(xiv). Draining the pulp having a high content of cellulose on a continuously sliding conveyor for the production of paper coils;

(xv). Continuous pressing with rollers.

Advantageously the described production process of pulp does not involve the use of chlorine or derivates for the bleaching operation, obtaining satisfactory results with important advantages from the environmental point of view and from the disposal costs of the working residues.

The collection product can be a just collected product (green), as well as an already partially macerating product, as well as a product which was previoulsy dryed and successively re-humidified, possibly with addition of anti fermenting agents.

With reference to the collection phase it will be apparent that, depending on how the collection itself occurs, in the collection product also elements other than marine plants and/or algae marine can be present, e.g. sand, other vegetals, etc. To eliminate possibile foreign bodies having larger dimensions is made the following sieving phase is done, for example by means of vibrating screens or sieves, both in a humid condition and in a dry condition. The possibly present sand, instead, will be eliminated by means of washing the collection product itself, preferably after the sieving phase, but it will be apparent that the two phases also could be inverted.

Relatively to the treatment phase of the humid washing product by means of a treatment in an oven this phase is equivalent to a preliminary cooking of the product, but the inventors, during the tests which were carried out have found that this phase can also be omitted if the collection product is already partially macerated before the collection or before its use. The treatment can occur in a range of temperatures between 80°C and 250° and for a time between 10 and 60 minutes, preferably for a time between 15 and 30 minutes. The treatment temperature as well as the treatment time can change depending on to the maceration degree of the product subjected to the treatment as well as on the quantity of the product subjected to the treatment and on the arrangement of the product in the cooking chamber. For example for a product quantity

equal to 3-6 kg of collection product that substantially has not undergone a maceration the treatment can occur at a temperature of 180° - 220° for times on the order of 15-30 minutes, with most short times being preferred in the case in which the product to be treated is spread enough inside the treatment chamber, while most long times will be preferred in the case in which the product to be treated is amassed and concentrate. In a similar way most long times will be necessary for higher quantities of product to be treated. If the product is already partially macerated, then lower treatment times will be sufficient and if the product is at a greater maceration state the treatment can also be omitted.

The scraping phase is needed to increase the etcheable surface of the reactive which is used in the following phases. In the performed tests this operation has been made manually but it can be made automatic, for example by means of a passage in a mill or in cylinders; the increasing of the chemically etcheable surface of the product is obtained by means of the scraping of the product, with a partial defibration/breakage of the fibers.

Referring to the disgregation phase of the fibers by means of boiling in a solution of sodium hydroxide, it will continue until the desired maceration degree is reached. The quantities of sodium hydroxide to be used, as well as the time of the treatment can change depending on the collection product quality. Indicatively, anyway the desired maceration degree can be defined by the end average dimension of the obtained disgregated fibers. Also other disgregating agents can be used provided that they have the characteristic not to excessively disgregate the cellulose fibers. The chemical disgregation can also be coupled to a mechanical disgregation, even if it can be omitted depending on the maturation degree of the collection product and/or on the maceration degree. Referring to the quantity of sodium hydroxide, for example using 99% sodium hydroxide in a solid form, the use is provided of 100-200g of sodium hydroxide for every 4 kg of product to be submitted to disgregation in a quantity of water so as to obtain the superficial covering of the matter to be treated, about 10-20 liters. However it

will be obvious that the solution of sodium hydroxide can also be prepared starting by sodium hydroxide in solution, obtaining concentrations corresponding the indicated ones.

The successive separation phase of the fibers can occur for example by means of filtering.

By means of washing with water, as previously explained, one can act on the pH until the disappearing of the basic pH in favour of a neutral pH with a recovery of the corresponding basic liquid phase which can successively be utilized again in the process.

Referring to the bleaching phase of the fibers it occurs by means of a treatment with a chemical bleaching agent, preferably by means of a heat treatment, preferably with hydrogen peroxide in an aqueous solution. The concentrations of chemical bleaching agent can change depending on the properties of the bleaching agent itself, as well as depending on the desired bleaching degree. For example with regard to hydrogen peroxide, starting from 40 volume hydrogen peroxide, the use is provided of 150-300 ml of 40 volume hydrogen peroxide for every 4 kg of product to be submitted to bleaching in a quantity of water so as to obtain the superficial covering of the matter to be treated, about 10-20 liters. Obviously the hydrogen peroxide can also be supplied starting from starting solutions with different concentrations, e.g. 130 hydrogen peroxide diluted 1/4. In general, therefore, for every 4 kg of product to be submitted to bleaching one can use hydrogen peroxide in a quantity such as to supply concentrations corresponding to the ones which are obtained adding in water 40 volume hydrogen peroxide for every 4 kg of product to be submitted to bleaching in quantities between 150 and 300 ml of 40 volume hydrogen peroxide, in a quantity of water so as to obtain the superficial covering of the matter to be treated, which for 4 kg of product is equal to about 10-20 liters. Preferably the hydrogen peroxide will be gradually added in successive times, modulating its quantity depending on the bleaching state and on the desired end quality. The treatment preferably occurs in hot conditions

at a temperature between 60°C and the boiling-point. The treatment continues for a time between 15-60 minutes depending on the desired quality of the finished product, namely of the color, most long treatment time corresponding to a greater bleaching.

The successive suspension phase in water of the product obtained after the filtering and washing phase of the bleached fibers will preferably occur in a container in which the product which was obtained in the previous phases is placed adding water so as to obtain the superficial covering of the product itself.

The inventors found that the bonding agent addition can occur with good results first or after or during the triturating phase or also both before, after and during the triturating phase. Therefore, in general, the process according to the present invention can comprise a phase of addition of a bonding agent or glue which can occur in a phase (x) successively to the phase (ix) and previously to the phase (xi) and/or simultaneously to phase (xi) and/or in a phase (xii) following the phase (xi). Preferably this addition occurs before the triturating phase to obtain a better amalgamation of the components. Possibly the addiction of the bonding agent can occur successively in the case in which the preparation phase of the pulp is separated by the phase of its effective use for the production of the paper. As a matter of fact the present invention also allows to stop the process after the triturating phase and before the addition of the bonding agent or anyway in other intermediate stages, for example also to allow the delivery or the preservation of the product, which can possibly be filtered and/or addittivated with possible anti – fermenting agents and/or partially dried for its successive use. If the addition of the bonding agent occurs after the triturating phase, also a mixing phase to amalgamate the components will be needed. The bonding agent addition will occur in quantities in the range between 10 and 90 ml for every 4 kg of the product, even more preferably in quantities between 25 and 50 ml for every 4 kg of the product, even more preferably 35 ml for every 4 kg of the product, the bonding agent being preferably vinyl glue. For bonding agents of a different type with respect to the vinyl glue, the preferred

quantities could undergo changing depending on the properties of the bonding agent itself.

Examples will follow showing the process in a greater detail.

Example I

Following the described process Posidonia oceanica marine plants have been collected which have been preliminarily cleaned-up from fibres and undesired materials by means of sieving, e.g. foreign bodies which was possibly present.

Quantities of 4 - 4,5 Kg of sieved Posidonia oceanica marine plants have been taken.

The sieved Posidonia oceanica marine plants have been washed in water and have been left in a suspension condition for 15 minutes in water in order to let the sand decant.

The Posidonia oceanica marine plants have been heated by means of passage in a stove for 15 - 20 minutes in order to improve their workability.

The thus obtained product has been submitted to a scraping treatment in order to increase the etcheable surface of the reactive which is used in the following phases.

The thus obtained product has been boiled with 150g of 99% sodium hydroxide in solid form to in a quantity of water so as to obtain the superficial covering of the product to be treated, about 20-25 litres. The treatment has been continued until a desired disgregation degree was reached, obtaining the disgregation of the fibres. In certain tests a mechanical agitation action has been used obtaining better results and/or shorter times.

The disgregated fibers have been separated by means of filtering with a recovery of the corresponding liquid phase; the corresponding recovered liquid phase can be reutilized for successive treatments by reintegration of sodium hydroxide or it can be disposed after neutralizing the same.

A bleaching operation has been performed by means of heat treatment with 225 ml of 40 volume hydrogen peroxide in a quantity of water so as to obtain the superficial

covering of the matter to be treated, about 20-25 litres. The treatment temperature was 80°C.

Successively one have proceeded with a washing phase of the the mass of bleached fibres with a consequent pH measurement and the washing procedure has been continued until the disappearing of the basic pH in favour of a neutral pH.

A suspension in water of the obtained product has been prepared and one proceeded with a trituration of the fibres in the suspension.

Successively 30-35 ml of a bonding agent have been added, which in the disclosed example was vinylic glue and one proceeded with the mixing of the thus obtained mixture until the same was homogenized.

In this experimental phase the drawing of the obtained pulp having a high content of cellulose occurred following the following steps:

(xiv). Drawing the pulp having a high content of cellulose from the withdrawal basin by means of a screen;

(xv). Applying a rug on the screen;

(xvi). Positioning a first felt on the rug on the opposed side with respect to the side with the pulp having a high content of cellulose;

(xvii). Applying a first rigid support on the first felt, the rigid support having sizes corresponding to the sizes of the screen;

(xviii). 180 degrees overturning of the assembly consisting of first rigid support, first felt, rug, pulp having a high content of cellulose and screen;

(xix). Removing the screen;

(xx). Positioning a second felt on the pulp having a high content of cellulose in correspondence of the opposite side with respect to the side on which the rug was placed;

(xxi). Applying a second rigid support on the second felt, the rigid support having sizes corresponding to the sizes of the screen, forming a sandwich construction;

(xxii). Pressing and exsiccation of the sandwich construction obtained at the previous phase for 6 - 8 hours obtaining a sheet of paper;

(xxiii). Verification of the paper sheet and possible re-humidification with reintroduction in the press and exsiccation;

(xxiv). Removing and drawing the paper sheet.

In particular a certain quantity of fibers and bonding agent solution has been separated by a screen having A4 sheet sizes. On the screen a clean and undamaged rug has been applied in correspodence of the future paper sheet and the rug has been padded in order to let the fibers adhere to the same. A felt was then placed on the rug on the opposed side with respect to the side with the fibres and a plywood rectangle has been applied above the felt. The assembly was then overturned and the rug with the sheet was detached from the net of the screen. Another and another felt rug were then applied on the surface covered by the fibers, encompassing everything with an additional plywood rectangle, therefore obtaining a sandwich construction consisting of: plywood, felt, rug, fibers, rug, felt, plywood. The thus obtained sandwich construction has been placed in a press for 6 - 8 hours. Successively the drying of the sheets has been completed, maintaining the rug in a tensioned condition. Once the drying was completed the sheets have been detached.

With the indicated quantities a hand-crafted sheet of paper was obtained having a weight of about 6 gr., corresponding to a basic weigh of 50g/m2 having a A4 size with Havana yellow coloring.

Example II

Another test was carried out following exactly the same steps of the example I, in the same quantities, but with the addition of the bonding agent before the triturating phase. It has been observed that with this process a better amalgamation of the bonding agent with the triturated fibers is obtained, obtaining a qualitatively better end product.

Example III

Another test was carried out following exactly the same steps of the example I or in an equivalent way of the example II, in the same quantities. In the case in which the sheets, after the drying phase showed pleating, one proceeded with a re-humidification of the sheet itself with an additional successive passage in the press. In the example the additional humidification of the sheet occurred by means of a sponge. After the extraction of the sheet from the press one observed that an effective elimination of the previously present pleating was obtained.

Example IV

Proceeding as in the example I, in the disgregation phase different quantities have been tested of sodium hydroxide obtaining satisfactory results in a range between 100 and 200 gr. for every 4 kg of product, with the best results obtained for values of about 120 gr. of 99% sodium hydroxide in solid form in a water quantity so as to obtain the superficial covering of the matter to be treated, about 10-20 liters.

Example V

Proceeding as in the example I, in the bleaching phase different quantities of 40 volume hydrogen peroxide have been tested obtaining satisfactory results in a range between 150 and 300 gr. for every 4 kg of product, with the best results obtained for values of about 180 gr. of peroxide gr. of 40 volume hydrogen peroxide.

Example VI

Proceeding as in the example I, different quantities of bonding agent have been tested, in particular vinyl glue, obtaining satisfactory results in a range between 10 and 90 ml each 4 kg of triturated product, preferably in quantity included between 25 and 50 ml for every 4 kg of triturated product, with the best results obtained for values of about 35 ml for every 4 kg of triturated product.

Example VII

Proceeding as in the example I, the real content of fanerogame marine has been analyzed in relation with the available collection product, finding that the described method finds an advantageous application in the case in which the collection product

has a fanerogame marine content equal or higher than 75%, the remaining 25 % possibly consisitng of other types of algae or marine plants. Good results were obtained even with a fanerogame marine content equal or higher than 95% in weight of the dry total collection product after sieving.

Example VIII

Proceeding as in the example I, different trituration degrees of the fibers have been tested, observing that the trituration phase must not be excessively prolonged to avoid to have too much small fibers. In general good results have been found with sizes of the fibers corresponding to those obtained in the production process of the paper starting from recycled paper. It will be apparent that depending on the used trituration device and on the introduced quantities the trituration times can be different.

The description of this invention has been made with reference to the enclosed figures showing a preferred embodiment of the invention itself, but it is evident that many possible alterations, modifications and variations will be immediately apparent to those skilled in the art in light of the foregoing description. Thus, it should be understood that the invention is not limited by the foregoing description, but embraces all such alterations, modifications and variations in accordance with the spirit and scope of the appended claims.

Claims

1. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives, comprising the steps of:

(i). Sieving the collection product eliminating possible foreign bodies which are present in the collection product;

(ii). Washing the sieved product by means of water removing possible sand which can be present;

(v). Obtaining disgregated fibers by means of disgregation of the fibers by means of a treatment with a chemical disgregating agent which does not etches the cellulose fibers, possibly combined with a mechanical disgregation treatment;

(vi). Separation of the fibers from the liquid phase by means of filtration recovering the corresponding liquid phase;

(vii). Bleaching the fibers obtained from the previous phase by means of a treatment with a chemical bleaching agent;

(viii). Filtering, washing by means of water and/or pH balancing treatment of the bleached fibers and obtainment of an essentially neutral pH;

(ix). Suspension of the product obtained from the previous phase in water in a container;

(xi). Triturating the suspension obtained from the previous phase obtaining a pulp with a high content of cellulose;

said method being further characterised in that said collection product is a marine plants collection product.

2. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said collection product is a collection product of marine plants preferably with a marine plants content equal or higher to 75 % in weight

of the dry total collection product after sieving, even more preferably with a marine plants content equal or higher to 95 % in weight of the dry total collection product after sieving.

3. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 2 characterised in that said marine plants are fanerogame marine.

4. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 2 characterised in that said marine plants are selected from the group consisting of Zostera, Posidonia, Cymodocea, Syringonium, Thalassia, Halophila, Thalassodendron.

5. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 2 characterised in that said marine plants are selected from the group consisting of Cymodocea nodosa, Cymodocea rotundata, Cymodocea serrulata, Syringonium filiforme, Syringonium isoetifolium, Halophila beccarii, Halophila decipiens, Halophila minor, Halophila ovalis, Zostera marina, Zostera noltii, Posidonia oceanica, Posidonia australis, Posidonia sinuosa, Thalassia hemprichii, Thalassia testudinum.

6. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 5 characterised in that it includes a further phase (iii) following to the phase (ii), said phase (iii) providing a treatment of the washed product at a temperature between 80°C and 250° and for a time between 10 and 60 minutes, preferably for a time between 15 and 30 minutes, even more preferably at a temperature between 180° - 220° for a time between 15 and 30 minutes, the time and the temperature being selected depending on the maceration degree of the collection

product.

7. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 6 characterised in that it includes a further phase (iv) prior to the phase (v), said phase (iv) being a scraping phase providing a scraping treatment of the product..

8. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said scraping phase occurs by means of a passage of the product in a mill or in cylinders.

9. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 8 characterised in that said disgregation phase (v) of the fibres by means of said treatment with said disgregating chemical agent occurs by means of a boiling treatment in aqueous solution of sodium hydroxide.

10. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said disgregation phase (v) of the fibers by means of said treatment with said disgregating chemical agent occurs by means of a boiling treatment in aqueous solution of sodium hydroxide in concentrations corresponding to those obtained dissolving 99% sodium hydroxide in solid form in quantities between 100g and 200g of sodium hydroxide for every 4 kg of product to be submitted to disgregation in a water quantity so as to obtain the superficial covering of the matter to be treated.

11. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 10 characterised in that said phase (vii) relative to the bleaching of the fibers occurs by means of treatment with hydrogen peroxide in an

aqueous solution preferably in hot conditions at a temperature between 60°C and the boiling-point.

12. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said treatment with hydrogen peroxide in an aqueous solution occurs with hydrogen peroxide in an aqueous solution in concentrations corresponding to those obtained adding in water 40 volume hydrogen peroxide for every 4 kg of product to be submitted to bleaching in quantities between 150 and 300 ml of 40 volume hydrogen peroxide, in a water quantity so as to obtain the superficial covering of the matter to be treated.

13. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said treatment with hydrogen peroxide is continued for a time between 15 and 60 minutes depending on the end bleaching degree.

14. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 13 characterised in that it includes a further phase of bonding agent addition, said bonding agent addition phase being able to occur in a further phase (x) after the phase (ix) and before the phase (xi) and/or simultaneously with respect to the phase (xi) and/or in a further phase (xii) after the phase (xi).

15. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said bonding agent is added in quantities between 10 and 90 ml for every 4 kg of product, preferably in quantities between 25 and 50 ml for every 4 kg of product, even more preferably 35 ml for every 4 kg of product.

16. Method to obtain pulp having a high content of cellulose for the use in a process of

production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 14 to 15 characterised in that said bonding agent is vinyl glue.

17. Pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives characterised in that said pulp having a high content of cellulose is obtained by means of a method to obtain pulp having a high content of cellulose according to any of the previous claims 1 to 16.

18. Paper, paperboard, cardboard, substitutes and derivatives obtained by pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives characterized in that at least 50 % of said pulp having a high content of cellulose is obtained by means of a method to obtain pulp having a high content of cellulose according to any of the previous claims from 1 to 16.

19. Paper, paperboard, cardboard, substitutes and derivatives obtained by pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives characterized in that 100 % of said pulp having a high content of cellulose is obtained by means of a method to obtain pulp having a high content of cellulose according to any of the previous claims from 1 to 16.

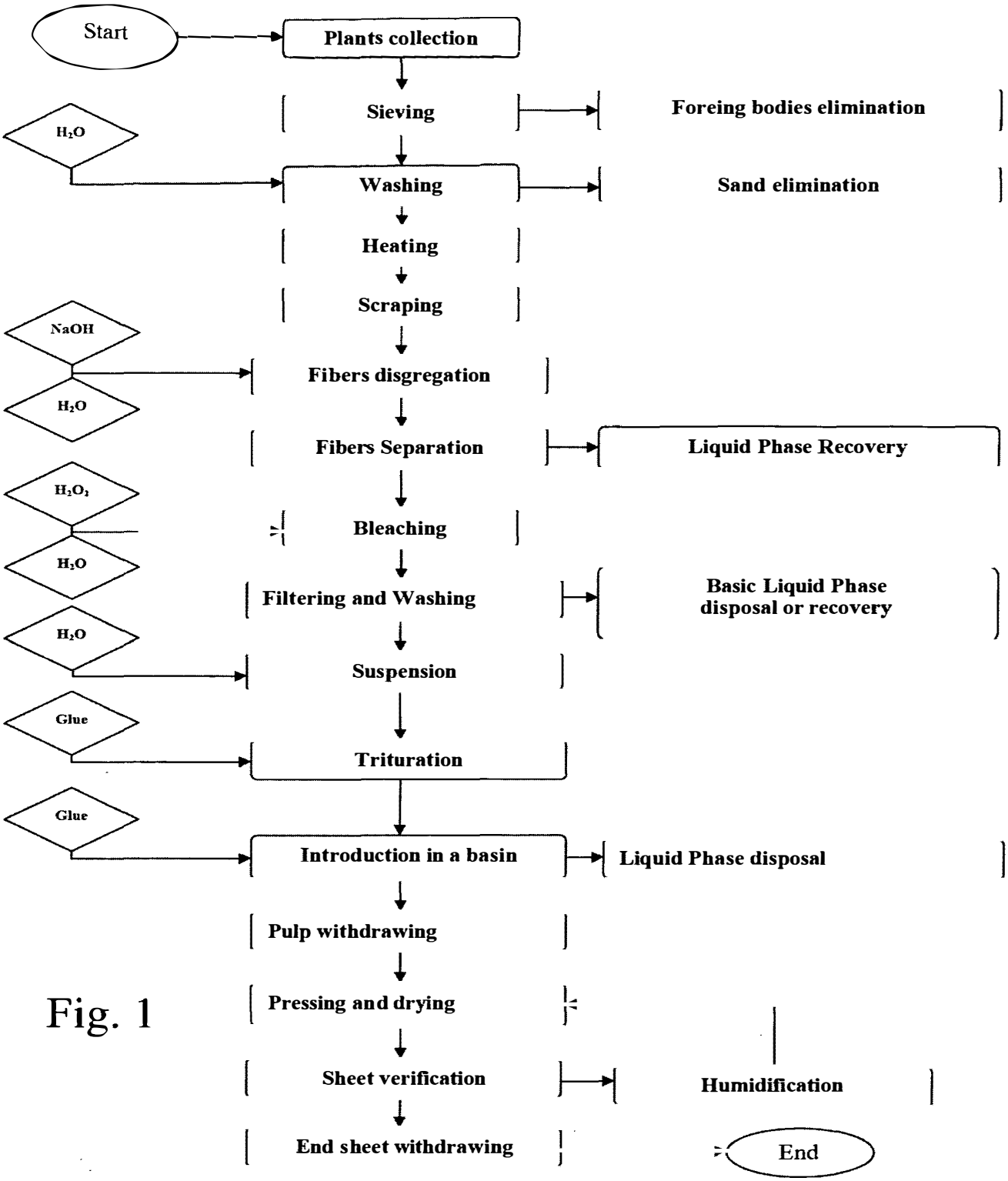

Start
Plants collection
Sieving
Foreing bodies elimination
H₂O
Washing
Sand elimination
Heating
Scraping
NaOH
Fibers disgregation
H₂O
Fibers Separation
Liquid Phase Recovery
H₂O₂
Bleaching
H₂O
Filtering and Washing
Basic Liquid Phase disposal or recovery
H₂O
Suspension
Glue
Trituration
Glue
Introduction in a basin
Liquid Phase disposal
Pulp withdrawing
Pressing and drying
Sheet verification
Humidification
End sheet withdrawing
End

Fig. 1

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International application No
PCT/EP2010/004390

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

Minimum documentation searched (classification system followed by classification symbols)
D21C D21B

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. |
|---|---|---|
| X | US 5 500 086 A (SAKAI MASAYASU [JP] ET AL) 19 March 1996 (1996-03-19) column 3, line 5 - column 4, line 21; claims 1, 3 | 1 |
| X | WO 94/04745 A1 (INT TECH MANAGEMENT ASS [US]) 3 March 1994 (1994-03-03) page 2, line 3 - page 3, line 11 page 6, line 23 - page 9, line 37 | 1 |

☐ 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

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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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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Lanniel, Geneviève |

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP2010/004390

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 5500086 A | 19-03-1996 | NONE | |
| WO 9404745 A1 | 03-03-1994 | AU 5005993 A | 15-03-1994 |



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

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

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(54) **Title**: HIGHLY DURABLE TOWEL COMPRISING NON-WOOD FIBERS

(57) **Abstract**: The present invention relates to tissue products comprising high yield hesperaloe fiber having improved wet performance, such as improved absorbency, CD Wet/Dry Ratio and CD Wet Durability. The addition of high yield hesperaloe pulp fibers surprisingly improves the CD Wet/Dry ratio without negatively affecting the absorbency of the tissue product. For example, tissue products of the present invention generally have an Absorbent Capacity greater than about 6.0 g/g, such as from about 8.0 to 8.0 g/g. As such the tissue products are durable when wet, but are still sufficiently absorbent. This balance of absorbency and wet strength is not found in the prior art without resorting to adding latex binders or the like to the tissue product.

# HIGHLY DURABLE TOWEL COMPRISING NON-WOOD FIBERS

## BACKGROUND OF THE DISCLOSURE

In the development and manufacture of paper products, particularly paper towels for the consumer market, it is a continual objective to improve the absorbent characteristics of the product. For cleaning up some spills, the consumer needs high absorbent capacity. For some uses, consumers want a fast rate of absorbency. For other uses, a combination of high absorbent capacity and fast absorbent rate is desired. At the same time, constraints on achieving this objective include the need to maintain or reduce costs in order to provide the consumer with the highest possible value, which in part means minimizing the amount of fiber in the product.

## SUMMARY OF THE DISCLOSURE

The present inventors have successfully used hesperaloe fibers to produce a tissue that is highly absorbent while also being durable when wet. As such the tissue products of the present invention may have an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry ratio greater than about 0.30. The desirable absorbency and wet durability are achieved by forming a tissue product from wood and non-wood fibers and more specifically high yield hesperaloe pulp fibers. In achieving these properties the inventors have overcome the negative to other important properties, such as bulk and stiffness, typically associated with substituting conventional wood papermaking fibers with non-wood fibers. 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 Northern softwood kraft (NSWK) fibers.

Accordingly, in certain embodiments, the invention provides tissue products in which hesperaloe fibers replace at least about 50 percent of the NSWK, more preferably at least about 75 percent and still more preferably all NSWK while maintaining or improving absorbency and without negatively effecting stiffness and bulk.

In other embodiments the present invention provides tissue products comprising a multi-layered tissue web where one or more of the layers comprise a blend of hesperaloe fibers and softwood kraft fibers, wherein the softwood kraft fibers comprise less than about 10 weight percent of the tissue product.

In still other embodiments the present invention provides a tissue product comprising greater than about 20 weight percent high yield hesperaloe fiber, the tissue product having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.



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In yet other embodiments the present invention provides single-ply through-air dried tissue product comprising at least about 20 weight percent high yield hesperaloe pulp fibers, the tissue product having a basis weight from about 30 to about 60 gsm, a GMT from about 1500 to about 2500 g/3" and an Absorbent Capacity greater than about 7.0 g/g.

In other embodiments the present invention provides tissue product comprising at least one multi-layered through-air dried tissue web comprising a first and a second layer, the first layer being substantially free from high yield hesperaloe pulp fibers and the second layer consisting essentially of high yield hesperaloe pulp fibers, the tissue product having a Wet CD Durability from about 1.75 to about 2.0 and a Stiffness Index less than about 6.0.

## 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.



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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 10 cc/g, more preferably greater than about 11 cc/g and still more preferably greater than about 12 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 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. GM Slope generally is expressed in units of kg.

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. While the GMT may vary tissue products prepared according to the present disclosure generally have a GMT greater than about 1,400 g/3", such as from about 1,400 to about 2,500 g/3".

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 (typically having units of kg), divided by the geometric mean tensile strength (typically having units of grams per three inches).

$$Stiffness\ Index = \frac{\sqrt{MD\ Tensile\ Slope\ (kg) x\ CD\ Tensile\ Slope(kg)}}{GMT\ (g/3")} \cdot x\ 1{,}000$$

While the Stiffness Index may vary tissue products prepared according to the present disclosure generally have a Stiffness Index less than about 8.0 and more preferably less than about 6.0.

As used herein, the term "Absorbent Capacity" is a measure of the amount of water absorbed by the paper towel product in the vertical orientation and is expressed as grams of water absorbed per gram of fiber (dry weight). Absorbent Capacity is measured as described in the Test Methods section and generally has units of grams per gram (g/g). While the Absorbent Capacity may vary tissue products prepared according to the present disclosure generally have an Absorbent Capacity greater than about 6.0 g/g and more preferably greater than about 7.0 g/g.

As used herein the term "CD Wet/Dry Ratio," refers to the ratio of the wet CD tensile strength to the dry CD tensile strength, measured as described in the Test Methods Section, below. While the

CD Wet/Dry Ratio may vary, tissue products prepared as described herein generally have a CD Wet/Dry Ratio greater than about 0.28 and more preferably greater than about 0.30, such as from about 0.28 to about 0.32. Generally the foregoing ratios are achieved at Wet CD Tensile greater than about 400 g/3", more preferably greater than about 425 g/3" and still more preferably greater than about 450 g/3".

As used herein the term "Wet CD Durability," refers to the CD Wet Stretch multiplied by 100, divided by the CD Wet Tensile (having units of g/3") and is a measurement of the wet CD extensibility of a product at a given wet tensile strength. At CD Wet Tensile strengths greater than about 400 g/3" the inventive tissue products of the present invention generally have Wet CD Durability greater than about 1.75 and more preferably greater than about 2.0.

As used herein the term "Wet Strength Efficiency," refers to the CD Wet/Dry Ratio divided by the add-on amount of wet strength resin (measured in kilograms per dry metric ton of fiber) multiplied by 100 and is a measure of the amount of wet strength generated relative to dry strength normalized by the amount of wet strength added.

## DETAILED DESCRIPTION OF THE DISLOSURE

Generally, the present invention provides tissue product having a CD Wet/Dry ratio that meets or exceeds satisfactory levels without the excess use of a wet strength resin. The satisfactory level of CD Wet/Dry ratio is generally greater than about 0.30. The satisfactory level of CD Wet/Dry ratio is surprisingly achieved by forming a tissue product from wood and non-wood fibers and more specifically high yield hesperaloe pulp fibers. Generally CD Wet/Dry ratios may be achieved with the addition of at least about 5 percent, by weight of the tissue product, such as from about 5 to about 50 percent and more preferably from about 15 to about 45 percent high yield hesperaloe pulp fibers.

The addition of high yield hesperaloe pulp fibers surprisingly improves the CD Wet/Dry ratio without negatively affecting the absorbency of the tissue product. For example, tissue products of the present invention generally have an Absorbent Capacity greater than about 6.0 g/g, such as from about 6.0 to 8.0 g/g. As such the tissue products are durable when wet, but are still sufficiently absorbent. This balance of absorbency and wet strength is not found in the prior art without resorting to adding latex binders or the like to the tissue product.

Further, the aforementioned wet-strength properties may be achieved with only modest additions of conventional wet-strength resin. For example, in certain embodiments the tissue products comprise less than about 15 kg of wet-strength resin per metric ton of furnish, such as from about 3 to about 15 kg, and more preferably from about 3 to about 10 kg. Rather than employ an excessive

amount of wet-strength resin, the improved wet-strength properties are achieved by the addition of high yield hesperaloe pulp fibers during the manufacture of the tissue product, such as from about 5 to about 50 percent, by weight of the product, and more preferably from about 20 to about 40 percent, by weight.

