood Kraft. The never-dried Hardwood (HW) and Softwood (SW) are sulfite.)

Also, several types of previously used non-wood cellulose pulp fibres have been found to display lower breaking length/average fibre length ratio than what is proposed in the above. For example, tested samples of dried bagasse fibre pulp was found to have an average ratio of 2.6, dried bamboo fibre pulp an average ratio of 1.2 and dried wheat fibre pulp an average ratio of 3.5.

For example, the non-wood cellulose fibres may be never-dried non-wood cellulose pulp fibres and the non-wood cellulose fibres may have a breaking length/average fibre length ratio of more than 3.7, such as more than 4.0 or more than 4.5.

The non-wood cellulose pulp fibres as proposed herein may be used together with hardwood cellulose pulp fibres and/or softwood cellulose pulp fibres.

As mentioned in the above, optionally, a portion of or all non-wood cellulose pulp fibres are never-dried non-wood cellulose pulp fibres.

Optionally, the non-wood cellulose fibres are used with softwood cellulose pulp fibres. In this case, a portion of or all softwood cellulose fibres may be never-dried softwood cellulose pulp fibres.

For example, the softwood cellulose pulp fibres may comprise never-dried hardwood cellulose pulp fibres and/or dried softwood cellulose pulp fibres.

Optionally, the non-wood cellulose fibres are used with hardwood cellulose pulp fibres. In this case, a portion of or all hardwood cellulose fibres may be never-dried hardwood cellulose pulp fibres.

For example, the hardwood cellulose pulp fibres may comprise never-dried hardwood cellulose pulp fibres and/or dried hardwood cellulose pulp fibres.

Optionally, the non-wood cellulose pulp fibres as proposed herein may be achieved by treatment by a non-pressurised process.

Optionally, the non-wood cellulose pulp fibres as proposed herein may be achieved by treatment by a process with no use of sulfur.

For example, the non-wood cellulose pulp fibres may be achieved by treatment using methods similar to the methods described EP 2 048281 A1, EP 2 247781 B1, US20130129573 A1, EP 2 034 090 A1, US20110281298 A1, and/or US20130129573 A1.

Additionally or alternatively, the non-wood cellulose pulp fibres may be achieved by treatment using methods similar to the methods described in WO2020264311 A1, WO2020264322 A1, US20190091643 A1, US2592983.

For example, the non-wood cellulose pulp fibres may be achieved by the Phoenix Process TM, of Sustainable Fiber Technologies Inc.

It will be understood that the features as discussed in the above as being contributing to the non-wood cellulose pulp fibres being suitable for use in tissue paper materials and tissue paper products may be used separately or in different combinations.

Optionally, the non-wood cellulose pulp fibres are derived from agricultural waste or byproduct.

Optionally, the non-wood cellulose pulp fibres are derived from a member of the Pocacea family. For example, the non-wood cellulose pulp fibres may be derived from wheat straw, rice straw, barley straw, oat straw, rye grass, costal Bermuda grass, Arundo donax, miscanthus, bamboo, and/or sorghum. Another example of a member of the Pocacea family is sugar cane, from which non-wood cellulose pulp fibres may be derived, for example from sugar cane bagasse.

Optionally, the non-wood cellulose pulp fibres are derived from a member of the Cannabaceae family. For example, the non-wood cellulose pulp fibres may be derived from hemp and/or hop.

Optionally, the non-wood cellulose pulp fibres are derived from agricultural waste or byproducts. For example, the non-wood cellulose pulp fibres may be derived from agricultural waste or byproducts of the members of the Pocacea family and/or

Cannabaceae family such as exemplified in the above, i.e. including agricultural waste or byproducts from wheat straw, rice straw, barley straw, oat straw, rye grass, bagasse from sugar cane, hemp or hop. In another example, the non-wood cellulose pulp fibres may be derived from agricultural waste or byproducts such as banana harvest residue (belongs to the family Musaceae), pineapple residue (belongs to the family Bromeliaceae), nut shell waste, bagasse from agave, hop residue and/or corn stover.

Optionally, the non-wood cellulose pulp fibres are derived from kenaf (belongs to the family Malvaceae), switchgrass , succulents, alfalfa (belongs to the family Fabaceae), flax straw (belongs to the family Linaceae), palm fruits (Elaeis or Arecaceae), and/or avocado (Lauraceae).

Optionally, the non-wood cellulose pulp fibres are derived from one or more of wheat straw, rice straw, barley straw, oat straw, rye grass, costal Bermuda grass, Arundo donax, miscanthus, bamboo, sorghum, banana harvest residue, pineapple residue, nut shell waste, sugar cane bagasse, industrial hemp, and/or members of the Cannabaceae family, kenaf, switchgrass, succulents, alfalfa, corn stover, and flax straw.

Optionally, the non-wood cellulose pulp fibres are derived from wheat straw, oat straw, barley straw, and/or rye grass. For example, the non-wood cellulose pulp fibres may be derived from agricultural waste or byproducts of wheat straw, oat straw, barley straw, and/or rye grass.

For example, the non-wood cellulose pulp fibres may be derived from wheat straw, such as from agricultural waste or byproducts of wheat.

Optionally, the non-wood cellulose pulp fibres are derived from residues from sugar production. For example, the non-wood cellulose pulp fibres may be residues from beet.

Optionally, the non-wood cellulose pulp fibres are derived from sugarcane bagasse.

Optionally, the non-wood cellulose pulp fibres are derived from agave. For example, the non-wood cellulose pulp fibres may be derived from resides from agave syrup production or derived from agave bagasse.

Although the present disclosure relates primarily to tissue paper made of non-wood fibres, it is understood that the non-wood cellulose pulp fibres as described herein may also find use in other applications e.g. in wound care, in absorbent articles, for example diapers, sanitary napkins, and incontinence articles, in beauty care, and/or in nonwoven materials and products.

Herein, the non-wood cellulose pulp fibres as described in the above are proposed to be used to form a non-wood tissue ply, comprising non-wood cellulose pulp fibres in an amount of at least 10% by dry weight of the non-wood tissue ply.

Optionally, said non-wood tissue ply comprises non-wood cellulose pulp fibres in an amount of at least 15% by dry weight of the non-wood tissue ply.

Optionally, said non-wood tissue ply comprises non-wood cellulose pulp fibres in an amount of at least 20% by dry weight of the non-wood tissue ply.

Optionally, said non-wood tissue ply comprises non-wood cellulose pulp fibres in an amount of at least 30% by dry weight of the non-wood tissue ply.

Optionally, said non-wood tissue ply comprises non-wood cellulose pulp fibres in an amount of at least 40% by dry weight of the non-wood tissue ply.

Optionally, said non-wood tissue ply comprises non-wood cellulose pulp fibres in an amount from 20 to 50% by dry weight of the non-wood tissue ply.

Optionally, said non-wood tissue ply comprises non-wood cellulose pulp fibres in an amount from 25 to 35% by dry weight of the non-wood tissue ply.

Optionally, said non-wood tissue ply comprises non-wood cellulose pulp fibres in an amount of less than 70 % by dry weight of the non-wood tissue ply.

Optionally, said non-wood tissue ply comprises non-wood cellulose pulp fibres in an amount of less than 60 % by dry weight of the non-wood tissue ply.

Optionally, the non-wood tissue ply further comprises wood pulp fibres, such as hardwood cellulose pulp fibres and/or softwood cellulose pulp fibres.

Optionally, the non-wood tissue ply further comprises wood pulp fibres in an amount such that the wood pulp fibre amount plus the non-wood fibre amount constitutes 100% dry weight of the tissue paper ply.

Optionally, the hardwood/softwood dry weight proportion of the wood pulp fibres in the non-wood tissue ply is less than 95/5.

Optionally, the hardwood/softwood dry weight proportion of the wood pulp fibres in the non-wood tissue ply is less than 90/10.

Optionally, the hardwood/softwood dry weight proportion of the wood pulp fibres in the non-wood tissue ply is less than 80/20.

Optionally, said non-wood cellulose pulp fibres are present throughout the non-wood tissue ply. In other words, at least some non-wood cellulose pulp fibres may be found in all parts of the ply, e.g. in all layers of the ply. The non-wood cellulose pulp fibres need not be uniformly distributed, but may be a result of e.g. stratified distribution of the non-wood cellulose pulp fibres. For example, the non-wood cellulose pulp fibres may be homogenously distributed in the ply. In another example, the non-wood cellulose pulp fibres may be heterogeneously distributed in the ply.

Optionally, when said non-wood tissue ply comprises two or more layers, at least one layer of the non-wood tissue ply comprises non-wood fibres. For example, said at least one layer maybe an outer layer of the non-wood tissue ply.

Optionally, when said non-wood tissue ply comprises two or more layers, each out of said two or more layers may comprise non-wood fibres.

Optionally, the non-wood tissue ply is produced by conventional wet press technology (CWP). By “is produced” means that the tissue paper material has been manufactured using conventional wet press technology, i.e. the tissue paper material is a CWP tissue

paper material. For example, the tissue paper material may be a dry crepe tissue paper material.

Optionally, the non-wood tissue ply is produced by structured tissue technology. By "is produced" means that the tissue paper material has been manufactured using structured tissue technology, i.e. the tissue paper material is a structured tissue paper material.

Optionally, the non-wood tissue ply is produced by TAD (Through Air Drying) technology.
Optionally, the non-wood tissue ply is produced by ATMOS technology.
Optionally, the non-wood tissue ply is produced by UCTAD technology.
Optionally, the non-wood tissue ply is produced by textured NTT technology.
Optionally, the non-wood tissue ply is produced by eTAD technology, such as Advantage eTAD technology from Valmet.
Optionally, the non-wood tissue ply is produced by QRT technology.
Optionally, the non-wood tissue ply is produced by PrimeLine TEX technology.

In accordance with the invention, there is provided tissue paper materials and tissue paper products including the non-wood tissue ply as described in the above with the non-wood cellulose pulp fibres as described in the above.

In accordance with the invention, there is provided a stack of a tissue paper product including the non-wood tissue ply as described in the above with the non-wood cellulose pulp fibres as described in the above.

In accordance with a first aspect of the invention, there is provided a stack according to claim 1. Hence, there is provided a stack of tissue paper product, wherein the tissue paper product is forming panels having a length, and a width perpendicular to said length, said panels being piled on top of each other to form a stack height, said tissue paper product comprising at least one non-wood tissue ply, the non-wood tissue ply comprising non-wood pulp fibres being present in an amount of at least 10% by dry weight of the non-wood tissue ply, and the stack having a density of at least 0.12 g/cm3.

It has been found, that a tissue paper product comprising a non-wood tissue ply comprising an amount of the non-wood tissue fibres as described in the above, not only may be made to display suitable properties for a tissue paper product, but that these properties may be maintained also after production of a stack of the tissue paper product.

The tissue paper product comprising the non-wood tissue fibres are hence compressible to relatively high densities, without properties such as absorbency or softness being severely affected.

Optionally, as mentioned in the above, the non-wood tissue ply may be made using structured tissue technology. The structured tissue technology used for producing the tissue paper product may, as mentioned in the above, for example be one out of TAD (Through Air Drying), ATMOS, textured NTT, UCTAD, eTAD, QRT and PrimeLineTEX technology.

Optionally, the stack may have a density of at least 0.15 g/cm3.

Optionally, the stack may have a density of at least 0.20 g/cm3.

Optionally, the stack may have a density less than 0.50 g/cm3.

Optionally, the stack may have a density less than 0.40 g/cm3.

For example, the stack may have a density in the range between from 0.20 g/cm3 to 0.40 g/cm3.

For example, the stack may have a density in the range from 0.25 g/cm3 to 0.35 g/cm3.

Optionally, the tissue paper product may be a single-ply product consisting of said non-wood tissue ply.

Alternatively, the tissue paper product may be a multi-ply product comprising at least two plies, such as three plies, four plies or more plies.

Optionally, when said tissue paper product is a multi-ply product comprising at least two plies, all of the plies may be non-wood tissue plies as defined in the above. The non-wood tissue plies may comprise the same amount of non-wood pulp fibres. Alternatively, the non-wood tissue plies may comprise different amounts of non-wood pulp fibres.

Optionally, the tissue paper product is folded to form the panels of the stack. Thus, the tissue paper product may be in the form of a continuous web, optionally separated by perforation lines, and folded to form the panels in the stack. Alternatively, the tissue paper product may be in the form of separate tissue paper products. The separate tissue paper products may be folded, for example in a two panel fold, a three panel fold or a four panel fold, to form the panels of the stack. Tissue paper products having more than four panels

may also be used in the stacks as disclosed herein. Optionally, the separate tissue paper products may be interfolded.

Optionally, the tissue paper product has a basis weight less than 100 gsm.

Optionally, the tissue paper product has a basis weight of less than 80 gsm.

Optionally, the tissue paper product has a basis weight of less than 60 gsm.

Optionally, the tissue paper product has a basis weight of more than 15 gsm.

Optionally, the tissue paper product has a basis weight of more than 20 gsm.

Optionally, the tissue paper product has a GMT tensile strength of at least 60 N/m.

Optionally, the tissue paper product has a GMT tensile strength of at least 70 N/m.

Optionally, the tissue paper product has a GMT tensile strength of at least 80 N/m.

For example, the tissue paper product has a GMT tensile strength of at least 100 N/m.

For example, the tissue paper product has a GMT tensile strength of at least 150 N/m.

For example, the tissue paper product has a GMT tensile strength of at least 200 N/m.

For example, the tissue paper product has a GMT tensile strength of at least 300 N/m.

For example, the tissue paper product has a GMT tensile strength of at least 400 N/m.

Optionally, the tissue paper product has an absorption of at least 7 g/g.

Optionally, the tissue paper product has an absorption of at least 8 g/g.

The absorption may for example be less than 13 g/g. For example, the absorption may be less than 10 g/g.

Optionally, the tissue paper product has a thickness in the range between from 0.1 to 0.8 mm, as obtained after removal of the tissue product from the stack, and with the tissue paper product in an unfolded state.

Optionally, the tissue paper product has a thickness in the range between from 0.1 to 0.6 mm, as obtained after removal of the tissue product from the stack, and with the tissue paper product in an unfolded state.

Optionally, the tissue paper product has a thickness in the range between from 0.1 to 0.3 mm, as obtained after removal of the tissue product from the stack, and with the tissue paper product in an unfolded state.

Optionally, the tissue paper product is a single-ply tissue paper product consisting of a non-wood ply as described in the above.

Optionally, the tissue paper product is a multi-ply tissue paper product comprising two or more plies, wherein one or more ply is a non-wood ply as described in the above.

The properties of the tissue paper product as set out in the above relates to properties of the unfolded tissue paper product as obtained immediately after the removal from the stack. Measurements may be made after the stack has been stored, for example after storage of the stack for three weeks.

BRIEF DESCRIPTION OF THE DRAWINGS

With reference to the appended drawings, below follows a more detailed description of embodiments of the invention cited as examples.

In the drawings:

Fig. 1a is a diagram illustrating the dry strength in the machine direction of the tissue paper products from stacks with different non-wood fibre content in relation to the density of the stacks obtained in a first trial;

Fig. 1b is a diagram illustrating the dry strength in the cross direction of the tissue paper products from stacks with different non-wood fibre content in relation to the density of the stacks obtained in the first trial;

Fig. 2 is a diagram illustrating the absorption of the tissue paper products from stacks with different non-wood fibre content in relation to the density of the stacks obtained in the first trial;

Fig. 3 is a diagram illustrating the thickness of the tissue paper products from stacks with different non-wood fibre content in relation to the density of the stacks obtained in the first trial;

Fig. 4 illustrates the force needed to compress the stacks to the different densities for three different tissue paper products with different amount of non-wood fibre content obtained in the first trial;

Fig. 5 illustrates the force needed to compress the stacks to the different densities for three different tissue paper products with different amount of non-wood fibre content obtained in a second trial; and

Fig. 6 is a diagram illustrating the thickness of the tissue paper products from stacks with different non-wood fibre content in relation to the density of the stacks after one week of storage of the stacks from the second trial;

Fig. 7 is a diagram similar to the diagram of Fig. 6 but obtained after one month of storage of the stacks from the second trial.

DETAILED DESCRIPTION

To investigate whether the tissue paper products comprising the non-wood fibres are suitable for forming stacks, and thereby useful for storage, distribution and dispensing of the tissue paper products, two trials with tissue paper products were performed.

In both trials the tissue paper products were made using structured tissue technology, in this case using ATMOS technology. The tissue paper products were 1 ply products intended for use as hand towels. The basis weight was 30 gsm.

Pulps

The non-wood fibre pulp was derived from wheat straw, being treated according to the Phoenix TM process by Sustainable Fiber Solutions Inc. The non-wood fibre pulp was never-dried pulp. This type of non-wood fibre pulp generally has lignin content of less than 15% and a hemicellulose content of more than 15%.

The conventional short fibre content was Hardwood cellulose fibre pulp, made fibre of Eucalyptus. The Eucalyptus fibre pulp was dried pulp, BEK (Bleached Eucalyptus Kraft).

The conventional long fibre content was made out of Softwood Cellulose fibre pulp. In this example, the Softwood cellulose fibre pulp was dried pulp, NBSK (Northern bleached softwood kraft).

The non-wood fibre pulp of the first trial and the non-wood fibre pulp of the second trail were slightly different.

The breaking length, average fibre length and breaking length/average fibre length ratio of the non-wood of the first trial (Non-wood (1)), the non-wood of the second trial (Non-wood

(2)), the softwood pulp (NBSK) and eucalyptus fibre pulp (BEK) were as indicated in the table below:

	Non-wood (1)	Non-wood (2)	NBSK	BEK
Breaking length [m]	3775	5233	2915	1724
Average fibre length[µm]	748	857	2094	714
Breaking length/av fibre length	5.05	6.10	1.39	2.41

Trial 1

1 ply tissue paper materials (base sheets) were made using the above-mentioned pulps for Trial 1, and using ATMOS technology.

Three versions of the tissue paper materials were made.

A first version, comprising 0% dry weight non-wood fibres.

A second version, comprising 25% dry weight non-wood fibres.

A third version, comprising 50% dry weight non-wood fibre.

The non-wood pulp, the softwood pulp and the eucalyptus pulp were blended in pulper with the recipes for the different versions of tissue paper products as indicated in the table in the below, sent to the dump chest and metered to the machine stock system.

	Variant 1 0% Non-wood	Variant 2 25% Non-wood	Variant 3 50% Non-wood
Softwood Pulp (NBSK)	60%	45%	30%
Eucalyptus Pulp (BEK)	40%	30%	20%
Non-wood Pulp (1)	0%	25%	50%

The average properties of the three variants (0%, 25%, 50%) of the tissue paper materials obtained are indicated in the table in the below.

Amount Non-wood	Basis weight (g/m²)	Thickness (mm)	MD dry (N/m)	CD dry (N/m)	MD stretch (%)	MD wet (N/m)	CD wet (N/m)
0%	26.5	0.23	528	378	19.9	130	96
25%	28.8	0.24	599	525	14.9	147	106
50%	29.1	0.26	651	611	16	138	102

The tissue paper materials were cut to form separate tissue paper products. The dimensions of the tissue paper products were 22.8 cm x 24.1 cm. The tissue paper products were folded in a 3-panel fold and piled on top of each other to form stacks. Each stack comprised 250 tissue paper products, i.e. 3 x 250 =750 panels.

Five stacks were produced of each one out the first, second and third version of the tissue paper product.

The method of producing the stacks involved compressing the stack to a density higher than a target density of the stack for a predetermined time period, and then releasing the stack to assume said target density.

Each one of the five stacks of each version of the tissue paper product was produced with a different target density.

When producing stacks, more force will be required to compress the tissue paper products with increasing target density of the stacks. The maximum compression force in kN as needed to compress the stacks to the different target densities of the three versions of the tissue paper products is noted in the table below.

		Non-wood fibre amount		
Bundle density (g/cm^3)	**Final height (cm)**	**0%**	**25%**	**50%**
0.19	11.3	2.04	2.14	2.32
0.27	7.9	15.81	15.40	15.09
0.38	5.6	80.12	67.22	69.13

Fig. 5 illustrate the maximum compression force for the three tissue paper product versions over the different stack densities. As may be seen in Fig. 5, the three curves seem to follow approximately the same behavior for densities between 0.19 and about 0.25 g/cm3. For densities greater than 0.25 g/cm3, the curves deviate, such that the compression force required to compress the tissue paper product with 0% non-wood fibre content is greater than the compression force required to compress the tissue paper products with 25 % and 50% non-wood fibre content.

The stacks were packaged and then stored within their packaging for 3 weeks.

Then, the packaging was removed and various properties of the tissue paper products from the different stacks were measured.

The results are indicated in the table below:

Non-wood amount	Density	Grammage	Thickness	MD strength	CD strength	Absorption
	g/cm3	g/m^2	mm	N/m	N/m	g/g
0%	0,13	30,3	0,24	582	445	8,8

0%	0,19	29,9	0,22	569	448	8,9
0%	0,27	29,6	0,2	587	426	8,4
0%	0,32	29,3	0,19	565	423	8,5
0%	0,38	29,5	0,15	591	422	8,1
25%	0,13	30,1	0,23	646	510	8,9
25%	0,19	29,9	0,21	592	501	8,7
25%	0,27	29,7	0,17	627	500	8,7
25%	0,30	29,7	0,18	636	513	8,5
25%	0,38	28,4	0,15	639	488	8,5
50%	0,13	30,5	0,23	637	567	8,5
50%	0,19	29,5	0,22	625	540	8,8
50%	0,27	29,0	0,2	640	530	8,3
50%	0,30	29,1	0,2	655	568	8,3
50%	0,38	28,6	0,17	629	527	8

Thus, the five stacks of Version 1 of the tissue paper material, which contains no non-wood fibre, may be seen as a reference.

In the following, the results of the measurements will be discussed with reference to the drawings.

Fig. 1a is a diagram illustrating the dry MD strength of the stacks of different non-wood content and density. As may be seen in Fig. 1a, the Dry MD strength does not vary much between the stack densities ranging between approximately 0.10 and 0.40 kg/dm3. Surprisingly, the stacks of Variant 1, where the tissue paper product comprises 0 % non-wood fibre displays the lowest dry MD strength for all densities. The diagram shows that the tissue paper products comprising 25% non-wood fibre or 50% non-wood fibre maintains their dry MD strength after having been compressed to form a stack of the different densities at least as well as the tissue paper product comprising 0% non-wood fibre.

Fig. 1b is a diagram illustrating the dry CD strength of the stacks of different non-wood content and density. Similar to Fig. 1a, Fig. 1b shows that the tissue paper products comprising 25% non-wood fibre or 50% non-wood fibre maintains their dry CD strength after having been compressed to form a stack of the different densities at least as well as the tissue paper product comprising 0% non-wood fibre.

Fig. 2 is a diagram illustrating the absorption of the stacks of different non-wood content and density. Absorption is generally adversely affected by the tissue paper products being compressed into stacks of relatively high density. However, it may be seen from Fig. 3 that the tissue paper products comprising 25% non-wood fibre or 50% non-wood fibre maintain their absorption after having been compressed to form a stack of the different densities about as well as the tissue paper product comprising 0% non-wood fibre.

Fig. 3 is a diagram illustrating the thickness of the stacks of different non-wood content and density. Thickness is known to generally be adversely affected by the tissue paper products being compressed into stacks of relatively high density. However, it may be seen from Fig. 3 that the tissue paper products comprising 25% non-wood fibre or 50% non-wood fibre maintains their thickness after having been compressed to form a stack of the different densities slightly better than the tissue paper product comprising 0% non-wood fibre.

Trial 2

1 ply tissue paper materials (base sheets) were made using pulps NBSK, BEK and Non-wood (2) for Trial 2 as described in the above, and using ATMOS technology.

Three versions of the tissue paper materials were made.

A first version, comprising 0% dry weight non-wood fibres.

A second version, comprising 25% dry weight non-wood fibres.

A third version, comprising 50% dry weight non-wood fibre.

The non-wood pulp, the softwood pulp and the eucalyptus pulp were blended in pulper with the recipes for the different versions of tissue paper products as indicated in the table in the below, sent to the dump chest and metered to the machine stock system.

	Variant 1	Variant 2	Variant 3

	0% Non-wood	25% Non-wood	50% Non-wood
Softwood Pulp (NBSK)	46%	21%	0%
Eucalyptus Pulp (BEK)	54%	54%	50%
Non-wood Pulp (2)	0%	25%	50%

The average properties of the three variants (0%, 25%, 50%) of the tissue paper materials obtained are indicated in the table in the below.

Amount Non-wood	Basis weight (g/m²)	Thickness (mm)	MD dry (N/m)	CD dry (N/m)	MD stretch (%)	MD wet (N/m)	CD wet (N/m)
0%	30.4	0.23	692	479	16.07	175	88
25%	31.1	0.26	579	362	16.2	144	67
50%	26.0	0.27	478	401	15.17	86	71

Fig. 5 illustrates the maximum compression force for the three tissue paper product variants over the different stack densities. In this trial, the two curves for 0% straw fibres and 25 % straw fibres seem to follow approximately the same behavior for densities between 0,19 and about 0.25 g/cm3, whereas the curve for 50% straw fibre deviates slightly. For densities greater than 0.25 g/cm3, the curves deviate, such that the compression force required to compress the tissue paper product with 0% non-wood fibre content is greater than the compression force required to compress the tissue paper products with 25 % non-wood fibre content. The compression force required to compress the tissue paper products with 50% non-wood fibre content is only slightly higher than the force needed to compress the tissue paper products with 0 % non-wood fibre content at densities over about 0.30 g/cm3.