Accordingly, in certain embodiments the tissue products generally comprise high yield hesperaloe pulp fibers derived from non-woody plants in the genus Hesperaloe in the family Agavaceae. Suitable species within the genus Hesperaloe 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 process 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.



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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 amount of SSWK, by weight of the tissue product, is less than about 10 percent and more preferably less than about 5 percent.

In addition to the use of high yield hesperaloe pulp fiber the tissue products of the present invention are preferably prepared without the addition of binders, particularly latex binders and more specifically carboxyl-functional latex emulsion polymers, such as those described in US Patent Nos. 6,187,140 and 7,462,258. Latex binders, such as those disclosed in the foregoing references, have been used previously in the manufacture of tissue products to improve wet performance. These binders, however, add manufacturing complexity and cost. Therefore, it is desirable to produce a tissue product, such as the inventive tissues, without the use of binders and more specifically latex binders.

Further, tissues prepared according to the present disclosure are not treated with a sizing agent, such as alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA), either during the tissue manufacturing process or after formation and drying of the tissue web. Rather, the tissue webs are prepared by adding hesperaloe fibers and in certain embodiments a wet strength resin, to the papermaking furnish prior to formation of the web, to enhance the wet-strength properties of the finished web. Unlike conventional sizing agents, which reduce the adsorption rate of water into the sheet, hesperaloe fibers and conventional wet-strength resins allow the sheet to adsorb water as intended during the end use but maintain sheet integrity and strength when wetted.

Rather than employ latex binders or sizing agents, the tissue products typically comprise a conventional wet-strength resin. Useful conventional wet strength resins include diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), epichlorhydrin resin(s), polyamide-epichlorohydrin (PAE), or any combinations thereof, or any resins to be considered in these families of resins. Particularly preferred wet strength resins are polyamide-epichlorohydrin (PAE) resins. Commonly PAE resins are formed by first reacting a polyalkylene polyamine and an aliphatic dicarboxylic acid or dicarboxylic acid derivative. A polyaminoamide made from diethylenetriamine and adipic acid or esters of dicarboxylic acid derivatives is most common. The resulting polyaminoamide is

then reacted with epichlorohydrin. Useful PAE resins are sold under the tradename Kymene® (commercially available from Ashland, Inc., Covington, KY).

Generally the conventional wet-strength resin is added to the fiber furnish prior to formation of the tissue web. The amount of the wet-strength resin can be less than about 10 kg per ton of furnish, more preferably less than about 8 kg per ton of furnish and still more preferably less than about 5 kg per ton of furnish. Generally the add-on level of wet-strength resin will be from about 1 to about 10 kg per ton of furnish and more preferably from about 3 to about 8 kg per ton of furnish and still more preferably from about 3 to about 5 kg per ton of furnish.

Although such low add on levels of wet strength are generally not considered to be suitable for achieving exceptional wet performance, such as a CD Wet/Dry Ratio greater than about 0.30, it has now been discovered that the use of high yield hesperaloe pulp fibers yields tissue products having a CD Wet/Dry Ratio greater than about 0.30 and in certain embodiments greater than about 0.32, such as from about 0.30 to about 0.35. The combination of conventional wet strength resin, such as PAE resins, and hesperaloe fiber have a synergistic effect. Accordingly, when the CD Wet/Dry Ratio and Wet CD Durability are concerned, the combination of wet-strength resin addition and hesperaloe fiber according to the invention provides a synergistic effect which has not been disclosed previously. This synergistic effect is valuable, since it makes it possible to achieve a higher wet-strength level without the excessive use of wet-strength resin.

Table 1 illustrates the desirable increase in wet-strength properties that can be achieved via the combination of high yield hesperaloe fiber (HYH) and a conventional wet-strength resin. The samples have a basis weight of about 36 gsm and comprised a single through-air dried ply. The samples comprised either a blend of NSWK (40 wt%) and EHWK (60 wt%) or HYH (40 wt%) and EHWK (60 wt%). As the table illustrates, at a constant level of wet-strength addition, a higher wet/dry tensile level can be achieved via the addition of HYH.

TABLE 1

| HYH (wt%) | Wet Strength (kg/MT) | CD Wet/Dry Ratio | Delta CD Wet/Dry Ratio (%) | Wet Strength Efficiency |
|---|---|---|---|---|
| - | 9 | 0.22 | - | 2.4 |
| 40 | 9 | 0.3 | 36 | 3.3 |
| - | 14 | 0.24 | - | 1.7 |
| 40 | 14 | 0.31 | 29 | 2.2 |

The improvement in wet tensile properties is further evident when the inventive tissue products are compared to commercially available tissue products. As illustrated in the table below, the inventive tissue products display both wet durability, such as a CD Wet/Dry Ratio greater than about 0.30 and



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good absorbency, such as an Absorbent Capacity greater than about 6.0 g/g and more preferably greater than about 7.0 g/g, such as from about 6.0 to about 7.5 g/g. In certain aspects the inventive tissue products also have improved Wet CD Durability relative to commercially available tissue products, such as a Wet CD Durability greater than about 1.5 and more preferably greater than about 1.75, such as from about 1.5 to about 2.0.

TABLE 2

| Product | Plies | Wet CD Tensile (g/3") | Wet CD Stretch (%) | CD Wet/Dry Ratio | Wet CD Durability | Absorbent Capacity (g/g) |
|---|---|---|---|---|---|---|
| Invention | 1 | 418 | 8.2 | 0.32 | 1.96 | 7.1 |
| Scott | 1 | 855 | 7.5 | 0.34 | 0.88 | 5.5 |
| Scott Naturals | 1 | 811 | 11.3 | 0.33 | 1.39 | 4.7 |
| Viva Vantage | 1 | 969 | 8.2 | 0.34 | 0.85 | 3.9 |
| Bounty Basic | 1 | 1040 | 7.2 | 0.47 | 0.69 | 4.9 |

Accordingly, in one embodiment tissue products comprise at least one multi-layered tissue web, the tissue product having a CD Wet/Dry Ratio greater than about 0.30 an Absorbent Capacity greater than about 6.0 g/g and still more preferably greater than about 6.5 g/g. Preferably the web comprises two layers, and more preferably three layers, wherein the hesperaloe fiber is selectively disposed in only one of the layers and the other layers are substantially free from hesperaloe fiber. In other embodiments, the web comprises two outer layers and a middle layer, where the hesperaloe fiber is selectively disposed in the middle layer. While in one embodiment it is preferred that the tissue web comprise a three-layered tissue having hesperaloe fiber selectively incorporated into the middle layer, it should be understood that tissue products made from the foregoing multi-layered web can include any number of plies and the plies may be made from various combinations of single- and multi-layered tissue webs. Further, tissue webs prepared according to the present invention 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.

As noted previously, the instant tissue products have a high degree of absorbent capacity such as an Absorbent Capacity greater than about 6.0 g/g, such as from about 6.0 to about 7.0 g/g and more preferably from about 6.5 to about 7.0 g/g, while also having a CD Wet/Dry Ratio greater than about 0.30, such as from about 0.30 to about 0.40. Generally the foregoing absorbent capacities and wet strengths are achieved at basis weights from about 30 to about 60 grams per square meter (gsm) and more preferably from about 35 to about 50 gsm and still more preferably from about 40 to about 50 gsm.

In addition to having satisfactory absorbent properties, the tissue products generally have improved wet CD performance. For example, in certain embodiments the tissue products have a Wet CD Durability greater than about 1.75, such as from about 1.75 to about 2.5 and more preferably from about 2.0 to about 2.5. At the foregoing Wet CD Durability levels the tissue products may have a Wet CD Stretch greater than about 8.0 percent, such as from about 8.0 percent to about 10.0 percent and more preferably from about 9.0 to about 10.0 percent.

While having improved properties, the tissue products prepared according to the present disclosure continue to be strong enough to withstand use by a consumer. For example, inventive tissue products generally have a geometric mean tensile (GMT) greater than about 1200 g/3", such as from about 1200 to about 3000 g/3", more preferably from about 1200 to about 2500 g/3" and still more preferably from about 1600 to about 2400 g/3".

Not only are the instant tissue products absorbent and strong enough to withstand use, they are generally flexible and have good hand feel. As such the tissue products may have a GM Slope less than about 10.0 kg, such as from about 4.0 to about 10.0 kg and more preferably from about 4.0 to about 8.0 kg. The foregoing GM Slopes are generally achieved at relatively modest GMT, such as from about 1200 to about 2500 g/3", and more preferably from about 1200 to about 2200 g/3". At these GM Slopes and GMT, the tissue products may have a Stiffness Index less than about 8.0, such as from about 4.0 to about 8.0 and more preferably from about 4.0 to about 6.0.

In one particularly preferred embodiment the inventive tissue product comprises a single-ply, multi-layered, through-air-dried web, wherein a first layer comprises wood pulp fibers and a second layer comprises high yield hesperaloe pulp fibers, the first layer being substantially free of hesperaloe fibers and the product comprising from about 20 to about 50 percent, by weight, hesperaloe fibers. The foregoing tissue product generally has a CD Wet/Dry Ratio greater than about 0.30 an Absorbent Capacity greater than about 6.0, while having a Stiffness Index less than about 6.0, such as from about 4.0 to about 6.0.

Webs useful in preparing tissue products according to the present disclosure can vary depending upon the particular application. In general, in addition to hesperaloe fibers, the webs can be made from any suitable type of fiber. For instance, the base web can be made from cellulosic fibers, and more preferably cellulosic pulp fibers. Suitable cellulosic fibers for use in connection with this invention include secondary (recycled) papermaking fibers and virgin papermaking fibers in all proportions. Such fibers include, without limitation, hardwood and softwood fibers.

Tissue webs made in accordance with the present disclosure can be made with a homogeneous fiber furnish or can be formed from a stratified fiber furnish producing layers within the

single- or multi-ply product. Stratified base webs can be formed using equipment known in the art, such as a multi-layered headbox. Both strength and softness of the base web can be adjusted as desired through layered tissues, such as those produced from stratified headboxes.

When constructing a web from a stratified fiber furnish, the relative weight of each layer can vary depending upon the particular application. For example, in one embodiment, when constructing a web containing three layers, each layer can be from about 15 to about 40 percent of the total weight of the web, such as from about 25 to about 35 percent of the weight of the web. Generally the hesperaloe fibers will comprise from about 5 to about 50 percent, by weight, of the web.

The tissue products 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.

In a particularly preferred 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.

In one embodiment the web is formed using a twin wire former having a papermaking headbox that injects or deposits a furnish of an aqueous suspension of papermaking fibers onto a plurality of forming fabrics, such as the outer forming fabric and the inner forming fabric, thereby forming a wet tissue web. 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 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 greater than 20 percent, more specifically between about 20 to about 40 percent, and more specifically between 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 30 to about 70 percent and more preferably from about 40 to about 60 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. Such molding to the contours of the surface of the transfer fabric 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 through-air drying fabric. Typically, the transfer fabric travels at approximately the same speed as the through-air drying fabric.

However, a second rush transfer may be performed as the web is transferred from the transfer fabric to the through-air drying fabric. This rush transfer is referred to as occurring at the second position and is achieved by operating the through-air drying fabric at a slower speed than the transfer fabric.

In addition to rush transferring the wet tissue web from the transfer fabric to the through-air drying fabric, the wet tissue web may be macroscopically rearranged to conform to the surface of the through-air drying fabric with the aid of a vacuum transfer roll or a vacuum transfer shoe. If desired, the through-air drying fabric can be run at a speed slower than the speed of the transfer fabric 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 to the topography of the through-air drying fabric.

While supported by a through-air drying fabric, the wet tissue web is dried to a final consistency of about 94 percent or greater by a through-air dryer. The web then passes through the winding nip between the reel drum and the reel and is wound into a roll of tissue for subsequent converting.

## TEST METHODS

Wet and Dry Tensile

Samples for tensile strength testing are prepared by cutting a 3 inches (76.2 mm) by 5 inches (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 4 ± 0.04 inches. The jaws are operated using pneumatic-action and are rubber coated. The minimum grip face width is 3 inches (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.

Wet tensile strength measurements are measured in the same manner, but after the center portion of the previously conditioned sample strip has been saturated with distilled water immediately prior to loading the specimen into the tensile test equipment. More specifically, prior to performing a wet CD tensile test, the sample must be aged to ensure the wet strength resin has cured. Two types of aging were practiced: natural and artificial. Natural aging was used for older samples that had already aged. Artificial aging was used for samples that were to be tested immediately after or within days of manufacture. For natural aging, the samples were held at 73°F, 50 percent relative humidity for a period of 12 days prior to testing. Following this natural aging step, the strips are then wetted individually and tested. For artificially aged samples, the 3-inch wide sample strips were heated for 4 minutes at 105 ± 2°C. Following this artificial aging step, the strips are then wetted individually and tested. Sample wetting is performed by first laying a single test strip onto a piece of blotter paper (Fiber Mark, Reliance Basis 120). A pad is then used to wet the sample strip prior to testing. The pad is a green, Scotch-Brite brand (3M) general purpose commercial scrubbing pad. To prepare the pad for testing, a full-size pad is cut approximately 2.5 inches long by 4 inches wide. A piece of masking tape is wrapped around one of the 4-inch long edges. The taped side then becomes the "top" edge of the wetting pad. To wet a tensile strip, the tester holds the top edge of the pad and dips the bottom edge in approximately 0.25 inches of distilled water located in a wetting pan. After the end of the pad has been saturated with water, the pad is then taken from the wetting pan and the excess water is removed from the pad by lightly tapping the wet edge three times across a wire mesh screen. The wet edge of the pad is then gently placed across the sample, parallel to the width of the sample, in the approximate center of the sample strip. The pad is held in place for approximately one second and then removed and placed back into the wetting pan. The wet sample is then immediately inserted into the tensile grips so the wetted area is approximately centered between the upper and lower grips. The test strip should be centered both horizontally and vertically between the grips. (It should be noted that if any of the wetted portion comes into contact with the grip faces, the specimen must be discarded and the jaws dried off before resuming testing.) The tensile test is then performed and the peak load recorded as the CD wet tensile strength of this specimen. As with the dry CD tensile test, the characterization of a product is determined by the average of at least six, but in the case of the examples disclosed, twenty representative sample measurements.



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Absorbency

As used herein, "vertical absorbent capacity" is a measure of the amount of water absorbed by a paper product (single-ply or multi-ply) or a sheet, expressed as grams of water absorbed per gram of fiber (dry weight). In particular, the vertical absorbent capacity is determined by cutting a sheet of the product to be tested (which may contain one or more plies) into a square measuring 100 millimeters by 100 millimeters (± 1 mm.) The resulting test specimen is weighed to the nearest 0.01 gram and the value is recorded as the "dry weight." The specimen is attached to a 3-point clamping device and hung from one corner in a 3-point clamping device such that the opposite corner is lower than the rest of the specimen, then the sample and the clamp are placed into a dish of water and soaked in the water for 3 minutes (± 5 seconds). The water should be distilled or de-ionized water at a temperature of 23 ± 3°C. At the end of the soaking time, the specimen and the clamp are removed from the water. The clamping device should be such that the clamp area and pressure have minimal effect on the test result. Specifically, the clamp area should be only large enough to hold the sample and the pressure should also just be sufficient for holding the sample, while minimizing the amount of water removed from the sample during clamping. The sample specimen is allowed to drain for 3 minutes (± 5 seconds). At the end of the draining time, the specimen is removed by holding a weighing dish under the specimen and releasing it from the clamping device. The wet specimen is then weighed to the nearest 0.01 gram and the value recorded as the "wet weight". The vertical absorbent capacity in grams per gram = [(wet weight - dry weight)/dry weight]. At least five (5) replicate measurements are made on representative samples from the same roll or box of product to yield an average vertical absorbent capacity value.

## EXAMPLE

Base sheets were made using a through-air dried papermaking process commonly referred to as "uncreped through-air dried" ("UCTAD") and generally described in US Patent No. 5,607,551, the contents of which are incorporated herein in a manner consistent with the present invention. Inventive base sheets were produced from a furnish comprising northern softwood kraft (NSWK), eucalyptus kraft (EHWK) and high yield hesperaloe fiber (HYH) using a layered headbox fed by three stock chests such that the webs having three layers (two outer layers and a middle layer) were formed. The outer layers comprised 100 percent EHWK for both the control and inventive samples. The center layer was 100 percent NSWK for the control sample; for the inventive sample, the center layer was 100 percent HYH. The layer splits, by weight of the web, are detailed in Table 3, below.

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



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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 tissue web was formed on a Voith Fabrics TissueForm V forming fabric, vacuum dewatered to approximately 25 percent consistency and then subjected to rush transfer when transferred to the transfer fabric. The layer splits, by weight of the web, are detailed in Table 4, below. The transfer fabric was the fabric described as t1207-11 (commercially available from Voith Fabrics, Appleton, WI). The web was then transferred to a through-air drying fabric. Transfer to the through-drying fabric was done using vacuum levels of greater than 10 inches of mercury at the transfer. The web was then dried to approximately 98 percent solids before winding.

TABLE 3

| Sample | Layer Split (Air/Middle/Fabric wt%) | HYH (wt%) | Wet Strength (kg/MT) |
|---|---|---|---|
| Control | 30/40/30 | - | 8 |
| Inventive 1 | 30/40/30 | 40 | 8 |

The base sheet webs were converted into rolled towel products by calendering using a conventional polyurethane/steel calender comprising a 4 P&J polyurethane roll on the air side of the sheet and a standard steel roll on the fabric side. The finished product comprised a single ply of base sheet. The finished products were subjected to physical testing, the results of which are summarized in Table 4.

TABLE 4

| | Control 1 | Inventive 1 |
|---|---|---|
| BW (gsm) | 39.3 | 39.0 |
| Wet CDT (g/3") | 515 | 418 |
| Wet CDS (%) | 10.7 | 8.2 |
| Wet CD Durability | 2.08 | 1.96 |
| CD Wet/Dry | 0.31 | 0.31 |
| Absorbent Capacity (g/g) | 6.2 | 7.1 |
| Wet Strength Efficiency | 3.89 | 3.89 |
| Dry GMT (g/3") | 2217 | 1821 |
| Dry CDT (g/3") | 1655 | 1340 |
| Dry GM Slope (kg) | 7.2 | 7.7 |
| Stiffness Index | 3.25 | 4.23 |

The foregoing is one example of an inventive tissue product prepared according to the present disclosure. In a first embodiment the invention provides a tissue product comprising greater than about

20 weight percent high yield hesperaloe fiber having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.

In a second embodiment the invention provides the tissue product of the first embodiment having a Wet CD Durability of greater than about 1.75.

In a third embodiment the invention provides the tissue product of the first embodiment having an Absorbent Capacity from about 7.0 to about 7.5 g/g, a CD Wet/Dry Ratio from about 0.30 to about 0.35.

In a third embodiment the present invention provides the tissue product of the first or the second embodiments having a GMT from about 1200 to about 2600 g/3".

In a fourth embodiment the present invention provides the tissue product of any one of the first through the third embodiments having a Stiffness Index from about 4.0 to about 6.0.

In a fifth embodiment the present invention provides the tissue product of any one of the first through the fourth embodiments having a basis weight from about 34 to about 60 gsm.

In a sixth embodiment the present invention provides the tissue product of any one of the first through the fifth embodiments having wet CD stretch greater than about 8 percent, such as from about 8 to about 10 percent.

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 comprises a single-ply multi-layered web having a first, a second and a third layer.

In an eighth embodiment the present invention provides the tissue product of any one of the first through the seventh embodiments wherein the tissue product comprises from about 20 to about 50 weight percent high yield hesperaloe fiber.

In a ninth embodiment the present invention provides the tissue product of any one of the first through the eighth embodiments wherein the tissue product comprises at least one through-air dried tissue web.

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 comprises at least one multi-layered through-air dried tissue web.

In still other embodiments the disclosure provides a tissue product of any one of the foregoing embodiments wherein the tissue product comprises at least one multi-layered through-air dried tissue web comprising a first fibrous layer and a second fibrous layer, the first fibrous layer comprising wood

pulp fibers and the second fibrous layer consisting essentially of high yield hesperaloe fibers and wherein the hesperaloe fibers comprise from about 20 to about 40 weight percent of the through-air dried web.



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**WHAT IS CLAIMED IS:**

1. A tissue product comprising greater than about 20 weight percent high yield hesperaloe fiber having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.

2. The tissue product of claim 1 having a Wet CD Durability of greater than about 1.75.

3. The tissue product of claim 1 having a GMT from about 1500 to about 3000 g/3".

4. The tissue product of claim 1 having a Stiffness Index from about 4.0 to about 6.0.

5. The tissue product of claim 1 having a basis weight from about 30 to about 60 gsm.

6. The tissue product of claim 1 having a wet CD stretch greater than about 8.0 percent.

7. The tissue product of claim 1 wherein the tissue product comprises a single-ply multi-layered web having a first layer comprising conventional wood pulp fibers and a second layer consisting essentially of high yield hesperaloe pulp fiber.

8. The tissue product of claim 1 wherein the tissue product comprises at least one through-air dried tissue web.

9. A tissue product comprising at least one multi-layered through-air dried tissue web comprising a first and a second layer, the first layer being substantially free from high yield hesperaloe pulp fibers and the second layer consisting essentially of high yield hesperaloe pulp fibers, the tissue product having a Wet CD Durability from about 1.75 to about 2.0 and a Stiffness Index less than about 6.0.

10. The tissue product of claim 9 having CD Wet/Dry Ratio from about 0.28 to about 0.32.

11. The tissue product of claim 9 having an Absorbent Capacity from about 6.5 to about 7.5.

12. The tissue product of claim 9 having a GM Slope less than about 8.0 kg.

13. The tissue product of claim 9 having a basis weight from about 30 to about 60 gsm and a GMT from about 1500 to about 2500 g/3".

14. The tissue product of claim 9 wherein the tissue product is substantially free from softwood kraft pulp fibers.



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15. The tissue product of claim 9 wherein the high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.

16. A single-ply through-air dried tissue product comprising at least about 20 weight percent high yield hesperaloe pulp fibers, the tissue product having a basis weight from about 30 to about 60 gsm, a GMT from about 1500 to about 2500 g/3" and an Absorbent Capacity greater than about 7.0 g/g.

17. The single-ply through-air dried tissue product of claim 16 having a Wet CD Durability from about 1.75 to about 2.0.

18. The single-ply through-air dried tissue product of claim 16 having a Stiffness Index less than about 6.0.

19. The single-ply through-air dried tissue product of claim 16 wherein the tissue product comprises from about 20 to about 40 weight percent high yield hesperaloe fiber and is substantially free from softwood kraft pulp fibers.

20. The single-ply through-air dried tissue product of claim 16 wherein high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.



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**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/US2015/033175**

**A. CLASSIFICATION OF SUBJECT MATTER**

**A47K 7/00(2006.01)i, 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 7/00; D21H 11/12; D21H 17/28; D21H 17/00; D21H 27/00; B31F 1/12; A47K 10/16

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, web, hesperaloe fiber, non-woody, pulp, absorbent

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | US 5320710 A (REEVES, R. H. et al.) 14 June 1994<br>See abstract; claims 1-7. | 1-20 |
| Y | US 2013-0269892 A1 (KIMBERLY-CLARK WORLDWIDE, INC.) 17 October 2013<br>See claims 1, 3; paragraphs [0013], [0038], [0045]. | 1-20 |
| A | US 2014-0093704 A1 (SHI, B. et al.) 03 April 2014<br>See abstract; claims 1-9. | 1-20 |
| A | US 2015-0129143 A1 (CARGILL, INCORPORATED) 14 May 2015<br>See claims 1, 2, 9. | 1-20 |
| A | US 2003-0192662 A1 (HEATH, M. S. et al.) 16 October 2003<br>See abstract; claim 1. | 1-20 |

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

☒ See patent family annex.

* Special categories of cited documents:
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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



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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:

$$CD\ Durability = \frac{CD\ TEA\ (\mathrm{g} \bullet \mathrm{cm/cm2})}{CD\ Tensile\ (g/3")} \cdot x\ 1{,}000$$

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:

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



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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.

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.



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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, 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 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



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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).



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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.



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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<br>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<br>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<br>See paragraphs [0027], [0081], [0089] and claims 1, 10-11. | 1-20 |
| A | US 2005-0236122 A1 (MULLALLY et al.) 27 October 2005<br>See paragraphs [0013], [0016], [0089] and claims 1, 9, 26. | 1-20 |
| A | US 2013-0199741 A1 (STAGE et al.) 08 August 2013<br>See claims 1-6 and table 8. | 1-20 |

☐ 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
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"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)
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"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
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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**(54) Title**: TISSUE PAPER COMPRISING PULP FIBERS ORIGINATING FROM MISCANTHUS AND METHOD FOR MANUFACTURING THE SAME

**(57) Abstract**: The present invention relates to a tissue paper web composed of one or more layers wherein at least one layer comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus wherein the pulp fibers are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof. The use of Miscanthus pulp fibers according to the present invention can lead to a major absolute increase in tensile strength along with good softness values.

# Tissue paper comprising pulp fibers originating from Miscanthus and method for manufacturing the same

## DESCRIPTION

The present invention relates to a soft and strong tissue paper comprising fibers originating from a plant belonging to the genus Miscanthus, in particular from *Miscanthus Gigantheus.* The present invention also pertains to a process for the manufacture of said tissue paper as well as to products, e.g. toilet paper, hand towels, household towels etc., obtained by this process.

## BACKGROUND OF THE INVENTION

Tissue paper-based materials find extensive use in modern society. Toilet paper, paper towels such as hand towels or household (kitchen) towels, facial tissues and tissue handkerchiefs are staple items of commerce. These products are typically made from papermaking pulp comprising fibers of both hardwood and softwood types.

Among the most important physical properties of these products are their strength, their softness, their absorbency, primarily for aqueous systems, and their lint and dust resistance. These physical properties are generally tuned for addressing common consumer demand.

Tissue paper products are often exposed to extremely varied strength requirements in the wet and the dry state, respectively. For instance, it must be ensured, in the case of household paper (paper towels) that they retain their strength at least for a specific period of time when exposed to aqueous liquids or moisture-containing food. On the other hand, toilet paper should dissolve in water, sometime after use, in order to prevent the sewage systems from clogging up. Furthermore, toilet paper must not immediately lose its strength properties during use for apparent reasons.

At the same time, tactile properties such as softness are extremely important as tissue paper-based products are intended to come in intimate contact with the

body and skin. Therefore, tissue paper-based products must exhibit sufficient softness in order to ensure consumer's comfort.

However, strength and softness are generally conflicting properties. If strength rises, the softness of the tissue paper will decline due to the increase of fiber to fiber bonds. Conversely, if softness increases, the strength is decayed due to limited fiber to fiber bonds.

The prior art describes many processes for achieving a good balance between strength and softness, or increasing one property without detrimentally affecting another.

EP 0 029 269 A1 discloses a multi-layered tissue paper, and tissue paper-based products made thereof, such as toilet tissue and facial tissues, having a smooth and soft top surface. The tissue paper comprises a velutinous top layer being the outwardly facing surface formed from at least 60% by weight of short hardwood fibers, such as Northern Hardwood Sulfite and/or Eucalyptus Hardwood, united to a furnish comprising long softwood fibers. The short papermaking fibers disposed on the outer layer exhibit sufficient free end portions to achieve softness, whereas the long-fiber furnish ensures strength. However, for some applications this tissue paper does not exhibit sufficient strength, primarily in the dry state.

Another common measure for modifying the strength and softness properties of tissue papers consists in adding strengthening and/or softening compositions to tissue-based materials. In this regard, the prior art describes strengthening resins, such as polyamidoamine-epichlorine resins. However, the isolated use of strengthening resins generally provides a tissue paper which is fairly stiff and has almost the haptic properties of normal paper. Consequently, strengthening resins are often used in combination with softening compositions which, in turn, reduce strength since softeners also interact with inter-fiber hydrogen bonds.

WO 94/10381 A1 discloses soft and strong tissue paper webs which can be used in toweling, napkin, facial tissue, and toilet tissue products. The tissue paper webs generally comprise a cellulose-based furnish, such as a mixture of Northern softwood kraft and eucalyptus fibers, and a chemical softening composition comprising a cationic surfactant as softener. However, surfactants weaken the bonds between fibers in the tissue webs. As a result, the tissue paper webs do not

exhibit sufficient strength. The loss of strength due to the surfactant is hence compensated by the addition of a binding resin, such as a polyamidoamine-epichlorohydrin resin.

Likewise, US 5,397,435 and US 5,312,522 disclose tissue paper-based products such as paper towels, facial tissues and toilet tissues, comprising a combination of a chemical softening composition containing a surfactant such as a quaternary ammonium compound, and a strengthening resin such as a polyamide-epichlorohydrin resin. However, as outlined above, the use of softening and strengthening chemical compositions in combination generally does not provide a significant improvement, because the effect of one composition (e.g. softening or strengthening) is often compromised by the opposite effect caused by the other.

In addition, it can be desirable to reduce the amount of chemicals such as softening and/or strengthening chemical compositions in tissue paper. This applies primarily to cases where these chemical compositions tend to irritate the skin or trigger allergic reactions in some users. Furthermore, the biological degradability of some softening and/or strengthening chemical compositions in the environment has raised concerns.

WO 96/06223 A1 proposes a tissue sheet composed of northern softwood kraft and eucalyptus hardwood kraft, comprising a combination of "debonding" agents and strengthening agents added in a layer-wise fashion, in order to maximize the effectiveness of each additive while minimizing the interaction of the additives with each other. However, the addition of different chemical compositions in a layer-wise fashion significantly increases the complexity of the manufacturing process.

These are typical examples for the generally occurring problem in the art of tissue paper making that the above-mentioned properties conflict with each other in so far as attempts to improve one property is detrimental for another.

Further, it has been noted that, in tissue paper making processes, the primary (embryonic) fibrous webs containing eucalyptus pulp fibers sometimes do not show the desired strong adhesion to the Yankee cylinder when the web is subjected to the final drying and creping steps.

Starting from commonly used tissue paper products using mixtures of softwood and eucalyptus pulps, it is an object of the present invention to provide tissue paper webs and products having improved properties, in particular improved strength and good softness.

It is a further object of the present invention to provide a process for manufacturing such tissue paper webs. According to one aspect of the present invention, a process is provided which involves an improved adhesion of the "primary" fibrous webs to the Yankee cylinder during the final drying and creping steps of the process.

## SUMMARY OF THE PRESENT INVENTION

The present invention relates to a soft and strong tissue paper web composed of one or more layers wherein at least one of these layers comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus, in particular from *Miscanthus Gigantheus*. The present invention also relates to tissue paper products such as toilet paper, hand towels, household towels, handkerchiefs, napkins and facial tissues manufactured from said tissue paper web.

The present invention also relates to a process for the manufacture of a tissue paper web comprising the steps of

(a) providing pulp fibers comprising fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*;
(b) forming an aqueous suspension of the fibers;
(c) feeding the suspension to a tissue-making headbox;
(d) depositing the suspension onto a wire to form a wet web;
(e) dewatering the wet web; and
(f) drying and creping the web,

The pulp fibers are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment, and mixtures thereof.

The tissue paper web and tissue paper products of the present invention are distinguished by their excellent strength and good softness.

The present invention includes the following embodiments ("Items"):

1. Tissue paper web composed of one or more layers wherein at least one layer comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus wherein the pulp fibers are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof.

2. Tissue paper web according to Item 1 wherein the pulp fibers originate from *Miscanthus Gigantheus*, *Miscanthus Sinensis*, or *Miscanthus Sacchariflorus*, and preferably from *Miscanthus Gigantheus*.

3. Tissue paper web according to Item 1 or 2 wherein the pulp fibers, which originate from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* are present in an amount of at least 5 wt.-%, preferably in an amount of from 10 wt.-% to 90 wt.-%, more preferably in an amount of from 15 wt.-% to 80 wt.-%, even more preferably 20 wt.-% to 70 wt.-%, based on the total weight of the tissue paper web.

4. Tissue paper web according to any of Items 1, 2 or 3 wherein the web is composed of two or three layers made from different pulps wherein at least one of these layers is made from pulp comprising the pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*.

5. Tissue paper web according to any of Items 1, 2, 3 or 4 wherein the remaining fibers present in said tissue paper web are selected from pulp fibers comprising hardwood fibers, such as eucalyptus, beech, aspen, acacia or birch fibers; softwood fibers such as pine, spruce, red cedar, hemlock, and larch fibers; and non-wood fibers such as cotton, bagasse, hemp, linen, sisal, straw or flax fibers.

6. Tissue paper web according to Item 4 or 5, wherein the web is composed of two layers wherein
(i) the first layer is made from pulp fibers (i-a) consisting of fibers originating from at least one plant belonging to the genus Miscanthus, preferably from

*Miscanthus Gigantheus,* and optionally hardwood fibers, or from pulp fibers (i-b) comprising, or consisting of, fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* softwood fibers, and optionally hardwood fibers, and
(ii) a second layer is made from pulp fibers comprising or consisting of softwood fibers.

7. Tissue paper web according to Item 6, wherein
(i) the first layer is made from pulp fibers (i-a), wherein the weight ratio of fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* to hardwood fibers, if present, is 100/0 to 10/90, preferably 100/0 to 20/80, and
(ii) the second layer is made from pulp comprising, or consisting of, softwood fibers,
and wherein the weight proportion of pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* based on the total weight of the tissue paper web is preferably 10 to 90 wt.-%, more preferably 10 to 80 wt.-%, in particular 25 to 75 wt.-%, such as 40 to 70 wt.-%.

8. Tissue paper web according to Item 6, wherein
(i) the first layer is made from pulp fibers (i-b) consisting of fibers originating from at least one plant belonging to the genus Miscanthus and preferably from *Miscanthus Gigantheus* (MG), softwood fibers (SW), and optionally hardwood fibers (HW), wherein the weight ratio MG / HW / SW in %, based on the total weight of pulp fibers (i-b), is 10 to 90 / 0 to 50 / 10 to 90, preferably 20 to 80 / 0 to 50 / 20 to 80, and
(ii) the second layer is made from pulp fibers comprising, or consisting of, softwood fibers, and wherein the weight proportion of pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* based on the total weight of the tissue paper web is preferably 10 to 50 wt.-% , such as 10 to 30 wt.-%.

9. Tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7 or 8, wherein the pulp fibers originating from *Miscanthus Gigantheus* are obtained in a chemical, chemo-mechanical or high yield chemical pulping process,

preferably the soda process or the CTMP process (Chemo-Thermo-Mechanical Pulping).

10. Tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7, 8 or 9, wherein the hardwood pulp fibers originate from eucalyptus and/or the softwood pulp fibers are Northern Bleached Softwood Kraft (NBSK) fibers, wherein the NBSK fibers are preferably refined to a degree of fineness of 19 to 35°SR.

11. Tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10, wherein (i) all fibers present in the web are primary pulp fibers, or (ii) a mixture of primary and secondary (recycled) pulp fibers wherein the proportion of secondary (recycled) pulp fibers does not exceed 90 wt.-% based on the tissue paper web.

12. Tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 which is composed of one or more layers wherein the pulp fibers originating from at least one plant belonging to the genus Miscanthus fulfill the following requirements:

(i) average fiber length of from 0.5 to 1.2 mm, preferably from 0.8 to 1.0 mm;

(ii) average fiber diameter of from 10 to 25 µm; and

(iii) average fiber wall thickness of from 3.0 to 5.0 µm.

13. Tissue paper product comprising at least one ply made from the tissue paper web according to any of Item 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12.

14. Tissue paper product according to Item 13, wherein the tissue paper product is selected from toilet paper, hand towel, household towel, handkerchiefs, napkins and facial tissues.

15. Tissue paper product according to Item 13 or 14 wherein the tissue paper product is a toilet paper composed of 2 to 4 plies, wherein preferably at least one outer ply, more preferably both outer plies, is/are made from the tissue paper web of Item 7, and the outer ply/plies is/are arranged such that, in the toilet paper, the first layer thereof (i), which comprises the pulp fibers originating from at least one plant belonging to the genus Miscanthus,

preferably from *Miscanthus Gigantheus*, is located on the outer surface of the toilet paper.

16. Tissue paper product according to Item 13 or 14 wherein the tissue paper product is a hand towel or household towel composed of 2 to 4 plies, wherein preferably at least one ply, optionally all plies, is/are made from the tissue paper web of Item 7 or the tissue paper web of Item 8.

17. Tissue paper product according to any of Items 13, 14, 15 or 16 wherein the tissue paper product is free of a softener and/or is free of a strengthening resin.

18. Process for the manufacture of a tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12, comprising the steps of:

(a) providing chemical pulp fibers comprising fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*;
(b) forming an aqueous suspension of said pulp fibers;
(c) feeding the suspension to a tissue-making headbox;
(d) depositing the suspension onto a wire to form a wet web;
(e) dewatering the wet web; and
(f) drying and creping the web.

Where the present description refers to "preferred" embodiments/features, combinations of these "preferred" embodiments/features shall also be deemed as disclosed as long as this combination of "preferred" embodiments/features is technically meaningful.

Hereinafter, the use of the term "comprising" should be understood as disclosing, as a more restricted embodiment, the term "consisting of" as well.

## FIGURES

Figure 1 - Schematic drawing showing the creping process on a Yankee cylinder with a creping blade. Figure 1 gives a survey on the terminology used for the

various angles influencing the creping process. In Figure 1 the following reference numbers represent:

(1) Yankee cylinder,
(2) Crepe pocket angle,
(3) Bevel angle,
(4) Blade holder angle,
(5) Sheet take-off angle,
(6) Creped sheet, and
(7) Stick out.

## DETAILED DESCRIPTION OF THE PRESENT INVENTION

### 1. Tissue paper web

The tissue paper web of the present invention is composed of one or more layers wherein at least one layer comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus.

The term "tissue paper" as used herein covers the "base (raw) tissue paper" ("**tissue paper web**") as obtained from the tissue paper machine as well as one-ply or multi-ply final products ("**tissue paper products**") made of base tissue, and tailored to the end user's needs by further converting steps.

As "**tissue paper web**" we understand the one-ply base tissue as obtained from the tissue machine. The tissue paper web is a sheet of paper made by a process comprising the steps of: forming an aqueous suspension of pulp fibers i.e. the so-called "furnish", depositing said aqueous suspension onto a wire to form a wet web, dewatering, drying and creping the web.

The tissue paper web has a basis weight of 8 to 50 g/m$^2$, in particular 10 to 30 g/m$^2$, especially 12 to 25 g/m$^2$.

The tissue paper web of the present invention is composed of one or more layers (i.e. single-layered web or multi-layered web). The term "**layer**" refers to a stratum within the web having a defined fiber 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. This technique is well-known to those skilled in the art. It renders possible the use of different kinds of fibers in each layer of the web. The “multi-layered” tissue paper web of the present invention may have 2 to 5, typically 2 or 3 layers.

The term “**ply**” as used herein refers to the one or more plies of tissue paper in the final tissue paper product as are obtained after processing (“converting”) one or more base tissue paper webs. Each individual ply consists of a tissue paper web comprising one or more layers, e.g. one, two, three or four layers.

Based on the underlying compatibility of the production processes (wet forming), "tissue" production is counted among the papermaking techniques. The production of tissue is distinguished from paper production by its extremely low 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 crepe doctor or in the latter instance as a result of 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 imparting to the tissue a 3D structure by means of 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 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, properties which are frequently referred to as bulk softness, a high surface softness, 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. These properties allow tissue paper to be used, for example, as cleaning cloths (e.g. household towels), sanitary products (*e.g.* toilet paper, hand towels), paper handkerchiefs, cosmetic wipes (facial tissues) or as serviettes/napkins.

The tissue paper web of the invention and the tissue paper products made therefrom are characterized by their content of pulp fibers originating from at least one plant belonging to the genus Miscanthus.

The "**Miscanthus**" genus includes about 15 perennial rhizomatous grasses. Miscanthus grasses are usually found throughout a wide climatic range, from the tropics and subtropics to the temperate regions of Northern Asia and Europe. According to the present invention, the fibers can be selected from fibers originating from the species *Miscanthus Floridulus*, *Miscanthus Sacchariflorus*, *Miscanthus Sinensis*, *Miscanthus Gigantheus*, *Miscanthus Tinctorius*, and *Miscanthus Transmorrisonensis*.

It is preferred that the pulp fibers originate from *Miscanthus Sacchariflorus*, *Miscanthus Sinensis*, and *Miscanthus Gigantheus*. It is even more preferred that the pulp fibers originate from *Miscanthus Gigantheus*.

When the aforementioned pulp fibers originating from at least one plant belonging to the genus Miscanthus are used to form the tissue paper web of the present invention, the resulting tissue paper web/product exhibits improved properties, in particular improved strength and good softness. When pulp fibers originating from *Miscanthus Gigantheus* are used, the improvement of strength is even more pronounced while good softness is maintained.

Further, when the aforementioned pulp fibers originating from at least one plant belonging to the genus Miscanthus are used to form the tissue paper web of the present invention, the resulting tissue paper web/product exhibits excellent absorption for aqueous systems.

It is furthermore believed that the tissue paper web/product of the present invention, comprising pulp fibers originating from at least one plant belonging to

the genus Miscanthus, can exhibit **antimicrobial / antibacterial properties** which are natural attributes of plants belonging to the genus Miscanthus.

The tissue paper web of the present invention contains the aforementioned pulp fibers originating from at least one plant belonging to the genus Miscanthus in an amount of at least 5 wt.-%, preferably in an amount of 10 wt.-%, more preferably in an amount of from 10 wt.-% to 80 wt.-%, and even more preferably 20 wt.-% to 70 wt.-%, based on the total weight of the tissue paper web.

The "**pulp fibers**" used in the present invention are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof.

"**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.

In the present invention, use can also be made of **mechanical pulps subjected to chemical pre-treatment**, such as chemo-mechanical pulp (CMP pulp), or chemo-thermo- mechanical pulp (CTMP pulp).

According to one embodiment of the invention, the claimed tissue paper web and tissue paper products do not include fibrous material made from wood entirely by mechanical means, i.e. purely mechanical pulps such as groundwood pulp and refined mechanical pulp.

The pulp fibers originating from at least one plant belonging to the genus Miscanthus are preferably obtained in a chemical, chemo-mechanical (CMP) or high yield chemical pulping process. The use of alkaline chemical pulping or pretreatment processes is preferred. The pulp fibers are preferably obtained by employing the soda pulping process or the CTMP process (Chemo-Thermo-Mechanical Pulping) as described e.g. by P. Cappelletto et al. in *Industrial Crops and Products,* 11 (2000) 205-210. The pulp fibers are more preferably obtained by the soda pulping process. Kraft cooking could be used as well.

Further, the pulp fibers originating from at least one plant belonging to the genus Miscanthus can be prepared and/or treated by common techniques. For instance,

said pulp fibers can be bleached by using chlorine-free bleaching steps in view of the production of environmentally sound products and process steps.

According to one embodiment, the pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*, have a length of from 0.5 to 1.2 mm, preferably from 0.8 to 1.0 mm, a diameter of from 10 to 25 µm, e.g. 13 to 21 µm, preferably 13 to 15 µm, and a wall thickness of from 3.0 to 5.0 µm. The fiber dimensions are mean (average) values, which can be determined by techniques well-known in the art such as described by C. Ververis et al. in *Industrial Crops and Products 19 (2004) 245-254*.

In the following, for the sake of brevity, we will refer to pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*", and being selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof as "***MG pulp fibers***".

According to one embodiment, the tissue paper web is composed of two or three layers made from different pulps wherein at least one of these layers is made from pulp comprising MG pulp fibers.

According to one further embodiment, the remaining fibers present in the tissue paper web of the invention, i.e. the fibers being not MG pulp fibers, are selected from pulp fibers comprising **hardwood fibers**, such as eucalyptus, beech, aspen, acacia or birch fibers; **softwood fibers** such as pine, spruce, red cedar, douglas fir, hemlock, and larch fibers; and **non-wood fibers** such as cotton, bagasse, hemp, linen, sisal, straw or flax fibers.

As "**hardwood fibers**" we understand fibrous pulp derived from the woody substance of deciduous trees (angiosperms). Typically, hardwood fibers are "short" fibers having a length of from 1 to 2 mm, a diameter of from 15 to 30 µm, and a wall thickness of from 2 to 3 µm. Hardwood such as Eucalyptus is normally pulped by the Kraft process.

The hardwood fibers usable in the present invention preferably originate from eucalyptus, beech, aspen, acacia and birch, more preferably from eucalyptus.

As "**softwood fibers**" we understand fibrous pulp derived from the woody substance of coniferous trees (gymnosperms). Typically, softwood fibers are "long" fibers having a length of from 3 to 4 mm, a diameter of from 30 to 40 µm, and a wall thickness of from 3 to 4 µm. They are normally pulped by the Kraft process.

The softwood fibers usable in the present invention preferably originate from pine, spruce, red cedar, douglas fir, hemlock, and larch. More preferably, the softwood fibers usable in the present invention are Northern Bleached Softwood Kraft (NBSK) fibers. Preferably, at least part of the NBSK fibers to be used is refined, more preferably to a degree of fineness of 19 to 35°SR, e.g. 19 to 26°SR.

As "**non-wood fibers**" we understand fibrous pulp derived from the non-woody substance of plants such cotton, bagasse, hemp, linen, sisal, straw or flax.

According to one preferred embodiment, the tissue paper web is composed of two layers wherein

(i) the first layer is made from

(i-a) pulp fibers consisting of MG pulp fibers, and optionally hardwood fibers, or

(i-b) from pulp fibers comprising, or consisting of, MG pulp fibers, softwood fibers, and optionally hardwood fibers, and

(ii) a second layer is made from pulp fibers comprising, or consisting, of softwood fibers.

Although it is frequently preferred that the second layer is made from pulp fibers consisting (only) of softwood ("SW") fibers the present invention also extends to embodiments in which this layer is made from pulp fibers comprising softwood fibers and other pulp fibers such as MG pulp fibers and/or hardwood fibers and/or non-wood fibers such as bagasse fibers or the other fibers mentioned hereinbefore. These other pulp fibers are then preferably used in an amount of up to 60 wt.-% based on the total weight of pulp fibers being present in the second layer.

Considering an exemplary case of 80% MG pulp fibers in total, one may for instance split the furnish for technical reasons in 50% MG pulp fibers in the first layer while the second layer consists of 30% MG pulp fibers plus 20% SW pulp fibers, each based on the total weight of the tissue paper web. In an alternative embodiment 50% MG pulp fibers are used in first layer and 30% Eucalyptus plus 20% SW pulp fibers in the second layer.

The above also applies to the following embodiments where the second layer is made from pulp comprising, or consisting of, softwood fibers.

According to one further preferred embodiment, especially suitable for the manufacture of toilet tissue paper, the tissue paper web is composed of two layers wherein

(i) the first layer is made from pulp fibers consisting of MG pulp fibers, and optionally hardwood fibers,

(i-a) wherein the weight ratio of MG pulp fibers to hardwood fibers, if present, is 100/0 to 20/80, and

(ii) the second layer is made from pulp comprising, or consisting of, softwood fibers,

and wherein the weight proportion of MG pulp fibers based on the total weight of the tissue paper web is preferably 10 to 80 wt.-%, in particular 25 to 75 wt.-%, such as 40 to 70 wt.-%.

According to one further preferred embodiment, especially suitable for the manufacture of household towel and hand towel, the tissue paper web is composed of two layers wherein

(i) the first layer is made from

(i-b) pulp fibers consisting of MG pulp fibers, softwood fibers (SW), and optionally hardwood fibers (HW), wherein the weight ratio MG / HW / SW in %, based on the total weight of pulp fibers (i-b), is 10 to 90 / 0 to 50 / 10 to 90, preferably 20 to 80 / 0 to 50 / 20 to 80, e.g. 20 to 70 / 10 to 50 / 20 to 70, or 20 to 80 / 0 / 20 to 80 or 20 to 50 / 0 to 30 / 40 to 60, and

(ii) the second layer is made from pulp fibers comprising, or consisting of, softwood fibers,

and wherein the weight proportion of MG pulp fibers based on the total weight of the tissue paper web is preferably 10 to 50 wt.-%, such as 10 to 30 wt.-%.

The MG pulp fibers used in the present invention can be refined fibers and are preferably unrefined. The remaining fibers present in the tissue paper web of the invention (i.e. the fibers being not MG pulp fibers) can be **unrefined fibers, refined fibers** and mixtures thereof. Preferably, at least a part of the softwood fibers (i.e. long fibers) to be used, optionally all softwood fibers, are refined. Preferably, the hardwood fibers (i.e. short fibers) to be used are unrefined.

According to one embodiment, the hardwood pulp fibers originate from eucalyptus and/or the softwood pulp fibers are Northern Bleached Softwood Kraft (NBSK) fibers, wherein the NBSK fibers are preferably refined to a degree of fineness of 19 to 35°SR, in particular 19 to 26°SR, e.g. 19 to 24°SR.

As "**unrefined fibers**" we understand fibers as naturally occurring or being obtained by their respective preparation process (chemical or mechanical pulping, recycling etc.). Although being dependent on the fiber source, unrefined hardwood and softwood pulp fibers typically have a freeness value of about 12 to 15°SR. By contrast, unrefined MG pulp fibers (as coming from the pulp mill) can have a SR value in the range of 34 to 36°SR, typically about 35°SR. The unrefined fibers used in the tissue paper web and product of the invention usually stem from hardwood. Also MG pulp fibers are typically used as they come from the paper mill without further refining. However, the unrefined fibers to be used can also stem from softwood, e.g. softwood like spruce digested by sulfite processes.

As "**refined fibers**" we understand fibers which have been subjected to refining processes. Such processes are well known to those skilled in the art. Refined fibers typically have a freeness value of more than 15 to less than 35°SR. In the present invention, the softwood fibers are preferably refined to a degree of fineness of 19 to 35°SR, in particular 19 to 26°SR, such as 19 to 24°SR. The refined fibers usually stem from softwood.

If long refined fibers and unrefined fibers are to be combined, be it in a single-layered ply as a true mixture or in multi-layered plies based on separate pulp streams, they are preferably used in a ratio of from 90/10 to 10/90, more preferably 80/20 to 20/80, most preferably from 75/25 to 40/60.

Further, the pulp fibers present in the tissue paper web of the invention can be a primary fibrous material, a secondary fibrous material (recycled pulp) and mixtures thereof.

According to one embodiment, (i) all fibers present in the tissue paper web are primary pulp fibers, or (ii) a mixture of primary and secondary (recycled) pulp fibers. Preferably, the proportion of secondary (recycled) pulp fibers, if present, does not exceed 90 wt.-%, based on the total weight of the tissue paper web. It is more preferred that the proportion thereof is 70 wt.-% or less, e.g. 50 wt.-% or less.

As "**primary pulp fibers**" we understand fibers as obtained from the pulping process of woody substances (e.g. hardwood, softwood) and non-woody substances (e.g. cotton, bagasse, hemp, Miscanthus etc.) which have not previously been used in a manufacturing process.

As "**secondary pulp fibers**" we understand fibers that have previously been used in a manufacturing process (e.g. paper- or tissue-making), and have been reclaimed (recycled) as raw material for the process of the present invention. Secondary pulp fibers can be recycled from e.g. waste paper by common techniques in the art.

The tissue paper web of the present invention may include **softening and/or strengthening chemical compositions**.

In one embodiment, the tissue paper web of the present invention is free of softener (debonder). In one further embodiment, the tissue paper web of the present invention is free of strengthening chemical additives, such as strength resins, for instance free of the water-soluble cationic or anionic polymers described below. The tissue paper web of the present invention can also be free of both softener (debonder) and strengthening chemical additives.

When the tissue paper web includes a softener and/or a strengthening resin, a water-soluble cationic polymer, a water soluble anionic polymer and/or a cationic surfactant-based softener as described, e.g. in European patent EP 1 583 869 B1 can be used.

1.a Water-Soluble Cationic Polymer

When a water-soluble cationic polymer is used, it is possible to add the same to the pulp fibers in such an amount that 0.01 to 5 wt.-%, in particular 0.01 to 3 wt.-%, such as 0.5 to 2 wt.-% (e.g. 0.5 to 1.5 wt.-%), based on the total amount of fibers (dry weight, EN 20638:1993) is retained.

The cationic polymer to be used contains cationic groups, such as positively charged quaternary nitrogen atoms in sufficient amounts to impart the molecule water solubility. The term "water-soluble" means solubility in water (at 20°C) of at least 1 g/l, in particular at least 10 g/l, more particularly at least 20 g/l.

Preferably, the cationic water-soluble polymer is a wet strength agent. It 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. Suitable materials are described in further detail in US 3,998,690 and EP 1 583 869 B1.

The most preferred types of cationic polymer are 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. Examples of these are the well-known Kymene ® resins available from Ashland.

1.b Water-Soluble Anionic Polymer

When a water soluble anionic polymer is used, it can be added to the cellulosic fibers in such an amount that 0.01 to 3 wt.-%, in particular 0.1 to 2 wt.-%, such as

0.2 to 1 wt.-%, based on the total amount of untreated cellulosic fibers (dry weight according to DIN EN 20638) is retained by the fibers.

As "water-soluble anionic polymers" we understand those polymers having a sufficient amount of anionic groups, such as carboxy groups to be water soluble. As "water-soluble" we understand solubility in water (at 20°C) of at least 1 g/l, in particular at least 10 g/l, and more particularly at least 20 g/l.

The water soluble anionic polymer can be selected among known anionic dry strength agents. Suitable dry strength agents are described in European patent EP 1 583 869 B1.

The water soluble anionic polymer can be 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. Starch-based polymers, vinyl copolymers of carboxylic acids and cellulose-based polymers are preferred. 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.

The above anionic polymers also include anionic polymers of acrylamide. These can be made by hydrolysis of an acrylamide polymer or copolymer by means known to the art, or by copolymerizing acrylamide with acrylic acid or sodium acrylate and optionally another monomer under radical initiation, again by means known to the art. Also operable are poly(acrylic acid) or its salts such as sodium polyacrylate or ammonium poylacrylate. Other operable polymers in this group are poly(acrylic acid) and its salts, and poly(sodium acrylate).

Use can be made of commercially available anionic polymers, having carboxyl (or carboxylate salt) contents of about 0.5 to about 14 millequivalents per gram such as CMC.

The above-explained water soluble cationic polymer is used in higher amounts than the water soluble anionic polymer. Preferably the weight ratio cationic polymer/anionic polymer is from 1/1 to 10/1, more preferably 2/1 to 7/1, most preferably 3/1 to 5/1.

1.c Cationic Surfactant-Based Softener

According to one embodiment, the tissue paper web/product of the present invention is free of softening chemical additives (e.g. softener / debonder).

When a softener is used, a cationic surfactant-based softener (in the prior art sometimes referred to as "debonder") can be added to the cellulosic fibers in such an amount that 0.005 to 3 wt.-%, in particular 0.01 to 2.5 wt.-%, such as 0.5 to 2 wt.-%, based on the total amount of untreated cellulosic fibers (dry weight according DIN EN 20638) are retained by the fibers.

The softener may be selected from quaternary ammonium compounds (e.g. quaternized protein compounds, silicone quaternaries or quatemized protein compounds) or cationic phospholipids of the type as described in WO 97/04171. All suitable surfactant-based softeners have the presence of a cationic unit (preferably quaternary ammonium unit) and a long chain aliphatic group having preferably 8 to 24, more preferably 14 to 22 carbon atoms in common. The long chain aliphatic group is preferably directly linked to the cationic group.

The quaternary ammonium compounds can also be selected from those conforming to Formula I, II, III, IV or V disclosed in [0079] to [0091] of EP 1 583 869 B1.

**2. Tissue paper product**

The present invention also relates to a tissue paper product comprising at least one ply made from the tissue paper web.

To achieve the desired finished products such as toilet tissues and hand towels, the one ply base tissues with typical basis weights from 12 g/m² to 38 g/m² are

combined in a subsequent converting step to the final ply count which may be 2 to 5 depending on the targeted properties of the final tissue paper product.

The total basis weight of multiple-ply tissue products preferably does not exceed 75 g/m$^2$ and more preferably is lower than 65 g/m$^2$, e.g. lower than 55 g/m$^2$.

In order to optimally use its strength and softness properties, it is desirable to employ the tissue paper web of the invention, i.e. one comprising MG pulp fibers, in one or both outer plies of the final tissue product, since these come in contact with the body and skin of the user.

When the tissue paper web of the invention is multi-layered, it is desirable that the outer layer(s) of the outer ply/plies, i.e. the layers which come into contact with the user's body and skin, comprise MG pulp fibers. A tissue paper product distinguished by its excellent strength and good softness is thus produced.

The tissue paper product of the present invention is preferably selected from toilet paper, hand towel, household towel, handkerchiefs, serviettes/napkins and facial tissues.

According to one preferred embodiment, the tissue paper product is a **toilet paper** composed of 2 to 5 plies, e.g. 2 to 4 plies, wherein preferably at least one outer ply, more preferably both outer plies, is/are made from the tissue paper web of the invention.

More preferably, this applies to the previously described "further preferred embodiment" of a tissue paper web having a first layer (i) and a second layer (ii), which was stated to be especially suitable for the manufacture of toilet tissue paper and can be used in least one outer ply, more preferably both outer plies of a toilet paper having e.g. 2, 3, 4 or 5 plies.

In this product, it is preferred that the outer ply/plies is/are arranged such that, in the toilet paper, the first layer thereof (i), which comprises the MG pulp fibers is located on the outer surface of the toilet paper. As a result, improved strength and soft feeling when applied on the user's skin can be achieved.

According to one further preferred embodiment, the tissue paper product is a **hand towel** or **household towel** composed of 2 to 5, e.g. 2 to 4 plies. Preferably, at least one ply, optionally all plies, is/are made from the tissue paper web of the present invention.

More preferably, this applies to the previously described "further preferred embodiment" of a tissue paper web having a first layer (i) and a second layer (ii), which was stated to be especially suitable for the manufacture of hand towel or household towel and can be used in least one outer ply, more preferably both outer plies of a hand towel having e.g. 2, 3, or 4 plies or household towel having e.g. 2, 3, 4 or 5 plies.

According to one further preferred embodiment, the tissue paper product of the present invention (e.g. toilet paper, hand towel and household towel) is free of a softener and/or is free of a strengthening additive, e.g. resin.

**3. Process for the manufacture of tissue paper webs and tissue paper products**

The present invention also relates to a process for the manufacture of a **tissue paper web** as described before and below, the process comprising the steps of:

(a) providing pulp fibers comprising fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus* i.e. MG pulp fibers;

(b) forming an aqueous suspension of said pulp fibers;

(c) feeding the suspension to a tissue-making headbox;

(d) depositing the suspension onto a wire to form a wet web;

(e) dewatering the wet web; and

(f) drying and creping the web.

(a) The pulp fibers to be used in the aforementioned process can be prepared by common techniques known in the art, for instance, fractionating, sorting, washing, floating, cleaning, thickening and/or fiberizing.

When refined pulp fibers are to be used in the aforementioned process, said fibers can be refined by using techniques well-known in the art. Typically, the fibrous material to be refined is transported to a refiner unit. Fibrillation of fibers during refinement (beating) occurs either by the fibers themselves or by the refining bars. During refinement, the fibers are subjected to a variety of physical loads. Axial and tangential shearing and compressive forces acting upon the fiber play a particular role as regards fiber refining. The associate change in fiber morphology involves, but is not limited to, tearing open and removing the fibrous materials' outer wall layer (primary wall) and/or exposing the fibers and fibrillation out of the wall layers and/or partially shorting the total fiber unit and/or shearing off fibrils.

(b) After providing the pulp fibers comprising MG pulp fibers, an aqueous suspension is produced therefrom. The aqueous suspension preferably contains the pulp fibers in an amount of from 3 to 4 wt.-%, based on the water content. The aqueous suspension is then diluted to consistencies in the order of 0.5 to 1.5 wt.-%, preferably of 0.8 to 1.2 wt.-%.

In one embodiment of the invention, the aqueous suspension can be treated with the anionic and cationic water soluble polymer described before. Preferably, aqueous solutions are used for adding these chemicals but it is also possible to add them in substance.

Generally, it is preferred to add the anionic polymer first (prior to the cationic polymer) in order to ensure an optimal interaction with the cellulosic fibers, if these chemicals are to be added. After a period of time of preferably 30 seconds to 24 hours, in particular 1 to 30 minutes, the cationic polymer is also given to the aqueous slurry. Again, it is preferred to let a certain period of time pass (preferably from 1 to 30 minutes) before the aqueous slurry is conducted to the headbox and dewatered. A different order of addition can also be used as described in EP 1 583 869 B1.