The produced stacks were packaged and stored.

Then, the thickness of the unfolded tissue paper products when removed from the stacks were measured after one week of storage and after one month of storage, as illustrated in Fig. 6 and Fig. 7, respectively.

Fig. 6 is a diagram illustrating the thickness of the stacks of different non-wood content and density after one week of storage. It may be seen from Fig. 6 that the tissue paper products comprising 25% non-wood fibre or 50% non-wood fibre both maintain their thickness after having been compressed to form a stack of the different densities slightly better than the tissue paper product comprising 0% non-wood fibre.

Fig. 7 is a diagram illustrating the thickness of the stacks of different non-wood content and density after one month of storage. Again, it may be seen from Fig.7 that the tissue paper products comprising 25% non-wood fibre or 50% non-wood fibre both maintain their thickness after having been compressed to form a stack of the different densities slightly better than the tissue paper product comprising 0% non-wood fibre, also after one month of storage.

Conclusion

In conclusion, for the stacks of different densities comprising tissue paper products comprising 25% or 50 % non-wood fibres, the measured properties indicate that the tissue paper products from the stacks comprising non-wood fibres will perform in a manner comparable to the tissue paper product comprising 0% non-wood fibres, coming from a stack with a similar density.

Thus, in summary, the results indicate that the tissue paper products comprising non-wood tissue fibres may be formed to stacks with relatively high densities, and that the stacks may be stored without the properties of the tissue paper products falling beyond an acceptable level. Instead, the tissue paper products comprising the non-wood tissue fibres perform as well as the tissue paper products comprising no non-wood tissue fibres, after compression to and storage in stacks of similar densities. The benefits for the environment resulting when using non-wood fibres may hence be achieved without requiring adaptation of storage systems, distribution, dispensers or use of the tissue paper products.

Further, in some regards the tissue paper products including the non-wood cellulose pulp fibres perform even better than the tissue paper products without non-wood fibre. For example, the results indicate that with the tissue paper products comprising non-wood

cellulose pulp fibres, stacks with relatively higher densities may be achieved using a relatively lower compression force, if compared to stacks comprising tissue paper products without non-wood cellulose pulp fibre. This is advantageous in view of production, where relatively lower compression pressures are generally desired in an industrial production line.

DEFINITIONS

Tissue paper material: As tissue paper material we understand herein the one-ply base tissue as obtained from a tissue machine.

Layer: The tissue paper material may comprise one or more layers, i.e. it may be a single-layered or a multi-layered web. The term "layer" refers to a stratum within the web having a defined fibre composition. The one or more layers is/are formed by depositing one or more streams of pulp furnishes onto a wire with a pressurized single-or multi-layered headbox.

Ply: The term "ply" as used herein refers to the one or more plies of tissue paper material in the final tissue paper product as are obtained after processes, i.e. converting, one or more base tissue webs. Each individual ply consists of a tissue paper material comprising one or more layers, e.g. one, two, or three layers.

Hardwood: As hardwood we understand herein fibrous pulp derived from the woody substance of deciduous trees (angiosperms). For example, hardwood includes eucalyptus. Typically, hardwood fibres are relatively short fibres. For example, the hardwood fibres may have an average fibre length less than 1700 µm. The hardwood fibres may for example have a diameter of 15 to 40 µm and a wall thickness of 3 to 5 µm.

Softwood: as softwood we understand fibrous pulp derived from the woody substance of coniferous trees (Gymnosperms). Typically, softwood fibres are relatively long fibres. For example, the softwood fibres may have an average fibre length above 1700 µm, such as above 1950 micron, for example the soft wood fibres may have an average fibre length in a range from 1700 to 2500. µm. The softwood fibres may for example have a diameter of from 30 to 80 µm, and a wall thickness of from 2 to 8 µm.

Conventional short fibres: As conventional short fibres we understand herein hardwood fibres as described in the above. Generally, the conventional short fibres may have an average fibre length less than 1700 µm.

Conventional long fibres: As conventional long fibres we understand herein softwood fibres as described in the above. Generally, the conventional long fibres may have an average fibre length greater than 1700 µm.

CWP & structured tissue technology:

As described in the above, paper tissue webs can be produced in several ways. Conventional paper machines have been used for many years for that purpose, to produce such conventional webs at a relatively low cost.

An example of a conventional paper tissue web process is the dry crepe process which involves creping on a drying cylinder, the so-called yankee cylinder, by means of a crepe doctor. Wet creping can be used as well, if there are lower demands on the tissue quality. The creped, finally dry raw tissue paper, the so-called base tissue, is then available for further processing into the paper product for a tissue paper product.

Recently, more advanced methods have been developed, such as e.g. Through Air Drying (TAD), Advanced Tissue Molding System (ATMOS) and similar methods for producing structured tissue webs. A common feature for these latter methods is that they result in a more structured web with a lower density than a web produced on a conventional paper machine.

As used herein the term CWP technology (Conventional Wet Pressed technology) refers to conventional paper web processes, in which the tissue is formed on a forming fabric and dewatered by pressing with one or more pressure roll nips. The process may involve transfer of the sheet to a Yankee dryer and removing the sheet from the Yankee surface by a doctor blade in a creping process. CWP technology as used herein includes for example dry crepe technology, wet crepe technology, and flat NTT (New Tissue Technology).

As used herein, the term structured tissue technology relates to the newer technologies for producing a structured tissue web. Such methods will not employ the high pressure used to dewater the web in the CWP process. Therefore, structured tissue technology is

sometimes referred to as non-compressing de-watering technology. The structured tissue technology may for example be TAD (Thru-Air-Dried), UCTAD (Uncreped-Through-Air-Dried) or ATMOS (Advanced-Tissue- Molding-System), textured NTT, QRT, PrimeLineTEX technology and eTAD technology.

The structured tissue technology methods are known from prior art, for example TAD is known from US5853547; and ATMOS from US 7744726, US7550061 and US7527709; and UCTAD from EP 1 156925 and WO 02/40774.

TAD technology has been developed since the 1960's and is well known to a person skilled in the art. It generally involves developing functional properties of the tissue by moulding the fibre mat on a structured fabric. This results in the fibre mat forming a structured tissue which may acquire high bulk and absorption due to air passing through the web while drying the web when still on the structured fabric.

ATMOS technology is a production method developed by Voith and which is also well known to a person skilled in the art.

Another example is textured NTT (New Tissue Technology). Textured NTT was designed to overcome some of the limitations of ATMOS by pressing at even higher pressures before transferring to the Yankee. A shoe press is used in the first pressing section between the former felt and a belt with cells designed to provide absorptive capacity and increase strength. The NTT technology may reduce the Yankee Hood drying load as compared to ATMOS.

Yet other examples are Prime Line Tex technology as rendered available by Andritz for production of textured tissue, and eTAD technology as rendered available by Valmet.

METHODS

Lignin content:

The measurement of residual lignin content in the pulp fibres has been carried out according to the draft standard ISO/DIS 21436: Pulps-Determination of lignin content – Method of acid hydrolysis 1), which includes:

i) the gravimetric measurement of the residue after acid hydrolysis (AIL : Acid Insoluble Lignin or Klason Lignin), also described in the Tappi T222 om-02 method 2 ; and

ii) the measurement of soluble lignin (ASL : Acid Soluble Lignin), also described in the technical note Tappi UM2503 .

3.1) Sample preparation: The samples were disintegrated with a grinder/mixer. Their dry matter contents were determined before analysis, by drying in an oven of an aliquot of 2-3 g at 105°C, according to the ISO 638 standard 4 .

3.2) Measurement of acid insoluble lignin (AIL or Klason lignin) after acid hydrolysis An aliquot of ~1 g was hydrolysed with a solution of sulfuric acid, firstly at ambient temperature (2 h) and then under reflux during 4 h (Procedure B of the future standard). After cooling, the suspension was filtered and washed and the solid residue was collected, dried and weighted. The acid insoluble lignin content in the sample was determined by difference between the dry hydrolysis residue weight and the ash weight, reported to the dry mass content of the initial sample. Note 1 : Detection limit (DL) ~0.1% ; Quantification limit (QL) ~0.5%.

3.3) Measurement of acid soluble lignin. The absorbance at 205 nm of the hydrolysate (i.e. the filtrate collected during the filtration of the suspension, cf 3.2), were measured. The acid soluble lignin content (ASL) was determined according to the predefined extinction coefficient of the lignin (i.e. 110 L/g.cm). Note 2 : : Detection limit (DL) ~0.1% ; Quantification Limit (QL) ~0.5% Remark: This quantification method is sensitive to the contaminants being present into the sample. Each compound other than hemicelluloses and cellulose and the acid insoluble minerals are susceptible to interfere with the measurement of the hydrolysis residue and with the acid soluble lignin.

Hemicellulose

The determination of the contents of the main polysaccharides in the pulp (arabinane, galactane, glucane, xylene, and mannane) has been made by using high performance anion exchange chromatography with a pulsed amerometric detector, HPAE/PAD-Dionex® analysis of free monosaccharides (arabinose, galactose, glucose, xylose and mannose) after sulphuric acid hydrolysis of the sample pulp. The cellulose and the hemicellulose content in the pulp sample is determined according to standard method

ISO / DIS21437 – Pulps: Determination of carbohydrate (under publication) after calibration. The samples studied are chemical pulp which has not required extraction of aceton beforehand. In contrast, the samples have been dried. However, considering the pulp state (wet lap sheets), samples were grinded before analysis. Dry content of the grinded samples was measured according to NF EN ISO 638:2008.

Basically the method is quantifying the amounts of sugars (monosaccharides) after hydrolysis of cellulose and hemi using the ISO / DIS 21437 – Pulps: Determination of carbohydrate. Then, calculation is made backwards to estimate level of hemicelluloses (knowing proportion of sugars in hemi and cellulose)

Basis weight

Basis weight is determined in accordance with ISO 12625-6: 2016.

The basis weight is determined in g/m^2.

Thickness per sheet:

Thickness is determined in accordance with ISO 12625-3.

GMT strength:

GMT strength (Geometric Mean Tensile strength) refers to the square root of the product of the machine direction dry tensile strength and the cross-direction dry tensile strength of a tissue web/product.

The GMT strength is determined in accordance with ISO 12625-4.

A load cell of 100N was used.

Absorption:

Absorption is herein the water absorption capacity of the tissue paper. Water absorption capacity is the amount of water the sample is able to absorb, reported in g/g (i.e. g water / g material in sample).

Absorption was measured according to ISO12625-8:2011.

The water is deionized water, conductivity ≤ 0.25 mS/m at 25ºC, in accordance with ISO14487.

Average fibre length measurement:

Fibre length measurement was made using the standard for fibre analyser: ISO 16065-2:2014: Pulps – Determination of fibre length by automated optical analysis – Part 1: Unpolarized light method.

Length-weighted mean length was used and the average of the length – weighted fibre-length distribution.

Breaking length measurement

The breaking length is the calculated upper limit of length of a uniform paper strip that would support its own weight if it were suspended at one end. Breaking length (m) = 102 x T/R, where T = Tensile strength, N/m, and R = basis weight, g/m2.

The breaking length is a pulp characteristic obtained by tensile strength and basis weight measurements as measured on lab handsheets produced in accordance with EN ISO 5269-2. (Tensile strength: ISO 12625-4; basis weight: ISO 12625-6: 2016)

Ratio of breaking length measurement/average fibre length measurement

The ratio of breaking length/average fibre length is herein using the values of the fibre length measurement and the breaking length measurements as achieved according to the methods in the above, the average fibre length measurement being reported in µm, and the breaking length being reported in m.

It may be noted that the breaking length, as well as the average fibre length, are pulp characteristics. Thus the measurements are to be performed on the pulp as received from the pulping process, before reaching the papermaking process, such as before entering the stock preparation in a paper machine. Thus, the measurements are done prior to any mechanical and/or chemical and/or enzymatic treatment for strength adjustment which may occur during the paper making process.

Density:

Density was determined as weight in g/volume in cm3.

The dimensions of the stack were measured with the stack resting freely on a planar surface. No load was applied to the stack. For the height measurement, the highest point

of the stack was measured. The volume of the stack was determined from the measurements.

CLAIMS

1. A stack of tissue paper product, wherein the tissue paper product is forming panels having a length, and a width perpendicular to said length, said panels being piled on top of each other to form a stack height, said tissue paper product comprising at least one non-wood tissue ply, the non-wood tissue ply comprising non-wood pulp fibres being present in an amount of at least 10% by dry weight of the non-wood tissue ply, and the stack having a density of at least 0.12 g/cm3.

2. A stack according to claim 1, wherein the non-wood tissue ply is made using structured tissue technology.

3. A stack according to claim 2, wherein said structured tissue technology is one out of TAD (Through Air Drying), ATMOS, textured NTT, eTAD, QRT, UCTAD, and PrimeLineTEX technology.

4. A stack according to any one of the preceding claims, wherein the stack has a density of at least 0.15 g/cm3.

5. A stack according to any one of the preceding claims, wherein the stack has a density of at least 0.20 g/cm3.

6. A stack according to any one of the preceding claims, wherein the stack has a density in the range from 0.20 g/cm3 to 0.40 g/cm3.

7. A stack according to any one of the preceding claims, wherein the stack has a density in the range from 0.25 g/cm3 to 0.35 g/cm3.

8. A stack according to any one of the preceding claims, wherein the tissue paper product is a single-ply product consisting of said non-wood tissue ply.

9. A stack according to any one of the claims 1 to 8, wherein the tissue paper product is a multi-ply product comprising at least two plies, wherein one or more plies is a non-wood tissue ply comprising non-wood pulp fibres being present in an amount of at least 10% by dry weight of the non-wood tissue ply.

10. A stack according to any one of the preceding claims, wherein said tissue paper product is folded to form said panels of said stack.

11. A stack according to any one of the previous claims, wherein the tissue paper product in an unfolded state has a basis weight less than 100 gsm.

12. A stack according to any one of the previous claims, wherein the tissue paper product in an unfolded state has a GMT tensile strength of at least 60 N/m.

13. A stack according to any one of the previous claims, wherein the tissue paper product in an unfolded state has a GMT tensile strength of at least 70 N/m.

14. A stack according to any one of the preceding claims, wherein the tissue paper product in an unfolded state has a GMT tensile strength of at least 80 N/m.

15. A stack according to any one of the preceding claims, wherein the tissue paper product has an absorbency of at least 7 g/g.

16. A stack according to any one of the preceding claims, wherein the tissue paper product has an absorbency of at least 8 g/g.

17. A stack according to any one of the preceding claims, wherein the tissue paper product in an unfolded state has a basis weight of less than 80 gsm.

18. A stack according to any one of the preceding claims, wherein the tissue paper product in an unfolded state has a basis weight of less than 60 gsm.

19. A stack according to any one of the preceding claims, wherein the tissue paper product in an unfolded state has a thickness in the range between from 0.1 to 3.0 mm, as obtained after removal of the tissue product from the stack.

20. A stack according to any one of the preceding claims, wherein said tissue paper product is a one-ply tissue paper product and consists of said non-wood tissue ply.

21. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres contain at least 15% hemicellulose.

22. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres contain no more than 15 % lignin.

23. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres have an average fibre length of less than 1700 µm.

24. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres have an average fibre length of less than 1200 µm.

25. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres have an average fibre length of less than 900 µm.

26. A stack according to any one of the preceding claims, wherein the non-wood cellulose fibres have a breaking length of more than 3000 m.

27. A stack according to any one of the preceding claims, wherein the non-wood cellulose fibres have a breaking length/average fibre length ratio of more than 3.7.

28. A stack according to any one of the preceding claims, wherein the non-wood cellulose fibres have a breaking length/average fibre length ratio of more than 4.0.

29. A stack according to any one of the preceding claims, wherein the non-wood cellulose fibres have a breaking length/average fibre length ratio of more than 4.5.

30. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres are derived from a member of the Pocacea family, such as from wheat straw, rice straw, barley straw, oat straw, rye grass, costal Bermuda grass, Arundo donax, miscanthus, bamboo, bagasse from sugar cane, and/or sorghum.

31. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres are derived from a member of the Cannabaceae family, such as from hemp and/or hop.

32. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres are agricultural waste or byproduct, such as derived from agricultural waste or byproduct of the Pocacea family and/or Cannabaceae family such as exemplified in the above, including agricultural waste or byproduct from wheat straw, rice straw, barley straw, oat straw, rye grass,

bagasse from sugar cane, hemp or hop and/or wherein the non-wood cellulose pulp fibres are derived from agricultural waste or byproduct such as banana harvest residue (belongs to the family Musaceae), pineapple residue (belongs to the family Bromeliaceae), nut shell waste, bagasse from agave, hop residue and/or corn stover.

33. A stack according to any one of the preceding claims, wherein the non-wood cellulose pulp fibres are derived from kenaf (belongs to the family Malvaceae) , switchgrass , succulents, alfalfa (belongs to the family Fabaceae.), flax straw (belongs to the family Linaceae), palm fruits (Elaeis or Arecaceae), and/or avocado (Lauraceae).

34. A stack according to any one of the preceding claims, wherein said non-wood tissue ply or plies comprises said non-wood cellulose pulp fibres in an amount of at least 15% by dry weight.

35. A stack according to any one of the preceding claims, wherein said non-wood tissue ply or plies comprises said non-wood cellulose pulp fibres in an amount of at least 20% by dry weight.

36. A stack according to any one of the preceding claims, wherein said non-wood tissue ply or plies comprises said non-wood cellulose pulp fibres in an amount of less than 70 % by dry weight.

37. A stack according to any one of the preceding claims, wherein said non-wood tissue ply or plies comprises said non-wood cellulose pulp fibres in an amount of less than 60 % by dry weight.

38. A stack according to any one of the preceding claims, wherein said non-wood tissue ply further comprises wood pulp fibres, such as hardwood cellulose pulp fibres and/or softwood cellulose pulp fibres.

39. A stack according to any one of the preceding claims, wherein said non-wood tissue ply comprises wood pulp fibres in an amount such that the wood pulp fibre amount plus the non-wood fibre amount constitutes 100% dry weight of the non-wood tissue ply.

40. A stack according to claim 38 or 39, wherein the hardwood/softwood dry weight proportion of the wood pulp fibres in said non-wood tissue ply is less than 95/5.

41. A stack according to any one of the claims 38 to 40, wherein the hardwood/softwood dry weight proportion of the wood pulp fibres in said non-wood tissue ply is less than 90/10.

42. A stack according to any one of the claims 38 to 41, wherein the hardwood/softwood dry weight proportion of the wood pulp fibres in said non-wood tissue ply is less than 80/20.

43. A stack according to any one of the previous claims, wherein said non-wood cellulose pulp fibres are present throughout the non-wood tissue ply or plies.

44. A stack according to any one of the previous claims, wherein said non-wood tissue ply or plies comprises two or more layers, and at least one layer comprises non-wood fibres.

45. A stack according to any one of the preceding claims, wherein a portion or all non-wood cellulose pulp fibres are never-dried non-wood cellulose pulp fibre.

46. A stack according to any one of the preceding claims, comprising softwood cellulose pulp fibres and wherein a portion or all softwood cellulose fibres are never-dried softwood cellulose pulp fibres.

47. A stack according to any one of the preceding claims, comprising hardwood cellulose pulp fibres and wherein a portion or all hardwood cellulose fibres are never-dried hardwood cellulose pulp fibres.

48. A stack according to any one of the preceding claims, the tissue paper product being for personal hygiene, such as toilet paper, hand wipes, paper napkins, facial wipes, handkerchiefs or the tissue paper product being a kitchen towel or industrial wipe.

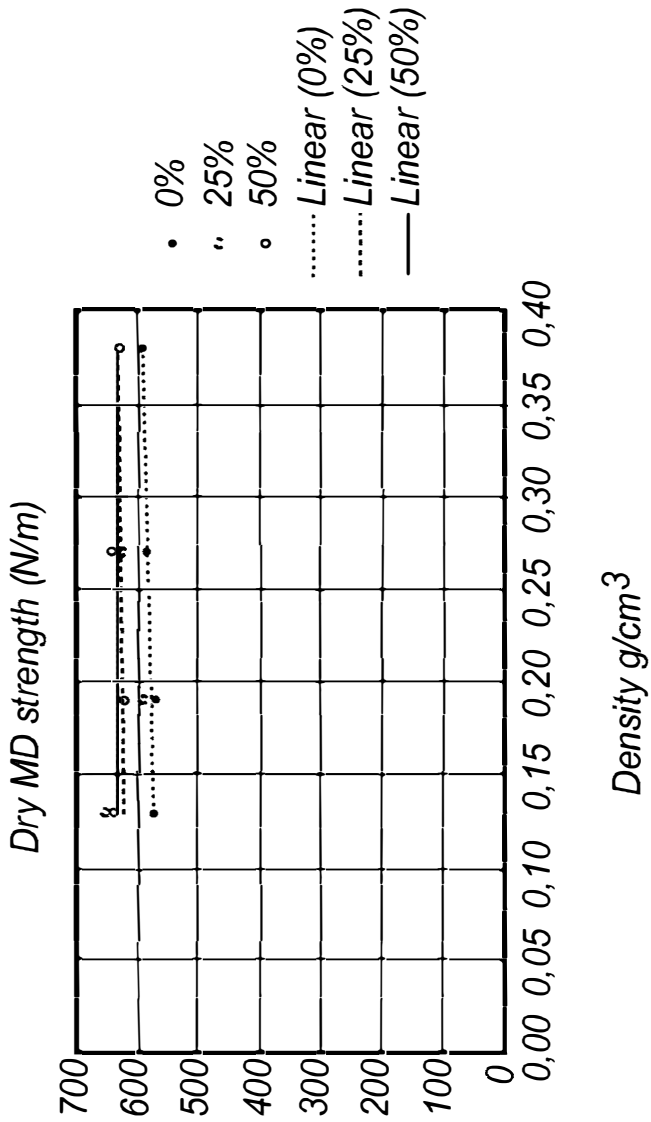

Dry MD strength (N/m)
700
600
500
400
300
200
100
0
0,00 0,05 0,10 0,15 0,20 0,25 0,30 0,35 0,40
Density g/cm3
0%
25%
50%
Linear (0%)
Linear (25%)
Linear (50%)

Fig. 1A

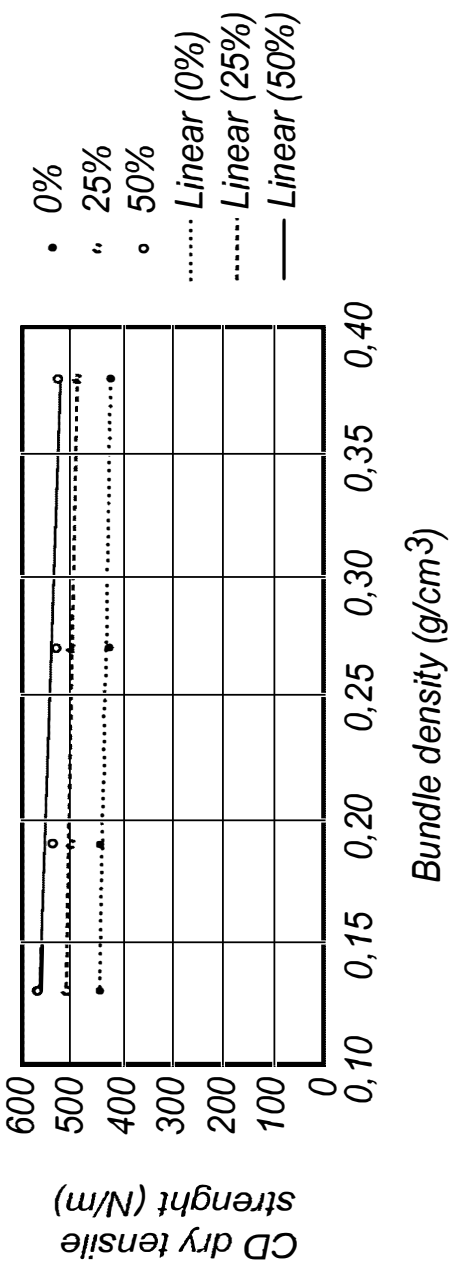

CD dry tensile strenght (N/m)
600
500
400
300
200
100
0
0,10
0,15
0,20
0,25
0,30
0,35
0,40
Bundle density (g/cm3)
0%
25%
50%
Linear (0%)
Linear (25%)
Linear (50%)