(c) In step (c) the suspension is fed to a tissue-making headbox in line with methods known in the art. In a typical process, a low consistency pulp furnish is provided in a pressurized (e.g. multi-layered) headbox. The headbox has an opening for delivering a thin deposit of pulp furnish onto the Fourdrinier wire to form a wet web in the following step (d) in which the suspension is deposited onto a wire to form a wet web. According to one preferred embodiment of the invention,

softness and strength of the base tissue are influenced by producing a multi-layer tissue paper web if a specifically constructed headbox (i.e. multi-layered headbox) is used to form the primary fibrous web having physically different layers of fibrous material.

(d) The wet laying step and the further production steps are also performed in line with methods known in the art. Tissue paper can be formed by placing the fibers on one or between the two continuously revolving wires of the paper-making machine while simultaneously removing the main quantity of water of dilution until dry-solids contents of 8 to 35% are obtained.

The forming wire is often referred to in the art as a Fourdrinier wire. Once the furnish is deposited on the forming wire, it is referred to as a web. The particular techniques and equipment for making webs according to the process just described are well-known to those skilled in the art.

(e) The web is then typically dewatered to a fiber consistency of between about 8% and about 35% (total web weight basis) by gravity or vacuum dewatering, and further dewatering the web by pressing operations wherein the web is subjected to pressure developed by opposing mechanical members, for example cylindrical rolls. A shoe press such as the NipcoFlex-T available from Voith can be used for the pressing operations.

(f) In conventional tissue making processes, the formed primary fibrous web is dried in one or more steps by mechanical and thermal means until a final dry-solids content of usually about 93 to 97% is obtained. The drying is followed by the crepe process which crucially influences the properties of the finished tissue product. The creping step involves creping on a usually 4.5 to 6 m diameter drying cylinder, the so-called Yankee cylinder, by means of a crepe doctor with the aforementioned final dry-solids content of the base tissue paper (wet creping can be used if lower demands are made of the tissue quality). The creped, finally dry base tissue paper (base tissue) is then available for further processing into the tissue paper product according to the invention.

When the tissue paper is creped on the Yankee cylinder, the blade holder angle (reference number (4) in Figure 1) is preferably determined to be from 10 to 35°. In conventional tissue making processes, values of from 11 to 13° are typically

employed. If through-air-drying (TAD) technology as explained below is used, the blade holder angle preferably ranges from 20 to 35°, in particular 22 to 30°.

When practising the present invention, the geometry of the doctor blade relative to the tissue surface may also have an impact on the properties of the product obtained. Thus, thickness and relative wet strength may increase, when the bevel angle is increased from 20° over 25° to 30°. As “level angle” we understand the angle (3) given in Figure 1.

The inventors of the present invention have surprisingly found that in the present tissue paper making processes, the primary (embryonic) fibrous webs containing MG pulp fibers strongly adheres to the Yankee cylinder in the final drying and creping steps. Furthermore, the inventors have observed that due to the strong adhesion of the web to the Yankee cylinder, finer creping is achieved and a smoother tissue surface is obtained. The strong and controlled adhesion of the web to the Yankee cylinder generally facilitates the tissue paper making process.

Instead of the conventional tissue making process described above, the invention can also make use of a modified technique in which an improvement in specific volume is achieved through wet-shaping of the still wet primary (embryonic) fibrous web by means of a 3D-structured fabric or plastic belt and/or by a special kind of drying as in TAD processes. In this way an improvement in the bulk softness of the thus made tissue paper is achieved as well. The TAD (through-air-drying) technique 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 80%, before final contact drying on the Yankee cylinder, by blowing hot air through the fibrous web. Pressing the "primary" fibrous web is hence not required for TAD processes. 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 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.

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 base 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 "internal" nor external 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.

When processing ("converting") the base fibrous web or base 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, laminating, folding, imprinting, perforating, application of lotions, smoothing, stacking, rolling up. Chemical ply adhesion can be performed by using an adhesive such as Kappasil and Kappaflex adhesives available from Kapp-Chemie GmbH.

To produce multi-ply tissue paper products, such as handkerchiefs, toilet paper, hand towels, household towels etc., 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, which has already been optionally wound up in several plies, to the finished 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 packages 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.

These converting techniques are known in the art.

The present invention is now further illustrated by the following examples.

## 4. Examples

The following test methods were used to evaluate the tissue papers produced. The test samples were conditioned for at least 12 hours at 50% relative humidity and 23 °C prior to testing.

### 4.1. Basis weight

The basis weight was determined according to EN ISO 12625-6:2005, Tissue Paper and Tissue Products, Part 6: Determination of grammage.

### 4.2. Caliper

The measurement is made by a precision micrometer (precision 0.001 mm) according to a modified method based on EN ISO 12625-3:2014, 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 $\pm$ 0.1 mm (10.0 $cm^2$ nominal area). The pressure applied is 2.0 kPa $\pm$ 0.1 kPa. The pressure foot is movable at a speed rate of 2.0 $\pm$ 0.2 mm/s.

A usable apparatus is a thickness meter type L & W SE050 (available from Lorentzen & Wettre, Europe).

The **base tissue** (web) to be measured is cut into pieces of 20 x 25 cm and conditioned in an atmosphere of 23°C, 50 % RH (Relative Humidity) for at least 12 hours. For the measurement, a stack of 10 base tissue paper sheets is prepared and placed beneath the pressure plate, which is then lowered. The thickness value for the stack is then read off 5 seconds after the pressure has been stabilized. The

thickness measurement is then repeated nine times with further samples treated and prepared in the same manner.

The mean value of the 10 values is taken as thickness of 10 base tissue sheets measured (in the following referred to as "**10-ply caliper**").

The **finished product** to be measured (i.e. a one-ply or multi-ply tissue paper product) is cut into pieces of 20 x 25 cm and conditioned in an atmosphere of 23°C, 50 % RH for at least 12 hours.

For the measurement one sheet is placed beneath the pressure plate which is then lowered. The thickness value for the sheet is then read off 5 seconds after the pressure has been stabilized. The thickness measurement is then repeated nine times with further samples treated in the same manner.

The mean value of the 10 values obtained is taken as thickness of one sheet ("**one-sheet caliper**") of the finished product (e.g. a two-ply hand towel) measured.

### 4.3. Bulk in $cm^3/g$

The bulk of the tissue paper was calculated with the following formula:

$X = t / w$

$X$ = bulk ($cm^3/g$)
$t$ = mean thickness of a sheet (µm)
$w$ = basis weight of the sheets ($g/m^2$)

### 4.4 Dry tensile strength in N/m (MD + CD)

The dry strength was determined according to EN ISO 12625-4: 2005, Tissue Paper and Tissue Products, Part 4: Determination of width-related breaking strength, elongation at break and tensile energy absorption.

The tensile tester used for the measurement featured two clamps of 50 mm width. Each clamp can grip the test piece firmly, but without damage, along a straight line

across the full width of the test piece (the clamping line). The distance between the clamping lines was set at 100 mm. For special tests, the distance is reduced if the available length of the sample is lower than 100 mm (e.g. toilet tissue in cross direction).

The tissue paper product to be measured, i.e. two sheets of a single-ply or multi-ply product, was cut into test pieces of 50 mm wide with parallel edges. Each sheet was cut into two different types of test pieces by cutting in the machine direction and in the cross direction. The obtained test pieces were then conditioned in an atmosphere of 23°C, 50 % RH (Relative Humidity) for at least 12 hours.

The test piece to be measured was placed between the clamps without any strain, and such that any observable slack is eliminated. At the beginning, a pre-tensile force of 25 cN is applied (zero of stretch) then the elongation rate between the clamps was kept constant at 5 cm/min. The maximum tensile force required to break the test piece was obtained. The measurement was repeated with six test pieces and the values obtained were averaged.

The dry tensile strength was calculated by means of the following formula:

Mean dry tensile strength [N/m] = (mean maximum tensile force [N] / initial width of the test piece [mm]) x $10^3$

Results were reported separately for the machine direction (MD) and the cross direction (CD).

### 4.5. Wet tensile strength in N/50mm (MD + CD)

The wet strength was determined according to EN ISO 12625-5:2005 Tissue Paper and Tissue Products, Part 5: Determination of wet tensile strength.

The apparatus used for the measurement was a vertical tensile strength tester featuring one clamp of 50 mm width, capable of gripping the test piece firmly without slippage. Below the clamp a thin metal bar and further below a vertically movable Finch Cup soaking device filled with water was arranged as is well known in the art.

To prepare the test pieces two sheets of a single-ply or multi-ply paper were each cut into test "strips" of 5 x 15 cm with parallel edges. From each sheet two types of test pieces were prepared by cutting in the machine direction (MD) and in the cross direction (CD).

To ensure that the wet strength of the samples had fully developed, the samples to be tested were artificially aged before conducting the tensile test measurement. Aging was achieved by heating the samples in an air-circulating drying cabinet to 80°C for a period of 30 min according to the ISO standard.

For the test the strip-shaped test piece was wound once around the metal bar in the Finch Cup soaking device in order to form a loop followed by fixing both ends of the test piece loop in the clamp arranged above the soaking device. The two ends of the test piece were fixed in the clamp without any strain, and such that the test span was set at 4.5 cm. To start the measurement the Finch cup filled with water was raised so that the bar and the strip are fully immersed in the water. After that the test piece was soaked for 15 seconds followed by immediately initiating the tensile test. The wet tensile force required to break the immersed test piece was determined at an elongation rate of 5 cm/min. The measurement was repeated with six test pieces and the values obtained were averaged.

The wet tensile strength was then calculated with the following formula:

Mean wet tensile strength [N/m] = (mean maximum tensile force [N] / initial width of the test piece [mm]) x $10^3$

Results were reported separately for the machine direction (MD) and the cross direction (CD).

### 4.6. Geometrical Mean Tensile Index (dry)

The geometrical mean tensile index was calculated in accordance with EN ISO 12625-4:2005 by the following formula:

Geometrical Mean Tensile Index [Nm/g] = SQRT ((Tensile Strength MD [N/m] x Tensile Strength CD [N/m]) / (Basis Weight [$g/m^2$])$^2$)

The basis weight of the tissue paper was determined in accordance with EN ISO 12625-6, Tissue Paper and Tissue Products, Part 6: Determination of grammage, as set forth in item 4.1 above.

### 4.7. Freeness value

The freeness value (in °SR) was measured according to DIN-ISO 5267/1; March 1999.

### 4.8. Softness

Softness was rated by a panel composed of at least five qualified persons.

The final tissue paper product (i.e. three-ply toilet paper, two-ply hand towel or two-ply household towel) is compared against softness standards. The evaluation procedure consists in assessing surface and bulk softness, grip and drapability. By judgment of the panelist the tested products are ranked against standards with a known softness value. The results of the individual panelists are averaged into a final softness value for the respective finished product.

Very slight differences in tissue softness can thus be quantified by comparison with tissue references to which softness values ranging from 1.5 to 4.0 had been previously allocated. Softness ratings were averaged across all panelists.

### 4.9. Absorption

The absorption (in g/g) was determined in accordance with PrENV 12625-8 Tissue Paper and Tissue Products, Part 8: *Determination of water-absorption time and water-absorption capacity*, in accordance with the basket-immersion test method described in EP 1 362 143 B1, item 5 - test method and Figur 1).

### 4.10. Starting materials, chemicals and tissue machine

**Pulp**

Three different types of pulp fibers were used as follows:

• Northern Bleached Softwood Kraft (NBSK) Pulp from Canfor Pulp Ltd., ECF 90 pulp grade ("SW pulp")
• Chemical pulp made from Eucalyptus hardwood fibers from Suzano Pulp and Paper, Brazil; Extra Prime Bleached Eucalyptus Kraft Pulp ECF grade ("HW pulp")
• Chemical pulp produced by SCA Hygiene Products from *Miscanthus Giganteus* ("MG pulp").

The "MG pulp" was produced using the soda pulping process. Soda pulping uses NaOH as the active cooking chemical to achieve the delignification which occurs at elevated temperatures. After the cooking the pulp was bleached using conventional bleaching agents and dried.

**Chemicals**

The chemicals used in the following examples are listed below:
• For the Yankee coating:
> Adhesive 2624 from Buckman;
> Plasticizer 2616 from Buckman;
> Release agent 2098e from Buckman
• Wet strength resin Kymene™ 557 H from Ashland (12,5% solids).
• Adhesives: Kappasil 260-4410, Kappaflex binder 72-0004. and Kappaflex grau 65-0012 were each purchased from Kapp-Chemie GmbH, Germany.

Hereinafter weight proportions ("kg/t") always refer to the amount of treated cellulosic fibers (dry weight).

**Tissue machine**

A conventional tissue paper making machine was adapted to make a three-ply toilet paper (Example 1), a two-ply hand towel (Example 2) and a two-ply household towel (Example 3). The machine was equipped with a Dry Crepe configuration and involved a two-layer headbox; a Crescent Former; a Suction Turning Roll; a NipcoFlex-T shoe press; a Yankee dryer with a drying hood; and a reel section to wind up the tissue paper.

The machine settings were kept throughout the trials in the following range(s):

| | |
|---|---|
| Yankee speed: | 1000 m/min |
| Shoe press line load: | 90 kN/m |
| Creping factor: | 13% |
| Dryness before Yankee: | 42 to 48% |
| Hood temperature: | 190 – 330 °C |
| Final tissue dryness: | 94 – 97% |

**Example 1-1 (Reference toilet paper)**

To achieve the desired finished toilet tissue paper one-ply base tissue was combined in a subsequent converting step to the final ply count (3). All three plies were produced in the same manner as described below:

The first furnish stream was prepared from unrefined HW pulp.

Then, SW pulp was refined to a freeness value of 21°SR to prepare a second furnish stream.

These two furnishes were supplied to the two chambers of a two-layer headbox. The furnish streams were kept separate through the headbox and deposited between a forming wire and a felt to form a two layer embryonic web containing 40 wt.-% of the refined SW pulp and 60 wt.-% of the unrefined HW pulp, respectively.

The embryonic web was dewatered in the shoe press to a dryness of about 42 to 48% and then led over the Yankee cylinder such that the HW pulp layer was in contact with the surface of the Yankee cylinder ("Y") and the SW pulp layer was opposite the Hood ("H").

After drying and creping, three two-layer base tissue paper webs having each a basis weight of about 17 g/m$^2$ and a 10-ply caliper of about 1,25 mm were obtained.

These three paper webs were bonded to each other by decor laminating / embossing and cut to size.

In the decor laminating / embossing step the three webs were fed through the nip of an embossing station including an embossing roll with protrusions forming a micro background and design elements (feathers) and a rubber roll arranged opposite thereto. Technical solutions where décor and background embossing are created by separate rolls / nips may be utilized too. Before the middle ply reached the nip, and after being superimposed with one outer web (ply), adhesive was selectively applied to those areas of the middle web (ply) that are joined together in the nip with the corresponding areas of the two outer webs (plies) by means of the protruding design elements of the embossing roll.

The adhesive used for bonding the three paper webs together was composed of 49 wt.-% water (452.16 kg), 46 wt.-% Kappasil (260-4410) (422.40 kg), 4.5 wt.-% Kappaflex binder (72-0004) (43.20 kg), and 0.5 wt.-% Kappaflex grau (65-0012) (4.42 kg), based on the total weight (922.18 kg) of the adhesive.

The three webs were fed to the embossing station and bonded in such a manner that the HW pulp layers (produced from the first furnish) of the two outer webs (plies) were located each on the outside of the three-ply toilet paper.

**Example 1-2 (Toilet paper with 12% MG pulp)**

A three-ply toilet paper was produced in the same manner as set forth in Example 1-1 apart from the following differences.

- The first furnish stream was a 1/4 mixture of unrefined MG pulp and unrefined HW pulp, respectively.
- The SW pulp used for the second furnish stream was refined to a slightly higher freeness value of 22°SR.

In the manufacture of the resulting two-layer webs, the SW pulp layer (40%) was located on the hood side, while the layer on the Yankee side included 12%MG pulp and 48%HW pulp, each based on the total weight of the web.

These three paper webs were bonded to each other by decor laminating / embossing and cut to size in the same manner as described in Example 1-1. They were bonded in such a manner that the MG pulp-containing layers (produced from

the first furnish stream) of the two outer webs (plies) were located each on the outside of the three-ply toilet paper.

**Example 1-3 (Toilet paper with 60% MG pulp)**

A three ply toilet paper was produced in the same manner as set forth in Example 1-1 apart from the following difference:

- The first furnish stream contained only unrefined MG pulp.

In the manufacture of the resulting two-layer webs, the SW pulp layer (40%) was located on the Hood side ("H"), while the layer on the Yankee side ("Y") included 60% MG pulp, each based on the total weight of the web.

These three paper webs were bonded to each other by decor laminating / embossing and cut to size size in the same manner as described in Example 1-1. They were bonded in such a manner that the MG pulp-containing layers of the two outer webs (plies) were located each on the outside of the three-ply toilet paper.

The properties of the toilet papers obtained in examples 1-1, 1-2 and 1-3 were evaluated according to the procedures explained hereinbefore. The results were as shown in table 1 below.

**Table 1**

| | Example 1-1 (Reference) | Example 1-2 | Example 1-3 |
|---|---|---|---|
| Pulp composition of plies (Y/H) | 60%HW/40%SW | (12%MG+48%HW)/ 40%SW | 60%MG/40%SW |
| Total basis weight ($g/m^2$) | 51.9 | 49.0 | 48.6 |
| Caliper /sheet[1] (µm) | 480 | 460 | 460 |
| Bulk ($cm^3/g$) | 9.25 | 9.39 | 9.47 |
| Dry MD tensile (N/m) | 238 | 236 | 274 |
| Dry CD tensile (N/m) | 124 | 128 | 136 |
| Geometrical Mean Tensile Index (Nm/g) | 3.3 | 3.5 | 4.0 |
| Softness | 2.2 | 2.2 | 2.1 |
| Absorption | 8.4 | 8.6 | 8.5 |

[1] "one sheet caliper" as described before

These test data show that the use of MG chemical pulp fibers according to the present invention can lead to a major absolute increase in tensile strength without concomitant loss of softness, or with only a minor loss of softness.

Further, it was surprisingly observed that, during the final drying and creping steps of the process, the embryonic fibrous webs of Examples 1-2 and 1-3, which contained MG pulp fibers, showed a better adhesion to the Yankee cylinder than the web of Reference Example 1-1, which contained eucalyptus pulp fibers instead.

**Example 2-1 (Reference hand towel)**

Two tissue paper plies were produced as described below.

SW pulp was refined to a freeness value of 21°SR and two different pulp slurries (furnishes) were prepared:

- The first furnish stream was a 1/1 mixture of refined SW pulp and unrefined HW pulp, respectively.
- The second furnish stream contained only refined SW pulp.
- 5.0 kg/t of Kymene™ 557H, based on the total pulp amount, was added to the first and second furnish streams.

These two furnish streams were supplied to the two-layer headbox. The furnish streams were kept separate through the headbox and deposited onto a Fourdrinier wire to form a two-layer embryonic web containing 50 wt.-% of refined SW pulp, and 50 wt.-% of the aforementioned 1/1 mixture of refined SW pulp and unrefined HW pulp.

The embryonic web was dewatered in the shoe press to a dryness of about 42 to 48% and then led over the Yankee cylinder such that the first furnish was in contact with the surface of the Yankee cylinder and the second furnish (SW pulp only) opposite the Hood.

Two two-layer base tissue paper webs having each a basis weight of about 21 g/m$^2$ and a 10-ply caliper of about 1.37 mm were obtained and wound up on jumbo rolls.

These two paper webs were bonded together by decor laminating / embossing, cut to size and reeled-up to a dispenser hand towel dispenser.

In the decor laminating / embossing step the two webs were fed through the nip of an embossing station including an embossing roll with protrusions forming a micro background and design elements (leaf and Tork® logo) and a rubber roll arranged opposite thereto. Before one web (ply) reached the nip, adhesive was selectively applied to those areas thereof that are joined together in the nip with the

corresponding areas of the other web (ply) by means of the protruding design elements of the embossing roll.

The adhesive used for bonding the two paper webs together was the same as used in Example 1-1.

In the bonding step the webs were superimposed and fed to the embossing station in such a manner that the layers containing only softwood pulp contacted each other and were located inside the two-ply hand towel (as shown in the table below).

| | layer | Pulp composition | Kymene |
|---|---|---|---|
| 1st ply | Outer 1) | 25%SW+25%HW | Yes |
| | Inner 2) | 50%SW | Yes |
| 2nd ply | Inner 2) | 50%SW | Yes |
| | Outer 1) | 25%SW+25%HW | Yes |

1) produced from 1st furnish / 2) produced from 2nd furnish

**Example 2-2 (Hand towel with 10% MG pulp)**

A two-ply hand towel was produced in the same manner as set forth in Example 2-1 apart from the following difference:

- The first furnish stream contained a 2/3/5 mixture of unrefined MG pulp, unrefined HW pulp and refined SW pulp, respectively.

Further, in accordance with the procedure of Example 2-1,

- the second furnish stream contained only refined SW pulp.
- 5.0 kg/t of Kymene™ 557H, based on the total pulp amount, was added to the first and second furnish streams.

In the manufacture of the resulting two-layer webs, the SW layer (50%) was on the hood side, while the layer on the Yankee side included 10% MG, 15% HW and 25% SW pulp, each based on the total weight of the ply.

Two two-layer base tissue paper webs having each a basis weight of about 21 g/m$^2$ and a 10-ply caliper of about 1,20 mm were obtained and wound up on jumbo rolls.

These two paper webs were bonded together by decor lamination / embossing, cut to size and reeled-up in the same manner as described in in Example 2-1. Correspondingly, in the final two-ply hand towel, the layers containing only softwood pulp contacted each other and the MG pulp-containing layers (produced from the first furnish) were located on the outside (as shown in the table below).

| | layer | Pulp composition | Kymene |
|---|---|---|---|
| 1$^{st}$ ply | Outer 1) | 10%MG+15%HW+25%SW | Yes |
| | Inner 2) | 50%SW | Yes |
| 2$^{nd}$ ply | Inner 2) | 50%SW | Yes |
| | Outer 1) | 10%MG+15%HW+25%SW | Yes |

1) produced from 1$^{st}$ furnish / 2) produced from 2$^{nd}$ furnish

**Example 2-3 (Hand towel with 25% MG pulp)**

The two webs constituting the two plies of a two ply hand towel were produced as described below.

A first web and a second web were produced in the same manner as explained in Example 2-1 apart from the following differences:

- The first furnish stream was a 1/1 mixture of refined SW pulp and unrefined MG pulp, respectively.

Further, in accordance with the procedure of Example 2-1,

- the second furnish stream contained only refined SW pulp.
- 5.0 kg/t of Kymene$^{TM}$ 557H, based on the total pulp amount, was added to the first and second furnish streams.

The two furnish streams were kept separate through the headbox and deposited onto a Fourdrinier wire in such a ratio so as to form a two-layer embryonic web

containing 75 wt.-% of refined SW pulp and 25 wt.-% of MG pulp, each based on the total amount of pulp (= total weight of the web).

In the manufacture of the resulting webs, the SW pulp layer (50%) was on the Hood side, while the layer on the Yankee side included 25% SW + 25% MG, each based on the total weight of the web.

The first and second base tissue paper web each had a basis weight of about 21 $g/m^2$ and a 10-ply caliper of about 1.20 mm and were wound up separately on jumbo rolls.

The first paper web and the second paper web were bonded together by decor lamination / embossing, cut to size and wound on a dispenser hand towel reel in the same manner as described in in Example 2-1.

In the final two-ply hand towel, the layers containing only softwood pulp contacted each other and the MG pulp-containing layers were located on the outside (as shown in the table below).

| | layer | Pulp composition | Kymene |
|---|---|---|---|
| 1st ply | Outer 1) | 25%SW+25%MG | Yes |
| | Inner 2) | 50%SW | Yes |
| 2nd ply | Inner 2) | 50%SW | Yes |
| | Outer 1) | 25%SW+25%MG | Yes |

1) produced from first furnish / 2) produced from 2nd furnish

The properties of the hand towels obtained in examples 2-1, 2-2 and 2-3 were evaluated according to the procedures explained hereinbefore. The results were as shown in table 2 below.

**Table 2**

| | Example 2-1 (Reference) | Example 2-2 | Example 2-3 |
|---|---|---|---|
| Pulp composition of plies (Y/H) | (25%SW+25%HW)/ 50%SW | (10%MG+15%HW +25%SW)/50%SW | (25%SW+25%MG)/ 50%SW |
| Total basis weight ($g/m^2$) | 42.8 | 40.0 | 41.4 |
| Caliper /sheet[1] (µm) | 250 | 260 | 260 |
| Bulk ($cm^3/g$) | 5.84 | 6.,50 | 6.28 |
| Dry MD tensile (N/m) | 615 | 759 | 751 |
| Dry CD tensile (N/m) | 321 | 323 | 349 |
| Geometrical Mean Tensile Index (Nm/g) | 10.4 | 12.4 | 12.4 |
| Absorption (g/g) | 6.4 | 6.2 | 6.5 |

[1] "one sheet caliper" as described before

These test data show that the use of MG chemical pulp fibers according to the present invention can lead to an absolute increase in tensile strength, when compared to HW pulp fibers, e.g. Eucalyptus.

Further, it was also surprisingly observed that, during the final drying and creping steps of the process, the embryonic fibrous webs of Examples 2-2 and 2-3 which contained MG pulp fibers showed a better adhesion to the Yankee cylinder than the web of Reference Example 2-1 which contained eucalyptus pulp fibers instead.

**Example 3-1 (Reference household towel)**

The same tissue paper webs as produced in Example 2-1 were used for manufacturing a two-ply household towel. The two tissue paper webs were superimposed and bonded (laminated) to each other by embossing in a nested configuration.

In the laminating / embossing step the two webs were fed through the nip of an embossing station including an embossing roll with protrusions forming a graphical pattern and a rubber roll arranged opposite thereto. Before one web (ply) reached the nip, the same adhesive as described in Example 1-1 was selectively applied to those areas of the web that are joined together in the nip with the corresponding areas of the other web (ply) by means of the protruding elements of the embossing roll.

**Example 3-2 (Household towel with 10% MG pulp)**

The same tissue paper webs as produced in Example 2-2 were used for manufacturing a two-ply household towel. The two tissue paper webs were laminated and embossed in the same manner as described in Example 3-1.

**Example 3-3 (Household towel with 25% MG pulp)**

The same tissue paper webs as produced in Example 2-3 were used for manufacturing a two-ply household towel. The two tissue paper webs were laminated and embossed in the same manner as described in Example 3-1.

The properties of the household towels obtained in examples 3-1, 3-2 and 3-3 were evaluated according to the procedures explained hereinbefore. The results were as shown in table 3 below.

**Table 3**

| | Example 3-1 (Reference) | Example 3-2 | Example 3-3 |
|---|---|---|---|
| Pulp composition of plies (Y/H) | (25%SW+25%HW)/ 50%SW | (10%MG+15%HW +25%SW)/50%SW | (25%SW+25%MG)/ 50%SW |
| Total basis weight ($g/m^2$) | 41.4 | 39.3 | 42.1 |
| Caliper /sheet[1] (µm) | 710 | 720 | 720 |
| Bulk ($cm^3/g$) | 17.15 | 18.32 | 17.10 |
| Dry MD tensile (N/m) | 453 | 577 | 612 |
| Dry CD tensile (N/m) | 190 | 191 | 237 |
| Geometrical Mean Tensile Index (Nm/g) | 7.1 | 8.4 | 9.0 |
| Softness | 5.,5 | 5,4 | 4.9 |
| Absorption (g/g) | 10.5 | 10.6 | 9.7 |

[1] "one sheet caliper" as described before

These test data show that the use of MG pulp fibers according to the present invention can lead to an absolute increase in tensile strength without significant loss of softness.

Further, it was surprisingly observed that, during the final drying and creping steps of the process, the embryonic fibrous webs of Examples 3-2 and 3-3 which contained MG pulp fibers showed a better adhesion to the Yankee cylinder than the web of Reference Example 3-1 which contained eucalyptus pulp fibers instead.

## CLAIMS

1. Tissue paper web composed of one or more layers wherein at least one layer comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus wherein the pulp fibers are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof.

2. Tissue paper web according to Claim 1 wherein the pulp fibers originate from *Miscanthus Gigantheus*, *Miscanthus Sinensis*, or *Miscanthus Sacchariflorus*, and preferably from *Miscanthus Gigantheus*.

3. Tissue paper web according to Claim 1 or 2 wherein the pulp fibers, which originate from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*, are present in an amount of at least 5 wt.-%, preferably in an amount of 10 wt.-% to 90 wt.-%, more preferably 15 wt.-% to 80 wt.-%, even more preferably 20 wt.-% to 70 wt.-%, based on the total weight of the tissue paper web.

4. Tissue paper web according to any of Claims 1 to 3 wherein the web is composed of two or three layers made from different pulps wherein at least one of these layers is made from pulp comprising the pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*.

5. Tissue paper web according to any of claims 1 to 4 wherein the remaining fibers present in said tissue paper web are selected from pulp fibers comprising hardwood fibers, such as eucalyptus, beech, aspen, acacia or birch fibers; softwood fibers such as pine, spruce, red cedar, douglas fir, hemlock, and larch fibers; and non-wood fibers such as cotton, bagasse, hemp, linen, sisal, straw or flax fibers.

6. Tissue paper web according to Claim 4 or 5, wherein the web is composed of two layers wherein
(i) the first layer is made from pulp fibers (i-a) consisting of fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* and optionally hardwood fibers, or from pulp fibers

(i-b) comprising, or consisting of, fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* softwood fibers, and optionally hardwood fibers, and
(ii) a second layer is made from pulp fibers comprising, or consisting, of softwood fibers.

7. Tissue paper web according to Claim 6, wherein
(i) the first layer is made from pulp fibers (i-a), wherein the weight ratio of fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* to hardwood fibers, if present, is 100/0 to 10/90, preferably 100/0 to 20/80, and
(ii) the second layer is made from pulp comprising, or consisting of, softwood fibers,
and wherein the weight proportion of pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* based on the total weight of the tissue paper web is preferably 10 to 90 wt.%, more preferably 10 to 80 wt.-%, in particular 25 to 75 wt.-%, such as 40 to 70 wt.-%.

8. Tissue paper web according to Claim 6, wherein
(i) the first layer is made from pulp fibers (i-b) consisting of fibers originating from at least one plant belonging to the genus Miscanthus and preferably from *Miscanthus Gigantheus* (MG), softwood fibers (SW), and optionally hardwood fibers (HW), wherein the weight ratio MG / HW / SW in %, based on the total weight of pulp fibers (i-b), is 10 to 90 / 0 to 50 / 10 to 90, preferably 20 to 80 / 0 to 50 /20 to 80, and
(ii) the second layer is made from pulp fibers comprising, or consisting of, softwood fibers, and wherein the weight proportion of pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* based on the total weight of the tissue paper web is preferably 10 to 50 wt-%, such as 10 to 30 wt.-%.

9. Tissue paper web according to any of claims 1 to 8, wherein the pulp fibers originating from *Miscanthus Gigantheus* are obtained in a chemical, chemo-mechanical or high yield chemical pulping process, preferably the soda process or the CTMP process (Chemo-Thermo-mechanical pulping).

10. Tissue paper web according to any of claims 1 to 9, wherein the hardwood pulp fibers originate from eucalyptus and/or the softwood pulp fibers are Northern Bleached Softwood Kraft (NBSK) fibers, wherein the NBSK fibers are preferably refined to a degree of fineness of 19 to 35°SR.

11. Tissue paper web according to any of claims 1 to 10, wherein (i) all fibers present in the web are primary pulp fibers, or (ii) a mixture of primary and secondary (recycled) pulp fibers wherein the proportion of secondary (recycled) pulp fibers does not exceed 90 wt.-% based on the tissue paper web.

12. Tissue paper web according to any of claims 1 to 11 which is composed of one or more layers wherein the pulp fibers originating from at least one plant belonging to the genus Miscanthus fulfill the following requirements:
(i) average fiber length of from 0.5 to 1.2 mm, preferably from 0.8 to 1.0 mm;
(ii) average fiber diameter of from 10 to 25 µm; and
(iii) average fiber wall thickness of from 3.0 to 5.0 µm.

13. Tissue paper product comprising at least one ply made from the tissue paper web according to any of claim 1 to 12.

14. Tissue paper product according to claim 13, wherein the tissue paper product is selected from toilet paper, hand towel, household towel, handkerchiefs, napkins and facial tissues.

15. Tissue paper product according to claim 13 or 14 wherein the tissue paper product is a toilet paper composed of 2 to 5 plies, wherein preferably at least one outer ply, more preferably both outer plies, is/are made from the tissue paper web of claim 7, and the outer ply/plies is/are arranged such that, in the toilet paper, the first layer thereof (i), which comprises the pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Giganteus*, is located on the outer surface of the toilet paper.

16. Tissue paper product according to claim 13 or 14 wherein the tissue paper product is a hand towel or household towel composed of 2 to 5 plies,

wherein preferably at least one ply, optionally all plies, is/are made from the tissue paper web of claim 7 or the tissue paper web of claim 8.

17. Tissue paper product according to any of claims 13 to 16 wherein the tissue paper product is free of a softener and/or is free of a strengthening resin.

18. Process for the manufacture of a tissue paper web according to any of Claims 1 to 12, comprising the steps of:

(a) providing chemical pulp fibers comprising fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Giganteus*;

(b) forming an aqueous suspension of said pulp fibers;

(c) feeding the suspension to a tissue-making headbox;

(d) depositing the suspension onto a wire to form a wet web;

(e) dewatering the wet web; and

(f) drying and creping the web.

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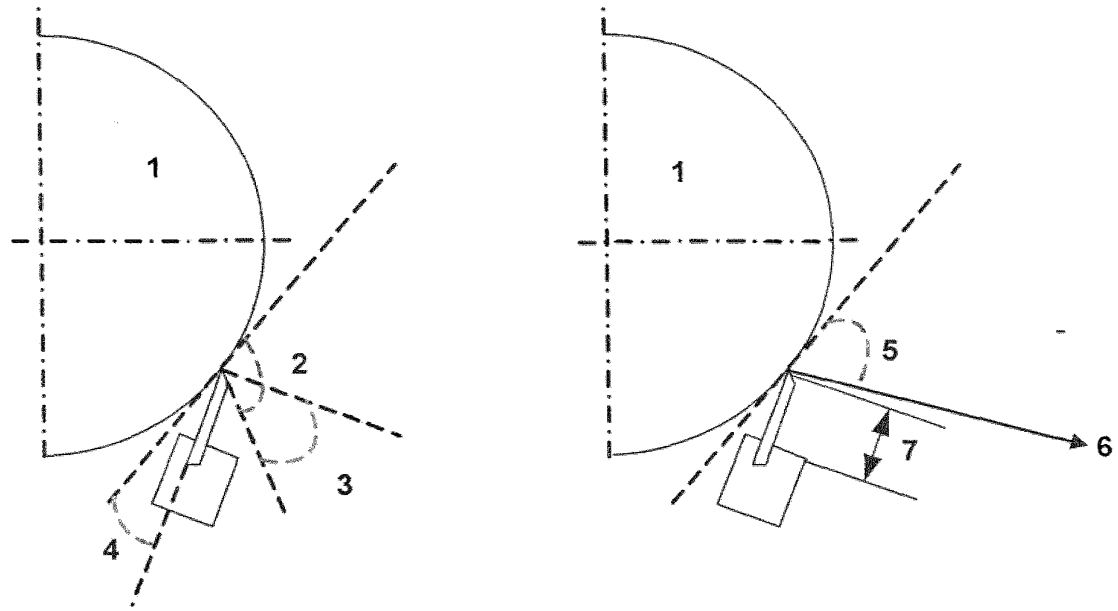



Figure 1

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/059326

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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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. |
|---|---|---|
| Y | KR 2015 0038853 A (UNIV CHONBUK NAT IND COOP FOUND) 9 April 2015 (2015-04-09) abstract | 1-3,18 |
| X | DE 10 2007 017061 A1 (VOITH PATENT GMBH [DE]) 16 October 2008 (2008-10-16) | 1,3,18 |
| Y | paragraphs [0014], [0015], [0022], [0042]; claims | 1-18 |
| Y | EP 1 583 869 A1 (SCA HYGIENE PROD GMBH [DE]) 12 October 2005 (2005-10-12) the whole document | 1-18 |

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

☒ See patent family annex.

* Special categories of cited documents :

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| 21 December 2015 | 08/01/2016 |

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|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Koegler-Hoffmann, S |



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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 |
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(54) **Title**: SOFT CREPED TISSUE

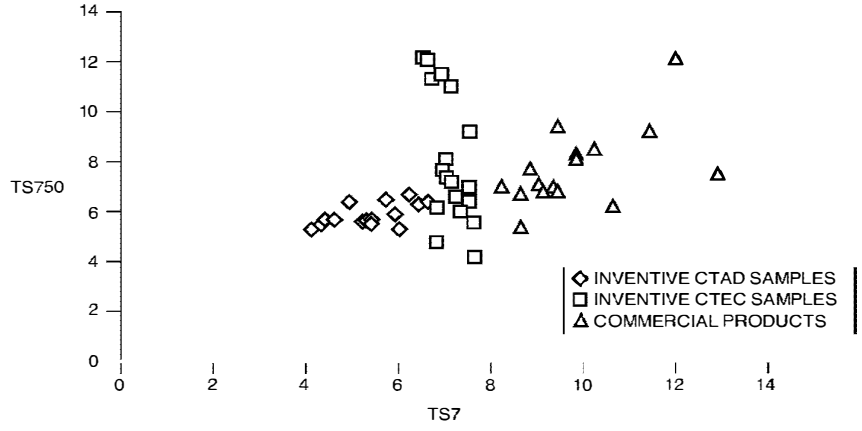



FIG. 1

(57) **Abstract**: The present disclosure is directed to creped tissue webs, and products produced therefrom. The creped tissue webs and tissue products made therefrom are soft and strong, such as having a TS7 value less than about 8.0. Moreover, the tissue of the present disclosure also preferably has low TS750 values such as less than about 7.0. Further, while webs prepared according to the present disclosure have low TS7, and in certain embodiments low TS750 values, they are also strong enough to withstand use.

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# SOFT CREPED TISSUE

## BACKGROUND

In the manufacture of paper products, such as facial tissues, bath tissues, napkins, wipes, paper towels, etc., it is often desired to optimize various properties of the products. For example, the products should have good bulk, a soft feel, and should have good strength. Unfortunately, however, when steps are taken to increase one property of the product, other characteristics of the product are often adversely affected.

For instance, it is very difficult to produce a high strength paper product that is also soft. In particular, strength is typically increased by the addition of certain strength or bonding agents to the product. Although the strength of the paper product is increased, various methods are often used to soften the product that can result in decreased fiber bonding. For example, chemical debonders can be utilized to reduce fiber bonding and thereby increase softness. Moreover, mechanical forces, such as creping or calendering, can also be utilized to increase softness.

However, reducing fiber bonding with a chemical debonder or through mechanical forces can adversely affect the strength of the paper product. For example, hydrogen bonds between adjacent fibers can be broken by such chemical debonders, as well as by mechanical forces of a papermaking process. Consequently, such debonding results in loosely bound fibers that extend from the surface of the tissue product. During processing and/or use, these loosely bound fibers can be freed from the tissue product, thereby creating lint, which is defined as individual airborne fibers and fiber fragments. Moreover, papermaking processes may also create zones of fibers that are poorly bound to each other but not to adjacent zones of fibers. As a result, during use, certain shear forces can liberate the weakly bound zones from the remaining fibers, thereby resulting in slough, i.e., bundles or pills on surfaces, such as skin or fabric. As such, the use of such debonders can often result in a much weaker paper product during use that exhibits substantial amounts of lint and slough. As such, a need currently exists for a paper product that is soft, yet strong enough to prevent sloughing. Moreover, there is a need for a product that can be produced without the excessive use of debonders.



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## SUMMARY

Typically to achieve a soft tissue the strength of the web is decreased and short, low coarseness fibers, treated with a chemical debonder, are disposed on the skin-contacting surface of the web. The softness levels achievable using such techniques, however, are limited by the user's desire to have a tissue that is strong enough to withstand use and to avoid large amounts of fibers sloughing from the tissue surface in-use. The present invention, however, overcomes these limitations to yield novel tissue webs that have improved softness, while maintaining sufficient strength.

Accordingly, in one aspect the disclosure provides a creped tissue web having a TS7 value less than about 8.0 dB $V^2$ rms.

In other aspects the disclosure provides a creped tissue web having a TS7 value less than about 8.0 dB $V^2$ rms and a TS750 value less than about 7.0 dB $V^2$ rms.

In yet other aspects the disclosure provides a creped tissue product comprising one or more plies, the tissue product having a geometric mean tensile (GMT) from greater than about 600 g/3" and a TS7 value of less than about 8 dB $V^2$ rms.

In still other aspects the disclosure provides a creped tissue web having a GMT from about 300 about 1000 g/3" and a TS7 value of less than about 8.0 dB $V^2$ rms.

In other aspects the disclosure provides a creped tissue web having a basis weight of greater than about 10 gsm and a TS7 value from about 4.0 to about 8.0 dB $V^2$ rms.

In still other aspects the present disclosure provides a multi-ply tissue product comprising two multi-layered creped tissue webs, the tissue webs having three superposed layers, an inner layer consisting essentially of softwood fibers and two outer layers consisting essentially of hardwood fibers, the inner layer being located between the two outer layers, wherein each web has a GMT greater than about 300 g/3" and a TS7 value of less than about 8.0 dB $V^2$ rms.

These and other features and aspects of the present disclosure are discussed in greater detail below.

## DEFINITIONS



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As used herein, the terms "TS7" and "TS7 value" refer to an output of an EMTEC Tissue Softness Analyzer ("TSA") (Emtec Electronic GmbH, Leipzig, Germany) as described in the Test Methods section. The units of the TS7 value are dB $V^2$ rms, however, TS7 values are often referred to herein without reference to units.

As used herein, the terms "TS750" and "TS750 value" refer to another output of the TSA as described in the Test Methods section. The units of the TS750 value are dB $V^2$ rms, however, TS750 values are often referred to herein without reference to units.

As used herein, the term "geometric mean tensile" (GMT) refers to the square root of the product of the machine direction tensile and the cross-machine direction tensile of the web, which are determined as described in the Test Method section.

As used herein, the term "tissue product" refers to products made from tissue webs and includes, bath tissues, facial tissues, paper towels, industrial wipers, foodservice wipers, napkins, medical pads, and other similar products.

As used herein, the terms "tissue web" and "tissue sheet" refer to a fibrous sheet material suitable for use as a tissue product.

As used herein, the term "caliper" is the representative thickness of a single 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" with Note 3 for stacked sheets. 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. Caliper may be expressed in mils (0.001 inches) or microns.

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

## DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of TS7 values (x-axis) versus TS750 values (y-axis) for various inventive and commercial tissue samples;

FIG. 2 is a plot of TS750 values (x-axis) versus GMT (y-axis) for various inventive and commercial tissue samples; and

FIG. 3 is a plot of TS7 values (x-axis) versus GMT (y-axis) for various inventive and commercial tissue samples.

## DETAILED DESCRIPTION

In general, the present disclosure is directed to creped tissue webs, and products produced therefrom. The creped tissue webs and tissue products made therefrom are soft and strong and as such generally have TS7 values less than about 8.0 and a geometric mean tensile ("GMT") greater than about 300 g/3" for single-ply tissue webs and greater than about 500 g/3" for multi-ply tissue products. In particularly preferred embodiments tissue produced according to the present disclosure also has a low TS750 value such as less than about 7.0. Further, while tissue prepared according to the present disclosure has low TS7, and in certain embodiments low TS750, it is also strong enough to withstand use. As such single-ply tissue webs prepared as disclosed herein preferably have a GMT greater than about 300 g/3", such as from about 400 to about 500 g/3".

Tissue webs and products having low TS7 and/or TS750 values may be prepared using a number of creped tissue making processes, such as conventional wet pressed (also referred to herein as "CTEC") and through-air dried (also referred to herein as "TAD"). Further, products having low TS7 and/or TS750 values may be prepared by post-treating the web by calendering or application of a topical additive such as a polysiloxane that makes a tissue product feel softer to the skin of a user. Suitable polysiloxanes that can be used in the present invention include amine, aldehyde, carboxylic acid, hydroxyl, alkoxyl, polyether, polyethylene oxide, and polypropylene oxide derivatized silicones, such as aminopolydialkylsiloxanes. When using an aminopolydialkysiloxane, the two alkyl radicals can be methyl groups, ethyl groups, and/or a straight, branched or cyclic carbon chain containing from about 3 to about 8 carbon atoms. Some commercially available examples of polysiloxanes include Y-14128, Y-14344, Y-14461 and FTS-226 (commercially available from Momentive Performance Materials, Albany, NY), and Dow Corning 8620, 2-8182, and 2-8194 (commercially available from Dow Corning Corporation, Midland, MI).



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When used, polysiloxanes may be combined with water and surfactants, such as nonionic ethoxylated alcohols, to form emulsions and applied to tissue webs. Since the process of the present invention can accommodate higher viscosities, however, the polysiloxanes can be added directly to a tissue web without having to be combined with water, a surfactant or any other dilution agent. For example, a neat composition, such as a neat polysiloxane can be applied to a web in accordance with the present disclosure.

Additionally, tissue webs and products having low TS7 and/or TS750 values may be prepared by applying a creping composition at high addition levels, such as greater than about 30 mg of solids per square meter of the creping surface, such as a Yankee Dryer. Still more preferably the creping composition is added to the creping surface at solids greater than about 50 mg/m$^2$, and even more preferably greater than about 100 mg/m$^2$, such as from about 50 to about 300 mg/m$^2$. The level of total solids add-on is preferably several times greater than traditional creping methods, which have typically employed add-on levels from about 2 to about 30 mg/m$^2$. Even at the increased add-on levels the present disclosure provides creping compositions that balance adhesion and release of the web from the Yankee Dryer, without the build-up of deposits of organic and/or inorganic components that can have a negative impact on creping efficiency.

When applied at high add-on levels to the Yankee Dryer, the creping compositions of the present disclosure develop proper coating equilibrium and a relatively constant Z-directional thickness of the coating on the dryer surface. When transferred to the web, the creping composition may form a continuous or a discontinuous film depending upon the additive composition and amount applied to the web. In other embodiments, the creping composition may be applied to a web such that the creping composition forms discrete treated areas on the surface of the web.

The thickness of the additive composition when present on the surface of a base sheet can vary depending upon the ingredients of the additive composition and the amount applied. In general, for instance, the thickness can vary from about 0.01 microns to about 10 microns. At higher add-on levels, for instance, the thickness may be from about 3 microns to about 8 microns. At lower add-on levels, however, the thickness may be from about 0.1 microns to about 1 micron, such as from about 0.3 microns to about 0.7 microns.

The area of the base sheet covered by the additive composition may vary from about 10 to about 100 percent of the surface area of one side of the base sheet. For instance,



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the additive composition may cover from about 20 to 100 percent of the surface area of the base sheet, such as from about 20 to about 90 percent, such as from about 20 to about 75 percent.

To achieve the desired creping efficiency and tissue product properties, tissue webs may be creped using a creping composition comprising at least one, and more preferably at least two, water-soluble polymers. For purposes herein, "water-soluble" means that the polymers dissolve completely in water to give a solution as opposed to a latex, dispersion, or suspension of undissolved particles.

In one embodiment the water-soluble polymer applied to the creping surface is an aqueous solution comprising a polyether, a polyamide, or a mixture of one or both with another water-soluble polymer. Suitable polyethers include (poly)ethylene oxide, (poly)propylene oxide, ethylene oxide/propylene oxide copolymers, (poly)tetra methylene oxide, poly vinyl methyl ether, and the like. Suitable polyamides include (poly)vinylpyrrolidone, (poly)ethyl oxazoline, (poly)amidoamine, (poly)acrylamide, polyethylene imine, and the like. Number average molecular weights for these components should be from about 10,000 to about 500,000.

Other water-soluble polymers which can be mixed with either of the water-soluble polymeric components used to form the creping composition include polyvinyl alcohol (PVOH), carboxymethylcellulose, hydroxypropyl cellulose, and the like.

In certain embodiments the creping composition may further comprise a polymeric component having an affinity for the fibers making up the web, such as a cationic polymer, and more specifically a cationic starch. As used herein the term "cationic starch" refers to a starch that has been chemically modified to impart a cationic constituent moiety. Suitable cationic polymers include cationic starches having a charge density of at least about 0.1 mEq/g, such as, for example, Redibond™ 2038 (Ingredion Incorporated, Westchester, IL) which has a charge density of about 0.22 mEq/g.

Particularly preferred cationic starches for use in the creping composition of the present disclosure are the tertiary aminoalkyl ethers and quaternary ammonium alkyl ethers, which include commercial cationic starches produced by Ingredion Incorporated, Westchester, IL, under the trade names Redibond™ and Optipro™. Grades with cationic

moieties only such as Redibond 5327™, Redibond 5330A™, and Optipro™ 650 are suitable, as are grades with additional anionic functionality such as Redibond 2038™.

The cationic component can be present in the creping composition in any operative amount and will vary based on the chemical component selected, as well as on the end properties that are desired. For example, in the exemplary case of Redibond 2038™, the cationic component can be present in the creping composition in an amount of about 10 to 90 wt %, such as 20 to 80 wt % or 30 to 70 wt % based on the total weight of the creping composition, to provide improved benefits.

Other suitable cationic components include cationic debonders and/or softeners. Cationic debonders and softeners are known in the papermaking art and are generally used as wet-end additives to enhance bulk and softness. Debonders are generally hydrophobic molecules that have a cationic charge. As wet end additives debonders function typically by disrupting inter-fiber bonding thereby increasing bulk and increasing perceived softness, but at the expense of a decrease in sheet strength. Softening agents are similar in chemistry to debonders, i.e., they are generally hydrophobic molecules that have a cationic charge. Examples of debonders and softening chemistries may include the simple quaternary ammonium salts having the general formula:

$$(R^{1'})_{4-b} - N^{+} - (R^{1''})_b\ X^{-}$$

wherein $R^{1'}$ is a $C_{1-6}$ alkyl group, $R^{1''}$ is a $C_{14-22}$ alkyl group, b is an integer from 1 to 3 and $X^{-}$ is any suitable counterion. Other similar compounds may include the monoester, diester, monoamide, and diamide derivatives of the simple quaternary ammonium salts. A number of variations on these quaternary ammonium compounds should be considered to fall within the scope of the present invention. Additional softening compositions include cationic oleyl imidazoline materials such as methyl-1-oleyl amidoethyl-2-oleyl imidazo linium methylsulfate commercially available as Mackernium CD-183 (McIntyre Ltd., University Park, IL) and Prosoft TQ-1003 (Ashland, Inc., Covington, KY).

In still other embodiments the creping composition comprises a water soluble cationic polyamide-epihalohydrin, which is the reaction product of an epihalohydrin and a polyamide containing secondary amine groups or tertiary amine groups. Commercially available preferred polyamide-epihalohydrins are sold under the trade names including Kymene™, Crepetrol™ and Rezosol™ (Ashland Water Technologies, Wilmington, DE).



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Compared to commercially available tissue, tissue products prepared according to the present disclosure generally have low TS7 values, such as less than about 8.0 and more preferably less than about 7.5, even more preferably less than about 7.0, and most preferably less than about 6.5, such as from about 4.0 to about 7.0. In other embodiments tissue products have low TS750 values, such as less than about 7.0, more preferably less than about 6.0, and still more preferably less than about 5.5, such as from about 4.0 to about 6.0. In other embodiments tissue products may have both a low TS7 value, such as less than about 8.0 and a low TS750 value, such as less than about 7.0, all while maintaining sufficient strength to withstand use, such as a GMT greater than about 400 g/3", such as from about 400 to about 1000 g/3".

Without wishing to be bound by theory, tissue webs and products produced therefrom are believed to achieve low TS7 and/or low TS750 values through the beneficial combination of improved tissue making methods and materials, such as, for example, high levels of low coarseness hardwood fibers, the addition of novel creping compositions at high add-on levels, the introduction of fine crepe structure to the creped tissue web and the post-treatment of the tissue web with calendering and/or topical treatment.

To illustrate the improvement over commercially available tissue, the table below compares inventive samples prepared as described herein with commercially available tissue.

TABLE 1

| | BW (gsm) | TS7 | TS750 | E (mm/N) | D (mm/N) |
|---|---|---|---|---|---|
| Kleenex● Ultra Facial Tissue | 25.7 | 9.4 | 6.8 | 3.58 | 3.67 |
| Kleenex● Lotion Facial Tissue | 27.9 | 9.0 | 7.1 | 3.54 | 3.69 |
| Kleenex● Anti-Viral Facial Tissue | 45.5 | 9.1 | 6.8 | 3.09 | 3.27 |
| Puffs Ultra Strong and Soft● Facial Tissue | 36.9 | 8.8 | 7.7 | 3.05 | 3.18 |
| Puffs Plus● Facial Tissue | 46.4 | 8.6 | 5.4 | 3.18 | 3.33 |
| Puffs Plus Lotion● Facial Tissue | 46.5 | 9.8 | 8.1 | 3.28 | 3.44 |
| Von's Ultra● Facial Tissue | 44.8 | 8.6 | 6.7 | 2.82 | 2.98 |
| Kroger Nice & Soft with Lotion | 46.2 | 9.3 | 7.0 | 3.11 | 3.32 |
| ShopRite Ultra Facial Tissue | 46.6 | 9.4 | 9.4 | 3.08 | 3.27 |
| Up&Up™ Ultra Facial Tissue | 46.4 | 8.2 | 7.0 | 3.45 | 3.65 |

| | | | | | |
|---|---|---|---|---|---|
| Up&Up™ Facial Tissue | 31.2 | 11.4 | 9.2 | 3.22 | 3.32 |
| Scotties® Facial Tissue | 31.2 | 12.0 | 12.1 | 2.84 | 2.92 |
| Publix ® Facial Tissue | 32.2 | 12.9 | 7.5 | 3.38 | 3.47 |
| Walgreens® Facial Tissue | 27.8 | 10.2 | 8.5 | 3.23 | 3.36 |
| Puffs® Facial Tissue | 29.6 | 10.6 | 6.2 | 3.43 | 3.53 |
| Kleenex® Facial Tissue | 28.4 | 9.8 | 8.3 | 3.27 | 3.40 |
| Inventive CTEC Sample | 29.6 | 7.6 | 6.0 | 2.7 | 3.2 |
| Inventive CTAD Sample | 29.8 | 4.1 | 5.3 | 2.68 | 3.36 |

The basis weight of tissue webs made in accordance with the present disclosure can vary depending upon the final product. For example, the process may be used to produce bath tissues, facial tissues, paper towels, and the like. In general, the basis weight of such fibrous products may vary from about 5 grams per square meter (gsm) to about 110 gsm, such as from about 10 gsm to about 90 gsm. For bath tissue and facial tissues products, for instance, the basis weight of the product may range from about 10 gsm to about 40 gsm.

Likewise, tissue web basis weight may also vary, such as from about 5 gsm to about 50 gsm, more preferably from about 10 gsm to about 30 gsm and still more preferably from about 14 gsm to about 20 gsm.

In multiple-ply products, the basis weight of each web present in the product can also vary. In general, the total basis weight of a multiple ply product will generally be from about 10 gsm to about 100 gsm. Thus, the basis weight of each ply can be from about 10 gsm to about 60 gsm, such as from about 20 gsm to about 40 gsm.

Tissue webs and products produced according to the present disclosure also have good bulk characteristics. For instance, bulk may vary from about 4 to about 15 $cm^3/g$, such as from about 5 to about 12 $cm^3/g$ or from about 6 to about 10 $cm^3/g$.

In addition to having good bulk, tissue webs and products prepared according to the present disclosure have improved softness and surface smoothness. For example, tissue webs prepared according to the present disclosure have TS7 values less than about 8.0, such as from about 5.0 to about 7.0 and in certain embodiments a TS750 value less than about 7.0, such as from about 4.0 to about 6.0. In a particularly preferred embodiment the present disclosure provides a tissue product comprising at least one creped tissue web having a basis weight of at least about 12 gsm, a GMT of at least about 300 g/3" and a TS7 value from about 5.0 to about 8.0.

Moreover, the low TS7 and/or TS750 values are achieved at relatively modest geometric mean tensile strengths. For example, tissue products prepared according to the

present disclosure have geometric mean tensile strengths of less than about 1000 g/3″, and more preferably less than about 900 g/3", such as from about 400 to about 1000 g/3".

In general, any suitable tissue web may be treated in accordance with the present disclosure. The tissue webs may then be converted into various tissue products, such as bath tissue, facial tissue, paper towels, napkins, and the like. Tissue products made according to the present disclosure may include single-ply or multiple-ply tissue products. For instance, in some aspects, the product may include two plies, three plies, or more.

Fibers suitable for making tissue webs comprise any natural or synthetic fibers including both nonwoody fibers and woody or pulp fibers. Pulp fibers can be prepared in high-yield or low-yield forms and can be pulped in any known method, including kraft, sulfite, high-yield pulping methods and other known pulping methods. Fibers prepared from organosolv pulping methods can also be used, including the fibers and methods disclosed in US Patent Nos. 4,793,898, 4,594,130, and 3,585,104. Useful fibers can also be produced by anthraquinone pulping, exemplified by US Patent No. 5,595,628.

Chemically treated natural cellulosic fibers can be used, for example, mercerized pulps, chemically stiffened or crosslinked fibers, or sulfonated fibers. For good mechanical properties in using web forming fibers, it can be desirable that the fibers be relatively undamaged and largely unrefined or only lightly refined. While recycled fibers can be used, virgin fibers are generally useful for their mechanical properties and lack of contaminants. Mercerized fibers, regenerated cellulosic fibers, cellulose produced by microbes, rayon, and other cellulosic material or cellulosic derivatives can be used. Suitable web forming fibers can also include recycled fibers, virgin fibers, or mixes thereof.

In general, any process capable of forming a web can also be utilized in the present disclosure. For example, a web forming process of the present disclosure can utilize creping, wet creping, double creping, recreping, double recreping, embossing, wet pressing, air pressing, through-air drying, hydroentangling, creped through-air drying, co-forming, airlaying, as well as other processes known in the art. For hydroentangled material, the percentage of pulp is about 70 to 85 percent and the balance of fiber is synthetic.

Also suitable for articles of the present disclosure are fibrous sheets that are pattern densified or imprinted, such as the fibrous sheets disclosed in any of the following

US Patent Nos. 4,514,345, 4,528,239, 5,098,522, 5,260,171, and 5,624,790, the disclosures of which are incorporated herein by reference to the extent they are non-contradictory herewith. Such imprinted fibrous sheets may have a network of densified regions that have been imprinted against a drum dryer by an imprinting fabric, and regions that are relatively less densified (e.g., "domes" in the fibrous sheet) corresponding to deflection conduits in the imprinting fabric, wherein the fibrous sheet superposed over the deflection conduits was deflected by an air pressure differential across the deflection conduit to form a lower-density pillow-like region or dome in the fibrous sheet.

Further, while webs having desired softness and strength may be produced without the use of chemical debonders to reduce the amount of fiber-fiber bonding within the web, in certain embodiments the fiber furnish used to form the base web may be treated with a chemical debonding agent. The debonding agent can be added to the fiber slurry during the pulping process or can be added directly to the headbox. Suitable debonding agents that may be used in the present disclosure include cationic debonding agents such as fatty dialkyl quaternary amine salts, mono fatty alkyl tertiary amine salts, primary amine salts, imidazoline quaternary salts, silicone, quaternary salt and unsaturated fatty alkyl amine salts. Other suitable debonding agents are disclosed in US Patent No. 5,529,665, which is incorporated herein by reference in a manner consistent herewith.

While the creped webs of the present disclosure achieve low TS7 values and/or TS750 values without post treatment, the webs may, in certain embodiments, be post treated to provide additional benefits. The types of chemicals that may be added to the web may include topical additive such as a polysiloxane that makes a tissue product feel softer to the skin of a user. Suitable polysiloxanes that can be used in the present invention include amine, aldehyde, carboxylic acid, hydroxyl, alkoxyl, polyether, polyethylene oxide, and polypropylene oxide derivatized silicones, such as aminopolydialkylsiloxanes. Other suitable additives may include compositions that supply skin health benefits such as mineral oil, aloe extract, vitamin-E, silicone, lotions in general, and the like. Such chemicals may be added at any point in the web forming process.

Tissue webs that may be treated in accordance with the present disclosure may include a single homogenous layer of fibers or may include a stratified or layered construction. For instance, the tissue web ply may include two or three layers of fibers. Each layer may have a different fiber composition. For example a three-layered headbox

generally includes an upper head box wall and a lower head box wall. Headbox further includes a first divider and a second divider, which separate three fiber stock layers.