Fig. 1B

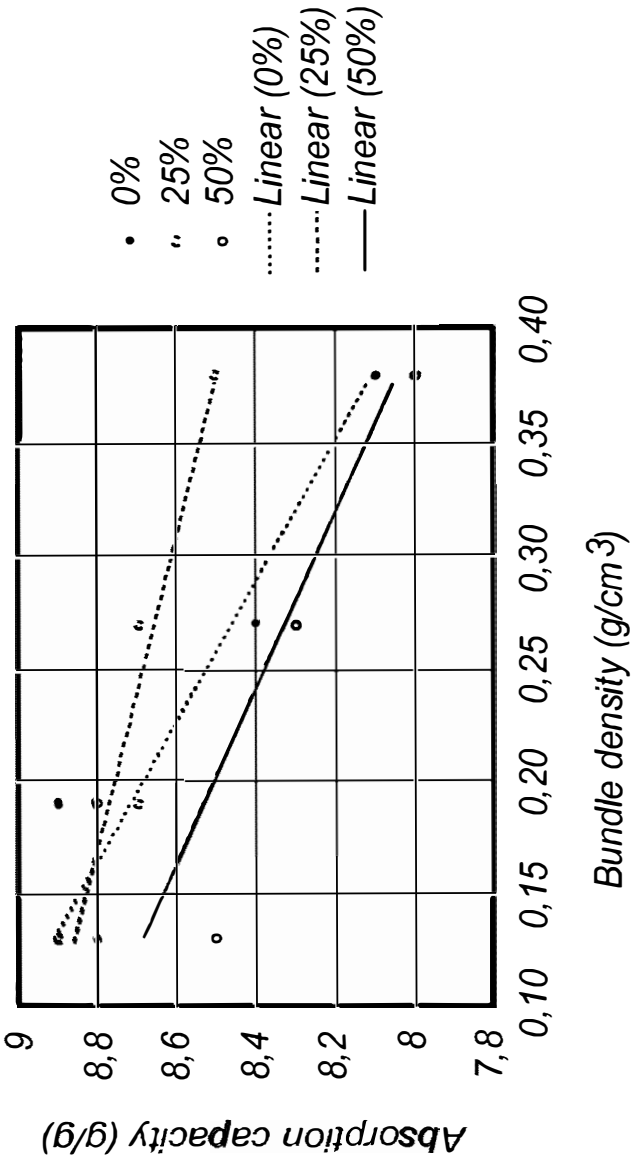

0%
25%
50%
Linear (0%)
Linear (25%)
Linear (50%)
Absorption capacity (g/g)
9
8,8
8,6
8,4
8,2
8
7,8
0,10
0,15
0,20
0,25
0,30
0,35
0,40
Bundle density (g/cm3)

Fig. 2

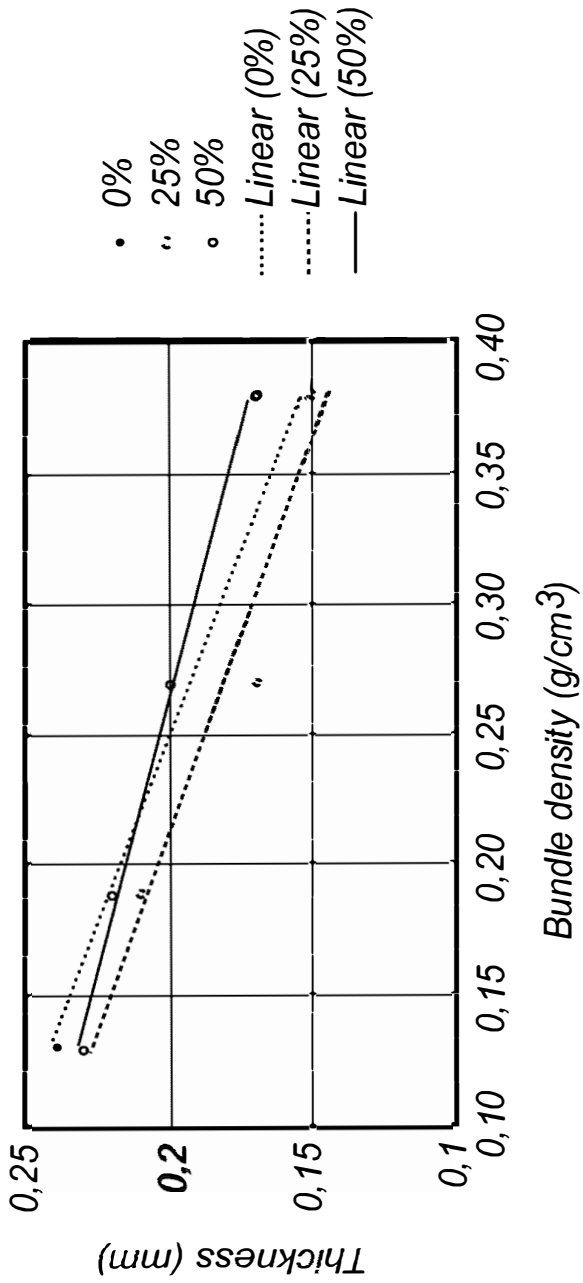

0%
25%
50%
Linear (0%)
Linear (25%)
Linear (50%)
0,25
0,2
0,15
0,1
Thickness (mm)
0,10
0,15
0,20
0,25
0,30
0,35
0,40
Bundle density (g/cm3)

Fig. 3

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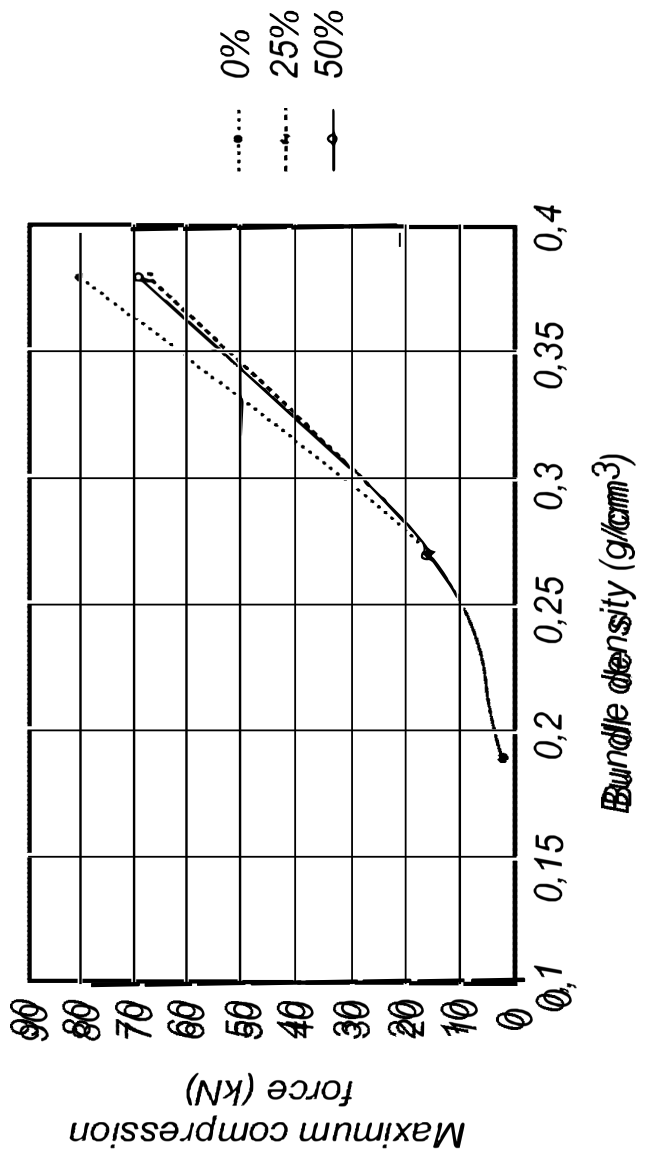


Fig. 4

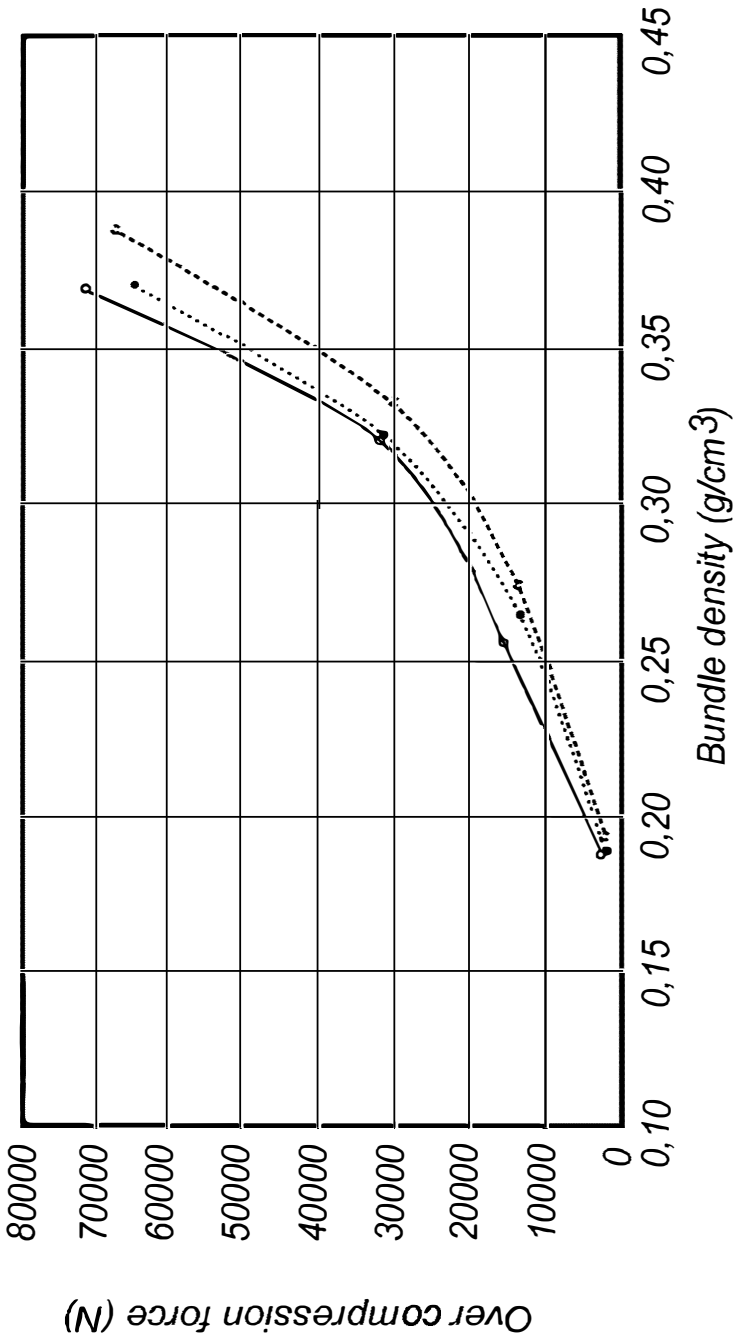

Over compression force (N)
80000
70000
60000
50000
40000
30000
20000
10000
0
0,10
0,15
0,20
0,25
0,30
0,35
0,40
0,45
Bundle density (g/cm3)
0% straw fibers
25% straw fibers
50% straw fibers

Fig. 5

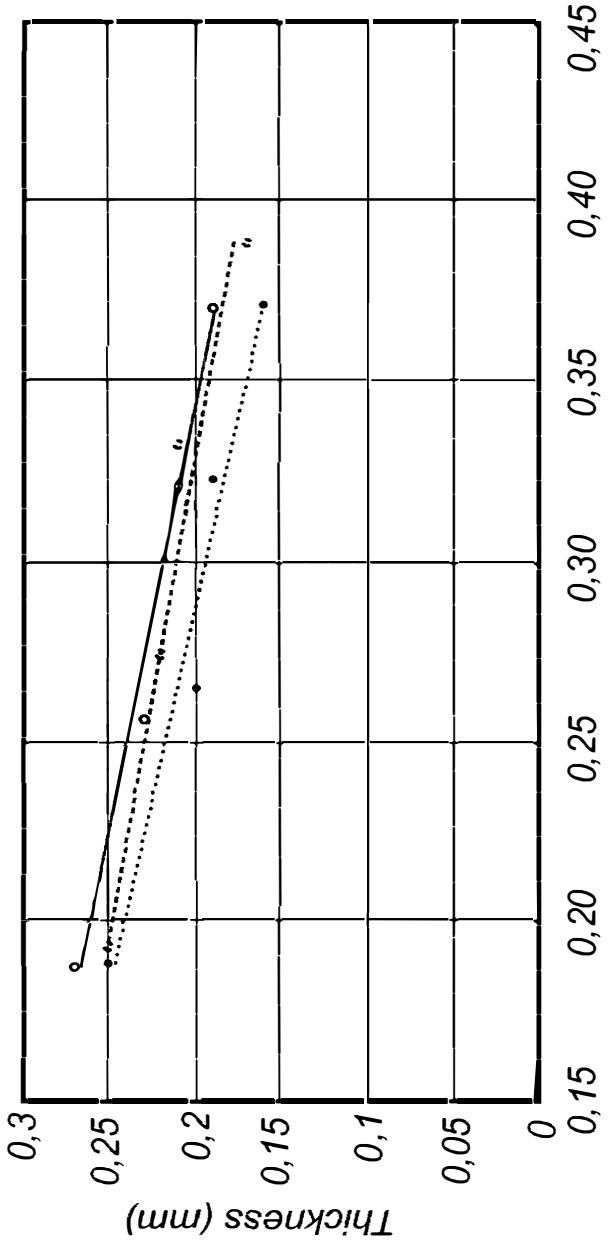

Thickness (mm)
0,3
0,25
0,2
0,15
0,1
0,05
0
0,15
0,20
0,25
0,30
0,35
0,40
0,45
Bundle density (g/cm3)
Linear (0% straw fibers)
0% straw fibers
Linear (25% straw fibers)
25% straw fibers
Linear (50% straw fibers)
50% straw fibers

Fig. 6

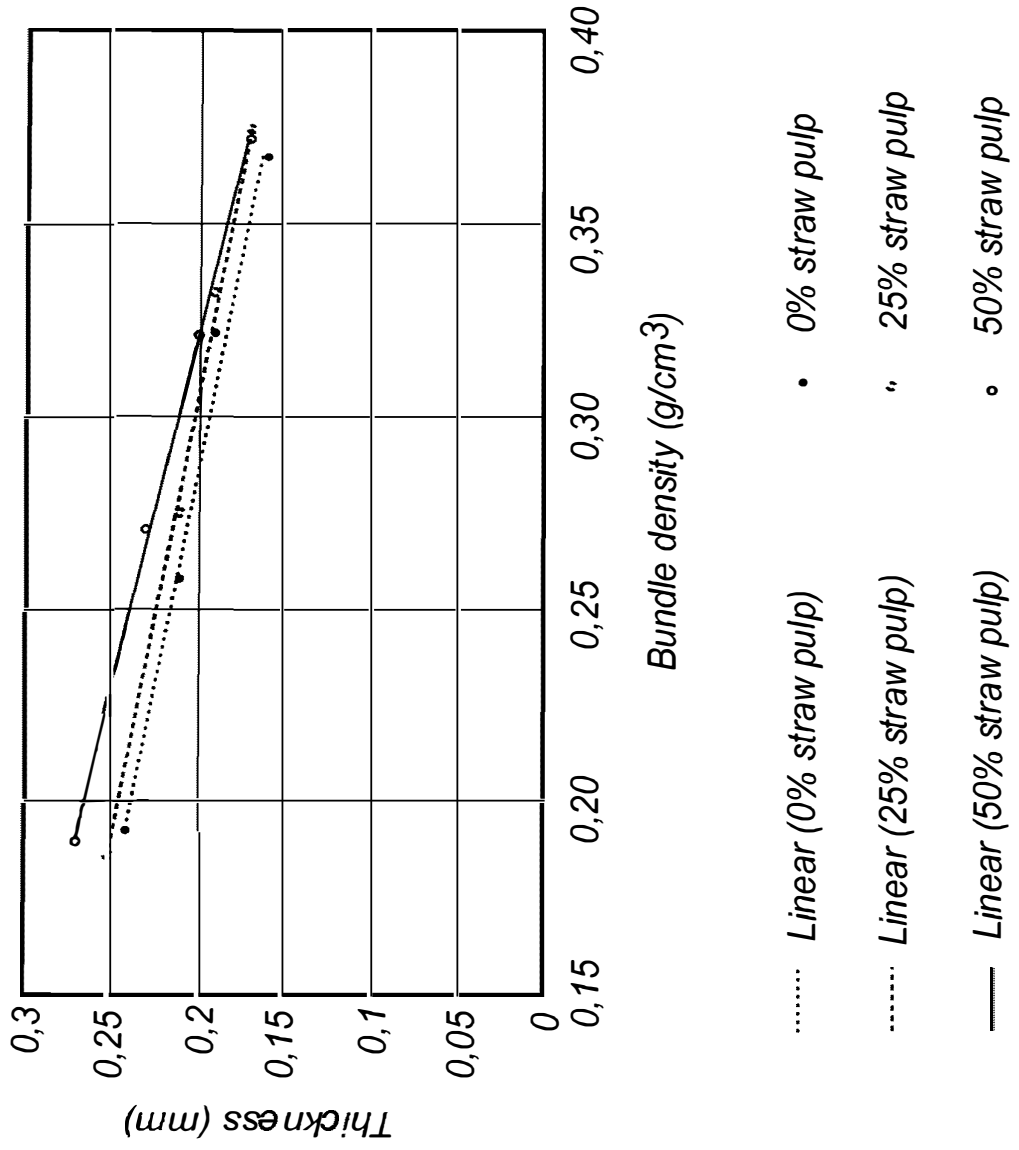

Thickness (mm)
0,3
0,25
0,2
0,15
0,1
0,05
0
0,15
0,20
0,25
0,30
0,35
0,40
Bundle density (g/cm3)
Linear (0% straw pulp)
0% straw pulp
Linear (25% straw pulp)
25% straw pulp
Linear (50% straw pulp)
50% straw pulp

Fig. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2021/050714

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: A47K, B65B, D04H, 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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 20150176220 A1 (OSTENDORF WARD WILLIAM ET AL), 25 June 2015 (2015-06-25); paragraphs [0066]-[0072], [0181]-[0190]; claims 1-3,13-17	1-48
	--	
Y	WO 2012087211 A1 (SCA HYGIENE PROD AB ET AL), 28 June 2012 (2012-06-28); claims 1-2	1-48
	--	
Y	US 20180354667 A1 (WALLENIUS HANS ET AL), 13 December 2018 (2018-12-13); paragraphs [0012]-[0021]; claims 1-5	1-48
	--	

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22-03-2022	22-03-2022

Name and mailing address of the ISA/SE	Authorized officer
Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Ingemar Wistrand Telephone No. + 46 8 782 28 00

Form PCT/ISA/210 (second sheet) (July 2019)

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 20180127920 A1 (MAULER DIRK ET AL), 10 May 2018 (2018-05-10); paragraphs [0030]-[0042]; claims 1-8,12-14	1-48
	--	
A	WO 2018156109 A1 (KIMBERLY CLARK CO), 30 August 2018 (2018-08-30); claim 1	1-48
	--	
A	WO 2013181302 A1 (PROCTER & GAMBLE), 5 December 2013 (2013-12-05); page 14, line 6 - line 11; claims 1,10	1-48
	--	
A	KR 102193309 B1 (HEALTHYTISSUE CO LTD), 22 December 2020 (2020-12-22); whole document; WPI abstract; machine translation	1-48
	--	

International application No.
PCT/SE2021/050714

Continuation of: second sheet

International Patent Classification (IPC)

B65B 25/14 (2006.01)
A47K 10/16 (2006.01)
B65B 63/02 (2006.01)
D04H 1/425 (2012.01)
D21H 11/12 (2006.01)
D21H 27/00 (2006.01)

US	20150176220	A1	25/06/2015	CA	2932638	C	08/06/2021
				DE	112014005955	T5	22/09/2016
				FR	3015213	A1	26/06/2015
				GB	2535413	A	17/08/2016
				MX	2016008139	A	16/09/2016
				US	20160237625	A1	18/08/2016
				US	11015297	B2	25/05/2021
				US	20200362517	A1	19/11/2020
				US	10697126	B2	30/06/2020
				US	10697125	B2	30/06/2020
				US	10697124	B2	30/06/2020
				US	10351997	B2	16/07/2019
				US	20190203422	A1	04/07/2019
				US	20190194874	A1	27/06/2019
				US	20190194873	A1	27/06/2019
				US	9909261	B2	06/03/2018
				US	20180051419	A1	22/02/2018
				US	20170226697	A1	10/08/2017
				US	9670620	B2	06/06/2017
				US	9322136	B2	26/04/2016
				WO	2015095431	A1	25/06/2015
WO	2012087211	A1	28/06/2012	AU	2010365875	A1	05/06/2014
				BR	112013015838	B8	24/09/2019
				CA	2821479	A1	28/06/2012
				CN	103281943	B	08/02/2017
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				ES	2751333	T3	31/03/2020
				HU	E045888	T2	28/01/2020
				MX	2013007028	A	13/09/2013
				MX	348139	B	30/05/2017
				RU	2013134138	A	27/01/2015
				UA	108528	C2	12/05/2015
				US	20130269893	A1	17/10/2013
				US	9556561	B2	31/01/2017

US	20180354667	A1	13/12/2018	AU	2015399433	B2	07/02/2019
				BR	112017020572	A2	03/07/2018
				CA	2981249	C	31/12/2019
				CN	107614385	B	11/10/2019
				CO	2017012291	A2	20/02/2018
				DK	3310671	T3	27/01/2020
				ES	2765495	T3	09/06/2020
				HK	1245739	A1	31/08/2018
				MX	2017015023	A	13/04/2018
				RU	2670170	C1	18/10/2018
				WO	2016209124	A1	29/12/2016
				ZA	201707067	B	28/08/2019
US	20180127920	A1	10/05/2018	AU	2015393147	A1	09/11/2017
				CN	107532385	A	02/01/2018
				CO	2017010865	A2	16/01/2018
				EC	SP17078850	A	28/02/2018
				EP	3289139	A1	07/03/2018
				HK	1246833	A1	14/09/2018
				MA	41084	A1	30/11/2018
				MX	2017013851	A	21/03/2018
				RU	2670867	C9	11/12/2018
				SG	11201708100	A	29/11/2017
				TN	2017000446	A1	12/04/2019
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				WO	2016173641	A1	03/11/2016
WO	2018156109	A1	30/08/2018	AU	2017400674	A1	05/09/2019
				BR	112019014276	A2	03/03/2020
				GB	2574744	A	18/12/2019
				KR	20190116335	A	14/10/2019
				MX	2019008742	A	02/10/2019
				US	20210292973	A1	23/09/2021
				US	11053643	B2	06/07/2021
				US	20200232166	A1	23/07/2020
WO	2013181302	A1	05/12/2013	CA	2875222	A1	05/12/2013
				DE	112013002760	T5	13/08/2015
				FR	2991345	A1	06/12/2013
				GB	2516403	B	20/04/2016
				MX	2014014392	A	05/02/2015
				MX	347274	B	20/04/2017
				US	9011641	B2	21/04/2015
				US	20130319625	A1	05/12/2013
KR	102193309	B1	22/12/2020	NONE			

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PGR2026-00078

(19) BUNDESREPUBLIK DEUTSCHLAND

DEUTSCHES PATENTAMT

(12) Gebrauchsmuster U1

(11) Rollennummer G 93 00 201.7

(51) Hauptklasse B31D 1/04

Nebenklasse(n) D21H 11/12

(22) Anmeldetag 09.01.93

(47) Eintragungstag 05.05.94

(43) Bekanntmachung im Patentblatt 16.06.94

(54) Bezeichnung des Gegenstandes
Serviette aus Manilafaser-Papier

(73) Name und Wohnsitz des Inhabers
Papierwerke Halstrick KGaA, 56316 Raubach, DE

(74) Name und Wohnsitz des Vertreters
Maxton, A., Dipl.-Ing.; Langmaack, J.,
Dipl.-Ing., Pat.-Anwälte, 50968 Köln

09.01.93

Bezeichnung: Serviette aus Manilafaser-Papier

Beschreibung:

Die Erfindung bezieht sich auf eine Papierserviette aus Faserstoff. Es ist bekannt, Papierservietten aus Hygienepapier herzustellen. Dabei handelt es sich insbesondere um Tissue, ein feines Papier, das nur wenig gekreppt wird. Dieses bekannte Papier ist so dünn, daß es sich zur Verwendung in einer Lage weniger eignet. Deshalb wird je nach Anforderung die Zahl der Lagen vervielfacht.

Zur Gewinnung eines hellen bekannten Papiers wird im Verlauf der Zellstoffherstellung im Anschluß an die Kochung gebleicht. Dabei hat sich in den vergangenen Jahren im Bereich der Bleiche ein technologischer Wandel vollzogen, nämlich von den traditionell chlorhaltigen zu umweltfreundlichen Bleichmitteln mit dem Ziel der Minimierung oder gar Vermeidung von Umweltbelastungen durch Bleichereiabwässer. Gleichwohl bleibt eine aufhellende Bleiche eine notwendige Bearbeitung, wenn ein helles Papier geschaffen werden soll.

Der Erfindung liegt die Aufgabe zugrunde, eine Serviette aus hellem Papier zu schaffen, das nicht gebleicht werden muß. Außerdem soll ein Rohstoff zur Herstellung der Serviette

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eingesetzt werden, der besonders umweltfreundlich ist. Der Rohstoff soll sich auch zur Herstellung einer einlagigen Serviette eignen.

Diese Aufgabe wird gemäß der Erfindung dadurch gelöst, daß die Papierserviette aus einem Papier hergestellt ist, welches aus dem Faserstoff einer Einjahrespflanze gewonnen worden ist. Als Einjahrespflanzen werden Pflanzenarten bezeichnet, die jährlich geerntet und nach ihrem chemischen Aufschluß als Faserstoffe der Papierherstellung dienen. Hierunter fallen insbesondere Stroh, Bambus und Bagasse. Die Umweltfreundlichkeit der Herstellung des Faserstoffes aus Einjahrespflanzen liegt darin, daß dabei ein jährlich nachwachsender Rohstoff verarbeitet wird.

In bevorzugter Ausgestaltung der Erfindung besteht der Faserstoff aus Hanf-Fasern, insbesondere aus Manilafasern. Manilafasern, die auch Abacafasern genannt werden, können aus den Fasersträngen der Blattscheiden von Faserbananen gewonnen werden. Diese Fasern sind von Natur aus hell und müssen nicht gebleicht werden. Es handelt sich um sehr lange und feste Fasern, so daß es möglich ist, hieraus gemäß der Erfindung auch eine einlagige Papierserviette herzustellen.

Dabei kann in weiterer Ausgestaltung der Erfindung die flächenbezogene Masse des Papiers kleiner als 10 g/m² sein. Eine solche Serviette ist dann aus einem ausgesprochen feinen und dünnen Papier hergestellt. Die Feinheit des Materials verleiht dem Papier einen eigentümlichen, textilähnlichen Charakter. Wenn auch gemäß einer bevorzugten Ausgestaltung der Erfindung der Faserstoff ungebleicht ist, besteht dennoch die Möglichkeit, gefärbte Papierservietten aus dem Faserstoff herzustellen.

Die Umweltfreundlichkeit des verarbeiteten Papiers besteht nicht zuletzt darin, daß ein natürlicher Rohstoff verarbeitet worden ist, der nicht gebleicht werden muß. Das Papier

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ist kompostierbar und verrottet innerhalb von zwei Wochen. Andererseits kann das Papier auch als Recyclingpapier verwertet werden.

Zwei Ausführungsbeispiele der Erfindung sind in der Zeichnung dargestellt. Es zeigen

Fig. 1 eine Serviette in der Draufsicht und

Fig. 2 eine weitere Serviette in der Draufsicht mit gegenüber derjenigen gemäß Fig. 1 unterschiedlicher Kontur.

Bei beiden Servietten handelt es sich um im wesentlichen runde, einlagige Papierservietten. Diese sind aus dem Papier gemäß der Erfindung hergestellt worden. Selbstverständlich können die Servietten in jeder beliebigen Form gestanzt sein. Insbesondere ist die Gestaltung der Ränder der Servietten in unterschiedlichster Weise möglich.

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Ansprüche:

1. Papierserviette aus Faserstoff, **gekennzeichnet** durch ein Papier aus dem Faserstoff einer Einjahrespflanze.

2. Papierserviette nach Anspruch 1, dadurch gekennzeichnet, daß der Faserstoff aus Hanf-Fasern besteht.

3. Papierserviette nach Anspruch 2, dadurch gekennzeichnet, daß der Faserstoff aus Manilafasern besteht.

4. Papierserviette nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die flächenbezogene Masse des Papiers kleiner als 10 g/m² ist.

5. Papierserviette nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß der Faserstoff ungebleicht ist.

6. Papierserviette nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß sie einlagig ist.

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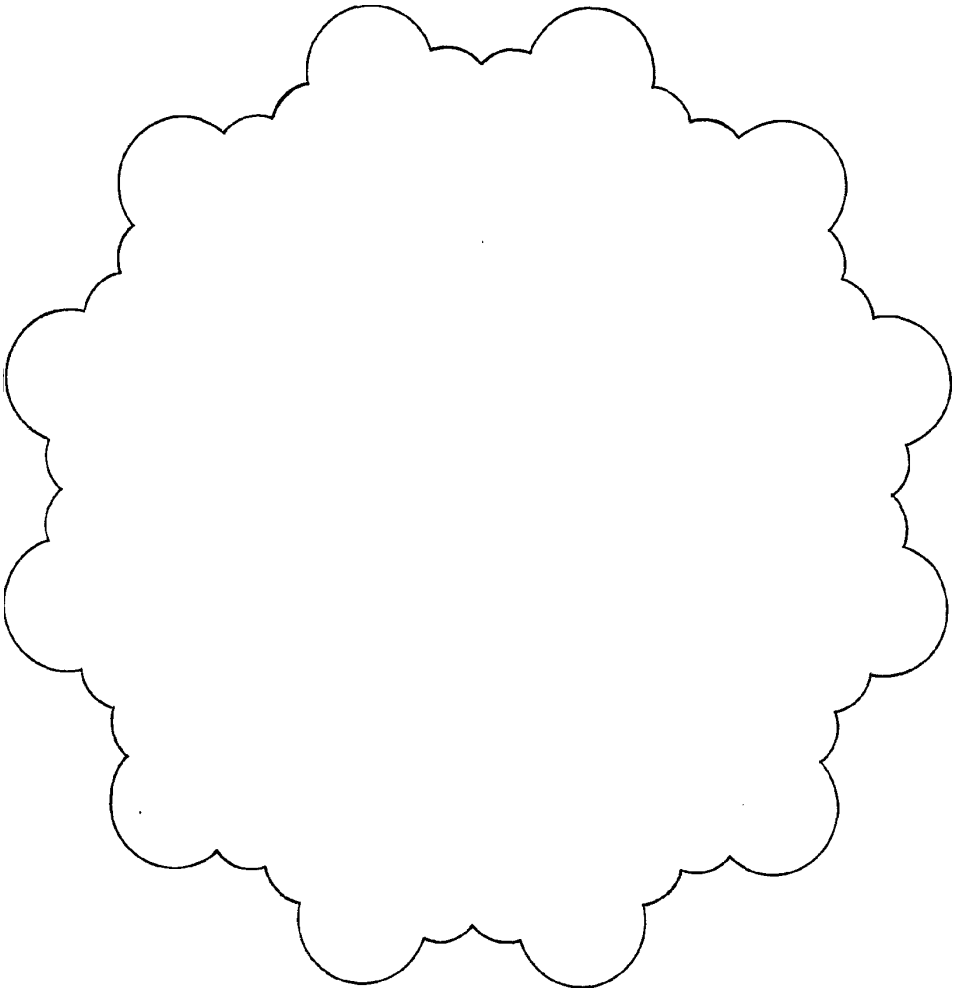


FIG.1

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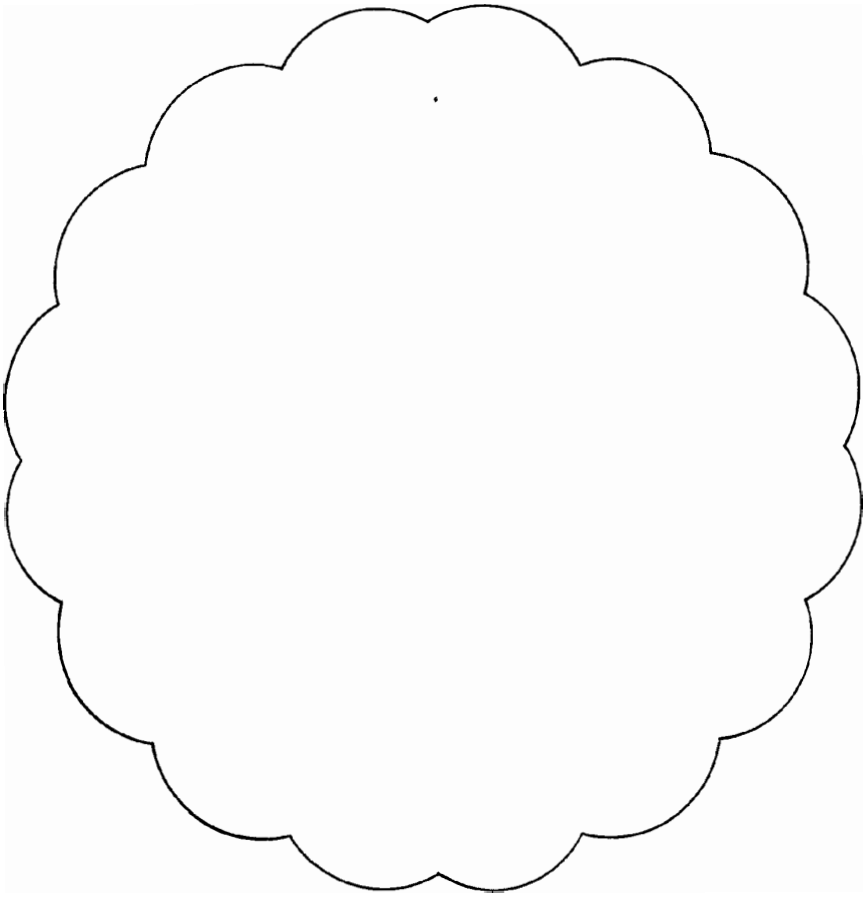


FIG.2

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DESCRIPTION DE8300201U1

[0001]

Name: Napkin made from Manila fiber paper

[0002]

Description:

[0003]

The invention relates to a paper napkin made of fiber material.

It is known to make paper napkins from sanitary paper.

This is particularly tissue, a fine paper that is only lightly creped. This known paper is so thin that it is less suitable for use in one layer. Therefore, depending on the requirements, the number of layers is multiplied.

[0004]

To obtain a bright, well-known paper, bleaching is carried out in the course of pulp production following cooking.

In recent years there has been a technological change in the area of bleaching, namely from traditionally chlorine-containing bleaching agents to environmentally friendly bleaching agents with the aim of minimizing or even avoiding environmental pollution caused by bleaching wastewater. Nevertheless, brightening bleach remains a necessary treatment if a light paper is to be created.

[0005]

The invention is based on the object of creating a napkin made of light-colored paper that does not have to be bleached.

There should also be a raw material for making the napkin

[0006]

be used, which is particularly environmentally friendly.

[0007]

The raw material is also said to be suitable for producing a single-layer napkin.

[0008]

This object is achieved according to the invention in that the paper napkin is made from paper which has been obtained from the fiber of an annual plant.

Annual plants are plant species that are harvested annually and, after being chemically digested, are used as fiber for paper production.

This particularly includes straw, bamboo and bagasse.

The environmental friendliness of producing fiber from annual plants lies in the fact that an annually renewable raw material is processed.

[0009]

In a preferred embodiment of the invention, the fiber consists of hemp fibers, in particular Manila fibers.

Manila fibers, also called abaca fibers, can be obtained from the fiber strands of the leaf sheaths of fiber bananas. These fibers are naturally light and do not require bleaching. These are very long and strong fibers, so that it is possible to produce a single-layer paper napkin from them according to the invention.

[0010]

In a further embodiment of the invention, the mass per unit area of the paper can be less than 10 g/m2.

Such a napkin is made from extremely fine and thin paper. The fineness of the material gives the paper a peculiar, textile-like character. Even if, according to a preferred embodiment of the invention, the fiber is unbleached, it is still possible to produce colored paper napkins from the fiber.

[0011]

The environmental friendliness of the processed paper lies not least in the fact that a natural raw material has been processed that does not need to be bleached.

The paper

[0012]

is compostable and rots within two weeks.

On the other hand, the paper can also be used as recycled paper.

[0013]

Two exemplary embodiments of the invention are shown in the drawing.

Show it

[0014]

Fig. 1 a napkin in top view and

[0015]

Fig. 2 shows another napkin in a top view

[0016]

compared to that according to FIG. 1 different contour.

[0017]

Both napkins are essentially round, single-layer paper napkins.

These were made from the paper according to the invention.

Of course, the napkins can be punched in any shape.

In particular, the edges of the napkins can be designed in a variety of ways.

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CLAIMS DE9300201U1

1.

Expectations:

2.

1. Paper napkin made of fiber, characterized by

3.

a paper made from the pulp of an annual plant. 5

4.

2. Paper napkin according to claim 1, characterized in that the fiber consists of hemp fibers.

5.

3. Paper napkin according to claim 2, characterized in that the fiber consists of Manila fibers.

6.

4. Paper napkin according to one of the preceding claims, characterized in that the mass per unit area of the

7.

Paper is smaller than 10 g/m2. 15

8.

5. Paper napkin according to one of the preceding claims, characterized in that the fiber is unbleached.

9.

6. Paper napkin according to one of the preceding claims, characterized in that it is single-layered.

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(12) (19) (CA) **Demande-Application**

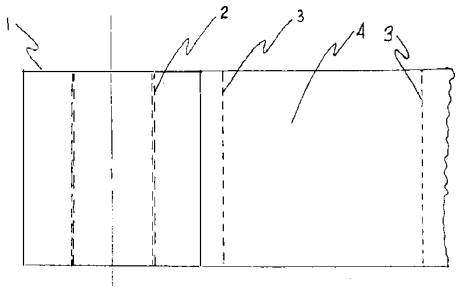
(21) (A1) **2,168,894**
(22) 1996/02/06
(43) 1997/08/07

(72) Fisher, Thomas Edward, CA

(51) Int.Cl.[6] D21H 27/00

(54) **PAPIER EN TISSU DE CHANVRE**

(54) **HEMP TISSUE PAPER**



(57) Le papier hygiénique est un produit très utilisé et très connu. L'invention constitue une amélioration tout en étant très différente du produit habituel composé de fibres cellulosiques du bois. L'invention est fabriquée à partir de fibres cellulosiques du chanvre, une ressource facilement renouvelable. Les fibres cellulosiques du chanvre proviennent surtout des plantes cannabis sativa ou cannabis sativa indica, mais elles peuvent aussi provenir de l'abaca ou des plantes de la famille musa textilis (chanvre de Manille), de l'agave sisalana (agave sisal), ou des plantes de la famille des mûriers. Les fibres cellulosiques du chanvre sont traitées jusqu'à l'obtention d'une pâte de fibres particulaires. La pâte est ensuite formée en minces couches de papier de soie dont les courtes fibres de chanvre ont une orientation aléatoire, ce produit étant l'objet de la présente invention. L'invention se présente habituellement, mais pas nécessairement, sous la forme d'une feuille continue de diverses largeurs et longueurs, selon son utilisation, et perforée à intervalles pour en faciliter la distribution La surface de la feuille peut être texturée ou non. L'invention est habituellement, mais pas nécessairement, enroulée autour d'un corps central vide. Le rouleau ainsi obtenu peut être formé d'une feuille à simple épaisseur ou d'une feuille à multiples épaisseurs. L'invention peut prendre d'autres formes, feuille à simple épaisseur ou à multiples épaisseurs, en fonction d'autres types de distributeurs. L'invention est distribuée à l'utilisateur sur un rouleau pour l'aider à éliminer les résidus ou fluides indésirables de son corps, du corps d'une autre personne, ou d'une surface ou d'un article quelconques. L'utilisateur emploie l'invention en prenant la quantité souhaitée de l'invention (du produit), qui se présente sous la forme convenant au distributeur. Une fois qu'il a obtenu la quantité voulue du produit, l'utilisateur lui donne une

(57) In a product commonly used and known as toilet paper and/or toilet tissue this invention is an improvement yet distinctively different from the known product composed from the wood cellulose fibers of trees. This invention is constructed from the easily renewable resource of hemp cellulose fibers. The hemp cellulose fibers are derived mainly from the plants cannabis sativa or cannabis sativa indica; however, also may be derived from the plants Abaca' or Musa Textilis plant family (Manila hemp), Agave Sisalana (Sisal hemp), or the Mulberry plant family. The hemp cellulose fibers are processed to a particulate fiber pulp. The pulp is then formed into a thin sheet tissue paper product, of randomly oriented short hemp fibers, which is the invention. The invention is usually, but not necessarily, in the form of a continuous sheet of various widths and various lengths, depending upon the application, and perforated at intervals to ease dispensing. The sheet product may or may not have an added designed texture to the surface. The invention is usually, but not always, formed into a roll around a hollow central core form of which the roll may be made up of a sheet of single lamination (ply) or a sheet of multiple laminations (plies) of the invention. The invention may be in the form of other shapes, also in a sheet of single lamination (ply) or multiple laminations (plies) of the invention, to facilitate other forms of dispensers. The invention is dispensed from the roll at the user's leisure to assist in one's removal of undesired residue(s) or fluid(s) from any portion of one's anatomy, someone else's anatomy, surface(s), or item(s). A person puts the invention to use by acquiring the desired amount of the invention (product) from whatever form of the product that the product has been shaped into to facilitate the dispenser. Once the desired amount is obtained one can form the

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(43) 1997/08/07

forme quelconque dans sa main. Il frotte ensuite le produit sur la partie de son anatomie ou de l'anatomie d'une autre personne, ou sur la ou les surfaces ou les objets dont il veut éliminer les fluides ou les résidus indésirables ou incommodants. L'utilisateur peut aussi déposer des objets sur le produit étendu à plat ou envelopper des objets du produit pour absorber et/ou enlever les fluides et/ou résidus indésirables.

product into numerous configurations in one's hand. After the user has configured the product as desired he or she rubs the product over the portion of their anatomy, and/or someone else's anatomy, and/or surface(s), and/or item(s) from which he or she wishes to remove the unwanted or uncomfortable fluid(s) and/or residue(s). The dispensed product may also be place out flat with items place on - or wrapped in - to absorb and/or remove fluid(s) and/or residue(s) from the items.

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ABSTRACT

In a product commonly used and known as toilet paper or toilet tissue, this invention is an improvement and yet distinctively different from the known product composed from the wood cellulose fibers of trees. This invention is constructed from the easily renewable resource of hemp cellulose fibers. The hemp cellulose fibers are derived mainly from the plants cannabis, cannabis sativa or cannabis sativa indica, however, also may be derived from the plants Abaca or Musa Textilis plant family (Manila hemp), Agava Sisalana (Sisal hemp) or various other hemp fiber producing plants. The hemp cellulose fibers are processed to a particulate pulp. The pulp is then formed into a thin sheet tissue paper product, of randomly oriented short hemp fibers, which is the invention. The invention is usually, but not necessarily, in the form of a long sheet of various widths and various lengths, depending upon the application, and perforated at intervals to ease dispensing. The sheet product may or may not have an added designed texture to the surface. The inventions is usually, but not always, formed into a roll around a hollow central core form of which the roll may be made of a sheet of single lamina (ply) or a sheet of multiple laminations (plies) of the invention. The invention may be in the form of other shapes, also in a single lamina (ply) or multiple laminations (plies) of the invention, to facilitate other forms of dispensers. The invention is dispensed from the roll at the user's discretion to assist in one's removal of undesired residue(s) or fluid(s) from any portion of one's anatomy, someone else's anatomy, surface(s) or item(s). A person puts the invention to use by acquiring the desired amount of the invention (product) from whatever form of the product that the product has been shaped into to facilitate the dispenser. Once the desired amount is obtained one can form the product into numerous configurations in one's hand. After the user has configured the product as desired he or she rubs the product over the portion of his/her anatomy, or someone else's anatomy, or surface(s), or

item(s) from which he or she wishes to remove the unwanted or uncomfortable fluid(s) or residue(s). The dispensed product may also be placed out flat with item(s) placed on - or wrapped in - to absorb or remove fluid(s) or residue(s) from the item(s).

SPECIFICATION

This invention relates to an article commonly known as toilet tissue paper that is generally used to extract the residue(s) or fluid(s) from
one's anatomy; however, the invention may be used to facilitate one's removal of undesired residue(s) or fluids from surface(s) or item(s) generally found in the household or workplace. The invention may be formed into another shape commonly known as facial tissue paper to be put to uses such as to blow one's nose, wipe makeup off one's face, clean ears as well as many other uses. The use of the article is generally to facilitate one's removal of undesired residue(s) or fluid(s) from portions of one's anatomy or someone else's anatomy. The invention may also be formed into another shape commonly known as absorbent paper towel to facilitate one's removal of undesired residue(s) or fluid(s) from anatomies or surface(s) or item(s) generally in the workplace or household.

It is common in an article of this type to use cellulose fibers derived from the composition of trees. This fiber source presents several unsatisfactory results. These cellulose fibers are difficult to transform from the raw material into the useful particulate fiber pulp furnish from which the commonly used article can be formed. The presently available article that is fashioned from tree cellulose fibers is by requiring inefficient processes to finish the product requiring sophisticated chemical processes to break down the raw material form and extract unwanted substances that are part of the raw material. As well large quantities of energy are required along with the chemical processes into the environment. Moreover, the extraction of the raw material from the global environment for the presently common article produces an unsatisfactory result and requires numerous years to be renewed.

I postulate that these disadvantages and unsatisfactory results may be overcome by replacing the base material with hemp cellulose fibers. The hemp cellulose fibers are derived mainly from the plants cannabis, cannabis sativa, cannabis sativa indica; however, also may be derived from the plants Abaca' or Musa Textilis plant family (manila hemp), Agava Sisalana (Sisal hemp), or various other hemp cellulose fiber producing plants. Such replacement provides a lenient raw material. The process of breaking down the hemp cellulose fibers from the naturally occurring form to the particulate fiber pulp furnish from which to fashion the new article is easier requiring less chemicals, less consumption of energy in the form of petroleum as well as reduction in production mill furnace emissions would improve global integrity by reducing greenhouse gas emissions and saving forest resources that clean and recycle the atmospheric gases and provides the required required life cycle qualities of the plant earth Moreover, the source of the hemp cellulose fibers is more accessible for harvesting and easily renewable within one year for most sources. The detriment to the global environment from which the new source of raw material is extracted is less harmful to animals species than that of the commonly used source for tree cellulose fibers.

The object of the invention is to produce a dry tissue paper of superior characteristics from the wet papermaking technique by employing different fiber utilization. Superior characteristics are achieved in the area of a more environmentally friendly product reducing detriment to the global environment. As well an implied condition of the term toilet tissue paper, facial tissue paper and absorbent paper towel sets out another object of

the invention. This is to achieve the same if not superior qualities in the areas of dry and wet strength, softness to touch (tactile properties), weight and density factors, and most importantly absorbency then that of the presently commonly used article with little or no chemical treatment and less energy consumption, the later being requirements of a more environmentally friendly product.

As indicated there are implied characteristics to be achieved or enhanced due to the natural qualities of hemp cellulose fibers. Wet and dry strength of the new article is naturally improved due to the superior tensile strength of hemp cellulose fibers compared to that of tree cellulose fibers. With the higher strength fiber a lower density product can be produced with the same strength characteristics of the presently commonly used product made from tree cellulose fibers. Hence, the structure of the new product has variations depending on the producer's aim and the end use of the product. One variation is a higher strength article fashioned with the same density characteristics of a tree cellulose fiber article. Another variation is a same strength article as that of a tree cellulose fiber product with a resultant lower density than that of a tree cellulose fiber article and yet others are higher strength and higher density article and lower strength with lower density. These are desired manufacturing variants depending on end use of the article and economical constraints.

Another inherent quality of hemp cellulose fibers is the ability of producing the same if not better softness properties than that of a product from tree cellulose fibers with little or no chemical treatment. All tree cellulose fibers are natural stiff and ruff. In order to acquire the desired qualities of toilet tissue paper, facial tissue paper and absorbent paper towel a vast amount of chemical reaction inhanced with heat energy or mechanical manipulation or a combination of the two are required to break down the naturally occurring formation of the tree cellulose fibers into a suitable fiber furnish to be supplied to the papermaking machinery. The naturally occurring formation of hemp cellulose fibers supplies a more lenient base material than that of the tree cellulose fibers. A naturally soft article can be produced from hemp cellulose fibers with little to no chemical reaction or heat energy. With simple mechanical manipulation alone a suitable hemp cellulose fiber furnish can be supplied to the wet-laid papermaking machinery. Mild treatments to the hemp cellulose fibers with chemicals and heat energy can be used to produce a more luxurious product if desired.

The use of the hemp cellulose fibers also provides the ability to manufacture a nonwoven web material that has the same or improved absorbency/strength ratio due to the naturally higher strength of hemp cellulose fibers. A lower density article can be produced with the same strength and higher absorbency than that of a tree cellulose fiber product. As well a higher strength same absorbency article can be produced or other variants depending on end use characteristics required and economical constraints. These are desirable qualities of absorbent towel.

With the tree cellulose fiber article the production starts with the acquisition of the base material from the greatly distributed and diminishing forest resource base. More and more energy in the form of petroleum is required to access and harvest the forest resource. Large amounts of petroleum are used to build roads and transport the base material to the

production mills specially as the resource diminishes and the allowable harvest areas become further and further from the production mills. As well more energy is required to manipulate the naturally occurring consolidated tree cellulose fiber formation into wood chips to be heat treated or mechanically manipulated or a combination of the two as well as chemically reacted into a fiber furnish for the papermaking machinery.

In comparision much less energy consumption is required to achieve the fiber furnish for the hemp cellulose fiber article. The hemp producing plants can be grown in much higher fiber per acre density than that of trees in a forest. As well a more centrally located fiber supply to production mill arrangement can be established to reduce energy consumption for transportation of base material. Together with easier harvesting due to agriculturally farm base fiber supply and six month to one year fiber source replacement generally reduces the amount of petroleum energy used and a reduction in the greenhouse gas production providing the postulated improvements in decreasing impact on the global environment. As well the consolidated hemp cellulose fiber formation easily breaks down with the use of the retting process to supply fibers for the pulping process. All in all the desired qualities of supply of fiber base material as well as structural and hysical characteristics can be improved with the use of hemp cellulose fibers with a benefit to the environment when compared to the presently used tree cellulose fiber supply.