Each of the fiber layers comprises a dilute aqueous suspension of papermaking fibers. The particular fibers contained in each layer generally depend upon the product being formed and the desired results. For instance, the fiber composition of each layer may vary depending upon whether a bath tissue product, facial tissue product or paper towel is being produced. In one aspect, for instance, the middle layer contains southern softwood kraft fibers either alone or in combination with other fibers such as high yield fibers. Outer layers, on the other hand, contain softwood fibers, such as northern softwood kraft. In an alternative aspect, the middle layer may contain softwood fibers for strength, while the outer layers may comprise hardwood fibers, such as eucalyptus fibers.

In general, any process capable of forming a base sheet may be utilized in the present disclosure. For example, an endless traveling forming fabric, suitably supported and driven by rolls, receives the layered papermaking stock issuing from the headbox. Once retained on the fabric, the layered fiber suspension passes water through the fabric. Water removal is achieved by combinations of gravity, centrifugal force and vacuum suction depending on the forming configuration. Forming multi-layered paper webs is also described and disclosed in US Patent No. 5,129,988, which is incorporated herein by reference in a manner that is consistent herewith.

Preferably the formed web is dried by transfer to the surface of a rotatable heated dryer drum, such as a Yankee dryer. In accordance with the present disclosure, the creping composition 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. Creping the 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 addition to applying the creping composition during formation of the tissue web, the creping composition may also be used in post-forming processes. For example, in one aspect, the creping composition may be used during a print-creping process. Specifically, once topically applied to a tissue web, the creping composition has been found well-suited to adhering the tissue web to a creping surface, such as in a print-creping operation.

Tissue webs made according to the present disclosure can be incorporated into multiple-ply products. For instance, in one aspect, a tissue web made according to the present disclosure can be attached to one or more other tissue webs for forming a wiping product having desired characteristics. The other webs laminated to the tissue web of the present disclosure can be, for instance, a wet-creped web, a calendered web, an embossed web, a through-air dried web, a creped through-air dried web, an uncreped through-air dried web, an airlaid web, and the like.

In certain embodiments, when incorporating a tissue web made according to the present disclosure into a multiple-ply product, it may be desirable to only apply the creping composition to one side of the tissue web and to thereafter crepe the treated side of the web. The creped side of the web is then used to form an exterior surface of a multiple-ply product. The untreated and uncreped side of the web, on the other hand, is attached by any suitable means to one or more plies.

## TEST METHODS

TS7 and TS750 Values

TS7 and TS750 values were measured using an EMTEC Tissue Softness Analyzer ("TSA") (Emtec Electronic GmbH, Leipzig, Germany). The TSA comprises a rotor with vertical blades which rotate on the test piece applying a defined contact pressure. Contact

between the vertical blades and the test piece creates vibrations, which are sensed by a vibration sensor. The sensor then transmits a signal to a PC for processing and display. The signal is displayed as a frequency spectrum. For measurement of TS7 and TS750 values the blades are pressed against sample with a load of 100 mN and the rotational speed of the blades is 2 revolutions per second.

To measure TS7 and TS750 values two different frequency analyses are performed. The first frequency analysis is performed in the range of approximately 200 Hz to 1000 Hz, with the amplitude of the peak occurring at 750 Hz being recorded as the TS750 value. The TS750 value represents the surface smoothness of the sample. A high amplitude peak correlates to a rougher surface. A second frequency analysis is performed in the range from 1 to 10 kHZ, with the amplitude of the peak occurring at 7 kHz being recorded as the TS7 value. The TS7 value represents the softness of sample. A lower amplitude correlates to a softer sample. Both TS750 and TS7 values have the units dB $V^2$ rms.

To measure the stiffness properties of the test sample, the rotor is initially loaded against the sample to a load of 100 mN. Then, the rotor is gradually loaded further until the load reaches 600 mN. As the sample is loaded the instrument records sample displacement (μm) versus load (mN) and outputs a curve over the range of 100 to 600 mN. The modulus value "E" is reported as the slope of the displacement versus loading curve for this first loading cycle, with units of mm displacement /N of loading force. After the first loading cycle from 100 to 600 mN is completed, the instrument reduces the load back to 100 mN and then increases the load again to 600 mN for a second loading cycle. The slope of the displacement versus loading curve from the second loading cycle is called the "D" modulus value.

Test samples were prepared by cutting a circular sample having a diameter of 112.8 mm. All samples were allowed to equilibrate at TAPPI standard temperature and humidity conditions for at least 24 hours prior to completing the TSA testing. Only one ply of tissue is tested. Multi-ply samples are separated into individual plies for testing. The sample is placed in the TSA with the softer (dryer or Yankee) side of the sample facing upward. The sample is secured and the measurements are started via the PC. The PC records, processes and stores all of the data according to standard TSA protocol. The reported values are the average of five replicates, each one with a new sample.



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Tensile

Samples for tensile strength testing are prepared by cutting a 3 inches (76.2 mm) x 5 inches (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 4±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 inches (76.2 mm), and the approximate height of a jaw is 0.5 inches (12.7 mm). The crosshead speed is 10±0.04 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.

For multiple-ply products tensile testing is done on the number of plies expected in the finished product. For example, 2-ply products are tested two plies at one time and the recorded MD and CD tensile strengths are the strengths of both plies.

## EXAMPLES

Example 1: Soft Creped Wet Pressed Tissue

Samples were made using a conventional wet pressed tissue-making process on a pilot scale tissue machine. Initially, northern softwood kraft (NSWK) pulp (Pictou Harmony Pulp, Northern Pulp, Nova Scotia, Canada) was dispersed in a pulper for 30 minutes at about 1.6 percent consistency at about 100°F. The NSWK pulp was refined in a batch refiner for about 4 minutes to a Canadian Standard Freeness (CSF) value of about 500 ml. The NSWK pulp was then transferred to a dump chest and subsequently diluted

with water to approximately 0.6 percent consistency. Softwood fibers were then pumped to a machine chest where they were further diluted with water to a consistency of about 0.3 percent and mixed with 2 kg/MT of Kymene● 920A on a dry-solids basis (Ashland Water Technologies, Wilmington, DE) prior to the headbox. The softwood fibers were added to the middle layer in the 3-layer tissue structure. The NSWK content contributed approximately 10 to 20 percent of the final sheet weight. The specific layer splits (dryer layer / middle layer / felt layer) are as set forth in Table 2.

Eucalyptus hardwood kraft (EHWK) pulp (Fibria Veracel pulp, Fibria, Sao Paulo, Brazil) was dispersed in a pulper for 30 minutes at about 1.6 percent consistency at about 100°F. The EHWK pulp was then transferred to a dump chest and diluted to about 0.6 percent consistency. The EHWK pulp was then pumped to a machine chest where they were further diluted with water to a consistency of about 0.15 percent and mixed with 2kg/MT of Kymene● 920A. These fibers were added to the dryer and felt layers of the 3-layer sheet structure and contributed approximately 80 to 90 percent of the final sheet weight. The specific layer splits (dryer layer / middle layer / felt layer) are as set forth in Table 2.

Debonder (ProSoft™ TQ-1003, Ashland, Inc., Covington, KY) was added to the machine chest supplying EHWK pulp to the dryer side of the three layered tissue structure. The amount of debonder added varied from 4 pounds per ton of fiber to 12 pounds of debonder per ton of EHWK pulp, depending on the sample (see Table 2 for details).

The pulp fibers from the machine chests were pumped to the headbox at a consistency of about 0.02 percent. Pulp fibers from each machine chest were sent through separate manifolds in the headbox to create a 3-layered tissue structure. The fibers were deposited onto a TissueForm V forming fabric (Voith Paper Fabrics, Wilson, NC) in an inclined fourdrenier type of former.

The wet sheet from the forming fabric, at about 10 to 20 percent consistency, was vacuum dewatered and then transferred to a Superfine Duramesh press felt (Albany International Corp., Rochester, NH). The wet tissue sheet, supported by the press felt, was passed through the nip of a pressure roll, in order to partially dewater the sheet to a consistency of about 40 percent. The wet sheet was then adhered the Yankee dryer by spraying the creping composition onto the dryer surface using a spray boom situated underneath the dryer.

TABLE 2

| Sample | Debonder Addition (lb/MT) | Layer Splits (%HW/%SW/%HW) |
|---|---|---|
| 1 | 0 | 50 / 20 / 30 |
| 2 | 4 | 50 / 20 / 30 |
| 3 | 0 | 50 / 20 / 30 |
| 4 | 0 | 50 / 20 / 30 |
| 5 | 4 | 50 / 20 / 30 |
| 6 | 6 | 50 / 20 / 30 |
| 7 | 12 | 50 / 20 / 30 |
| 8 | 0 | 60 / 10 / 30 |
| 9 | 8 | 60 / 10 / 30 |
| 10 | 0 | 60 / 10 / 30 |
| 11 | 12 | 60 / 10 / 30 |
| 12 | 12 | 60 / 10 / 30 |

The creping compositions generally comprised a mixture of PerForm● PC 1279 (Ashland, Inc., Covington, KY), ProSoft™ TQ-1003 (Ashland, Inc., Covington, KY) and Redibond● 2038A (Ingredion Incorporated, Westchester, IL) or a mixture of poly(ethylene oxide) (commercially available as Polyox™ N80 from Dow Chemical, Midland, MI) and polyvinyl alcohol (Celvol 523 from Celanese, Houston TX) . The creping compositions used to produce each of the samples is detailed in Table 3.

Creping compositions were prepared by dissolution of the solid polymers into water followed by stirring until the solution was homogeneous. Individual polymers were diluted depending on the desired spray coverage on the Yankee dryer. Alternatively, flow rates of the polymer solutions were varied to provide the desired amount of solids to the base web. The sheet was dried to about 98 to 99 percent consistency as it traveled on the Yankee dryer and to the creping blade. The Yankee dryer was heated with 30 to 35 psi of steam pressure to dry the sheet to a target sheet temperature of 240°F before the creping blade. The Yankee dryer was traveling at about 60 FPM, unless otherwise noted. The creping blade, an 80-Proto-HY02 Durablade● (BTG, Eclépens, Switzerland) with a 10 to 15 degree grind angle, was loaded at a pressure of 30 psig. The creping blade subsequently scraped the tissue sheet off of the Yankee dryer. The creped tissue base sheet was then wound onto a core traveling at about 47 to about 52 FPM into soft rolls for converting. The basis weight of the resulting tissue was about 14 gsm and the GMT ranged from about 300 to about 450 g/3".

The soft rolls were then either converted directly to tissue product by rewinding and plying so that both creped sides were on the outside of a 2-ply tissue product, or subject to post treatment. In the event that soft rolls were post treated, they were either calendered or treated with silicone (see Tables 3 and 4 for details). The calendering was between two steel rolls with a nip loading of 50 psi. Silicone treatment was completed by applying 1 percent (by dry weight) of Momentive Y-14868 silicone emulsion (commercially available from Momentive Performance Materials, Albany, NY) using rotogravure printing on the outside surface of each of the two plies.



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TABLE 3

| | Creping Composition | | | | |
|---|---|---|---|---|---|
| Sample | Component 1 (wt %) | Component 2 (wt %) | Component 3 (wt %) | Creping composition Add-on ($mg/m^2$) | Post Treatment |
| 1C | Redibond 2038A (65%) | TQ-1003 (35%) | - | 300 | Calendered |
| 1S | Redibond 2038A (65%) | TQ-1003 (35%) | - | 300 | Silicone |
| 2C | Redibond 2038A (65%) | TQ-1003 (35%) | - | 300 | Calendered |
| 2S | Redibond 2038A (65%) | TQ-1003 (35%) | - | 300 | Silicone |
| 3S | Redibond 2038A (75%) | TQ-1003 (25%) | - | 300 | Silicone |
| 4S | Redibond 2038A (75%) | TQ-1003 (25%) | - | 300 | Silicone |
| 5S | PVOH (80%) | Polyox (20%) | - | 300 | Silicone |
| 6S | PVOH (80%) | Polyox (20%) | - | 300 | Silicone |
| 7S | PVOH (80%) | Polyox (20%) | - | 300 | Silicone |
| 8S | PVOH (90%) | Polyox (10%) | - | 300 | Silicone |
| 9C | Redibond (30%) | PC1279 (40%) | TQ-1003 (30%) | 300 | Calendered |
| 9S | Redibond (30%) | PC1279 (40%) | TQ-1003 (30%) | 300 | Silicone |
| 10C | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 10S | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Silicone |
| 11C | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 11 | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | - |
| 12 | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | - |
| 12S | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Silicone |



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Table 4

| Sample | TS7 | TS750 | E (mm/N) | D (mm/N) | Single Sheet Caliper (μm) | 2-ply BW (gsm) | Bulk ($cm^3/g$) |
|---|---|---|---|---|---|---|---|
| 1C | 7.2 | 6.6 | 3.0 | 3.8 | 143 | 26.9 | 5.32 |
| 1S | 7.0 | 7.4 | 3.1 | 3.9 | 132 | 27.3 | 4.83 |
| 2C | 7.1 | 7.2 | 3.0 | 3.8 | 134 | 26.5 | 5.05 |
| 2S | 6.9 | 7.7 | 3.0 | 3.9 | 138 | 27.0 | 5.10 |
| 3S | 7.5 | 7.0 | 3.0 | 3.7 | 143 | 27.5 | 5.21 |
| 4S | 7.5 | 6.4 | 2.9 | 3.5 | 133 | 27.2 | 4.88 |
| 5S | 7.3 | 6.0 | 2.7 | 3.2 | 125 | 29.1 | 4.29 |
| 6S | 7.6 | 4.2 | 2.7 | 3.3 | 128 | 29.6 | 4.33 |
| 7S | 7.6 | 5.6 | 3.2 | 4.0 | 140 | 28.6 | 4.90 |
| 8S | 6.8 | 4.8 | 3.0 | 4.2 | 121 | 25.6 | 4.72 |
| 9C | 7.0 | 8.1 | 3.1 | 4.0 | 199 | 35.6 | 5.59 |
| 9S | 6.8 | 6.2 | 3.0 | 4.3 | 191 | 36.6 | 5.21 |
| 10C | 7.5 | 9.2 | 2.9 | 3.4 | 156 | 27.5 | 5.68 |
| 10S | 7.1 | 11.0 | 2.9 | 3.3 | 152 | 27.1 | 5.62 |
| 11C | 6.7 | 11.3 | 3.7 | 4.2 | 159 | 27.3 | 5.82 |
| 11 | 6.6 | 12.1 | 3.0 | 3.8 | 220 | 27.5 | 8.00 |
| 12 | 6.5 | 12.2 | 3.5 | 4.1 | 227 | 40.5 | 5.60 |
| 12S | 6.9 | 11.5 | 2.9 | 3.8 | 194 | 38.4 | 5.05 |

Example 2: Soft Creped Through-Air Dried Tissue

Additional inventive samples were made using a papermaking process commonly referred to as creped through-air-dried ("CTAD") in which the web is formed using a through-air dried tissue making process and creped after final drying.

Initially, northern softwood kraft (NSWK) pulp (Pictou Harmony Pulp, Northern Pulp, Nova Scotia, Canada) was dispersed in a pulper for 30 minutes at about 1.6 percent consistency at about 100°F. The NSWK pulp was refined in a batch refiner for about 4 minutes to a Canadian Standard Freeness (CSF) value of about 500 ml. The NSWK pulp was then transferred to a dump chest and subsequently diluted with water to approximately 0.6 percent consistency. Softwood fibers were then pumped to a machine chest where they were further diluted with water to a consistency of about 0.3 percent and mixed with 2 kg/MT of Kymene● 920A on a dry-solids basis (Ashland Water Technologies, Wilmington, DE) and 1 kg/MT of Baystrength 3000 (Kemira, Atlanta, GA) prior to the headbox. The softwood fibers were added to the middle layer in the 3-layer tissue structure.

The NSWK content contributed approximately 30 percent of the final sheet weight. The specific layer splits (dryer layer / middle layer / felt layer) are as set forth in Table 5.

Eucalyptus hardwood kraft (EHWK) pulp (Fibria Veracel pulp, Fibria, Sao Paulo, Brazil) was dispersed in a pulper for 30 minutes at about 2.3 percent consistency at about 100°F. The EHWK pulp was then transferred to a dump chest and diluted to about 1.0 percent consistency. The EHWK pulp was then pumped to a machine chest where they were further diluted with water to a consistency of about 0.22 percent and mixed with 2kg/MT of Kymene● 920A. These fibers were added to the dryer and felt layers of the 3-layer sheet structure and contributed to approximately 70 percent of the final sheet weight. The specific layer splits (dryer layer / middle layer / felt layer) are as set forth in Table 5.

Debonder (ProSoft™ TQ-1003, Ashland, Inc., Covington, KY) was added to the machine chest supplying EHWK pulp to the dryer side of the three layered tissue structure. The amount of debonder added varied from 4 pounds per ton of fiber to 12 pounds of debonder per ton of EHWK pulp, depending on the sample (see Table 5 for details).

The pulp fibers from the machine chests were pumped to the headbox at a consistency of about 0.02 percent. Pulp fibers from each machine chest were sent through separate manifolds in the headbox to create a 3-layered tissue structure. The web was formed on a TissueForm V forming fabric (Voith Paper fabrics, Wilson, NC), transferred to a Voith 2164 fabric (Voith Paper fabrics, Wilson, NC) and vacuum dewatered to roughly 25 percent consistency. The web was then transferred to a Voith Saturn 852 fabric (Voith Paper fabrics, Wilson, NC) for the TAD fabric. No rush transfer was utilized at the transfer to the TAD fabric. After the web was transferred to the TAD fabric, the web was dried, however the consistency was maintained low enough to allow significant molding when the web was transferred using high vacuum to the impression fabric. A vacuum level of at least 10 inches of mercury was used for the transfer to the impression fabric in order to mold the web as much as possible into the fabric. Two different impression fabrics were used, as shown in Table 5 – either a Voith Saturn 852 fabric (Voith Paper fabrics, Wilson, NC) with the long shute (LS) knuckles toward the sheet or a Voith Saturn 952 fabric (Voith Paper fabrics, Wilson, NC) with the long warp (LW) knuckles toward the sheet. The web was then transferred to a Yankee dryer and creped. Minimum pressure was used at the web



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transfer to minimize compaction of the web during the transfer to the Yankee dryer so as to maintain maximum web caliper.

TABLE 5

| Sample | Debonder (lb/MT) | Layer Splits (%HW/%SW/%HW) | Refining (min) | Impression Fabric |
|---|---|---|---|---|
| 13 | 0 | 35 / 30 /35 | 5 | Saturn 852 - LS |
| 14 | 0 | 35 / 30 /35 | 4 | Saturn 852 - LS |
| 15 | 6 | 35 / 30 /35 | 4 | Saturn 852 - LS |
| 16 | 0 | 35 / 30 /35 | 4 | Saturn 852 - LS |
| 17 | 0 | 35 / 30 /35 | 4 | Saturn 852 - LS |
| 18 | 0 | 35 / 30 /35 | 3 | Saturn 852 - LS |
| 19 | 0 | 35 / 30 /35 | 3 | Saturn 852 - LS |
| 20 | 0 | 35 / 30 /35 | 3 | Saturn 852 - LS |
| 21 | 12 | 35 / 30 /35 | 3 | Saturn 852 - LS |
| 22 | 4 | 35 / 30 /35 | 3 | Saturn 952 - LW |
| 23 | 4 | 35 / 30 /35 | 3 | Saturn 952 - LW |

The web was adhered to the Yankee dryer using one of the creping compositions specified in Table 6, below. The creping compositions were prepared by dissolution of the solid polymers into water followed by stirring until the solution was homogeneous. Individual polymers were diluted depending on the desired spray coverage on the Yankee dryer. Alternatively, flow rates of the polymer solutions were varied to provide the desired amount of solids to the base web. The sheet was dried to about 98 to 99 percent consistency as it traveled on the Yankee dryer and to the creping blade. The Yankee dryer was heated with 30 to 35 psi of steam to dry the sheet to a target sheet temperature of 240°F, as measured above the creping blade. The Yankee dryer was traveling at about 60 FPM, unless otherwise noted. The creping blade, an 80-Proto-HY02 Durablade● (BTG, Eclépens, Switzerland) with a 10 to 15 degree grind angle, was loaded at a pressure of 30 psig. The creping blade subsequently scraped the tissue sheet off of the Yankee dryer. The creped tissue basesheet was then wound onto a core traveling at about 47 to about 52 FPM into soft rolls for converting. The basis weight of the resulting tissue was about 14 gsm and the GMT ranged from about 300 to about 450 g/3".

TABLE 6

| Sample | Component 1 (wt %) | Component 2 (wt %) | Component 3 (wt %) | Creping composition Add-on ($mg/m^2$) | Post Treatment |
|---|---|---|---|---|---|
| 13C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Calendered |
| 14C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Calendered |
| 14S | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Silicone |
| 15C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Calendered |
| 16C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 60 | Calendered |
| 17C | Redibond 2038A (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 17S | Redibond 2038A (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Silicone |
| 18C | Redibond 2038A (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 19C | Redibond 2038A (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 20C | PVOH (80%) | N80 Polyox (20%) | - | 200 | Calendered |
| 20S | PVOH (80%) | N80 Polyox (20%) | - | 200 | Silicone |
| 21C | PVOH (80%) | N80 Polyox (20%) | - | 200 | Calendered |
| 21S | PVOH (80%) | N80 Polyox (20%) | - | 200 | Silicone |
| 22C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Calendered |
| 23C | PVOH (80%) | N80 Polyox (20%) | - | 200 | Calendered |

The soft rolls were then either converted directly to tissue product by rewinding and plying so that both creped sides were on the outside of a 2-ply tissue product, or subject to post treatment. In the event that soft rolls were post treated, they were either calendered or treated with silicone (see Tables 3 and 4 for details). The calendering was between two steel rolls with a nip loading of 50 psi. Silicone treatment was done by applying 1 percent (bone dry weight) of Momentive Y-14868 silicone emulsion (commercially available from



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Momentive Performance Materials, Albany, NY) using rotogravure printing on the outside surface of each of the two plies.

TABLE 7

| Sample | GMT (g/3") | TS7 | TS750 | E (mm/N) | D (mm/N) |
|---|---|---|---|---|---|
| 13C | 894 | 5.7 | 6.5 | 2.71 | 3.07 |
| 14C | 735 | 5.3 | 5.7 | 2.74 | 3.10 |
| 14S | 735 | 5.2 | 5.6 | 2.98 | 3.38 |
| 15C | 651 | 4.1 | 5.3 | 2.68 | 3.36 |
| 16C | 777 | 6.2 | 6.7 | 2.31 | 2.75 |
| 17C | 851 | 4.9 | 6.4 | 2.25 | 2.61 |
| 17S | 851 | 5.4 | 5.7 | 2.43 | 2.87 |
| 18C | 916 | 4.6 | 5.7 | 2.18 | 2.71 |
| 19C | 936 | 5.9 | 5.9 | 2.15 | 2.48 |
| 20C | 999 | 6.4 | 6.3 | 2.02 | 2.35 |
| 20S | 999 | 5.4 | 5.5 | 2.21 | 2.54 |
| 21C | 530 | 4.4 | 5.7 | 2.31 | 2.88 |
| 21S | 530 | 4.3 | 5.5 | 2.62 | 3.31 |
| 22C | 680 | 6.6 | 6.4 | 2.42 | 2.76 |
| 23C | 587 | 6.0 | 5.3 | 2.65 | 3.08 |

These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.



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We claim:

1. A creped tissue web having a TS7 value less than about 8.0 dB $V^2$ rms.

2. The creped tissue web of claim 1 having a TS750 value less than about 8.0 dB $V^2$ rms.

3. The creped tissue web of claims 1 or 2 having a TS750 value from about 4.0 to about 7.0 dB $V^2$ rms.

4. The creped tissue web of anyone of the foregoing claims wherein the TS7 value is less than about 7 dB $V^2$ rms.

5. The creped tissue web of anyone of the foregoing claims wherein the TS7 value is from about 4 to about 8 dB $V^2$ rms.

6. The creped tissue web of anyone of the foregoing claims wherein the basis weight of the web is at least about 10 gsm.

7. The creped tissue web of anyone of the foregoing claims wherein the basis weight is from about 10 to about 16 gsm.

8. The creped tissue web of anyone of the foregoing claims wherein the web has a GMT of at least about 300 g/3".

9. The creped tissue web of anyone of the foregoing claims wherein the web has a GMT from about 300 to about 500 g/3".

10. A creped multi-ply tissue product having a TS7 value less than about 8.0 dB $V^2$ rms.

11. The creped multi-ply tissue product of claim 10 having a TS750 value less than about 8.0 dB $V^2$ rms.

12. The creped multi-ply tissue product of claims 10 or 11 having a TS750 value from about 4.0 to about 7.0 dB $V^2$ rms.



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13. The creped multi-ply tissue product of anyone of claims 10 through 12 wherein the TS7 value is less than about 7 dB $V^2$ rms.

14. The creped multi-ply tissue product of anyone of claims 10 through 13 wherein the TS7 value is from about 4 to about 8 dB $V^2$ rms.

15. The creped multi-ply tissue product of anyone of claims 10 through 14 wherein the basis weight of the product is at least about 25 gsm.

16. The creped multi-ply tissue product of anyone of claims 10 through 15 wherein the basis weight of the product is from about 25 to about 32 gsm.

17. The creped multi-ply tissue product of anyone of claims 10 through 16 wherein the product has a GMT of at least about 600 g/3".

18. The creped multi-ply tissue product of anyone of claims 10 through 17 wherein the product has a GMT from about 600 to about 1000 g/3".

19. A creped multi-ply tissue product comprising at least one ply which comprises a creped tissue web having a first and second side, wherein a water-soluble creping composition selected from the group consisting of a polyether, a polyamide, a polyvinyl alcohol, a cationic starch, and a cationic polyamide-epihalohydrin, is disposed on at least the first or second side and the at least one ply has a TS7 value less than about 8.0 dB $V^2$ rms and a TS750 value less than about 7.0 dB $V^2$ rms.

20. The creped multi-ply tissue product of claim 19 wherein the product has a basis weight of at least about 20 gsm and GMT of at least about 600 g/3".