The papermaking process is that of the wet-laid nonwoven webs. The fiber utilized for the invention consists of hemp cellulose fibers mechanically manipulated - the process may also utilize some chemical or heat treatments or a combination of the two - to achieve the desired fiber pulp furnish to produce the article. The fiber pulp furnish for the article can be 100% cannabis, cannabis sativa, or cannabis sativa indica hemp fibers; however ,other plant hemp cellulose fibers may be utilized at any percentage ratios depending upon supply of fibers. The preferred amount is that of 100% cannabis, cannabis sativa, or cannabis sativa indica fibers. The article with the previously mentioned desirable characteristics is produced with the wet papermaking process usually associated with wet-laid nonwoven webs. In specific the use of water suspended hemp cellulose fiber particulates in a predetermined fiber density aqueous solution, depending on the quality of the article to be produced, being dispensed from a head box onto a continuous fiber collecting wire screen. The fibers collected on the wire form into randomly oriented three dimensional fiber maze that is a continuous nonwoven short fiber thin sheet material. The dispersant water passes through the screen and is easily collected and recycled or treated and discharged. The density of the article can be varied depending on the density of suspended hemp cellulose fibers, flow rates from the head box, and wire screen velocities. This technique is generally known as a Fourdrinier wire machine employment; however, there are other commercial papermaking machines that can be employed to manufacture the article. The sheet material formed as mentioned above can be, but not necessarily, textured during, before, or after the drying process that removes residual retained fiber dispersant. The resulting sheet material is the invented article. This article may be used as is to manufacture the packaged products of toilet tissue paper, facial tissue paper or absorbent paper towel or there may be further processing to form these packaged products from the article with laminated plies of the initial article.

Illustrated in figure 1 and 2 the roll 1 is the most useful form of the invention; however,

not the only form. The roll 1 is made up of a long sheet of the article 4 wound around, as depicted 5, the central hollow core form 2. This form of the article is best utilized by being placed in a dispenser near the source of use so as the article 4 may be used when required. In order to use the article 4 one unravels the article 4 from the roll 1 to an amount of the article 4 that is required, usually to a perforated location 3 on the article 4. A portion of the long sheet article 4 making up the roll 1 is torn off, usually at one of the many perforated locations 3 along the length of the long sheet article, to give a dispensed amount of the article 4. Once the desired amount of the article 4 has been dispensed one can place the article 4 in one's hand in any number of configurations in order to be utilized to remove undesired residue(s) or fluid(s) from one's or anyone's anatomy or item(s) generally found in the workplace or household.

The article 4 may be formed into other shapes to facilitate other types of dispensing; however, the main objective of use remains the same as described in the previous paragraph. Illustrations 3 and 4 depict another common form of the article 4. In figures 3 and 4 the article 4 is formed into a bundle 1 of any number of singular interlocking folded sheets of the article 4. Each sheet of the article 4 is folded at two locations 2. As the preceding sheet of the article 4 is pulled from the dispenser, to provide the dispensed portion of the article 4, the interlocked proceeding sheet of the article 4 is drawn into dispensing location. As well the article 4 may take on the form as illustrated in figure 1 and 2 or figures 3 and 4 so as to be used as an absorbent paper towel to clean residue(s) or fluid(s) from anatomies, windows, counters, vegetables, kitchen or household appliances, floors, tools, cars, or any other type of surface(s) or item(s) generally in the household or the workplace. The dispensed article 4 may also be placed out flat with item (s) placed on - or wrapped in - to absorb or emove fliud(s) or residue(s) from the item(s).

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1)An absorbent soft tissue paper consisting of 100% hemp cellulose fibers.

2)An absorbent soft tissue paper as defined in claim 1 wherein the hemp cellulose fibers are randomly oriented.

3)An absorbent soft tissue paper as defined in claim 1 or claim 2 that is porous, flat (or slightly textured) and thin sheet to be packaged and dispensed in a dry form exhibiting dry, soft, and flexible consistency as well as high absorbent tendency that is less 1 mm thickness.

4)A roll or sheet of absorbent soft tissue paper as defined in claim 1 or claim 2 or claim 3 and hereafter called hemp tissue paper.

5)Hemp tissue paper as defined in claims 1 to 4 in the form of a facial tissue.

6)Hemp tissue paper as defined in claims 1 to 4 in the form of a toilet tissue.

7)Hemp tissue paper as defined in claims 1 to 4 in the form of an absorbent paper towel.

8)Hemp tissue paper as defined in claim 1 to claim 7 wherein the hemp cellulose fibers are derived from one or more of the plant sources cannabis, cannabis sativa, cannabis sativa indica, Agava Sisalana, abaca, musa textilis plant families.

FIGURE 1

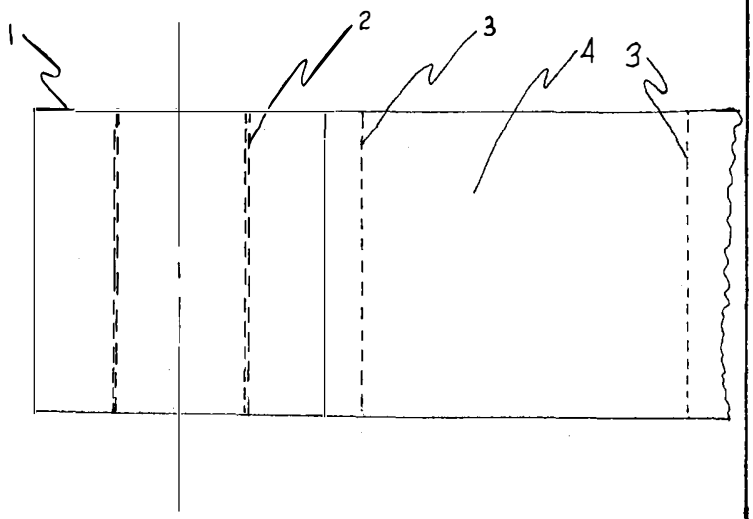


FIGURE 2

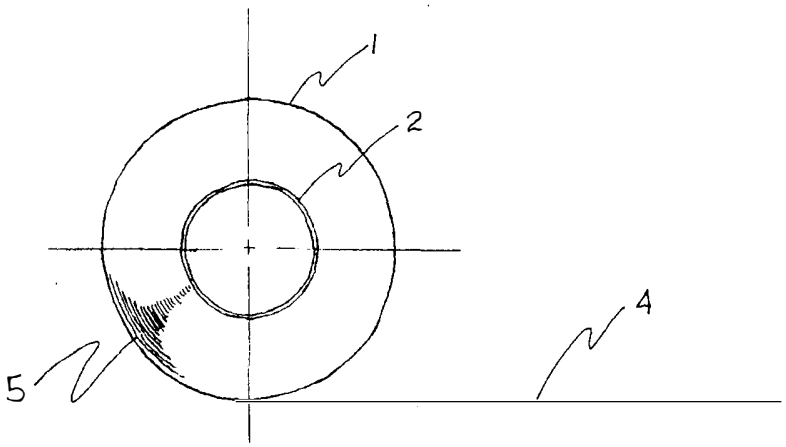


FIGURE 3

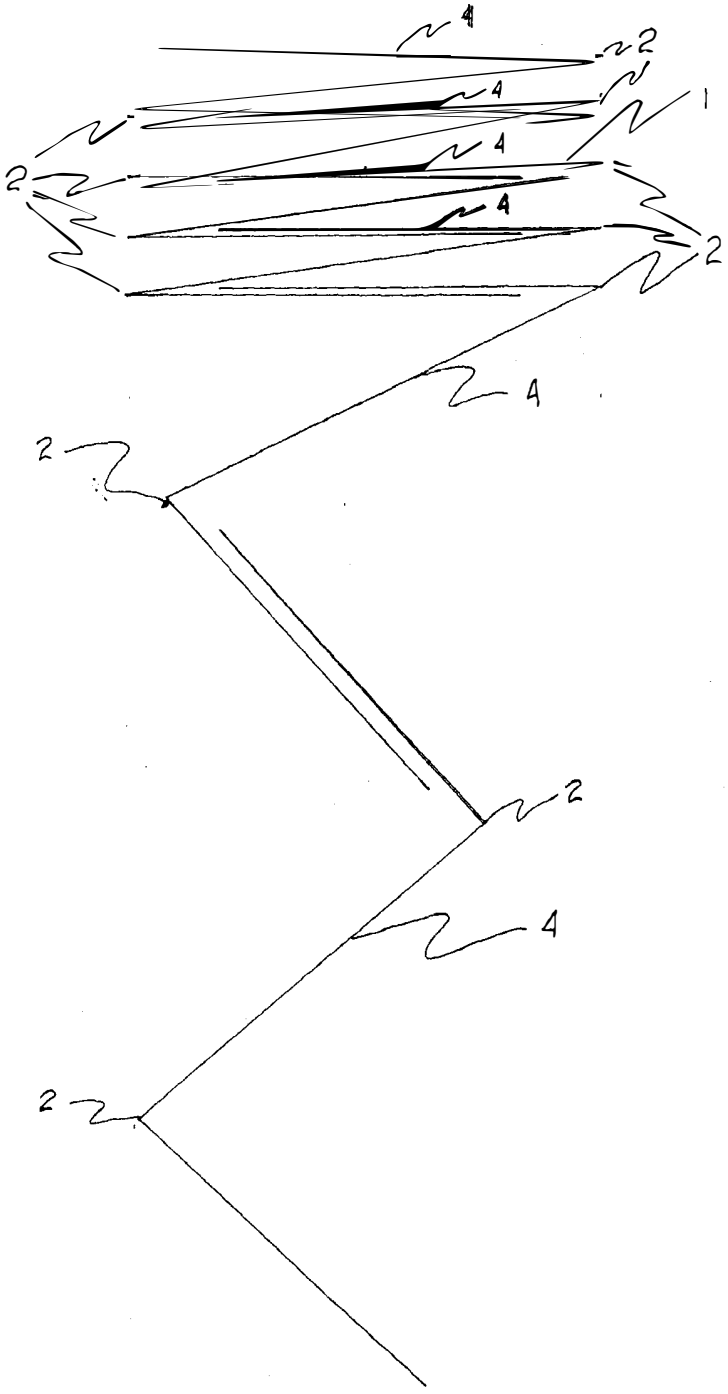
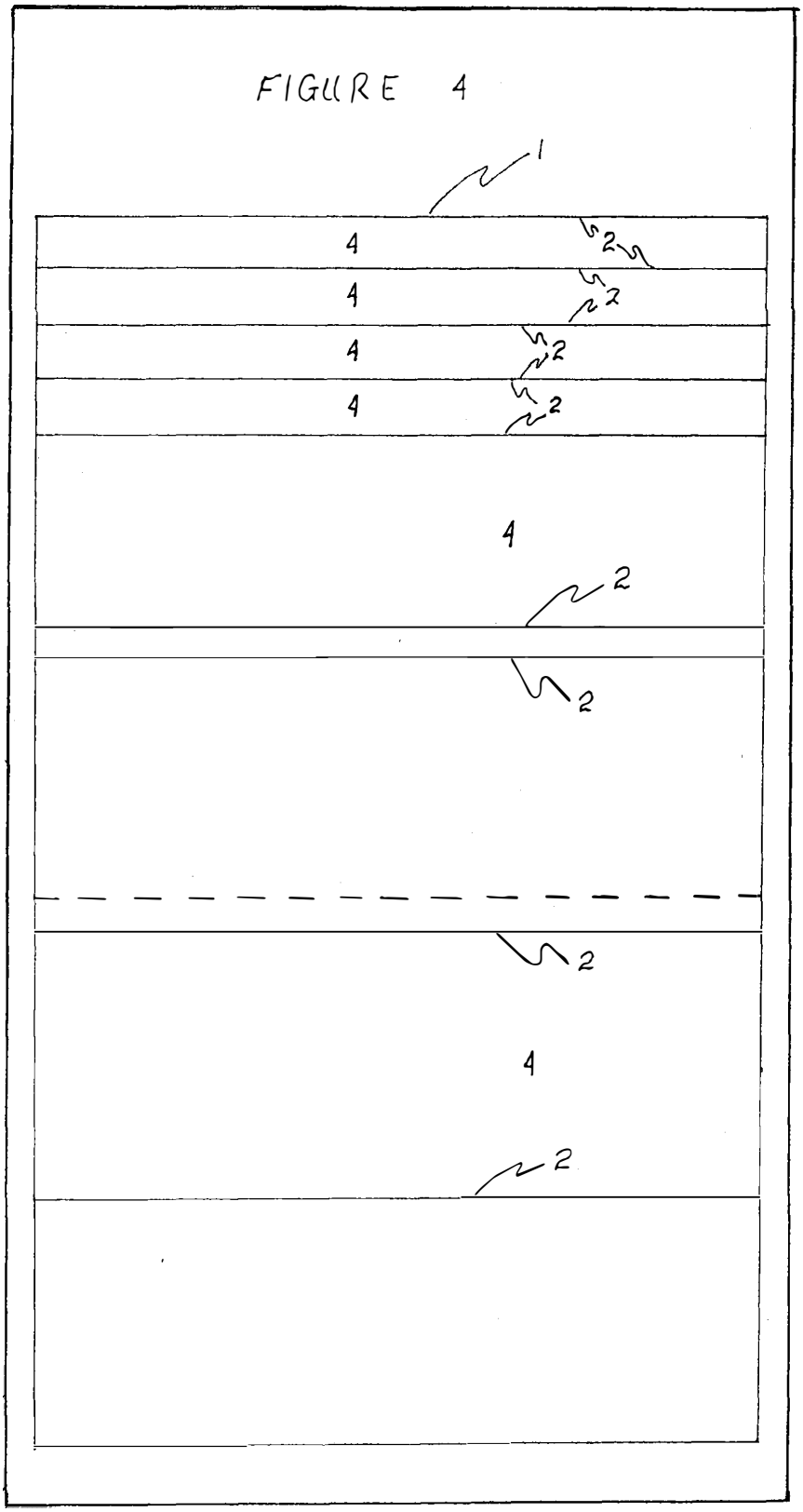


FIGURE 4



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

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(54) Title: LOTIONED TISSUE PAPER HAVING A SHORT WATER ABSORPTION TIME

(57) Abstract: The present invention relates Toilet paper based on tissue paper, said tissue paper being treated with an O/W emulsion comprising at least one non-ionic emulsifier, at least one anionic co-emulsifier, an oil component having a polarity of at least 20 mN/m or a mixture of oil components wherein at least 75 weight-% of the oils constituting the mixture have a polarity of at least 20mN/m, 6 to 35 weight % of water, based on the total weight of the emulsion, wherein the total amount of emulsifiers and co-emulsifiers is between 4 and 20 weight, preferably between 6 and 16 weight-%, based on the total weight of the emulsion. Since in the above lotion composition the external phase is aqueous, a web treated therewith can easily be wet by water and does not float on the water if it is to be disposed in a toilet. Moreover, this lotion shows an improved brightness after application on tissue paper, smell and rheology.

Lotioned tissue paper having a short water absorption time

FIELD OF INVENTION

The invention relates to a soft lotioned tissue paper web, which easily sinks in water due to a specific lotion based on an oil-in-water emulsion.

BACKGROUND ART

Based on the underlying compatibility of the production processes (wet laying), "tissue" production is counted among the paper making techniques. The production of tissue is distinguished from paper production by its extremely low basis weight of normally less than 65 g/m² and its much higher tensile energy absorption index. The tensile energy absorption index is arrived at from the tensile energy absorption in which the tensile energy absorption is related to the test sample volume before inspection (length, width, thickness of sample between the clamps before tensile load). Paper and tissue paper also differ in general with regard to the modulus of elasticity that characterizes the stress-strain properties of these planar products as a material parameter.

A tissue's high tensile energy absorption index results from the outer or inner creping. The former is produced by compression of the paper web adhering to a dry cylinder as a result of the action of a crepe doctor or in the latter instance as a result of a difference in speed between two wires ("fabrics"). In the latter technique, often referred to as "(wet) rush transfer", for instance the forming fabric of the paper machine is moved at greater speed than that of the fabric to which the formed paper web is transferred, for instance a transfer fabric or a TAD fabric (through air drying), so that the paper web is

somewhat bundled when it is taken up by the transfer fabric. Many prior art documents (e.g. EP-A-0 617 164, WO-94/28244, US-5 607 551, EP-A-0 677 612, WO-96/09435) refer to this as "inner creping", when they describe the production of "uncreped" tissue paper by rush transfer techniques. The inner and outer creping causes the still moist, plastically deformable paper web to be internally broken up by compression and shearing, thereby rendering it more stretchable under load than uncreped paper. Most of the functional properties typical of tissue and tissue products result from a high tensile energy absorption index (see DIN EN 12625-4 and DIN EN 12625-5).

Typical properties of tissue paper include the ready ability to absorb tensile stress energy, their drapability, good textile-like flexibility, a high specific volume with a perceptible thickness, as high a liquid absorbency as possible and, depending on the application, a suitable wet and dry strength as well as an interesting visual appearance of the outer product surface.

Softness is an important property of tissue products such as handkerchiefs, cosmetic wipes, toilet paper, serviettes/napkins, not to mention hand or kitchen towels, and it describes a characteristic tactile sensation caused by the tissue product upon contact with the skin.

Although the term "softness" is generally comprehensible, it is extremely difficult to define because there is no physical method of determination and, consequently no recognized industrial standard for the classification of different degrees of softness.

To be able to detect softness at least semi-quantitatively, softness is determined in practice by means of a subjective method. To do so, use is made of a

"panel test" in which several trained test persons give a comparative opinion.

In simplified terms, softness can be subdivided into its main characteristics, surface softness and bulk softness. Surface softness describes the feeling perceived when e.g. one's fingertips move lightly over the surface of the sheet of tissue. Bulk softness is defined as the sensory impression of the resistance to mechanical deformation that is produced by a tissue or tissue product manually deformed by crumpling or folding and/or by compression during the process of deformation.

One method for increasing bulk softness of tissue paper as taught by WO 96/25557 involves

a) wet-laying an aqueous slurry containing cellulosic fibres to form a web
b) applying a water soluble polyhydroxy compound to the wet web, and
c) drying and creping the web (wet web addition method).

It is further known from US 4,764,418 that some humectants such as polyethylene glycol contribute to the softness of tissue products if they are applied to a dry web.

The use of humectants, such as polyhydroxy compounds, in highly concentrated form, as softeners however, has the disadvantage that the humectant may, upon contact, draw too much moisture from the skin, for instance when blowing one's nose with a tissue handkerchief. Moreover the softening effect is not yet satisfactory.

WO 96/24723 teaches increasing the surface softness of tissue paper by applying discrete deposits of a water free lotion composition containing an oil and a wax. Since however, due to its solid consistency, the treatment composition remains

on the surface of the tissue paper, it cannot contribute to bulk softness. Further, water-free lotion compositions based on waxy or oily materials often feel unpleasantly greasy or oily.

Moreover, water-free lotions such as the one in WO 96/24723 often do not feel particularly pleasant to the skin.

EP A 1 029 977 relates to a composition for treating paper products, such as tissue products, comprising between 30 and 90 % by weight of oil, between 1 and 40 % by weight of wax, between 1 and 30 % by weight of an emulsifying agent and between 5 and 35 % by weight of water. These lotion compositions are based on W/O emulsions, are solid or semisolid at 30° C, and remain primarily at the surface of the tissue paper, although they penetrate the tissue paper somewhat more than the solid composition of WO 96/24723.

DE 199 06 081 A1 discloses emulsions containing (a) 5 to 25 % by weight polyol poly-12-hydroxy stearate, (b) 50 to 90 % by weight waxy esters, and (c) 5 to 25 % by weight waxes. This document further contains examples describing the treatment of tissue papers with W/O emulsions as defined above containing about 20 to 25 % water. These compositions are solid or semisolid at 30° C (Example 1 corresponds to lotion F of EP A 1 029 977) and demonstrate the same penetration behaviour as described above for the lotions of EP A 1 029 977.

However, tissue papers treated with water-in-oil (W/O) lotions often float on the water for a longer time and cannot be flushed down, if they are to be disposed in a toilet. This is a serious disadvantage, in particular for lotioned toilet papers which are becoming increasingly popular due to their softness and pleasant feel on the skin of the user.

WO 97/30216 discloses a softening lotion composition for treating tissue. The composition is aqueous and liquid, and includes as active ingredients

(a) one or more saturated straight fatty alcohols having at least 16 C atoms in a preferred amount of 35 to 90 % by weight,
(b) one or more waxy esters having a total of at least 24 C atoms in a preferred amount of 1 to 50 % by weight,
(c) optionally non-ionic and/or amphoteric emulsifiers, preferably oil-in-water emulsifiers, and
(d) optionally 0 to 50 % mineral oil.

The lotion composition comprises 1 to 50 % by weight active ingredients and consequently 50 to 99 % by weight of water. According to the teaching of WO 97/30217, this aqueous composition is combined with a quaternary ammonium compound.

If such high water content lotions are applied to tissue paper, they can strongly affect the strength properties (dry strength or wet strength, if additional water, *e.g.* from body fluids is absorbed by the tissue paper).

WO 02/057547 A2 relates to a lotioned fibrous web, in particular tissue paper web having a short water absorption time. This web is treated with a lotion composition based on an O/W emulsion comprising

A) at least one oil
B) an (O/W) emulsifier or (O/W) emulsifier combination, and
C) 6 to 35 wt.-% of water, based on the total weight of the lotion composition.

The oil component may be selected from glycerides, natural plant oils, dialk(en)yl ethers, dialk(en)yl carbonates, hydrocarbon-based oils, waxy esters and silicon oils. The specific combination of hydrocarbon-based oils, such as mineral oil and fatty ester emollients is not disclosed. On a

concrete level, this international application also pertains to a lotioned tissue paper wherein the lotion comprises as main components 5.3 wt.-% polyglyceryl poly(12-hydroxystearate) (Dehymuls® PGPH), 5.3 wt.-% lauryl glucosid, 3.0 wt.-% glyceryl stearate, 30.0 wt.-% cocoglyceride, 30.0 wt.-% di-N-octylcarbonate, 1.5 wt.-% bisabolol and 4.0 wt.-% glycerol. This lotion is also disclosed as "composition 1" in WO 02/056841.

Although this lotion shows a good stability under usual conditions, stability problems may occur if it is stored for very long times or at higher temperatures. Moreover, it was noted that specifically the incorporation of plant extracts may cause an undesired coloring which lowers the whiteness (brightness) of tissue paper treated therewith. In addition, some customers perceived an undesired smell if this lotion was stored over a longer period of time.

In view of the above, one object of the present invention involves providing a lotion-treated toilet paper that overcomes the disadvantages of prior art formulations.

In a first aspect, the present invention is intended to provide a lotioned toilet paper which can be easily disposed of in a toilet, since it does not float on the water for long.

In a further aspect, the present invention seeks to provide a lotioned toilet paper, the strength properties of which are not greatly deteriorated by the application of lotion.

A further technical object of the present invention is to provide a lotioned toilet paper web which feels very pleasant to the skin and is not oily or greasy to the touch.

Moreover, the present invention also aims at providing a lotioned toilet paper web which shows an enhanced degree of whiteness (brightness).

It is one further technical object of the present invention to provide a toilet paper treated with a lotion composition that can be applied at relatively low temperatures.

Finally, it is one further technical object of the present invention to provide a toilet paper treated with a lotion composition wherein said lotion composition shows a suitable, in particular improved balance of critical properties including stability, softness and/or sensory impression, compatibility with plant extracts and application temperature.

Further technical objects may become apparent to a skilled person when studying the following description.

SUMMARY OF THE INVENTION

This technical object is solved by a toilet paper based on tissue paper, said tissue paper being treated with an O/W emulsion comprising

at least one non-ionic emulsifier,
at least one anionic co-emulsifier,
one oil component having a polarity of at least 20 mN/m or a mixture of oil components wherein at least 75 weight-% of the oils constituting the mixture have a polarity of at least 20mN/m,
6 to 35 weight % of water, based on the total weight of the emulsion,
wherein the total amount of emulsifiers and co-emulsifiers is between 4 and 20 weight, preferably

between 6 and 16 weight-%, based on the total weight of the emulsion.

This emulsion gives a lotion-like feel to the user of the toilet paper and is at least partially transferable. Further, if desired, the toilet paper is capable of transferring active agents to the skin of the user. For this reason the terms "emulsion" and "lotion" will be used throughout the present specification as synonyma. Since in the above emulsion/lotion composition the external phase is aqueous, a web treated therewith can be easily wet by water and therefore shows an excellent sinking behaviour in water. The water absorption time (measured according to DIN V ENV 12625-8 of May 2001 "Water absorption time, water absorption capacity - manual and automated test method", identical with the corresponding prestandard explained in WO 02/057547) is preferably is less than 1 min, more preferably less than 30 sec, in particular less than 10 sec.

Moreover, the lotion/emulsion also contributes to the bulk softness of the toilet paper since it preferably migrates into the tissue paper.

FIGURE

Figure 1 shows a rheology profile of the lotion according to the Example wherein the viscosity was determined in relation to the temperature of the measurement.

DETAILED DESCRIPTION OF THE INVENTION

The lotioned toilet paper of the invention is typically obtained by applying the aforementioned lotion composition to a dry tissue web (without lotion). Preferably, the residual water content of the tissue web is no more than 10 % by weight.