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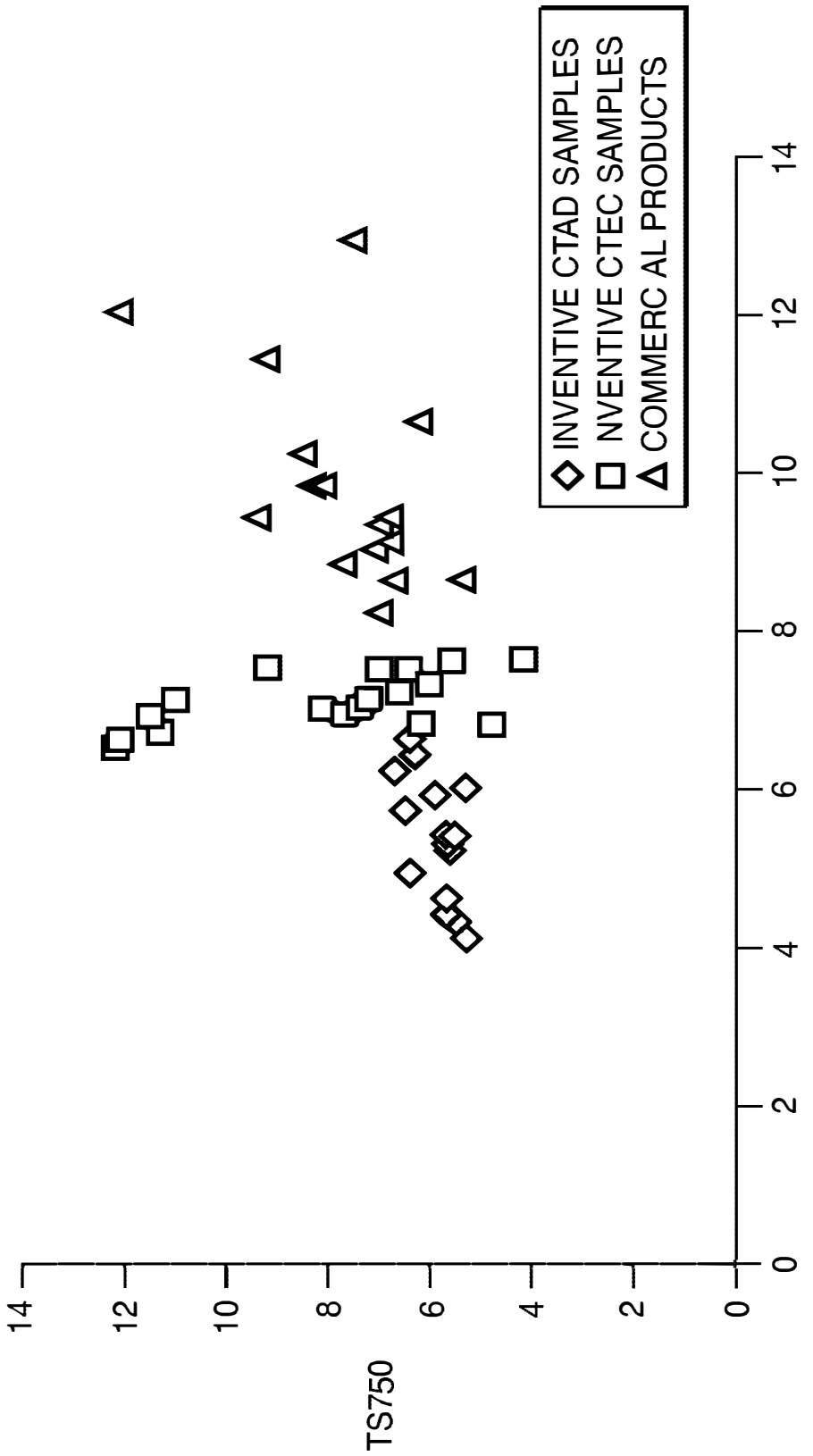

INVENTIVE CTAD SAMPLES
NVENTIVE CTEC SAMPLES
COMMERC AL PRODUCTS
TS750
TS7
0
2
4
6
8
10
12
14

FIG. 1

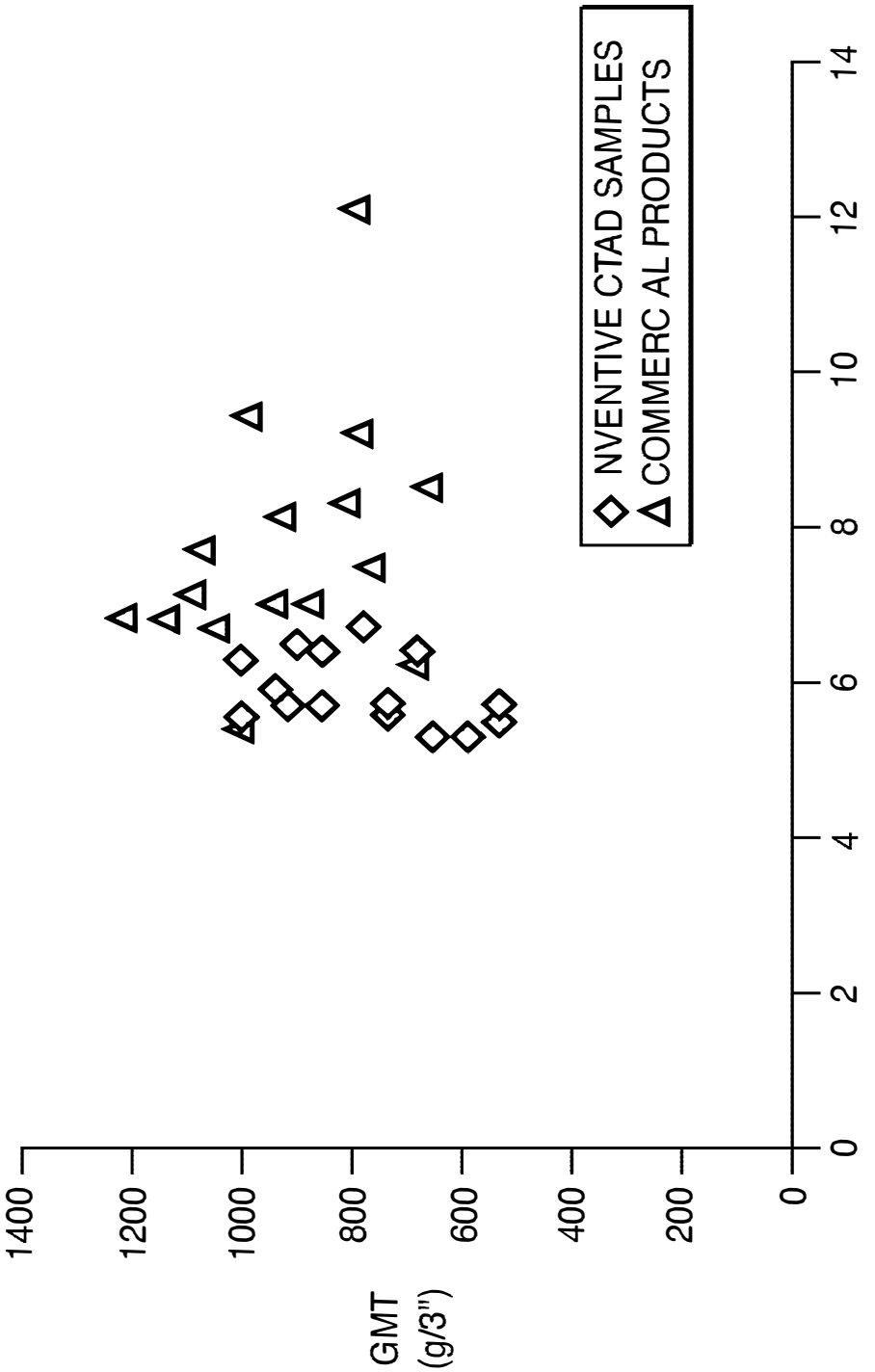

NVENTIVE CTAD SAMPLES
COMMERC AL PRODUCTS
GMT (g/3")
TS750
0
200
400
600
800
1000
1200
1400
0
2
4
6
8
10
12
14

FIG. 2

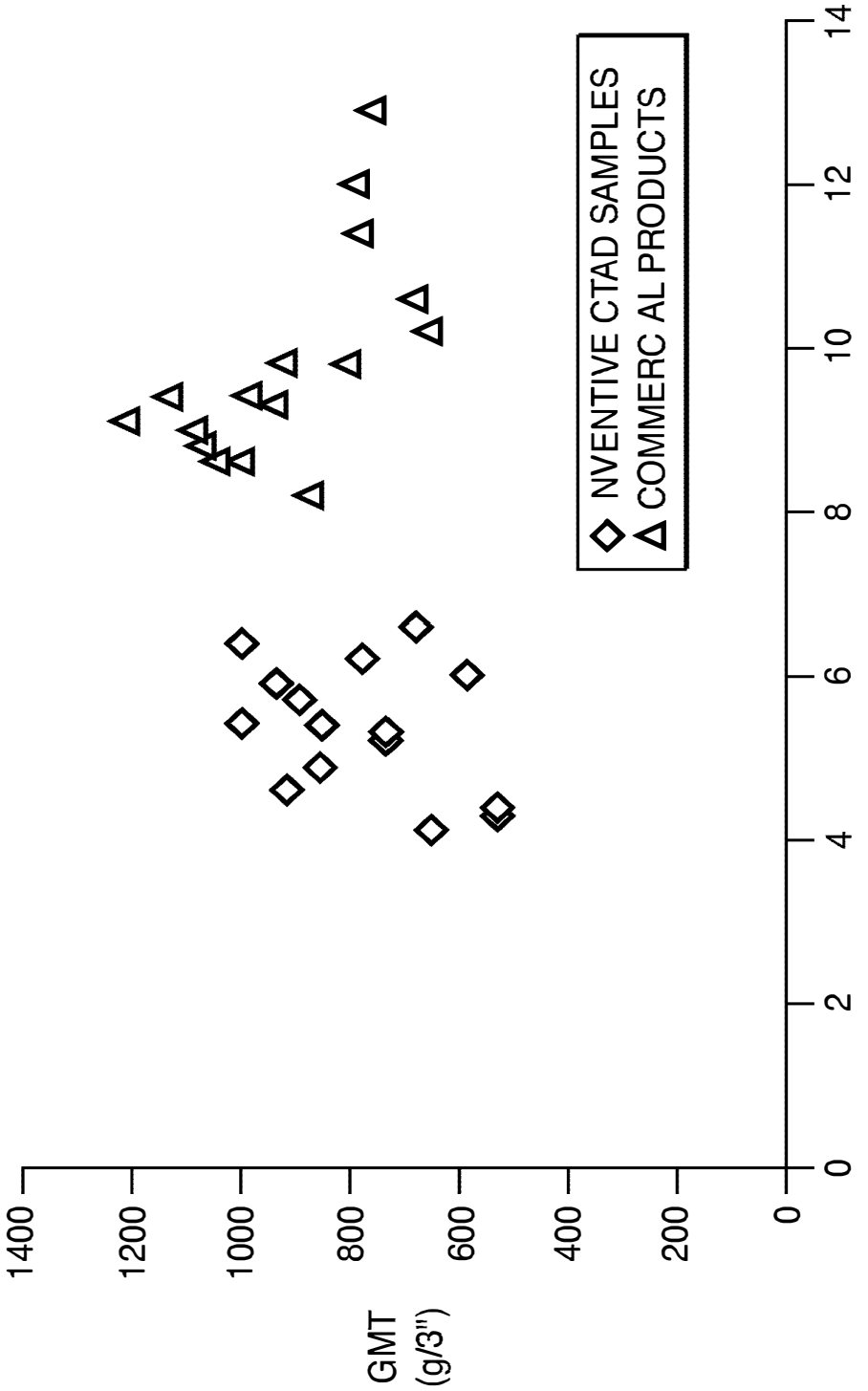

GMT (g/3")
1400
1200
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
TS7
NVENTIVE CTAD SAMPLES
COMMERC AL PRODUCTS

FIG. 3

**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/IB2013/058817**

**A. CLASSIFICATION OF SUBJECT MATTER**

**D21H 27/40(2006.01)i, D21H 27/30(2006.01)i, D21H 27/00(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)
D21H 27/40; D21F 3/00; D21F 11/00; B32B 23/04; D21H 27/02; D21H 21/18; D21H 27/00; D21H 19/00; B31F 1/12; D21H 27/30

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: creping, tissue, TS7, TS750

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | US 2010-0065234 A1 (KLERELID, INGVAR BERNDT ERIK et al.) 18 March 2010<br>See abstract; claims 18 and 49. | 1-3,10-12,19,20 |
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☐ 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
25 February 2014 (25.02.2014)

Date of mailing of the international search report
**25 February 2014 (25.02.2014)**

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

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International application No.
**PCT/IB2013/058817**

**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.: 4-9,13-18
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.

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**PGR2026-00078**

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Information on patent family members

International application No.

**PCT/IB2013/058817**

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(54) **Title**: HIGHLY DURABLE TOWEL COMPRISING NON-WOOD FIBERS

(57) **Abstract**: The present invention relates to tissue products comprising high yield hesperaloe fiber having improved wet performance, such as improved absorbency, CD Wet/Dry Ratio and CD Wet Durability. The addition of high yield hesperaloe pulp fibers surprisingly improves the CD Wet/Dry ratio without negatively affecting the absorbency of the tissue product. For example, tissue products of the present invention generally have an Absorbent Capacity greater than about 6.0 g/g, such as from about 8.0 to 8.0 g/g. As such the tissue products are durable when wet, but are still sufficiently absorbent. This balance of absorbency and wet strength is not found in the prior art without resorting to adding latex binders or the like to the tissue product.

# HIGHLY DURABLE TOWEL COMPRISING NON-WOOD FIBERS

## BACKGROUND OF THE DISCLOSURE

In the development and manufacture of paper products, particularly paper towels for the consumer market, it is a continual objective to improve the absorbent characteristics of the product. For cleaning up some spills, the consumer needs high absorbent capacity. For some uses, consumers want a fast rate of absorbency. For other uses, a combination of high absorbent capacity and fast absorbent rate is desired. At the same time, constraints on achieving this objective include the need to maintain or reduce costs in order to provide the consumer with the highest possible value, which in part means minimizing the amount of fiber in the product.

## SUMMARY OF THE DISCLOSURE

The present inventors have successfully used hesperaloe fibers to produce a tissue that is highly absorbent while also being durable when wet. As such the tissue products of the present invention may have an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry ratio greater than about 0.30. The desirable absorbency and wet durability are achieved by forming a tissue product from wood and non-wood fibers and more specifically high yield hesperaloe pulp fibers. In achieving these properties the inventors have overcome the negative to other important properties, such as bulk and stiffness, typically associated with substituting conventional wood papermaking fibers with non-wood fibers. 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 Northern softwood kraft (NSWK) fibers.

Accordingly, in certain embodiments, the invention provides tissue products in which hesperaloe fibers replace at least about 50 percent of the NSWK, more preferably at least about 75 percent and still more preferably all NSWK while maintaining or improving absorbency and without negatively effecting stiffness and bulk.

In other embodiments the present invention provides tissue products comprising a multi-layered tissue web where one or more of the layers comprise a blend of hesperaloe fibers and softwood kraft fibers, wherein the softwood kraft fibers comprise less than about 10 weight percent of the tissue product.

In still other embodiments the present invention provides a tissue product comprising greater than about 20 weight percent high yield hesperaloe fiber, the tissue product having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.



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In yet other embodiments the present invention provides single-ply through-air dried tissue product comprising at least about 20 weight percent high yield hesperaloe pulp fibers, the tissue product having a basis weight from about 30 to about 60 gsm, a GMT from about 1500 to about 2500 g/3" and an Absorbent Capacity greater than about 7.0 g/g.

In other embodiments the present invention provides tissue product comprising at least one multi-layered through-air dried tissue web comprising a first and a second layer, the first layer being substantially free from high yield hesperaloe pulp fibers and the second layer consisting essentially of high yield hesperaloe pulp fibers, the tissue product having a Wet CD Durability from about 1.75 to about 2.0 and a Stiffness Index less than about 6.0.

## 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.



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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 10 cc/g, more preferably greater than about 11 cc/g and still more preferably greater than about 12 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 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. GM Slope generally is expressed in units of kg.

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. While the GMT may vary tissue products prepared according to the present disclosure generally have a GMT greater than about 1,400 g/3", such as from about 1,400 to about 2,500 g/3".

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 (typically having units of kg), divided by the geometric mean tensile strength (typically having units of grams per three inches).

$$Stiffness\ Index = \frac{\sqrt{MD\ Tensile\ Slope\ (kg) x\ CD\ Tensile\ Slope(kg)}}{GMT\ (g/3")} \cdot x\ 1{,}000$$

While the Stiffness Index may vary tissue products prepared according to the present disclosure generally have a Stiffness Index less than about 8.0 and more preferably less than about 6.0.

As used herein, the term "Absorbent Capacity" is a measure of the amount of water absorbed by the paper towel product in the vertical orientation and is expressed as grams of water absorbed per gram of fiber (dry weight). Absorbent Capacity is measured as described in the Test Methods section and generally has units of grams per gram (g/g). While the Absorbent Capacity may vary tissue products prepared according to the present disclosure generally have an Absorbent Capacity greater than about 6.0 g/g and more preferably greater than about 7.0 g/g.

As used herein the term "CD Wet/Dry Ratio," refers to the ratio of the wet CD tensile strength to the dry CD tensile strength, measured as described in the Test Methods Section, below. While the

CD Wet/Dry Ratio may vary, tissue products prepared as described herein generally have a CD Wet/Dry Ratio greater than about 0.28 and more preferably greater than about 0.30, such as from about 0.28 to about 0.32. Generally the foregoing ratios are achieved at Wet CD Tensile greater than about 400 g/3", more preferably greater than about 425 g/3" and still more preferably greater than about 450 g/3".

As used herein the term "Wet CD Durability," refers to the CD Wet Stretch multiplied by 100, divided by the CD Wet Tensile (having units of g/3") and is a measurement of the wet CD extensibility of a product at a given wet tensile strength. At CD Wet Tensile strengths greater than about 400 g/3" the inventive tissue products of the present invention generally have Wet CD Durability greater than about 1.75 and more preferably greater than about 2.0.

As used herein the term "Wet Strength Efficiency," refers to the CD Wet/Dry Ratio divided by the add-on amount of wet strength resin (measured in kilograms per dry metric ton of fiber) multiplied by 100 and is a measure of the amount of wet strength generated relative to dry strength normalized by the amount of wet strength added.

## DETAILED DESCRIPTION OF THE DISLOSURE

Generally, the present invention provides tissue product having a CD Wet/Dry ratio that meets or exceeds satisfactory levels without the excess use of a wet strength resin. The satisfactory level of CD Wet/Dry ratio is generally greater than about 0.30. The satisfactory level of CD Wet/Dry ratio is surprisingly achieved by forming a tissue product from wood and non-wood fibers and more specifically high yield hesperaloe pulp fibers. Generally CD Wet/Dry ratios may be achieved with the addition of at least about 5 percent, by weight of the tissue product, such as from about 5 to about 50 percent and more preferably from about 15 to about 45 percent high yield hesperaloe pulp fibers.

The addition of high yield hesperaloe pulp fibers surprisingly improves the CD Wet/Dry ratio without negatively affecting the absorbency of the tissue product. For example, tissue products of the present invention generally have an Absorbent Capacity greater than about 6.0 g/g, such as from about 6.0 to 8.0 g/g. As such the tissue products are durable when wet, but are still sufficiently absorbent. This balance of absorbency and wet strength is not found in the prior art without resorting to adding latex binders or the like to the tissue product.

Further, the aforementioned wet-strength properties may be achieved with only modest additions of conventional wet-strength resin. For example, in certain embodiments the tissue products comprise less than about 15 kg of wet-strength resin per metric ton of furnish, such as from about 3 to about 15 kg, and more preferably from about 3 to about 10 kg. Rather than employ an excessive



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amount of wet-strength resin, the improved wet-strength properties are achieved by the addition of high yield hesperaloe pulp fibers during the manufacture of the tissue product, such as from about 5 to about 50 percent, by weight of the product, and more preferably from about 20 to about 40 percent, by weight.

Accordingly, in certain embodiments the tissue products generally comprise high yield hesperaloe pulp fibers derived from non-woody plants in the genus Hesperaloe in the family Agavaceae. Suitable species within the genus Hesperaloe 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 process 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.



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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 amount of SSWK, by weight of the tissue product, is less than about 10 percent and more preferably less than about 5 percent.

In addition to the use of high yield hesperaloe pulp fiber the tissue products of the present invention are preferably prepared without the addition of binders, particularly latex binders and more specifically carboxyl-functional latex emulsion polymers, such as those described in US Patent Nos. 6,187,140 and 7,462,258. Latex binders, such as those disclosed in the foregoing references, have been used previously in the manufacture of tissue products to improve wet performance. These binders, however, add manufacturing complexity and cost. Therefore, it is desirable to produce a tissue product, such as the inventive tissues, without the use of binders and more specifically latex binders.

Further, tissues prepared according to the present disclosure are not treated with a sizing agent, such as alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA), either during the tissue manufacturing process or after formation and drying of the tissue web. Rather, the tissue webs are prepared by adding hesperaloe fibers and in certain embodiments a wet strength resin, to the papermaking furnish prior to formation of the web, to enhance the wet-strength properties of the finished web. Unlike conventional sizing agents, which reduce the adsorption rate of water into the sheet, hesperaloe fibers and conventional wet-strength resins allow the sheet to adsorb water as intended during the end use but maintain sheet integrity and strength when wetted.

Rather than employ latex binders or sizing agents, the tissue products typically comprise a conventional wet-strength resin. Useful conventional wet strength resins include diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), epichlorhydrin resin(s), polyamide-epichlorohydrin (PAE), or any combinations thereof, or any resins to be considered in these families of resins. Particularly preferred wet strength resins are polyamide-epichlorohydrin (PAE) resins. Commonly PAE resins are formed by first reacting a polyalkylene polyamine and an aliphatic dicarboxylic acid or dicarboxylic acid derivative. A polyaminoamide made from diethylenetriamine and adipic acid or esters of dicarboxylic acid derivatives is most common. The resulting polyaminoamide is

then reacted with epichlorohydrin. Useful PAE resins are sold under the tradename Kymene® (commercially available from Ashland, Inc., Covington, KY).

Generally the conventional wet-strength resin is added to the fiber furnish prior to formation of the tissue web. The amount of the wet-strength resin can be less than about 10 kg per ton of furnish, more preferably less than about 8 kg per ton of furnish and still more preferably less than about 5 kg per ton of furnish. Generally the add-on level of wet-strength resin will be from about 1 to about 10 kg per ton of furnish and more preferably from about 3 to about 8 kg per ton of furnish and still more preferably from about 3 to about 5 kg per ton of furnish.

Although such low add on levels of wet strength are generally not considered to be suitable for achieving exceptional wet performance, such as a CD Wet/Dry Ratio greater than about 0.30, it has now been discovered that the use of high yield hesperaloe pulp fibers yields tissue products having a CD Wet/Dry Ratio greater than about 0.30 and in certain embodiments greater than about 0.32, such as from about 0.30 to about 0.35. The combination of conventional wet strength resin, such as PAE resins, and hesperaloe fiber have a synergistic effect. Accordingly, when the CD Wet/Dry Ratio and Wet CD Durability are concerned, the combination of wet-strength resin addition and hesperaloe fiber according to the invention provides a synergistic effect which has not been disclosed previously. This synergistic effect is valuable, since it makes it possible to achieve a higher wet-strength level without the excessive use of wet-strength resin.

Table 1 illustrates the desirable increase in wet-strength properties that can be achieved via the combination of high yield hesperaloe fiber (HYH) and a conventional wet-strength resin. The samples have a basis weight of about 36 gsm and comprised a single through-air dried ply. The samples comprised either a blend of NSWK (40 wt%) and EHWK (60 wt%) or HYH (40 wt%) and EHWK (60 wt%). As the table illustrates, at a constant level of wet-strength addition, a higher wet/dry tensile level can be achieved via the addition of HYH.

TABLE 1

| HYH (wt%) | Wet Strength (kg/MT) | CD Wet/Dry Ratio | Delta CD Wet/Dry Ratio (%) | Wet Strength Efficiency |
|---|---|---|---|---|
| - | 9 | 0.22 | - | 2.4 |
| 40 | 9 | 0.3 | 36 | 3.3 |
| - | 14 | 0.24 | - | 1.7 |
| 40 | 14 | 0.31 | 29 | 2.2 |

The improvement in wet tensile properties is further evident when the inventive tissue products are compared to commercially available tissue products. As illustrated in the table below, the inventive tissue products display both wet durability, such as a CD Wet/Dry Ratio greater than about 0.30 and

good absorbency, such as an Absorbent Capacity greater than about 6.0 g/g and more preferably greater than about 7.0 g/g, such as from about 6.0 to about 7.5 g/g. In certain aspects the inventive tissue products also have improved Wet CD Durability relative to commercially available tissue products, such as a Wet CD Durability greater than about 1.5 and more preferably greater than about 1.75, such as from about 1.5 to about 2.0.

TABLE 2

| Product | Plies | Wet CD Tensile (g/3") | Wet CD Stretch (%) | CD Wet/Dry Ratio | Wet CD Durability | Absorbent Capacity (g/g) |
|---|---|---|---|---|---|---|
| Invention | 1 | 418 | 8.2 | 0.32 | 1.96 | 7.1 |
| Scott | 1 | 855 | 7.5 | 0.34 | 0.88 | 5.5 |
| Scott Naturals | 1 | 811 | 11.3 | 0.33 | 1.39 | 4.7 |
| Viva Vantage | 1 | 969 | 8.2 | 0.34 | 0.85 | 3.9 |
| Bounty Basic | 1 | 1040 | 7.2 | 0.47 | 0.69 | 4.9 |

Accordingly, in one embodiment tissue products comprise at least one multi-layered tissue web, the tissue product having a CD Wet/Dry Ratio greater than about 0.30 an Absorbent Capacity greater than about 6.0 g/g and still more preferably greater than about 6.5 g/g. Preferably the web comprises two layers, and more preferably three layers, wherein the hesperaloe fiber is selectively disposed in only one of the layers and the other layers are substantially free from hesperaloe fiber. In other embodiments, the web comprises two outer layers and a middle layer, where the hesperaloe fiber is selectively disposed in the middle layer. While in one embodiment it is preferred that the tissue web comprise a three-layered tissue having hesperaloe fiber selectively incorporated into the middle layer, it should be understood that tissue products made from the foregoing multi-layered web can include any number of plies and the plies may be made from various combinations of single- and multi-layered tissue webs. Further, tissue webs prepared according to the present invention 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.

As noted previously, the instant tissue products have a high degree of absorbent capacity such as an Absorbent Capacity greater than about 6.0 g/g, such as from about 6.0 to about 7.0 g/g and more preferably from about 6.5 to about 7.0 g/g, while also having a CD Wet/Dry Ratio greater than about 0.30, such as from about 0.30 to about 0.40. Generally the foregoing absorbent capacities and wet strengths are achieved at basis weights from about 30 to about 60 grams per square meter (gsm) and more preferably from about 35 to about 50 gsm and still more preferably from about 40 to about 50 gsm.

In addition to having satisfactory absorbent properties, the tissue products generally have improved wet CD performance. For example, in certain embodiments the tissue products have a Wet CD Durability greater than about 1.75, such as from about 1.75 to about 2.5 and more preferably from about 2.0 to about 2.5. At the foregoing Wet CD Durability levels the tissue products may have a Wet CD Stretch greater than about 8.0 percent, such as from about 8.0 percent to about 10.0 percent and more preferably from about 9.0 to about 10.0 percent.

While having improved properties, the tissue products prepared according to the present disclosure continue to be strong enough to withstand use by a consumer. For example, inventive tissue products generally have a geometric mean tensile (GMT) greater than about 1200 g/3", such as from about 1200 to about 3000 g/3", more preferably from about 1200 to about 2500 g/3" and still more preferably from about 1600 to about 2400 g/3".

Not only are the instant tissue products absorbent and strong enough to withstand use, they are generally flexible and have good hand feel. As such the tissue products may have a GM Slope less than about 10.0 kg, such as from about 4.0 to about 10.0 kg and more preferably from about 4.0 to about 8.0 kg. The foregoing GM Slopes are generally achieved at relatively modest GMT, such as from about 1200 to about 2500 g/3", and more preferably from about 1200 to about 2200 g/3". At these GM Slopes and GMT, the tissue products may have a Stiffness Index less than about 8.0, such as from about 4.0 to about 8.0 and more preferably from about 4.0 to about 6.0.

In one particularly preferred embodiment the inventive tissue product comprises a single-ply, multi-layered, through-air-dried web, wherein a first layer comprises wood pulp fibers and a second layer comprises high yield hesperaloe pulp fibers, the first layer being substantially free of hesperaloe fibers and the product comprising from about 20 to about 50 percent, by weight, hesperaloe fibers. The foregoing tissue product generally has a CD Wet/Dry Ratio greater than about 0.30 an Absorbent Capacity greater than about 6.0, while having a Stiffness Index less than about 6.0, such as from about 4.0 to about 6.0.

Webs useful in preparing tissue products according to the present disclosure can vary depending upon the particular application. In general, in addition to hesperaloe fibers, the webs can be made from any suitable type of fiber. For instance, the base web can be made from cellulosic fibers, and more preferably cellulosic pulp fibers. Suitable cellulosic fibers for use in connection with this invention include secondary (recycled) papermaking fibers and virgin papermaking fibers in all proportions. Such fibers include, without limitation, hardwood and softwood fibers.

Tissue webs made in accordance with the present disclosure can be made with a homogeneous fiber furnish or can be formed from a stratified fiber furnish producing layers within the



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single- or multi-ply product. Stratified base webs can be formed using equipment known in the art, such as a multi-layered headbox. Both strength and softness of the base web can be adjusted as desired through layered tissues, such as those produced from stratified headboxes.

When constructing a web from a stratified fiber furnish, the relative weight of each layer can vary depending upon the particular application. For example, in one embodiment, when constructing a web containing three layers, each layer can be from about 15 to about 40 percent of the total weight of the web, such as from about 25 to about 35 percent of the weight of the web. Generally the hesperaloe fibers will comprise from about 5 to about 50 percent, by weight, of the web.

The tissue products 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.

In a particularly preferred 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.

In one embodiment the web is formed using a twin wire former having a papermaking headbox that injects or deposits a furnish of an aqueous suspension of papermaking fibers onto a plurality of forming fabrics, such as the outer forming fabric and the inner forming fabric, thereby forming a wet tissue web. 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 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 greater than 20 percent, more specifically between about 20 to about 40 percent, and more specifically between 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 30 to about 70 percent and more preferably from about 40 to about 60 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. Such molding to the contours of the surface of the transfer fabric 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 through-air drying fabric. Typically, the transfer fabric travels at approximately the same speed as the through-air drying fabric.



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However, a second rush transfer may be performed as the web is transferred from the transfer fabric to the through-air drying fabric. This rush transfer is referred to as occurring at the second position and is achieved by operating the through-air drying fabric at a slower speed than the transfer fabric.

In addition to rush transferring the wet tissue web from the transfer fabric to the through-air drying fabric, the wet tissue web may be macroscopically rearranged to conform to the surface of the through-air drying fabric with the aid of a vacuum transfer roll or a vacuum transfer shoe. If desired, the through-air drying fabric can be run at a speed slower than the speed of the transfer fabric 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 to the topography of the through-air drying fabric.

While supported by a through-air drying fabric, the wet tissue web is dried to a final consistency of about 94 percent or greater by a through-air dryer. The web then passes through the winding nip between the reel drum and the reel and is wound into a roll of tissue for subsequent converting.

## TEST METHODS

Wet and Dry Tensile

Samples for tensile strength testing are prepared by cutting a 3 inches (76.2 mm) by 5 inches (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 4 ± 0.04 inches. The jaws are operated using pneumatic-action and are rubber coated. The minimum grip face width is 3 inches (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.

Wet tensile strength measurements are measured in the same manner, but after the center portion of the previously conditioned sample strip has been saturated with distilled water immediately prior to loading the specimen into the tensile test equipment. More specifically, prior to performing a wet CD tensile test, the sample must be aged to ensure the wet strength resin has cured. Two types of aging were practiced: natural and artificial. Natural aging was used for older samples that had already aged. Artificial aging was used for samples that were to be tested immediately after or within days of manufacture. For natural aging, the samples were held at 73°F, 50 percent relative humidity for a period of 12 days prior to testing. Following this natural aging step, the strips are then wetted individually and tested. For artificially aged samples, the 3-inch wide sample strips were heated for 4 minutes at 105 ± 2°C. Following this artificial aging step, the strips are then wetted individually and tested. Sample wetting is performed by first laying a single test strip onto a piece of blotter paper (Fiber Mark, Reliance Basis 120). A pad is then used to wet the sample strip prior to testing. The pad is a green, Scotch-Brite brand (3M) general purpose commercial scrubbing pad. To prepare the pad for testing, a full-size pad is cut approximately 2.5 inches long by 4 inches wide. A piece of masking tape is wrapped around one of the 4-inch long edges. The taped side then becomes the "top" edge of the wetting pad. To wet a tensile strip, the tester holds the top edge of the pad and dips the bottom edge in approximately 0.25 inches of distilled water located in a wetting pan. After the end of the pad has been saturated with water, the pad is then taken from the wetting pan and the excess water is removed from the pad by lightly tapping the wet edge three times across a wire mesh screen. The wet edge of the pad is then gently placed across the sample, parallel to the width of the sample, in the approximate center of the sample strip. The pad is held in place for approximately one second and then removed and placed back into the wetting pan. The wet sample is then immediately inserted into the tensile grips so the wetted area is approximately centered between the upper and lower grips. The test strip should be centered both horizontally and vertically between the grips. (It should be noted that if any of the wetted portion comes into contact with the grip faces, the specimen must be discarded and the jaws dried off before resuming testing.) The tensile test is then performed and the peak load recorded as the CD wet tensile strength of this specimen. As with the dry CD tensile test, the characterization of a product is determined by the average of at least six, but in the case of the examples disclosed, twenty representative sample measurements.