Unless stated otherwise, the terms "liquid" and "solid" refer to the physical state at 23°C. Moreover, it should be noted that the use of "comprising" is intended to cover the more limiting expressions "essentially consisting of" and "consisting of".

1. Lotion

By mixing and homogenizing at least one oil (mixture), a non-ionic (O/W) emulsifier or non-ionic (O/W) emulsifier combination, an anionic co-emulsifier and water, a stable oil-in-water (O/W) emulsion is obtained.

The lotion composition can be a semi-solid or a viscous liquid at room temperature (23° C), the latter being preferred.

In the first case, it typically has a viscosity of less than 30,000 mPa•s at 25° C (measured with a Brookfield-RVF viscosimeter, spindle 3, 10 rpm). Then, the lotion composition primarily remains on the surface of the fibrous substrate, contributing to surface softness of the product, and to a lesser extent to bulk softness.

In a preferred embodiment, the lotion has a fairly low viscosity in comparison to known semi-solid lotion compositions for tissues. This low viscosity contributes to an excellent penetration behaviour and prevents it from remaining on the surface of a single or multi-ply tissue product. In the case of single-ply tissues, it fully penetrates and softens the ply. In the case of multi-ply tissue products, the lotion composition reaches the inner plies, thereby greatly enhancing bulk softness. Such a low viscosity lotion preferably has a viscosity of 100 to 10,000 mPa•s, preferably 500 to 3,000 mPa•s at 25° C (measured with a Brookfield-RVF viscosimeter, spindle 3, 10 rpm)

If measured by a rheometer, the lotion used in the present invention shows a viscosity [mPa•s] of less than 1, preferably less than 0.8, in particular less than 0.5 (e.g. 0.01 to 0.3) in the temperature range of 20 to 60°C (shear rate D=50 1/sec, CR mode (rotation), constant heating from 20 to 60°C over 450 sec, number of measuring points 200), as shown in Figur 1. The measurement was conducted with a Haake RheoStress RS1 rheometer (now available from Thermo Electron) under the following additional conditions regarding measurement geometry: sensor C35/2° Ti, A-factor of 89090.000 Pa/Nm, M-factor of 28.650 (1/s)/(rad/s), moment of inertia: 1.769e-06 kg m^2, attenuation of 30.00 and slit width 0.105 mm. The tempering device used was TCP/P (Peltier/Plate).

The viscosity of the lotion can be adjusted, as known in the art, by the use of higher or lower amounts of solid components, in particular the consistency regulators mentioned below. Further the homogenization of the lotion (energy influx) may have an impact on the final viscosity. The melting range of the optionally present solid components, as measured according to DSC analysis of the final lotion composition, preferably lies within the temperature range of 25° to 70° C, in particular 30° to 60° C.

This lotion/emulsion does not require the presence of silicone containing compounds, e.g. silicone oils or quaternary amine compounds in order to attain its softening effect, although their use is not excluded.

According to one embodiment the lotion/emulsion has the following composition

(a) at least one non-ionic emulsifier having an HLB value of less than 10, preferably $\leq$ 8, more preferably $\leq$ 5, e.g. 2 to 5,

(b) at least one further non-ionic emulsifier having an HLB value of more than 10, preferably $\geq$ 12, preferably from 12 to 20 (e.g. 15 to 18),
(c) at least one anionic co-emulsifier,
(d) one oil component having a polarity of at least 20 mN/m or a mixture of oil components wherein at least 75 weight-% of the oils constituting the mixture have a polarity of at least 20mN/m,
(e) 6 to 35 weight % of water, based on the total weight of the emulsion,
(f) optionally at least one consistency regulator,
(g) optionally at least one humectant, and
(h) optional further additives.

The individual components are explained below in further detail.

1.2. Nonionic O/W emulsifier

The emulsifier or emulsifier composition is of a non-ionic type and primarily has the function of forming an oil-in-water emulsion. It can also contribute to the softness of tissue paper. It can be suitably selected from known non-ionic O/W emulsifiers or combination thereof.

The emulsifier (combination) can be selected from the group of hydrophilic O/W emulsifiers. These hydrophilic emulsifiers may have an HLB value of 10 to 20. Such emulsifiers are known from the prior art and some are, for instance, listed in Kirk-Othmer, *Enclypedia Of Chemical Technology*, third edition, 1979, volume 8, page 913. According to the invention, the HLB value for ethoxylated products may also be calculated according to the formula: HLB $\equiv$ (100-L):5, wherein L is the weight percentage of hydrophilic groups, e.g. fatty alkyl or fatty acyl groups present in the ethoxylated products.

It is also possible to combine less polar and strongly polar emulsifiers such as emulsifiers (a) and (b) explained below:

(a) at least one non-ionic emulsifier having an HLB value of less than 10, preferably $\leq$ 8, more preferably $\leq$ 5, e.g. 2 to 5.

(b) at least one further non-ionic emulsifier having an HLB value of more than 10, preferably $\geq$ 12, preferably from 12 to 20 (e.g. 15 to 18).

The overall content of the (O/W) emulsifier (combination) is preferably 2 to 15 % by weight, for instance 1 to 7.5 weight-% (a) and 1 to 7.5 weight-% (b).

Preferably, a liquid O/W emulsifier is used, although the use of minor amounts of solid emulsifier is possible depending on the desired viscosity of the resulting lotion composition.

Component (a) preferably represents a liquid polyol polyester wherein a polyol having at least two hydroxy groups is esterified with at least one carboxylic acid having from 6 to 30 carbon atoms (in particular 16 to 22 C atoms) and having at least one hydroxy group or condensation products of this hydroxy fatty acid. Polyols include monosaccharides, disaccharides, and trisaccharides, sugar alcohols, other sugar derivatives, glycerol, and polyglycerols, *e.g.* diglycerol, triglycerol, and higher glycerols. Such polyol preferably has from 3 to 12, in particular 3 to 8 hydroxy groups and 2 to 12 carbon atoms (on average, if it is a mixture as in polyglycerols). The polyol preferably is polyglycerol, in particular that having the specific oligomer distribution described in WO 95/34528 (page 5).

The carboxylic acid used in the polyol polyester preferably is a fatty acid having from 6 to 30 carbon atoms (Hereinafter, unless stated otherwise, the term "fatty acid"

is not limited to the naturally occurring, even-numbered, saturated or unsaturated long-chain carboxylic acids, but also includes their uneven-numbered homologues or branched derivatives thereof). The fatty acid contains at least one hydroxy group. It can be a mixture of hydroxy fatty acids or a condensation product thereof (poly(hydroxy fatty acids)). The preferred carbon range for the above mentioned hydroxy fatty acid is from 16 to 22, in particular 16 to 18. A particularly preferred poly(hydroxy fatty acid) is the condensation product of hydroxy stearic acid, in particular 12-hydroxy stearic acid, optionally in admixture with poly(ricinoleic acid), said condensation product preferably having the properties described in WO 95/34528.

Preferred emulsifiers include the polyol poly(hydroxystearates), preferably polyol poly(12-hydroxystearates) described in WO 95/34528, in particular polyglycerol poly(hydroxystearates) having the characteristics disclosed in this document, *e.g.* polyglycerol-2 dipolyhydroxystearate, being available from Cognis Deutschland GmbH under the tradename Dehymuls® PGPH.

Component (b) is preferably selected from (b-1) to (b-6) and mixtures thereof:

(b-1) ethylenoxide or propylenoxide adducts of fatty alcohols having from 8 to 24 C atoms (in particular 12 to 22 C atoms), (C8-C15 alkyl)-phenol or polyols, containing 2 to 50 mol ethylenoxy and/or 0 to 5 mol propylenoxy units.

(b-2) Mono- or diesters (or mixtures thereof) derived from glycerol, poly-, oligo- or monosaccharides, sugar alcohols or sugar alcohol anhydrides (such as sorbitan), and linear or branched, saturated or unsaturated fatty acids having preferably 6 to 22 carbon atoms. These esters may also be ethoxylated

(→ EO units), *e.g.* polysorbate monolaurate + 20 EO or polysorbate mono-oleate + 20 EO. If the ester is to be liquid, the fatty acid can often be selected from short chain saturated fatty acid, *e.g.* as in sorbitan monolaurate or from fatty acids having at least one unsaturated fatty acid, as in sobitan sesquioleate. More preferably, component (b-2) represent $C_{12/18}$ fatty acid monoesters and diesters of addition products of 1 to 50 mol ethylene oxide onto glycerol;

(b-3) C12 to 18 fatty acid monoesters and diesters of addition products of 1 to 50 mol ethylene oxide onto glycerol.

(b-4) An alkyl mono-, oligo- and/or polyglycoside, preferably an alkyl mono- or oligo glycoside having 6 to 22 carbon atoms in the alkyl group and alkoxylated, preferably ethoxylated derivates thereof.

An alkyl(mono or oligo)glycoside is a nonionic surfactant wherein at least one hydroxy group (typically the C1 hydroxy of the first glycosyl) of a (mono or oligo)glycoside is linked via at least one ether bond (or ethyleneoxi and/or propyleneoxi units) with an alkyl group-bearing unit (preferably 6 to 28 C atoms in total). The alkyl(mono or oligo) glycoside preferably has the following generic structure (II):

$$R^2O(C_nH_{2n}O)_t\ (\text{glycosyl})_x\ \ (II)$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl group contains from 6 to 22 carbon atoms, in particular

from 8 to 16 carbon (*e.g.* 10 to 14 carbon atoms); n is 2 or 3, preferably 2, t is from 0 to about 10, preferably 0; x is at least 1, preferably from 1.1 to 5, more preferably 1.1 to 1.6, in particular 1.1 to 1.4, and "glycosyl" is a monosaccharide. The x value is to be understood as the average content of monosaccharide units (oligomerization degree).

The production of alkyl(oligo)glycoside useful in the present invention is known from the prior art and described, for instance in US-4,011,389, US-3,598,865, US-3,721,633, US- 3,772,269, US-3,640,998, US-3,839,318, or US-4,223,129.

To prepare these compounds, the alcohol or alkyl-polyethoxy alcohol is typically first formed and then reacted with the (oligo)glycosyl unit to form the (oligo)glycoside (attachment at the 1-position). The glycosyl units can be attached between the C1 position of further glycosyl(s) and the alkyl-group-bearing glycosyl unit's 2-, 3-, 4- and/or 6-position, preferably 6-position.

Preferred starting alcohols R^2OH are primary linear alcohols or primary alcohols having a 2-methyl branch. Preferred alkyl residues R^2 are for instance 1-octyl, 1-decyl, 1-lauryl, 1-myristyl, 1-cetyl, and 1-stearyl, the use of 1-octyl, 1-decyl, 1-lauryl, and 1-myristyl being particularly preferred.

Alkyl(oligo)glycosides useful in the invention may contain only one specific alkyl residue. Usually, the starting alcohols are produced from natural fats, oils or mineral oils. In this case, the starting alcohols represent mixtures of various alkyl residues.

In four specific (preferred) embodiments alkyl(oligo)-glycosides are used, wherein R^2 consists essentially of C8 and C10 alkyl groups, C12 and C14 alkyl groups, C8 to C16 alkyl groups, or C12 to C16 alkyl groups.

It is possible to use as sugar residue "(glycosyl)x" any mono- or oligosaccharide. Usually, sugars having 5 or 6 carbon atoms as well as the corresponding oligosaccharides are used. Such sugars include, for instance glucose, fructose, galactose, arabinose, ribose, xylose, lyxose, allose, altrose, mannose, gulose, idose, talose and sucrose. It is preferred to use glucose, fructose, galactose, arabinose, sucrose as well as their oligosaccharides, (oligo)glucose being particularly preferred.

In a preferred embodiment "laurylglucoside", a C12-C16 fatty alcohol-glucoside (x = 1.4), which can be obtained from Cognis Deutschland GmbH under the tradename Plantacare®, is used.

(b-5) partial esters based on linear, branched, unsaturated or saturated C_{6-22} fatty acids, ricinoleic acid and 12-hydroystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols, alkyl glucosides and polyglucosides; or

(b-6) polxsiloxane/polyalkyl/polyether copolymers and corresponding derivatives;
and mixtures thereof.

Of particular advantage from the group of O/W emulsifiers are, for example, Ceteareth-12, Ceteareth-20, PEG-30 Stearate, PEG-20 Glyceryl Stearate, PEG-40 Hydrogenated Castor Oil and Polysorbate 20.

Preferably, the weight ratio of non-ionic emulsifier (a) to further non-ionic emulsifier (b) is in the range of 1:0,5 to 1:2, preferably in the range of 1:0,7 to 1:1,5, most preferably in the range of 1:0,8 to 1:1,2.

Possible non-ionic emulsifiers are the following:

(1) products of the addition of 2 to 50 mol ethylene oxide and/or 0 to 20 mol propylene oxide onto linear fatty alcohols containing 8 to 40 carbon atoms, onto fatty acids containing 12 to 40 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group;

(2) $C_{12/18}$ fatty acid monoesters and diesters of addition products of 1 to 50 mol ethylene oxide onto glycerol;

(3) glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide addition products thereof;

(4) alkyl mono- and oligoglycosides containing 8 to 22 carbon atoms in the alkyl group and ethoxylated analogs thereof;

(5) addition products of 7 to 60 mol ethylene oxide onto castor oil and/or hydrogenated castor oil;

(6) other polyol esters and, in particular, polyglycerol esters other than polyol poly-12-hydroxystearates such as, for example, polyglycerol polyricinoleate or polyglycerol dimerate;

(7) addition products of 2 to 60 mol ethylene oxide onto castor oil and/or hydrogenated castor, oil;

(8) partial esters based on linear, branched, unsaturated or saturated C_{6-22} fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, - dipentaerythritol, sugar alcohols (for example sorbitol), alkyl and/or alkenyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example cellulose);

(9) wool wax alcohols;

(10) polysiloxane/polyalkyl/polyether copolymers and corresponding derivatives;

(11) mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol and/or mixed esters of fatty acids containing 6 to 22 carbon atoms, methyl glucose and polyols, preferably glycerol or polyglycerol, and

(12) polyalkylene glycols.

1.2. Anionic co-emulsifier

The emulsion/lotion used in the present invention also contains an anionic co-emulsifier as essential component. This anionic co-emulsifier (c) is preferably present in an amount of 0.01 to 10 wt.-%, more preferably 0.05 to 5 wt.-%, in particular 0.03 to 1.4 wt.-%, based on the total weight of the emulsion.

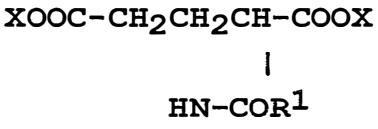
The anionic co-emulsifiers to be used in the O/W emulsion of the present invention are characterized by a water-solubilizing anionic group, such as for example a phosphate, sulphate, carboxylate or sulfonate group, and a lipophilic residue. Even though this is not always

mentioned in the following, the anionic co-emulsifier must also comprise for reasons charge neutrality a positive counter ion which is preferably selected from hydrogen, ammonium and alkali metals such as sodium or potassium. Accordingly, the anionic co-emulsifier is employed in salt form.

Dermatologically compatible anionic emulsifiers are known to the expert in large numbers from relevant manuals and are commercially available. More particularly, they are alkyl sulfates in the form of their alkali metal, ammonium or alkanolammonium salts, alkyl ether sulfates, alkyl ether carboxylates, acyl isethionates, acyl sarcosinates, acyl taurines with linear C_{12-18} alkyl or acyl groups and sulfosuccinates and acyl glutamates in the form of their alkali metal or ammonium salts. In a preferred embodiment of the invention the alkali metal salts of fatty acids, alkyl sulphate and alkyl phosphates are used with an alkyl moiety of C 12 to C 22. Among the anionic surfactants, alkali metal salts of fatty acids (such as e.g. sodium stearate, alkali metal salts of palmitic acid or behenic acid) and, in particular, alkyl sulfates (Lanette® E) and alkyl phosphates (Amphisol® K) are particularly suitable according to the invention because they lead to particularly stable and homogeneous emulsions. The term "fatty acid", as used in this context, is not restricted to the naturally occurring even numbered saturated and unsaturated long chain carboxylic acids. It also comprises uneven numbered homologues, as well as blanched or substituted derivates thereof. It is preferred to use saturated linear fatty acids such as lauric acid, myristic acid, palmitic acid or stearic acid. The amino acid can be any naturally occurring amino acid or synthetic analoge thereof including for instance alanine, valine, leucine, isoleucine, glycerine, serine, treonine. The amino acid is preferably selected from dicarboylic acids having from 3

to 8 carbon atoms and one amino function such as glutamic acid or asparginic acid (Asp).

Acyl glutamates are known anionic emulsifiers, e.g. corresponding to the following formula



in which R^1CO is a linear or branched acyl radical containing 6 to 22 carbon atoms and 0 and/or 1, 2 or 3 double bonds and X is hydrogen, an alkali metal and/or alkaline earth metal, ammonium, alkylammonium, alkanolammonium (e.g. triethanolammonium) or glucammonium. They are produced, for example, by Schotten-Baumann acylation of glutamic acid with fatty acids, fatty acid esters or chlorides. Corresponding commercial products are available, for example, from Hoechst AG, Frankfurt, Germany or from the Ajinomoto Co. Inc.,Tokyo, Japan. An overview of the production and properties of acyl glutamates was published by M. Takehara et al. in J. Am. Oil. Chem. Soc., 49, 143 (1972). Typical examples of suitable acyl glutamates suitable for the purposes of the invention are anionic surfactants derived from fatty acids containing 6 to 22 and preferably 12 to 18 carbon atoms, for example C 12/14 or C 12/18 cocofatty acid, lauric acid, myristic acid, palmitic acid and/or stearic acid. Sodium or potassium N-cocoyl and sodium or potassium N-stearoyl-L-glutamate are particularly preferred. Triethanolamine-salts of acyl glutamates are also preferred, especially the triethanolamine salt of N-cocoylglutamate and the triethanolamine salt of N-stearoyl-L-glutamate.

In a preferred embodiment of the invention the anionic co-emulsifier is present in an amount of 0.01 to 10,

preferably 0.05 to 5 weight-%, preferably 0.03 to 1.4 weight-% based on a total weight of the O/W emulsion.

The anionic co-emulsifier is preferably an acylglutamate or acylaspariginate wherein the acyl residue may also be derived from other carboxylic acids than the above-mentioned fatty acids. More preferably, the anionic core emulsifier is an acyl glutamate, preferably a stearoyl glutamate such as the commercially available sodium stearoylglutamate.

The anionic co-emulsifier is preferably present in an amount of 1 to 20 wt.-% based on the amount of the at least one further non-ionic emulsifier (b).

The anionic co-emulsifier helps to stabilize the O/W emulsion, in particular if the same contains a major amount of medium polar oils, for instance hydrocarbon-based oils such as mineral oil. Moreover, without wishing to be bound by theory, it would appear that the anionic co-emulsifier, in cooperation with the other emulsion component, also contributes to suppression of undesired smells.

1.3. Oil Component

Component (c) of the emulsion/lotion is an oil component having a polarity of at least 20 mN/m or a mixture of oil components wherein at least 75 weight-% of the oils constituting the mixture have a polarity of at least 20mN/m. Oils having a lower polarity tend to develop undesired smells over longer periods of storage. The polarity of an oil component is defined as the polarity (= polarity index) of an oil against water. The polarity of oil can be determined using a ringtensiometer (e.g. Krüss K 10), measuring the boundary layer energy, which is the boundary layer tension in mN/m. The lower limit is 5 mN/m. The method is suitable for

low viscosity liquids given that a boundary layer is present (that is the liquids are not miscible). The polarity of the oil is determined against water.

The term "oil" is used for water-insoluble, organic, natural and synthetic, cosmetically useful oils having emollient properties and preferably a liquid (also viscous) consistency at room temperature (23°).

Preferably, the oil or mixture of oils is present in an amount of 20 to 80 weight %, more preferably 30 to 75 weight-%, in particular 40 to 70 weight-%, based on the total weight of the emulsion.

Oil components having the required polarity are for instance liquid hydrocarbon-based oils such as mineral oil, synthetic triglyceride mixtures, vegetable oils, guerbet alcohols, liquid linear or branched carboxylic acid esters, liquid substituted cyclohexanes, symmetric or asymmetric dialk(en)ylethers having from 6 to 22 C atoms per alk(en)yl group, linear or branched dialk(en)ylcarbonates derived from 6 to 22 C atoms fatty alcohols, ring-opening products or epoxidized fatty acid esters and polyols, silicone oils and mixtures thereof.

The following table lists the polarity for the most common oils.

Common Oils (CFTA-terms)	Polarity index (mN/m)
Non-polar	
Isoparaffin (C12-C14)	53.0
Squalan	46.2
Isohexadekan (ARLAMOL ND)	43.8
Mineral oil (Paraffin oil perliquidum	43.7

Mineral oil (Paraffin oil subliquidum	38.3
Polar	
Cetylstearyloctanoat (purceline oil)	28.6
Dimethicone (silicon oil 20 cSt)	26.6
Isopropylpalmitate	25.2
Octyldodecanol	24.8
Dioctyladipat (ARLAMOL DOA)	24.5
Isopropylmyristat	24.2
Octylpalmitate (2-ethylhexylpalmitate)	23.1
Hexamethyldisiloxan	22.7
Isopropylstearate	21.9
Capryl/caprine acid triglyceride (neutral oil)	21.3
Isopropylisostearate	21.2
Jojoba oil	20.8
Cyclomethicone (ARLAMOL D4)	20.6
Peanut oil	20.5
Almond oil	20.3
Sunflower oil	19.3
Decyloleate	18.7
Avocado oil	18.3
Olive oil	16.9
Castor oil	13.7
Calendula oil	11.1
Wheat germ oil	8.3

Preferred embodiments of the oil component to be used in the present invention are illustrated below.

- Suitable hydrocarbon-based oils are known to a person skilled in the art. They have preferably 8 to 32, more preferably 12 to 25, in particular 15 to 20 carbon atoms, such as squalane, squalene, paraffinic oils, isohexadecane, isoeicosane, polydecene or dialkycyclohexane. Mineral oil usually refers to less viscous mixtures of hydrocarbons having from 16 to 20 carbon atoms. Mineral oil is a particularly preferred oil.

- Liquid synthetic glycerides are mono-, di- and/or tri ester (fatty acid ester) of glycerol (in particular di- and/or triester). Preferably the fatty acid component has from 6 to 24, more preferably 6 to 18, in particular 8 to 18 carbon atoms. The fatty acid can be branched or unbranched as well as saturated or unsaturated, saturated fatty acids being preferred. According to the invention, the use of liquid glycerides from plant source is preferred, in particular the use of a modified liquid coconut oil (INCI name: cocoglycerides, available under the trade name Myritol® 331 from Cognis Deutschland GmbH) which contains as main component a mixture of di- and triglycerides based on C8 to C18 fatty acids.

- Vegetable oils which may contain liquid glycerides as main component, such as soja oil, peanut oil, olive oil, macademia nut oil or jojoba oil.

- Guerbet alcohols are based on fatty alcohols having 6 to 18, preferably 8 to 10 carbon atoms, such as 2-ethylhexanol or 2-octyldodecanol.

- Liquid linear or branched carboxylic acid esters, preferably fatty acid esters are more preferably esters of monovalent carboxylic acids having at least one long chain alkyl or acyl residue (each having at

least 6 C atoms, in particular at least 12 C atoms). Preferred carboxylic ester type emollient oils include those having more than 6 carbon atoms in total, preferably more than 12 C atoms in total which comprise either an acyl or an alkyl residue having each 1 to 5 carbon atoms. According to even more preferred embodiments, the carboxylic acid ester has the following formula (I)

$$R^1COO\text{-}R^2$$

wherein (i) R^1CO represents an acyl residue having 6 to 28 carbon atoms, and R^2 represents an alkyl residue having 1 to 5 carbon atoms or (ii) R^1CO represents an acyl residue having 1 to 5 carbon atoms, and R^2 represents an alkyl residue having 6 to 28 carbon atoms.

In line with option (i), the acyl residue may be saturated or unsaturated (e.g. 1,2,3 double bonds), the saturated embodiments being preferred. The acyl residue, preferably the saturated acyl residue may be branched and is optionally substituted, although this is not preferred. Similarly, the alkyl residue, may be branched as in isopropyl and/or substituted. The acyl residue preferably has 12 to 22 carbon atoms, in particular, 14 to 20 carbon atoms. The alkyl residue preferably has 1 to 3 carbon atoms as in methyl, ethyl or (iso)propyl. Representative examples of such esters include methylpalmitate, methyl stearate, isopropyl laurate, isopropyl myristate, and isopropyl palmitate.

In line with option (ii) the acyl residue may be branched and/or substituted for instance by hydroxy. According to one embodiment of option (ii), the acyl residue has 2 to 4 carbon atoms. The alkyl residue preferably has 12 to 22 carbon atoms, in particular 14 to 20 carbon atoms. It may be saturated or unsaturated

(*e.g.* one, two or three double bonds), saturated embodiments being preferred. Moreover, the alkyl residue may also be branched and/or substituted. Suitable fatty ester emollients of type (ii) include lauryl lactate and cetyl lactate.

- Substituted cyclohexanes, in particular substituted cyclohexanes.

- Symmetric or asymmetric, linear or branched dialk(en)ylethers having from 6 to 22 carbon atoms (per alk(en)yl group, preferably having 12 to 24 C atoms as total number of C atoms), such as di-n-octylether (dicaprylylether), di-(2-ethylhexyl)ether, laurylmethylether, octylbutylether or didocecylether.

- Dialk(en)ylcarbonates having preferably at least one C6 to 22 alkyl or alkenyl group (preferred total number of C atoms: not more than 45 including the C atom for the carbonate unit). The alkyl or alkenyl group can be straight or branched. The alkenyl unit may display more than one double bond. These carbonates can be obtained by transesterification of dimethyl or diethyl carbonate in the presence of C6 to C22 fatty alcohols according to known methods (cf. Chem. Rev. 96, 951 (1996)). Typical examples for dialk(en)ylcarbonates are the (partial) transesterification products of caprone alcohol, capryl alcohol, 2-ethylhexanol, n-decanol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachidyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol as well as their technical mixture,

which are for instance obtained by high pressure hydrogenisation of technical methyl esters on fat or oil basis. Particularly suitable in view of their low viscosity at 20°C are dihexyl-, dioctyl-, di-(2-ethylhexyl)- or dioleylcarbonat. Thus it is preferred to use either short chain (C6 to C10) alkyl or alkenyl carbonates.

- Ring-opening products of epoxidized fatty acid esters and polyols.

- Cosmetically useful silicone oils (*e.g.* those of US-4,202,879 and US-5,069,897).

In a further preferred embodiment, the above oil components are suitably selected among low viscosity oils, *i.e.* oils having a viscosity of 1 – 100 mPa•s, in particular 1 – 50 mPa•s (*e.g.* 1-20 mPaS) measured with a Höppler falling sphere viscosimeter at 20° C (method "*Deutsche Gesellschaft für Fettchemie*" DGF C-IV 7), in order to achieve the desired penetration behaviour on tissue paper.

According to one embodiment, the emulsion comprises a mixture of oils and at least 80, preferably at least 90 weight% of the oils constituting the mixture have a polarity of at least 20 mN/m.

According to one preferred embodiment, the emulsion comprises one oil having a polarity of at least 35 mN/m or a mixture of oils wherein at least 30, preferably at least 40, more preferably at least 50 weight% of the oils constituting the mixture have a polarity of at least 35 mN/m.

According to one preferred embodiment, the emulsion comprises a hydrocarbon-based oil, preferably mineral oil as sole oil component or a mixture of (d-1) a hydrocarbon based oil,

preferably mineral oil and (d-2) at least one further oil, which is preferably selected from the afore-mentioned oils other than hydrocarbon-based oils.

According to one further preferred embodiment, the hydrocarbon-based oil (d-1), preferably mineral oil constitutes at least 40 weight-%, more preferably at least 50 weight-% of all oil components (d).

The further oil component (d-2) is preferably selected from liquid carboxylic acid esters comprising either an acyl or an alkyl residue having each 1 to 5 carbon atoms.

According to one preferred embodiment, the carboxylic acid ester has the following formula (I)

(I)

$$R^1COO-R^2$$

wherein (i) R^1CO represents an acyl residue having 6 to 28 carbon atoms, and R^2 represents an alkyl residue having 1 to 5 carbon atoms or (ii) R^1CO represents an acyl residue having 1 to 5 carbon atoms, and R^2 represents an alkyl residue having 6 to 28 carbon atoms, option (i) being more preferred.

Option (i) includes the aforementioned more preferred embodiments.

1.4. Water

The lotion composition contains 6 to 35 % by weight, preferably 12 to 32 % by weight, more preferably 10 to 30% by weight, in particular 20 to 30 % by weight of water. The water contributes to a lotion-like pleasant feel to the skin of the user. Water, further, counteracts the

tendency of pure humectants (if present) to withdraw water from the human skin. On the other hand, the water content should not be much higher than 35 % by weight, since then the mechanical strength of the treated tissue paper may suffer to an undesired extent. Usually, the aqueous phase of the O/W emulsion contains water as a main component. However, if the water content is closer to the lower limit of the claimed range, it is preferred to add a corresponding amount of water-soluble, aqueous phase-forming components, preferably the humectant, to the lotion composition. Otherwise the discontinuous (oil) phase could be in too close contact, in order to maintain a stable O/W emulsion. In view of the above, the weight proportion of the aqueous phase is preferably more than 20, more preferably at least 22, in particular at least 23 weight %, based on the total weight of the lotion composition.

1.5. Humectant (optional)

The lotion composition preferably comprises from 0.5 to 15 % by weight, more preferably 1 to 10 % by weight, and in particular 2 to 8 % by weight (water-soluble) humectant.

The humectant performs multiple functions. First, it binds water and counteracts the tendency of water to evaporate. Moreover, the humectant can interact with other lotion components and then contributes to the softness of the tissue paper, in particular its bulk softness. The humectant can also influence the rheological properties of the lotion composition.

The humectant preferably is a polyhydroxy compound, which is understood to be an organic compound having at least two hydroxy groups and which preferably consists only of carbon, hydrogen, oxygen and nitrogen, in particular only

of C, H and O. It is further desirable that the humectant is not ionic.

Hydrophilic surfactants (having a HLB number of 10 or greater, see for instance US 4,764,418) can have humectant properties. It is preferred according to the invention that the humectant be free of major hydrophobic molecule parts, *e.g.* fatty acid or fatty alcohol residues.

Further, the humectant preferably has a liquid consistency, even though it is possible to use a minor amount of a solid, low melting point humectant depending on the desired viscosity and penetration behaviour of the final lotion.

If liquid humectants are to be employed, the molecular weight (weight average) preferably is less than 1,000, more preferably less than 800, and in particular not more than 600.

Examples of suitable humectants include: amino acids, pyrrrolidone, carboxylic acid, lactic acid and salts thereof, lactitol, urea and urea derivatives, uric acid, glucosamine, creatinine, cleavage products of collagen, chitosan or chitosan salts/derivatives and, in particular, polyols and polyol derivatives (for example glycerol, diglycerol, triglycerol, polyalkylene glycols, *e.g.* polypropylene glycol, butylene glycol, 1,2,6-hexantriol, polyethylene glycols, for instance polyethylene glycol having a weight average molecular weight of from about 200 to 600); neopentyl alcohols such as pentaerythritol or neopentyl glycol; sugar alcohols such as threitol, erythritol, adonitol (ribitol), arabitol, xylitol, dulcitol, maltitol, mannitol, inositol and sorbitol, carbohydrates such as D (+)- glucose, D (+)- fructose, D (+)- galactose, D (+)- mannose, L-gulose, saccharose, galactose, maltose, polyglycerols, polyoxypropylene

adducts of glycerol, methoxypolyethylene glycol, polyethylene glycol ethers of sugar alcohols, such as sorbitol, polyethylene glycol ethers of glycerol, ethoxylated sorbitol (Sorbeth-6, Sorbeth-20, Sorbeth-30, Sorbeth-40), honey and hydrogenated honey, hydrogenated starch hydrolyzates and mixtures of hydrogenated wheat protein and PEG-20-acetate copolymer, and combinations thereof. Hyaluronic acid may also be used as humectant.

Preferred humectants are glycerol, diglycerol and triglycerol, and particularly preferred is glycerol.

1.6. Consistency regulators (optional)

The viscosity of a lotion can be adjusted by using a corresponding amount of consistency regulators, which are typically solid.

The amount of consistency regulators depends on the desired viscosity of the final lotion composition. If a semi-solid consistency is to be obtained, the consistency regulators can be used in amounts of up to 30 % by weight, for instance 5 to 20 % by weight.

On the other hand, if it is intended to produce a low viscosity lotion composition which fully penetrates the fibrous web, lower amounts of consistency regulators should be used. In this case, the overall content of solid components, including the consistency regulators is preferably less than 15 % by weight, more preferably less than 10 % by weight, in particular less than 5 % by weight, e.g. 0.1 to 5% or 1 to 5% by weight.

The consistency regulator is suitably selected from solid, mono-, di- and triglycerides and mixtures thereof, solid fatty alcohols, waxes, as well as metal soaps. Preferred embodiments thereof are explained in the following:

- Glycerides are preferably the mono-, di- and/or triester of glycerol and fatty acids having from 6 to 30, in particular, 16 to 30 carbon atoms, whereby the term "fatty acid" is not restricted to the naturally occurring even-numbered, saturated and unsaturated carboxylic acids, but also includes their uneven-numbered homologues and isomers thereof. A skilled person can suitably select among known glycerides those having a solid consistency at 23° C, whereby the degree of esterification and unsaturation plays an important role. Usually, it is preferred to use glycerides wherein the fatty acid residues are predominantly saturated. In a more preferred embodiment, commercial mono-, di- and/or triglyceride (mixtures) are used, which are available from Cognis Deutschland GmbH under the tradenames Cutina® GMS or MD, or Novata® AB. Syncrowax® HGLC (available from Croda) may also be used. Particularly preferred is a glyceryl stearate (predominantly mono- and diester, some triester), which is marketed by Cognis Deutschland GmbH under the tradename Cutina® MD.

- Metal soaps:
  A metal soap of the following formula may be used:

$$(R^1COO)_n-X$$

  wherein R^1 represents a linear, saturated, or unsaturated acyl residue having 6 to 22 carbon atoms and optionally at least one hydroxy group, preferably 12 to 18 carbon atoms, X is an alkali metal (*e.g.* Li), earth alkali metal (*e.g.* Ca, Mg), or Al or Zn, and n is the valence of X. Preferred examples of the metal soap involve zinc, calcium, magnesium or aluminium stearate.

- Wax:
  The term "wax" is used as in the prior art for natural or synthetic materials which have a kneadable, solid or brittle consistency at room temperature, are finely to granularly crystalline, however not glass-like, and transparent to opaque. Useful waxes melt at a temperature above 35° C without decomposition and then (slightly above the melting point) have a fairly low viscosity (sometimes referred to as "lipophilic" waxes). Useful waxes are listed in DE-A 199 06 081.

- Fatty alcohols:
  Preferred fatty alcohols are those having at least 12, preferably 12 to 30 C atoms (*e.g.* C12-C24 or C24-C30), in particular the saturated embodiments thereof. Examples thereof involve lauryl alcohol, myristyl alcohol, cetearyl alcohol, erucyl alcohol, ricinol alcohol, isostearyl alcohol, arachidyl alcohol, behenyl alcohol, brassidyl alcohol as well as their guerbet alcohols. Further, it is possible to use fatty alcohol mixtures obtained by the reduction of naturally occurring fats and oils, such as beef tallow, peanut oil, rape oil, cotton seed oil, soy oil, sunflower oil, palm kernel oil, linseed oil, castor oil, corn oil, sesame oil, cocoa butter and coco oil. However, it is also possible to use synthetic alcohols such as the linear, even-numbered fatty alcohols obtained by Ziegler synthesis (Alfole®) or the partially branched alcohols by oxosynthesis (Dobanole®).

  It is also possible to use mixtures of these fatty alcohols, for instance the mixture of cetyl alcohol and stearyl alcohol which is commercially available as "cetearyl alcohol".

According to a particularly preferred embodiment of the present invention, the consistency regulator is selected from fatty alcohols, such as cetearyl alcohol.

1.7. Additives (optional)

Optionally, the lotion composition may contain up to 10 % by weight, in particular 0.1 to 5 % by weight additives, such as

- Preservatives which stabilize the lotion composition, such as methylisothiazolin(on) which may have a chlorine as substituent, *e.g.* 5-chloro-2-methyl-4-isothiazolin-3-on or 2-methyl-4-isothiazolin-3-on; phenoxyethanol or PHB ester, paraben preservatives, pentanediol, sorbic acid or other compounds as mentioned in "Kosmetikverordnung, Anlage 4, Teil A und B".
- Germicidal agent(s), *e.g.* those described in DE-199 06 081 A.
- Cosmetic agents, preferably from natural sources (plant extracts), having for instance a skin-soothing, antiphlogistic (reduction of skin irritation), wound-healing, cell-regenerating, anti-inflammatory and/or anti-itch effect such as allantoin; aloe vera extract; aloe barbadensis extract; chamomile extract containing azulene and α-bisabolol; echinacea; dragosantol; panthenol; liquorice root extract containing 18-glycyrrhetinic acid; lime tree extract containing quercetin and/or glyco-rutin; marigold (calendula oil); urea; phytosterols, optionally ethoxylated (available from Henkel under the tradename "Generol"); chitosan (acetylated chitin); anthocyanidins; gingko leaf extract containing quercetin and rutin; horse chestnut containing quercetin and campherol; vitamins or provitamins such as provitamin B5 or

Vitamin E; avocado oil; birch extract; arnica; extract of rose of Sharon or St. John's wort; teatree oil; cucumber, hops, or hamamelis extracts or ingredients, ethoxylated quaternary amines (itching inhibiter useful for lotioned toilet papers); the use of α-bisabolol being preferred;

- Perfume *e.g.* those described in DE 199 06 081; and/or
- Cosmetically useful Dyes and pigments, *e.g.* those described in "*Kosmetische Färbemittel*" (Cosmetic Colouring Agents), published by the *Farbstoffkommission der Deutschen Farbstoff-gemeinschaft*; Verlag Chemie, Weinheim, 1984, p. 81-106.

The above-mentioned cosmetic agent is normally present in a quantity of 0.01 to 10 weight-%, preferably 0.1 to 7 weight-%, and more particularly 1 to 5 weight-%. The emulsion to be used in the present invention preferably contains, as a cosmetic agent, at least one irritation-soothing/anti-inflammatory agent, which is intended in particular to sooth inflammatory skin processes or reddened, sore skin.

According to the invention, bisabolol, allantoin and panthenol and bisabolol are particularly preferred as cosmetic agents. Vitamins and vitamin precursors and protein hydrolyzates can also promote wound healing.

Also suitable are plant extracts which often contain a synergistic combination of wound-healing/irritation-soothing substances. These extracts are normally obtained by extraction of the whole plant. In individual cases, however, it can also be preferred to prepare the extracts exclusively from flowers and/or leaves of the plant.

As far as the plant extracts suitable for use in

accordance with the invention are concerned, reference is made in particular to the extracts listed in the Table beginning on page 44 of the **3rd Edition of the Leitfaden zur lnhaltsstoffdeklaration kosmetischer Mittel**, published by the Industrieverband Körperpflege- und Waschmittel e.V. (IKW), Frankfurt.

According to the invention, the extracts of, above all, camomile, aloe vera, hamamelis, lime blossom, horse chestnut, green tea, oak bark, stinging nettle, hops, burdock root, horse willow, hawthorn, almond, pine needle, sandalwood, juniper, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, mallow, lady's smock, creeping thyme, yarrow, thyme, balm, restharrow, coltsfoot, hibiscus, meristem, ginseng and ginger root are suitable.

One preferred type of cosmetic agents are plant extracts of the type as already mentioned above which often contain one or more wound-healing/soothing agents. Typically these extracts are prepared by extracting the entire plant. In some cases it can also be preferred to use solely the blossom and/or leaves of the plant. Preferred extracts are obtained from chamomile aloe vera, hamamelis, lime-blossom, sage and melissa. It is a particular merit of the present invention that plant extracts can be used without undesired colouring reactions of the emulsion.

Suitable extraction agents for the preparation of the plant extracts to be mentioned are water, alcohols and mixtures thereof. Among the alcohols, lower alcohols, such as ethanol and isopropanol, but especially polyhydric alcohols, such as ethylene glycol and propylene glycol, are preferably used both as sole extractant and in the form of mixtures with water, Plant extracts based on water/propylene glycol in a ratio of 1:10 to 10:1 have proved to be particularly suitable.

The above additives may be used separately or in combination.

1.8. Most preferred lotion

The most preferred lotion composition, which based on current knowledge reflects the best mode for carrying out the invention, comprises the following components:

(a) 2 to 15 weight %, preferably 3 to 7 weight % of a polyol polyester wherein a polyhydric alcohol having at least two hydroxy groups is esterified with at least one acid having from 6 to 30 carbon atoms and at least one hydroxy group or condensation product(s) of this hydroxy fatty acid,
(b) 2 to 15 weight %, preferably 3 to 7 weight-% of at one further non-ionic emulsifier, preferably at least one alkyl mono-, oligo- or polyglycoside,
(c) 0.01 to 10 weight-%, preferably 0.03 to 1.4 weight-% of at least one anionic emulsifier, preferably of carboxylate type.
(d) 40 to 70 weight % of an oil component having a polarity of at least 20 mN/m or a mixture of oil components wherein at least 75 weight-% of the oils constituting the mixture have a polarity of at least 20mN/m,
(e) 12 to 32 weight % water,
(f) optionally 1 to 5 weight % of at least one consistency regulator,
(g) optionally 1 to 5 weight % humectant,
(h) optionally 0.1 to 5 weight % further additives, preferably at least one irritation-soothing agent.

More preferably, the emulsion comprises (d) a mixture of (d-1) at least one hydrocarbon-based oil such as mineral oil and (d-2) at least one further oil selected from those defined

above. Even more preferably, the further oil (d-2) is a carboxylic acid ester represented by formula (I)

(I)

R^1COO-R^2

wherein R^1CO represents an acyl residue having 6 (more preferably 12) to 22 carbon atoms and R^2 represents an alkyl residue having 1 to 5 carbon atoms.

2. Preparation of lotion

The lotion composition (oil-in-water emulsion) can be prepared according to known methods (see for instance Karlheinz Schrader, Grundlagen und Rezepturen der Kosmetika, Hüthig Buch Verlag Heidelberg, Second Edition, 1989, pages 906 to 912).

One (low temperature) procedure which is only applicable if there are no solid components requiring melting for even distribution/dissolution involves mixing and homogeneously stirring the oil phase component(s), such as oil components (A) and emulsifier(s) (B) and other optional oil-phase components at room temperature (usually for approximately 10 min). The components of the water phase such as water, humectant, and possible water-soluble or water-dispersible additives such as perfume or preservatives are separately mixed at room temperature and slowly added to the mixture of oil-phase components during continuous stirring. After continued stirring (preferably for approximately 10 min) the resulting mixture is then homogenized (usually for approximately 10 min) with a suitable dispersion device such as supraton or stator-rotor homogenizers of the Ultraturrax type. As known from the prior art, homogenizing conditions may have an impact on the viscosity of the emulsion obtained.

According to one embodiment, which is applicable, if solid components such as consisting regulates require an increased temperature to be evenly distributed/dissolved in the oil phase, the lotion composition is prepared by mixing the oil phase and water phase components at a higher temperature. For this purpose, it is preferred to heat the oil phase and water phase components separately to about 80° C to 85° C. Then, at this temperature the water phase components are slowly added to the oil phase components while stirring, optionally homogenizing. After continued stirring, preferably for about 5 min, the mixture is allowed to cool while stirring in such a way that it remains in continuous motion. Simultaneously, the incorporation of air should be avoided. The mixture can then be homogenized with a suitable dispersion device such as supraton or stator-rotor homogenizers of Ultraturrax type, preferably at 60° to 65° C, in order to improve stability and structure. After a homogeneous state is reached, the composition is allowed to cool to room temperature. If perfume is added, it is generally preferred to include the same not at the highest preparation temperature, but during the cooling step and preferably before the emulsion has returned to room temperature.

If the viscosity is too high, it is possible for instance to reduce the energy influx during homogenization, in particular by lowering the rotational speed of the rotor/stator system.

3. Tissue paper to be treated

In accordance with the present invention, the tissue paper to be lotioned exists in the form of toilet paper, or is further processed to toilet paper after the lotioning step.

The present invention pertains to a toilet paper, that is a tissue paper product intended for sanitary use in a toilet, mainly provided in form of rolls with a certain number of sheets. It may be separated by a perforation line or as folded single sheets, c-folded or interfolded in the institutional area. Products of this type are made using a light weight dry creped, optionally through air dried or a non-creped technique and derive from a single ply, semi-finished, wet-laid tissue base paper that is composed of natural fibers and optionally other fiber materials. The origin of these fibers may be native or recycled. A typical grammage of a single ply tissue paper is from 10 g/m^2 up to 50 g/m^2.

The toilet paper products are coated or impregnated with the present lotion which provides a cream-like lotion perception.

Preferably the tissue paper contains as main component (in particular at least 80 % by weight, relative to the dry weight of the fibrous web, without lotion) cellulosic fibres, in particular pulp, although a proportional use of modified pulp fibers (*e.g.* from 10 to 50 weight %, relative to the total weight of the fibers) or the use of synthetic fibers suitable for web making (*e.g.* from 10 to 30 % by weight, relative to the total weight of the fibers) is covered by the invention.

Creped or "uncreped" tissue paper obtained by wet rush transfer as described in the section "Background Art" can be lotioned, the use of creped tissue paper being preferred. The tissue paper (or the final tissue paper product obtained therefrom) can be single-ply or multi-ply (typically 2 to 4). The penetration behaviour of a low viscosity lotion can be particular suitable for multi-ply toilet tissue paper, in particular 4-ply embodiments,

since the lotion can be almost evenly distributed over the outer and inner plies.

The tissue paper may be homogeneous or layered, wet-pressed or blow-dried (TAD-dried). The tissue paper includes, but is not limited to, felt-pressed tissue paper, pattern-densified tissue paper, uncompacted tissue paper or compacted tissue paper.

The starting material for the production of the tissue paper usually is a fibrous cellulosic material, in particular pulp.

If, however, linters or cotton is used as raw material for the production of tissue paper, usually no further pulping steps are needed. Due to the morphological structure, the cellulose already exists in an open state.

The starting pulps used may relate to primary fibrous materials (raw pulps) or to secondary fibrous materials, whereby a secondary fibrous material is defined as a fibrous raw material recovered from a recycling process. The primary fibrous materials may relate both to a chemically digested pulp and to mechanical pulp such as thermorefiner mechanical pulp (TMP), chemothermorefiner mechanical pulp (CTMP) or high temperature chemithermomechanical pulp (HTCTMP). Synthetic cellulose-containing fibres can also be used. Preference is nevertheless given to the use of pulp from plant material, particularly wood-forming plants. Fibers of softwood (usually originating from conifers), hardwood (usually originating from deciduous trees) or from cotton linters can be used for example. Fibres from esparto (alfa) grass, bagasse (cereal straw, rice straw, bamboo, hemp), kemp fibers, flax, and other woody and cellulosic fiber sources can also be used as raw materials. The corresponding fiber source is chosen in accordance with

the desired properties of the end product in a manner known from the prior art. For example, the fibers present in hardwood, which are shorter than those of softwood, lend the final product a higher stability on account of the higher diameter/length ratio. If softness of the product is to be promoted, which is important *e.g.* for tissue paper, eucalyptus wood is particularly suitable as a fiber source.

With regard to softness of the products, the use of chemical raw pulps is also preferred, whereby it is possible to use completely bleached, partially bleached, and unbleached fibers. The chemical raw pulps suitable according to the invention include *inter alia*, sulphite pulps, kraft pulps (sulphate process).

Before a raw pulp is used in the tissue making process, it may also be advantageous to allow further delignification to occur in a separate process step or employ a bleaching process to achieve a more extensive removal of lignin after the cooking process and to obtain a completely cooked pulp.

A preferred production process for tissue paper uses

a a forming section (for wet-laying a slurry of cellulosic fibrous material, typically pulp) comprising a headbox and wire portion, and

b the drying section (TAD (through air drying) or conventional drying on the yankee cylinder) that also usually includes the crepe process essential for tissues.

This is typically followed by

c the monitoring and winding area.

The tissue paper can be formed by placing the fibers, in an oriented or random manner, on one or between two continuously revolving wires of a paper-making machine while simultaneously removing the main quantity of water of dilution until dry-solid contents of usually between 12 and 35 % are obtained. It is possible to include additives in the paper furnish to improve the wet-strength or dry-strength or other properties of the finished tissue paper.

Drying the formed primary fibrous web occurs in one or more steps by mechanical and thermal means until a final dry- solids content of usually about 93 to 97 % is obtained. In the case of tissue making, this stage is followed by the crepe process which crucially influences the properties of the finished tissue product in conventional processes. The conventional dry crepe process involves creping on a drying cylinder having a diameter of usually 4.5 to 6 m, the so-called yankee cylinder, by means of a crepe doctor with the aforementioned final dry-solids content of the base ("raw tissue") tissue paper (wet creping can be used if lower demands are made of the tissue quality). The creped, finally dry base tissue paper is then available for further processing into the paper product or tissue paper product according to the invention.

Instead of the conventional tissue making process described above, the invention gives preference to the use of a modified technique in which an improvement in specific volume is achieved by a special kind of drying within process section b and in this way an improvement in bulk softness of the resulting tissue paper is achieved. This pre-drying process, which exists in a variety of subtypes, is termed the TAD (through air drying) technique. It is characterized by the fact that the "primary" fibrous web (like a non-woven) that leaves the

sheet making stage is pre-dried to a dry-solids content of about 80 % before final contact drying on the yankee cylinder by blowing hot air through the fibrous web. The fibrous web is supported by an air-permeable wire or belt and during its transport is guided over the surface of an air-permeable rotating cylinder drum. Structuring the supporting imprinting fabric or belt makes it possible to produce any pattern of compressed and uncompressed zones achieved by deflection of the fibres in the moist state, followed by pre-drying (TAD step) and leading the web through a pressure nip between a pressure roll and the Yankee cylinder surface, thereby resulting in increased mean specific volumes and consequently leading to an increase in bulk softness without decisively decreasing the strength of the fibrous web.

Another possible influence on softness and strength of base tissue lies in the production of a layering in which the primary fibrous web to be formed is built up by a specially constructed headbox in the form of physically different layers of fibrous material, these layers being jointly supplied as a pulp jet to the forming stage.

The one-ply intermediate products originating from the paper-making machine and made of lightweight paper usually dry-creped on a yankee cylinder by means of a crepe doctor are generally described as "tissue paper" or more accurately base tissue paper. The one-ply base tissue may be built up of one or a plurality of layers respectively.

All one-ply or multi-ply final products made of base tissue and tailored to the end user's needs, *i.e.* manufactured with a wide variety of requirements in mind, are known as "tissue products".

When processing the fibrous web or base tissue paper into the final tissue product, the following procedural steps

are normally used individually or in combination: cutting to size (longitudinally and/or cross cutting), producing a plurality of plies, producing mechanical and/or chemical ply adhesion, volumetric and structural embossing, folding, imprinting, perforating, smoothing, stacking, rolling up.

To produce multi-ply toilet paper products an intermediate step preferably occurs with so-called doubling in which the base tissue in the finished product's desired number of plies is usually gathered on a common multiply master roll.

The processing step from the base tissue that has already been optionally wound up in several plies to the finished tissue product occurs in processing machines which include operations such as repeated smoothing of the tissue, edge embossing, to an extent combined with full area and/or local application of adhesive to produce ply adhesion of the individual plies (base tissue) to be combined together, as well as longitudinal cut, folding, cross cut, placement and bringing together a plurality of individual tissues and their packaging as well as bringing them together to form larger surrounding packaging or bundles. The individual paper ply webs can also be pre-embossed and then combined in a roll gap according to the foot-to-foot or nested methods.

Embossing can be used for generating ply adhesion in multi-ply tissue papers. In order to ensure that the lotion does not lower the ply adhesion, the embossed regions may be left untreated. Further it is known from US-4,867,831 to use melted thermoplastics to achieve plybonding in lotioned tissue papers.

According to the invention the tissue paper to be treated with the lotion preferably has a basis weight of 10 to 50,

more preferably 11 to 40, even more preferably 12 to 20 g/m² per ply, in particular 13 to 17 g/m² per ply and a total basis weight (including all plies without lotion) of usually 10 to 80 g/m².

4. Application of Lotion on the Tissue Paper

As mentioned, lotion application typically takes place after the tissue paper web has been dried. A suitable point in time is for example directly after drying the web, shortly before combining the webs to form multiple plies or before forming the multi-ply web into the final tissue product. However, it is preferred first to laminate at least two single ply webs to a multiply web, followed by application of lotion. For tissue paper having two or more plies, the lotion composition may be applied to each ply or only to one or both outer plies. In a preferred production process for lotioned 4-ply (products), two 2-ply webs are each lotioned on only one side, followed by joining together the untreated sides of said 2-ply webs, thereby obtaining a 4 ply product. It can be preferred to apply the lotion composition to at least one, preferably both outer plies of multi-ply tissue webs, since then the advantageous penetration behavior of a low viscosity lotion composition can fully be developed by achieving a distribution as even as possible with respect to the z-direction (perpendicular) of the multi-ply tissue paper. The individual plies or the multi-ply structure may be patterned either before or after application of the lotion composition. Suitable application techniques include spraying, rotogravure printing or flexographic printing or application by means of rolls having a smooth surface. Preferably, the lotion composition is slightly heated, in particular to a temperature from 30° to 50° C, in particular 32 to 38°C before it is applied to the web.

Preferably, the lotion is applied in an amount of 1 to 10 g, in particular 2 to 5 g per m^2 treated surface, *i.e.* with the double the amount, if both surfaces are lotioned. The weight ratio lotion composition/web (single or multi-ply, dry weight) is preferably 3 to 30 %, more preferably 5 to 20 % by weight.

5. Test Method

The capacity of a lotioned tissue paper to sink in water was determined in line with DIN ENV 12625-8 of May 2001 "*Tissue paper and tissue products-Part 8: Determination of water absorption time, water absorption capacity -manual and automated test method*", which is identical with the method described in further detail in WO 02/057547 A2.

6. Example

A lotion composition containing the following ingredients was prepared at increased temperature as described above.

Table 1

Component	% by weight
Mineral oil	35.0
Isopropyl Palmitate	26.2
Aqua	23.9
Polyglyceryl-2 Dipolyhydroxystearate	4.0
Lauryl Glucoside	4.0
Glycerin[1]	3.0
Cetearyl Alcohol	3.0
Perfum Oil	0.5
Sodium Stearoyl Glutamate	0.1
Aloe Barbadensis Leaf Extract	0.1

Chamomilla Recutita (Matricaria) Flower Extract (and) Maltodextrin (and) Silica	0.1
Citric acid	0.09
Methylchloroisothiazolinone (and) Methylisothiazolinone	0.0014

[1] Citric acid is present for pH adjustment in the commercially available (from Cognis Deutschland GmbH) emulsifier combination Eumulgin ® VL 75 (based on PGPH, Laurylglucoside, glycerol and water) which was used for preparing the lotion.

Conductivity measurements showed that the above lotion is of O/W type.

This lotion composition was heated to about 35° C and applied with a rotogravure device on one side of two 2-ply webs in an amount of 3.5 g/m² each. Then the untreated side of one 2-ply web was partially coated with adhesive (cold glue or hotmelt) and then joined together in face to face relationship with the untreated side of the other 2-ply web, thereby obtaining a 4 ply web having lotion on both outer sides (total amount of lotion 7 g/m^2). The corresponding, but untreated 4-ply web showed a basis weight of about 65 g/m² and a thickness of about 505 µm, and a bulk of about 7.8 cm^3/g. This leads to an amount of about 11 % by weight lotion based on the weight of the four-ply tissue.

The sinking behaviour in water (water absorption time) of this lotioned tissue paper was determined in accordance with the DIN ENV 12625-8 as described above. The water absorption time was about 6 sec.

The viscosity/temperature dependence of this lotion as shown in Figure 1 displayed a favourable, relatively broad plateau

from 32°C to 36°C. It was measured with a Haake Rheostress RS1 rheometer under the conditions indicated before. Accordingly, this lotion can be easily applied on tissue web at relatively low temperatures.

Comparative Example

The above lotion was compared with the lotion of WO 02/057547 A2 in respect of their whiteness (according to Din EN 12625-7, item 7.3.2, color (D65/10°) and smell.

As a reference point for the whiteness analysis, the whiteness of unlotioned tissue paper was taken as 100%. It turned out that the lotioned toilet paper of the present invention surprisingly shows a degree of whiteness (brightness) that is improved by about 4% (80.4 and 80.3 versus 76,7 as measured for the lotioned toilet paper of WO 02/057547). The corresponding values were measured with a Minolta spectrophotometer CM-3610d.

Moreover, two toilet papers were treated with the same amount of the lotion shown in the example of WO 02/057547 A2 and the lotion of the present invention, respectively, both however without perfume. The lotioned toilet papers were stored over 12 weeks at a temperature of 40°C to accelerate aging. After 4, 8 and 12 weeks the toilet papers were presented to a test panel, which noticed after 8 weeks an off-odour (rancid odour) for the toilet paper made in line with WO 02/057547 A2. In contrast thereto, the toilet paper of the present invention did not develop any unpleasant odours.

In a second test, both toilet papers were treated with the respective perfume-containing lotions. The perfume had evaporated after 4 weeks. Again however, the test panel noticed after 8 weeks an off-odour (rancid odour) for the toilet paper made in line with WO 02/057547 A2, whereas

the toilet paper of the present invention never developed any unpleasant odours.

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25. Nov. 2005

CLAIMS

1. Toilet paper based on tissue paper, said tissue paper being treated with an O/W emulsion comprising

at least one non-ionic emulsifier,
at least one anionic co-emulsifier,
one oil component having a polarity of at least 20 mN/m or a mixture of oil components wherein at least 75 weight-% of the oils constituting the mixture have a polarity of at least 20mN/m,
6 to 35 weight % of water, based on the total weight of the emulsion,
wherein the total amount of non-ionic emulsifier(s) and anionic co-emulsifier(s) is between 4 and 20 weight, preferably between 6 and 16 weight-%, based on the total weight of the emulsion.

2. Toilet paper according to claim 1, characterized in that the emulsion comprises

(a) at least one non-ionic emulsifier having an HLB value of less than 10, preferably $\leq$ 8, more preferably $\leq$ 5, e.g. 2 to 5.
(b) at least one further non-ionic emulsifier having an HLB value of more than 10, preferably $\geq$ 12, preferably from 12 to 20 (e.g. 15 to 18).
(c) at least one anionic co-emulsifier
(d) one oil component having a polarity of at least 20 mN/m or a mixture of oil components wherein at least 75 weight-% of the oils constituting the mixture have a polarity of at least 20mN/m,
(e) 6 to 35 weight % of water, based on the total weight of the emulsion,
(f) optionally at least one consistency regulator, and
(g) optionally at least one humectant.

3. Toilet paper according to claim 1 or 2, wherein the emulsion comprises
   (a) at least one polyol polyester wherein a polyhydric alcohol having at least two hydroxy groups is esterified with at least one acid having from 6 to 30 carbon atoms and at least one hydroxy group, or condensation product(s) of this hydroxy fatty acid,

4. Toilet paper according to any of claims 1, 2 or 3, wherein the emulsion comprises
   (a) polyol poly-12-polyhydroxystearate, preferably polyglycerolpoly-12-hydroxy stearate.

5. Toilet paper according to any of claims 1, 2 or 3, wherein the emulsion comprises a further (b) non-ionic emulsifier selected from

   - (b-1) products of the addition of 2 to 50 mol ethylene oxide and/or o to 20 mol propylene oxide onto linear fatty alcohols containing 8 to 40 carbon atoms, onto fatty acids contains 12 to 40 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group.
   - (b-2) $C_{12/18}$ fatty acid monoesters and diesters of addition products of 1 to 50 mol ethylene oxide onto glycerol;
   - (b-3) glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide addition products thereof;
   - (b-4) alkyl mono-, oligo and/or polyglycosides, preferably alkyl mono- and oligo and their alkoxylated, preferably ethoxylated derivates.
   - (b-5) partial esters based on linear, branched, unsaturated or saturated C_{6-22} fatty acids,

ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols, alkyl glucosides and polyglucosides; or

- (b-6) polysiloxane/polyalkyl/polyether copolymers and corresponding derivatives;

and mixtures thereof

6. Toilet paper according to claim 5, wherein the non-ionic coemulsifier (B) is selected from (b-4) alkyl mono-, oligo- and/or polyglycosides and their alkoxylated derivatives.

7. Toilet paper according to any of claims 2 to 6, wherein the weight ratio of non-ionic emulsifier (a) to further non-ionic emulsifier (b) is in the range of 1:0.5 to 1:2.

8. Toilet paper according to any of claims 1 to 7, wherein the anionic co-emulsifier (c) is selected from phosphate- , sulphate- and carboxylate emulsifiers.

9. Toilet paper according to claim 8, wherein the anionic co-emulsifier (c) is a carboxylate emulsifier.

10. Toilet paper according to claim 8 or 9, wherein the anionic co-emulsifier (c) is an acyl glutamate, preferably a stearoyl glutamate.

11. Toilet paper according to any of claims 1 to 10, wherein the anionic co-emulsifier (c) is present in an amount of 0.01 to 10, preferably 0.05 to 5, more preferably 0.03 to 1.4 weight-%, based on the total weight of the emulsion.

12. Toilet paper according to any of claims 2 to 11, wherein the anionic emulsifier (c) is present in an amount of 1

to 20 weight-% based on the amount of the further non-ionic emulsifier (b).

13. Toilet paper according to any of claims 1 to 12, wherein the emulsion comprises a mixture of oils and at least 80, preferably at least 90 weight% of the oils constituting the mixture have a polarity of at least 20 mN/m.

14. Toilet paper according to any of claims 1 to 12, wherein the emulsion comprises one oil having a polarity of at least 35 mN/m or a mixture of oils wherein at least at least 30, preferably at least 40, more preferably at least 50 weight% of the oils constituting the mixture have a polarity of at least 35 mN/m.

15. Toilet paper according to any of claims 1 to 12 or 14, wherein the emulsion comprises a hydrocarbon-based oil, preferably mineral oil as sole oil component or a mixture of (d-1) a hydrocarbon based oil, preferably mineral oil and (d-2) at least one further oil.

16. Toilet paper according to claim 15, wherein the hydrocarbon-based oil (d-1), preferably mineral oil constitutes at least 40 weight-%, more preferably at least 50 weight-% of all oil components (d).

17. Toilet paper according to any of claims 1 to 16, wherein the emulsion comprises at least one oil selected from liquid synthetic triglyceride mixtures, vegetable oils, guerbet alcohols, liquid linear or branched carboxylic acid esters, liquid substituted cyclohexanes, symmetric or asymmetric dialk(en)ylethers having from 6 to 22 C atoms per alk(en)yl group, linear or branched dialk(en)ylcarbonates derived from 6 to 22 C atoms fatty alcohols, ring-opening products or epoxidized fatty acid esters and polyols, silicone oils and mixtures thereof.

18. Toilet paper according to any of claims 13, 14, 15 or 16, wherein the emulsion comprises a mixture of (d-1) a hydrocarbon-based oil and (d-2) at least one oil selected from those defined in claim 17, in particular a liquid linear or branched carboylic acid ester.

19. Toilet paper according to claim 17 or 18, wherein the liquid carboxylic acid ester comprises either an acyl or an alkyl residue having each 1 to 5 carbon atoms.

20. Toilet paper according to claim 19, wherein the carboxylic acid ester has the following formula (I)

(I)

$$R^1COO\text{-}R^2$$

wherein (i) R^1CO represents an acyl residue having 6 to 28 carbon atoms, and R^2 represents an alkyl residue having 1 to 5 carbon atoms or (ii) R^1CO represents an acyl residue having 1 to 5 carbon atoms, and R^2 represents an alkyl residue having 6 to 28 carbon atoms.

21. Toilet paper according to any of the preceding claims wherein the oil or mixture of oils is present in an amount of 20 to 80 weight %, preferably 40 to 70 weight-%, based on the total weight of the emulsion.

22. Toilet paper according to any of claims 1 to 21, wherein the emulsion further contains at least one irritation-soothing agent.

23. Toilet paper according to any of the preceding claims, characterized in that the emulsion composition further comprises at least one consistency regulator (f) in an amount of 0.1 to 15 weight %.

24. Toilet paper according to any of the preceding claims, characterized in that the emulsion composition further comprises at least one humectant (g), preferably glycerin in an amount of 0.5 to 15 weight %.

25. Toilet paper according to any of the preceding claims, wherein the emulsion has a viscosity of 100 to 10,000 mPa x s, preferably 500 to 3000 measured with a Brookfield RFV, spindle 3, 10rpm.

26. Toilet paper according to claim 1, characterized in that the emulsion comprises:

(a) 2 to 15 weight %, preferably 3 to 7 weight % of a polyol polyester wherein a polyhydric alcohol having at least two hydroxy groups is esterified with at least one acid having from 6 to 30 carbon atoms and at least one hydroxy group or condensation product(s) of this hydroxy fatty acid,
(b) 2 to 15 weight %, preferably 3 to 7 weight-% of at one further non-ionic emulsifier, preferably at least one alkyl mono, oligo or polyglycoside,
(c) 0.01 to 10 weight-%, preferably 0.03 to 1.4 weight-% of at least one anionic emulsifier, preferably of carboxylate type.
(d) 40 to 70 weight % of an oil component having a polarity of at least 20 mN/m or a mixture of oil components wherein at least 75 weight-% of the oils constituting the mixture have a polarity of at least 20mN/m,
(e) 12 to 32 weight % water,
(f) optionally 1 to 5 weight % of at least one consistency regulator,
(g) optionally 1 to 5 weight % humectant,

(h) optionally 0.1 to 5 weight % additives, preferably at least one irritation-soothing agent.

27. Toilet paper according to claim 26, wherein the emulsion comprises (d) a mixture of (d-1) at least one hydrocarbon-based oil such as mineral oil and (d-2) at least one further oil selected from those defined in claim 17.

28. Toilet paper according to claim 27, wherein the further oil (d-2) is a carboxylic acid ester represented by formula (I)

(I)

R^1COO-R^2

wherein R^1CO represents an acyl residue having 6 to 22 carbon atoms and R^2 represents an alkyl residue having 1 to 5 carbon atoms.

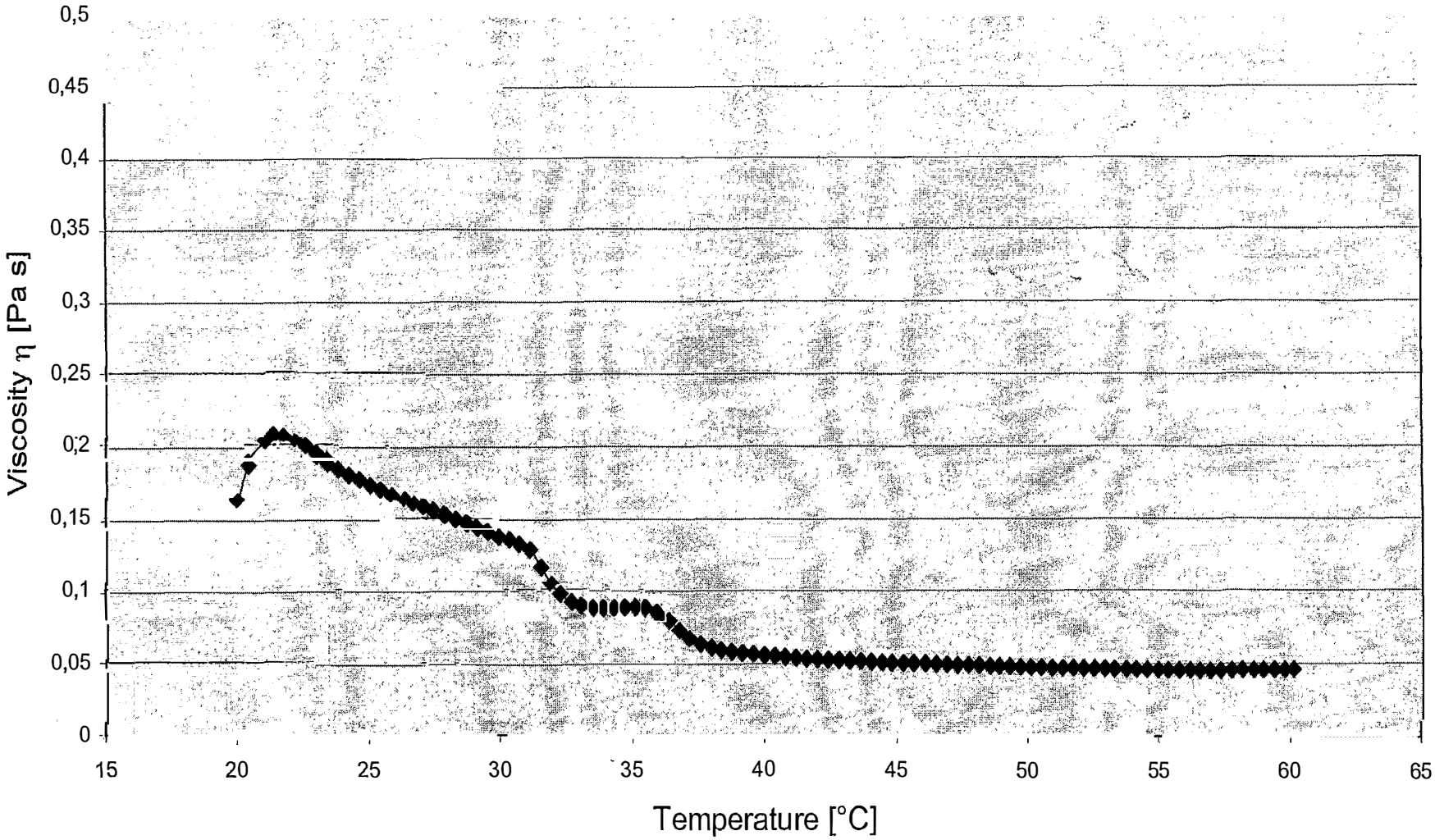
29. Toilet paper according to any of the preceding claims being a multi ply tissue paper.

30. Toilet paper according to claim 29, being a toilet paper having from 2 to 4 plies.

31. Toilet paper according to any of claims 1 to 30, wherein the emulsion is present in amount of 3 to 30 weight-%, based on the weight of the tissue paper.

Figure 1

Viscosity of the lotion of the Example in dependance of the temperature



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/012639

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H21/22 A61L15/34 C11D17/04 C11D1/83 C11D3/20

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)
A61L A47K C11D D21H

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/057547 A (SCA HYGIENE PRODUCTS GMBH) 25 July 2002 (2002-07-25) cited in the application claims 1-13	1-31
A	WO 96/24723 A (KIMBERLY-CLARK CORPORATION) 15 August 1996 (1996-08-15) cited in the application examples 1-6	1-31
A	EP 1 029 977 A (SCA HYGIENE PRODUCTS GMBH) 23 August 2000 (2000-08-23) cited in the application paragraph [0019]; claims 1-26	1-31
A	WO 95/16824 A (THE PROCTER & GAMBLE COMPANY) 22 June 1995 (1995-06-22) examples 1-11	1-31

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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

"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

"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

"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 September 2006	27/09/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Richards, Michael

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/012639

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 94/05856 A (THE PROCTER & GAMBLE COMPANY) 17 March 1994 (1994-03-17) claims 1-12	1-31
A	US 5 935 384 A (TANIGUCHI ET AL) 10 August 1999 (1999-08-10) claims 1-21	1-31
A	FR 2 538 238 A (SCERAB) 29 June 1984 (1984-06-29) claims 1-13	1-31
A	WO 98/24871 A (THE PROCTER & GAMBLE COMPANY) 11 June 1998 (1998-06-11) claims 1-11	1-31

Kimberly Clark EX1002, p. 1028
PGR2026-00078

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2005/012639

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 02057547 A	25-07-2002	AT 280271 T	15-11-2004
		BR 0206567 A	27-01-2004
		CN 1478166 A	25-02-2004
		DE 60201659 D1	25-11-2004
		DE 60201659 T2	27-10-2005
		EP 1225277 A1	24-07-2002
		ES 2232731 T3	01-06-2005
		MX PA03005150 A	22-09-2003
		PL 362306 A1	18-10-2004
WO 9624723 A	15-08-1996	AU 696144 B2	03-09-1998
		AU 4968696 A	27-08-1996
		BR 9607131 A	04-11-1997
		CA 2210338 A1	15-08-1996
		CN 1200781 A	02-12-1998
		DE 69618176 D1	31-01-2002
		DE 69618176 T2	14-08-2002
		EP 0808389 A1	26-11-1997
		HK 1003392 A1	26-04-2002
		JP 2001505257 T	17-04-2001
		PL 327467 A1	07-12-1998
		US 5665426 A	09-09-1997
		US 5650218 A	22-07-1997
		ZA 9600583 A	14-08-1996
EP 1029977 A	23-08-2000	AU 3155500 A	04-09-2000
		WO 0049228 A1	24-08-2000
		JP 2002537499 T	05-11-2002
WO 9516824 A	22-06-1995	AU 1295895 A	03-07-1995
		CA 2177038 A1	22-06-1995
		EP 0734474 A1	02-10-1996
		JP 3786686 B2	14-06-2006
		JP 9506682 T	30-06-1997
		US 5525345 A	11-06-1996
WO 9405856 A	17-03-1994	AT 152793 T	15-05-1997
		AU 679189 B2	26-06-1997
		AU 5011093 A	29-03-1994
		BR 9306990 A	24-12-2002
		CA 2142605 A1	17-03-1994
		DE 69310521 D1	12-06-1997
		DE 69310521 T2	18-09-1997
		DK 656970 T3	03-11-1997
		EP 0656970 A1	14-06-1995
		ES 2104168 T3	01-10-1997
		FI 950862 A	19-04-1995
		GR 3023346 T3	29-08-1997
		JP 8500858 T	30-01-1996
		JP 3217368 B2	09-10-2001
		NZ 255759 A	24-02-1997
		US 5494731 A	27-02-1996
US 5935384 A	10-08-1999	JP 3454997 B2	06-10-2003
		JP 9154764 A	17-06-1997
FR 2538238 A	29-06-1984	NONE	

Kimberly Clark EX1002, p. 1029
PGR2026-00078

INTERNATIONAL SEARCH REPORT

Information on Patent family members

International application No
PCT/EP2005/012639

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9824871 A	11-06-1998	AU 5367098 A	29-06-1998
		BR 9714834 A	26-12-2000
		CA 2273816 A1	11-06-1998
		CN 1244792 A	16-02-2000
		EP 0941062 A2	15-09-1999
		JP 2000506565 T	30-05-2000
		TW 420741 B	01-02-2001
		US 5908707 A	01-06-1999
		ZA 9710657 A	12-06-1998

Kimberly Clark EX1002, p. 1030
PGR2026-00078