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Absorbency

As used herein, "vertical absorbent capacity" is a measure of the amount of water absorbed by a paper product (single-ply or multi-ply) or a sheet, expressed as grams of water absorbed per gram of fiber (dry weight). In particular, the vertical absorbent capacity is determined by cutting a sheet of the product to be tested (which may contain one or more plies) into a square measuring 100 millimeters by 100 millimeters (± 1 mm.) The resulting test specimen is weighed to the nearest 0.01 gram and the value is recorded as the "dry weight." The specimen is attached to a 3-point clamping device and hung from one corner in a 3-point clamping device such that the opposite comer is lower than the rest of the specimen, then the sample and the clamp are placed into a dish of water and soaked in the water for 3 minutes (± 5 seconds). The water should be distilled or de-ionized water at a temperature of 23 ± 3°C. At the end of the soaking time, the specimen and the clamp are removed from the water. The clamping device should be such that the clamp area and pressure have minimal effect on the test result. Specifically, the clamp area should be only large enough to hold the sample and the pressure should also just be sufficient for holding the sample, while minimizing the amount of water removed from the sample during clamping. The sample specimen is allowed to drain for 3 minutes (± 5 seconds). At the end of the draining time, the specimen is removed by holding a weighing dish under the specimen and releasing it from the clamping device. The wet specimen is then weighed to the nearest 0.01 gram and the value recorded as the "wet weight". The vertical absorbent capacity in grams per gram = [(wet weight - dry weight)/dry weight]. At least five (5) replicate measurements are made on representative samples from the same roll or box of product to yield an average vertical absorbent capacity value.

## EXAMPLE

Base sheets were made using a through-air dried papermaking process commonly referred to as "uncreped through-air dried" ("UCTAD") and generally described in US Patent No. 5,607,551, the contents of which are incorporated herein in a manner consistent with the present invention. Inventive base sheets were produced from a furnish comprising northern softwood kraft (NSWK), eucalyptus kraft (EHWK) and high yield hesperaloe fiber (HYH) using a layered headbox fed by three stock chests such that the webs having three layers (two outer layers and a middle layer) were formed. The outer layers comprised 100 percent EHWK for both the control and inventive samples. The center layer was 100 percent NSWK for the control sample; for the inventive sample, the center layer was 100 percent HYH. The layer splits, by weight of the web, are detailed in Table 3, below.

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 tissue web was formed on a Voith Fabrics TissueForm V forming fabric, vacuum dewatered to approximately 25 percent consistency and then subjected to rush transfer when transferred to the transfer fabric. The layer splits, by weight of the web, are detailed in Table 4, below. The transfer fabric was the fabric described as t1207-11 (commercially available from Voith Fabrics, Appleton, WI). The web was then transferred to a through-air drying fabric. Transfer to the through-drying fabric was done using vacuum levels of greater than 10 inches of mercury at the transfer. The web was then dried to approximately 98 percent solids before winding.

TABLE 3

| Sample | Layer Split (Air/Middle/Fabric wt%) | HYH (wt%) | Wet Strength (kg/MT) |
|---|---|---|---|
| Control | 30/40/30 | - | 8 |
| Inventive 1 | 30/40/30 | 40 | 8 |

The base sheet webs were converted into rolled towel products by calendering using a conventional polyurethane/steel calender comprising a 4 P&J polyurethane roll on the air side of the sheet and a standard steel roll on the fabric side. The finished product comprised a single ply of base sheet. The finished products were subjected to physical testing, the results of which are summarized in Table 4.

TABLE 4

| | Control 1 | Inventive 1 |
|---|---|---|
| BW (gsm) | 39.3 | 39.0 |
| Wet CDT (g/3") | 515 | 418 |
| Wet CDS (%) | 10.7 | 8.2 |
| Wet CD Durability | 2.08 | 1.96 |
| CD Wet/Dry | 0.31 | 0.31 |
| Absorbent Capacity (g/g) | 6.2 | 7.1 |
| Wet Strength Efficiency | 3.89 | 3.89 |
| Dry GMT (g/3") | 2217 | 1821 |
| Dry CDT (g/3") | 1655 | 1340 |
| Dry GM Slope (kg) | 7.2 | 7.7 |
| Stiffness Index | 3.25 | 4.23 |

The foregoing is one example of an inventive tissue product prepared according to the present disclosure. In a first embodiment the invention provides a tissue product comprising greater than about



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20 weight percent high yield hesperaloe fiber having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.

In a second embodiment the invention provides the tissue product of the first embodiment having a Wet CD Durability of greater than about 1.75.

In a third embodiment the invention provides the tissue product of the first embodiment having an Absorbent Capacity from about 7.0 to about 7.5 g/g, a CD Wet/Dry Ratio from about 0.30 to about 0.35.

In a third embodiment the present invention provides the tissue product of the first or the second embodiments having a GMT from about 1200 to about 2600 g/3".

In a fourth embodiment the present invention provides the tissue product of any one of the first through the third embodiments having a Stiffness Index from about 4.0 to about 6.0.

In a fifth embodiment the present invention provides the tissue product of any one of the first through the fourth embodiments having a basis weight from about 34 to about 60 gsm.

In a sixth embodiment the present invention provides the tissue product of any one of the first through the fifth embodiments having wet CD stretch greater than about 8 percent, such as from about 8 to about 10 percent.

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 comprises a single-ply multi-layered web having a first, a second and a third layer.

In an eighth embodiment the present invention provides the tissue product of any one of the first through the seventh embodiments wherein the tissue product comprises from about 20 to about 50 weight percent high yield hesperaloe fiber.

In a ninth embodiment the present invention provides the tissue product of any one of the first through the eighth embodiments wherein the tissue product comprises at least one through-air dried tissue web.

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 comprises at least one multi-layered through-air dried tissue web.

In still other embodiments the disclosure provides a tissue product of any one of the foregoing embodiments wherein the tissue product comprises at least one multi-layered through-air dried tissue web comprising a first fibrous layer and a second fibrous layer, the first fibrous layer comprising wood

pulp fibers and the second fibrous layer consisting essentially of high yield hesperaloe fibers and wherein the hesperaloe fibers comprise from about 20 to about 40 weight percent of the through-air dried web.



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**WHAT IS CLAIMED IS:**

1. A tissue product comprising greater than about 20 weight percent high yield hesperaloe fiber having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.

2. The tissue product of claim 1 having a Wet CD Durability of greater than about 1.75.

3. The tissue product of claim 1 having a GMT from about 1500 to about 3000 g/3".

4. The tissue product of claim 1 having a Stiffness Index from about 4.0 to about 6.0.

5. The tissue product of claim 1 having a basis weight from about 30 to about 60 gsm.

6. The tissue product of claim 1 having a wet CD stretch greater than about 8.0 percent.

7. The tissue product of claim 1 wherein the tissue product comprises a single-ply multi-layered web having a first layer comprising conventional wood pulp fibers and a second layer consisting essentially of high yield hesperaloe pulp fiber.

8. The tissue product of claim 1 wherein the tissue product comprises at least one through-air dried tissue web.

9. A tissue product comprising at least one multi-layered through-air dried tissue web comprising a first and a second layer, the first layer being substantially free from high yield hesperaloe pulp fibers and the second layer consisting essentially of high yield hesperaloe pulp fibers, the tissue product having a Wet CD Durability from about 1.75 to about 2.0 and a Stiffness Index less than about 6.0.

10. The tissue product of claim 9 having CD Wet/Dry Ratio from about 0.28 to about 0.32.

11. The tissue product of claim 9 having an Absorbent Capacity from about 6.5 to about 7.5.

12. The tissue product of claim 9 having a GM Slope less than about 8.0 kg.

13. The tissue product of claim 9 having a basis weight from about 30 to about 60 gsm and a GMT from about 1500 to about 2500 g/3".

14. The tissue product of claim 9 wherein the tissue product is substantially free from softwood kraft pulp fibers.



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15. The tissue product of claim 9 wherein the high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.

16. A single-ply through-air dried tissue product comprising at least about 20 weight percent high yield hesperaloe pulp fibers, the tissue product having a basis weight from about 30 to about 60 gsm, a GMT from about 1500 to about 2500 g/3" and an Absorbent Capacity greater than about 7.0 g/g.

17. The single-ply through-air dried tissue product of claim 16 having a Wet CD Durability from about 1.75 to about 2.0.

18. The single-ply through-air dried tissue product of claim 16 having a Stiffness Index less than about 6.0.

19. The single-ply through-air dried tissue product of claim 16 wherein the tissue product comprises from about 20 to about 40 weight percent high yield hesperaloe fiber and is substantially free from softwood kraft pulp fibers.

20. The single-ply through-air dried tissue product of claim 16 wherein high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.



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**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/US2015/033175**

**A. CLASSIFICATION OF SUBJECT MATTER**

**A47K 7/00(2006.01)i, 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 7/00; D21H 11/12; D21H 17/28; D21H 17/00; D21H 27/00; B31F 1/12; A47K 10/16

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, web, hesperaloe fiber, non-woody, pulp, absorbent

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | US 5320710 A (REEVES, R. H. et al.) 14 June 1994<br>See abstract; claims 1-7. | 1-20 |
| Y | US 2013-0269892 A1 (KIMBERLY-CLARK WORDWIDE, INC.) 17 October 2013<br>See claims 1, 3; paragraphs [0013], [0038], [0045]. | 1-20 |
| A | US 2014-0093704 A1 (SHI, B. et al.) 03 April 2014<br>See abstract; claims 1-9. | 1-20 |
| A | US 2015-0129143 A1 (CARGILL, INCORPORATED) 14 May 2015<br>See claims 1, 2, 9. | 1-20 |
| A | US 2003-0192662 A1 (HEATH, M. S. et al.) 16 October 2003<br>See abstract; claim 1. | 1-20 |

☐ 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
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"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

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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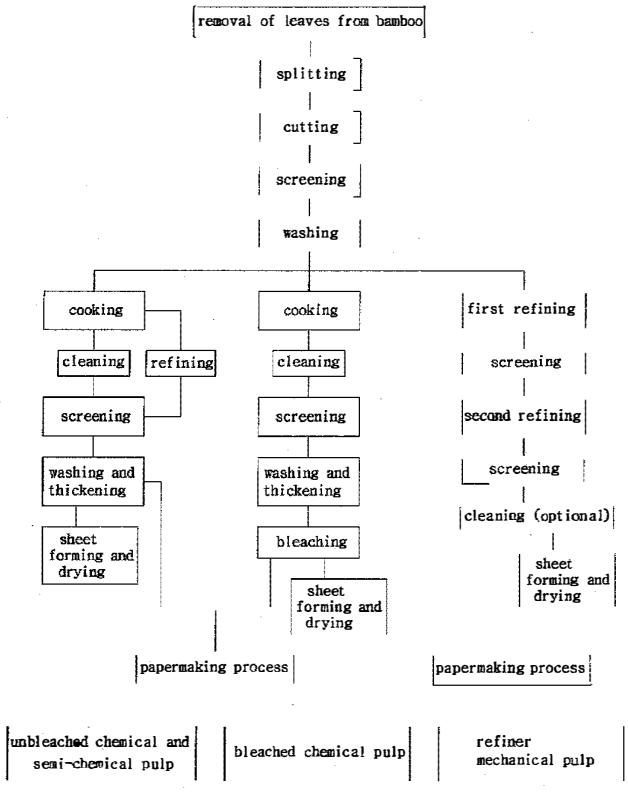
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*[Continued on next page]*

(54) **Title:** PROCESS FOR PRODUCING PULP UTILIZING BAMBOO AND PULP AND PAPERS PRODUCED USING THE SAME




(57) **Abstract:** Disclosed are a technique for producing high quality paper-making pulp capable of replacing wood pulp, utilizing bamboo and paper products produced using the same. The present invention can be applied to techniques for producing a variety of paper-making pulps which can be used in production of industrial papers, printing and writing papers, thin wrapping papers, toilet papers and special purpose papers from bamboo, and processes for producing a variety of paper products from the same. The present invention relates to a process for producing pulp utilizing bamboo, which is capable of producing pulp under mild conditions by facilitating penetration of liquid chemicals in chemical pulp production, is capable of simplifying manufacturing processes, and is also capable of maximizing pulp yield and minimizing weakening of pulp fibers, thereby maximizing pulp quality; and pulp and papers produced using the same.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

【DESCRIPTION】

【Invention Title】

PROCESS FOR PRODUCING PULP UTILIZING BAMBOO AND PULP AND PAPERS PRODUCED USING THE SAME

【Technical Field】

The present invention relates to a technology for producing high-quality paper-making pulp capable of substituting for wood pulp, and paper products, using a bamboo, and encompasses a technology for producing various paper-making pulps usable in the production of industrial paper, printing and writing paper, thin wrapping paper, toilet paper, non-woven fabric and special purpose paper, from bamboos, as well as a method for producing various papers from said pulps. The method according to the present invention can produce chemical pulp in mild conditions by facilitating the penetration of liquid chemicals in the production of the pulp, simplify a process, maximize pulp yield, and minimize the weakening of pulp fiber to maximize pulp quality. Also, the present invention relates to pulp produced using said method.

【Background Art】

Generally, papermaking pulps are recognized to be produced using wood.

In other words, because the papermaking pulps consist mostly of wood pulps, and it has recently became a great problem to produce the papermaking pulp while conserving forests due to the lack of wood resources and maintaining the environment, effects to produce the pulps using non-woody plant fibers and the like are being conducted.

Such non-woody plants include paper mulberry bast fibers, hemps, cottons, and Manila hemps, and Korean Patent Publication Nos. 98-9651 and 93-2604 disclose a method for producing pulp using rice-straw.

All such efforts can be considered as efforts to conserve trees, which can prevent environmental pollution.

In other words, these efforts aim to conserve trees by absorbing pollutants and carbon dioxide contained in the atmosphere through photosynthetic action while producing and supplying oxygen.

The development of industry and civilization really led to a great improvement in the quality of life of mankind, but involved a rapid increase in energy use, so that the emission of greenhouse gas was also rapidly increased, and thus the contamination of the global environment and side effects thereof became very severe.

In typical examples thereof, the depletion of the ozone layer in the South Pole becomes very rapidly severe, and misfortunes caused by a rapid change in weather, global warming and ecosystem destruction occur in the whole world.

Such environment pollution phenomena very rapidly progressed to reach a state that threatens the survival of mankind, and thus the Tokyo Protocol on the reduction of greenhouse gas emissions, which has been delayed due to the noncooperation of some of highly developed countries, became effective.

Accordingly, in manufactures in various countries, efforts to reduce greenhouse gas emissions are urgently required, and in severe cases, additional expenses for purchasing greenhouse gas emission rights are expected.

One means for solving this problem, which has recently received great attention, is a non-woody plant that eliminates the need for the felling of wood.

In other words, when this non-woody plant is used to produce pulp, there will be a great advantage in that wood, which is consumed in large amounts, needs to be felled.

Among the non-woody plants, a bamboo, which has recently attracted attention and is used as a raw material in the present invention, is produced in large amounts in Southeast Asia countries such as China and Myanmar and sufficiently grows to a usable degree only within about five months.

However, the use of the bamboo has shortcomings in that, because the compact structure of the bamboo is not considered, the pulping of the bamboo is not satisfactorily achieved, large amounts of chemicals and energy are consumed, and a bleaching process is conduced in strong conditions to reduce yield and to cause the decomposition and destruction of fiber, making the fiber weak.

A chlorine bleaching process using elemental chlorine provides the cause of dioxin generation.

Also, because bleaching powder that acts as the cause of the corrosion of an apparatus is used as a bleaching chemical, the durability of the production apparatus is highly problematic.

In addition, this processing problem acts as the cause of increasing chemical amount, energy consumption and production cost per unit pulp production.

Methods for producing papermaking pulp and paper using a bamboo, like the present invention, were also developed in

the prior art, but have not been widely used, the reason for which will now be described.

Even though the bamboo has a very compact and hard structure, a bamboo chip having a thickness of 3.2 mm and a length and width of 19 mm was prepared in the prior art. Because the penetration of liquid chemical into the chip was difficult, the cooking of the chip was not sufficiently performed, thus making bleaching difficult.

The application of the prior art as described above cannot efficiently produce pulp, reduces the quality of pulp and is very disadvantageous in environmental terms.

Japanese Patent 3,184,993 invented by Kikuchi Shingo is very disadvantageous in terms of pulp yield, pulp quality and the consumption of liquid chemicals, because bamboo leaves and stalks are all used. Also, the technology of the household industrial level, which is difficult to perform mass production, is applied, because the bamboo is simply treated with an alkali solution in atmospheric conditions.

The paper making method in said Japanese Patent is a method for producing a kind of fiber mat for use in special applications such as forest bath, deodorization, air purification and wall papers using household industrial means and is entirely different from a paper production method for mass production, which is suggested in the present invention.

Also, in US Patent No. 4,857,145 invented by Eduardo J. Villavicencio, a shredder is used to prepare bamboo chips having a length of 10-25 cm or more, which are then chemically digested.

In this case, although it is possible to minimize damage to fibers as stated by the inventor, the fibers

require a wide space for the storage thereof, because their volume is very large. Also, the fibers cannot be treated in large amounts during a digestion process.

Furthermore, because the thickness of the prepared bamboo chips is large, the fibers are pre-impregnated with black liquor or digestion chemicals at high pressure to facilitate the digestion of chemicals. For this reason, additional processes, facilities and energy are required.

Also, the dissociation of the fibers is induced by treatment such as an explosion process by repeating pressurization and depressurization in a digestion process.

This pulping process is unsuitable for the mass production of papermaking pulp, because it requires much time and results in a significant reduction in pulp quality.

Also, because the pulp discharged from a digester is treated with a refiner so as to disintegrate it into a fiber state, the fibers can be significantly damaged. Also, the pulp shows properties similar to those of semi-chemical pulp, and it is optionally carried out to bleach the pulp.

Accordingly, the pulp produced in said US Patent can be used as a raw material for the production of low-grade paper and industrial paper, but is not suitable for the production of high-grade printing and writing paper, toilet paper, thin paper, newsprint paper or medium-quality paper.

【Disclosure】

【Technical Problem】

The present invention has been made to solve the problems occurring in the prior art, and it is an object of the present invention to provide a method for producing high-quality papermaking pulp capable of substituting for wood

pulp, and paper products, using a bamboo. More specifically, it is an object of the present invention to provide a method for producing various papermaking pulps using a bamboo, which makes it possible to produce the pulp in mild conditions by facilitating the impregnation of liquid chemicals into the pulp, simplify a process, maximize the pulp yield and minimize the weakening of the pulp fiber to maximize the quality of the pulp, as well as pulp prepared using said method, and a method for producing paper products from said pulp. The pulp, which is produced in the inventive method, can be used to produce various paper products, including industrial paper, printing and writing paper, thin wrapping paper, toilet paper, non-woven fabric and special purpose paper.

【Technical Solution】

To achieve the above object, the present invention provides a method for producing pulp from a bamboo, the method comprising: a step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo to make bamboo chips; a step of screening the cut bamboo chips to filter out small fragments or impurities from the chips and washing the chips with water to remove contaminants from the bamboo chips; a step of cooking the screened bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked in the digester at high temperature, thus softening and pulping the bamboo chips; a step of cleaning the cooked pulp using a centrifugal cleaner so as to remove

contaminants introduced together with the bamboo; a step of screening the cleaned pulp, in which contaminants are removed from the cleaned pulp using a pressure screen, and an incompletely cooked of the pulp is fed back into the digester; a step of washing and thickening the screened pulp, in which a decker is used to wash the pulp, thus removing the chemical liquor, and to squeeze water, thus thickening the pulp; and a step of using the thickened pulp to produce unbleached chemical and semi-chemical bamboo pulp for industrial paper or liner paper for corrugated boards.

In another embodiment, the present invention provides a method for producing bleached chemical bamboo pulp for the production of tissue paper, wood-free paper, art paper or toilet paper, and a method for producing refiner mechanical pulp for the production of newsprint paper or medium-quality paper, each of the methods having modifications of said method for producing the unbleached chemical and semi-chemical bamboo pulps for industrial paper or liner paper for corrugated boards.

In still another embodiment, the present invention provides a method for producing industrial paper or liner paper for corrugated boards, the method comprising: a step of disintegrating the unbleached chemical or semi-chemical bamboo pulp produced according to said method; a step of refining the disintegrated pulp; a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp; a step of screening the pulp having the chemicals added thereto; a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard; a pressing step of pressing the web

obtained in the sheet forming step to remove water; a drying step of further removing water from the pressed web; a calendering step of making the thickness of the paper or paperboard uniform; a step of slitting and cutting the calendered paper into a sheet or roll and packing the sheet or roll.

In addition, the present invention provides a method for producing tissue paper, wood-free paper, art paper or toilet paper from bleached chemical bamboo pulp, and a method for producing newsprint paper or medium-quality paper from refiner mechanical pulp, each of the methods having modifications of said method for producing industrial paper and liner paper for corrugated boards.

【Description of Drawings】

FIG. 1 is a flow chart showing processes for producing bamboo pulps according to the present invention.

【Best Mode】

The present invention relates to methods for producing papermaking pulps using a bamboo, as well as pulps produced using said methods, and methods for producing papers using the pulps. The production methods have great characteristics and will now be described in detail.

Among the methods for producing pulps using a bamboo, the steps of the method for producing unbleached chemical and semi-chemical pulp for industrial paper or liner paper for corrugated boards will now be sequentially described with reference to FIG. 1.

Specifically, the method for producing unbleached chemical and semi-chemical pulp for the production of industrial paper or liner paper for corrugated boards

comprises: a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo; and a second step of screening the cut bamboo chips to filter out small fragments or impurities from the bamboo chips and washing the bamboo chips with water to remove contaminants from the bamboo chips.

Also, the method comprises: a third step of cooking the washed bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked in the digester at high temperature, thus softening and pulping the bamboo chips; and a fourth step of cleaning the cooked pulp using a centrifugal cleaner to remove contaminants introduced together with the bamboo.

If semi-chemical pulp is to be produced, the third step comprises conducting the cooking process in mild conditions and then conducting refining instead of the cleaning.

Also, the method comprises: a fifth step of screening the chips, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the pulp is fed back into the digester; and a sixth step of washing and thickening the chips, in which a decker is used to wash the pulp, thus removing the chemical liquor, and to squeeze water from the pulp, thus thickening the pulp.

In addition, the method comprises: a seventh step of forming a sheet from the washed and thickened pulp and drying the sheet, thereby producing unbleached chemical and semi-

chemical pulp for industrial paper or liner paper for corrugated boards.

The above-described steps will now be described in further detail. In the third step of cooking the bamboo chips, the amount of alkali (as $Na_2O$) added to water is 10-30 % based on the oven-dry weight of the bamboo chips (i.e., mass excluding the content of moisture in the bamboo chips), and the anthraquinon (AQ) is added in an amount of 0.01-2%.

In other words, the bamboo leaf contains a large amount of extracts unnecessary to produce pulp, but has a small amount of essential fibrous material.

Thus, because the bamboo leaf is of help to prepare pulp, but rather can act as the cause of increasing the consumption of chemicals, the bamboo leaf is removed before introducing the bamboo into a process for producing the pulp.

In other words, in the inventive method for producing the bamboo pulp, the bamboo leaf is not used and only the bamboo stalk is used.

Then, a longitudinal splitting step of longitudinally splitting the bamboo to a width of 1.5-3 mm is conducted.

Due to the compact structure of the bamboo, the impregnation of chemicals into the bamboo is significantly difficult compared to wood.

Thus, the production of the pulp must be started with the crushing of the bamboo. For this purpose, the bamboo is first longitudinally split into half, and the split bamboo is additionally split to a narrower width.

In this step, the bamboo is preferably split to a width of 1.5-2.0 mm.

This longitudinal splitting is a significantly

characteristic step of the present invention, and when the bamboo is split at random without considering orientation, fibrous material will not be uniformly split, but rather the fibrous material itself can be broken.

This reduces the strength of the produced pulp to reduce the quality thereof.

For this reason, in the inventive production method, the bamboo is used after it is longitudinally split several times to have narrow width.

It is also possible to use a method of splitting the bamboo in a one-step process using a device mounted with a plurality of blades.

Then, the step of transversely cutting the longitudinally split bamboo to a length of 10-30 mm is conducted.

In other words, in order to produce small bamboo chips which are easily filled and packed in a digester, the split bamboo is transversely cut to a length of 10-30 mm using a blade cutter.

If the length of the bamboo chips is too large, they cannot be effectively packed into the digester, and if the bamboo is cut to an excessively short length, large damage to fiber can occur, resulting in the reduction in the strength of the pulp.

Then, the second step of screening the cut bamboo chips to filter out small fragments or impurities from the chips and of washing the chips with water to remove contaminants from the chips is carried out.

In other words, even if small fragments which are generated in the step of cutting the bamboo are prepared into

pulp, the pulp is in a state in which the fibrous material was broken. Thus, these small fragments can weaken the strength of the pulp, increase the consumption of chemicals, and adversely affects dehydration in a papermaking machine.

Also, contaminants introduced during the cutting step are not of any help to produce the pulp.

Accordingly, if these small fragments and contaminants are all used in the production of the pulp, they will greatly reduce the yield (production rate) of the pulp and will adversely affect the quality of the pulp. For this reason, these are removed by screening.

Also, in other words, the contaminant, dust and the like attached to the bamboo chips are removed with water.

This can reduce the consumption of unnecessary chemicals in a cooking process and allows pure pulp to be obtained, thus improving the quality of the produced pulp.

Then, the third step is carried out, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked in the digester at high temperature, thus softening and pulping the bamboo chips.

The use of a prior sulfite process for the cooking of the bamboo chips has problems in that the fiber becomes weak and the yield of the pulp is low.

Thus, in the present invention, a soda-AQ process is applied in order to promote delignification and to prevent the decomposition of hemicellulose, thus increasing the yield and quality of the pulp.

In other words, the soda-AQ process comprises adding a liquor consisting of alkali (mainly NaOH), anthraquinone and water in a liquor ratio of 3.5-6.9 : 1 with respect to the oven-dry weight of the bamboo chips.

Also, in the soda-AQ process, the amount of alkali (as $Na_2O$) added to water is preferably 10-30 % based on the oven-dry weight of the bamboo chips (i.e., mass excluding the content of moisture in the bamboo chips), and the anthraquinon (AQ) is preferably added in an amount of 0.01-1%.

The cooking temperature in this cooking step is preferably 130-210 ℃, and the cooking time is preferably controlled within the range of 90-120 minutes depending on the polymerization degree and the quality of pulp to be produced.

As used herein, the term "oven-dry weight" means the mass of the bamboo chips that excludes the content of moisture in the bamboo chips.

Then, the fourth step of cleaning the bamboo chips using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo is conducted.

In other words, the centrifugal cleaner is used to remove contaminants introduced in the process together with the bamboo.

Then, a fifth step of screening the pulp is conducted, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the pulp is fed back into the digester.

In other words, non-disintegrated fibrous portions or contaminants are removed using the pressure screen.

A portion passed through the screen is sent to a

subsequent process, whereas a rejected portion remaining on the screen is filtered through a vibrating screen, a rejected portion remaining on the vibrating screen is wasted, and a fibrous portion or an incompletely cooked portion is sent back into the digester.

A sixth step of washing and thickening the pulp is conducted, in which a decker is used to wash the pulp, thus removing the chemicals from the pulp, and to squeeze water from the pulp, thus thickening the pulp.

The decker (not shown) is a machine that serves to wash the pulp and, at the same time, to thicken the pulp by squeezing water. Using this decker, the pulp is washed and thickened to a concentration suitable for the next step.

In this step, the washing operation is repeated at least three times in order to remove the remaining chemicals, fine powders and parenchyma cells as much as possible.

Then, a seventh step of forming the washed pulp into a sheet or roll is conducted, in which the washed pulp is made into a sheet and dried, thus completing the production of unbleached chemical and semi-chemical pulp for industrial paper or liner paper for corrugated boards.

To produce unbleached pulp for the production of industrial paper and liner paper, which have a more excellent quality, the cooking step in the above-described method is preferably carried out in the following conditions milder than those for the production of bleached chemical pulp: the content of active alkali: 12-14%; the content of AQ: 0.01 - 1%; liquor ratio: 3.5-6.9; cooking temperature: 130 - 150 ℃; and cooking time: 90-120 minutes.

Such conditions were determined through many

experiments conducted by the applicant.

Furthermore, said unbleached chemical and semi-chemical pulp for the production of industrial paper or liner paper for corrugated boards, bleached chemical pulp for the production of tissue paper, wood-free paper, art paper or toilet paper, and refiner mechanical pulp for the production of newsprint paper or medium-quality paper, can undergo a slitting, cutting and packing step.

However, it is preferable that the pulps should not be subjected to this slitting, cutting and packing step and should be immediately sent to a papermaking process to make paper and paperboard products.

It is to be understood that, if a pulp production factory and a paper production factory are separately placed, the slitting, cutting and packing step must be carried out.

The pulps are generally packed in the form of rolls or sheets.

In other words, it is preferable that the pulp produced in the pulping process is immediately fed into a papermaking process for use as a papermaking raw material without undergoing a drying process.

The bamboo pulp fiber has a structure and dimension different from those of wood pulp.

Such properties can be advantages in some terms depending on the intended use of the pulps, but can also be disadvantages in other terms.

Thus, depending on the quality requirement of paper to be produced, the blending or treatment of the pulps is required.

The method for producing the unbleached chemical and

semi-chemical bamboo pulp for the production of industrial paper and liner paper has been described above. Thus, a step of completing the production of bleached chemical pulp for use in the production of tissue paper, wood-free paper, art paper, non-woven fabric, special purpose paper and toilet paper will now be described.

Specifically, the method for producing bleached chemical pulp for the production of tissue paper, wood-free paper, art paper or toilet paper, using a bamboo, comprises: a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo; and a second step of screening the cut bamboo chips to filter out small fragments or impurities from the chips and washing the chips to remove contaminants from the chips.

Also, the method comprises: a third step of cooking the washed bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked in the digester at high temperature, thus softening and pulping the bamboo chips; and a fourth step of cleaning the cooked pulp using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo.

Also, the method comprises: a fifth step of screening the cleaned pulp, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the pulp is fed back into the digester; and a sixth step of washing and thickening the pulp, in which a decker is used to wash the pulp, thus removing the chemical

liquor from the pulp, and to squeeze water from the pulp, thus thickening the pulp.

In addition, the method comprises: a seventh step of bleaching the thickened pulp; and a eighth step of forming the bleached pulp into a sheets or roll and drying the sheet or roll, thereby producing bleached chemical pulp for the production of tissue paper, wood-free paper, art paper or toilet paper.

In other words, the method for producing the bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, special purpose paper or toilet paper is the same as the above-described method for producing the unbleached chemical and semi-chemical pulp for the production of industrial paper or corrugated board liner paper with respect to the first step to the sixth step, but it performs the cooking step in conditions stronger than those of the production of the unbleached chemical and semi-chemical pulp and comprises the seventh step of bleaching the pulps.

This is because the industrial paper and corrugated boards need not to be bleached, but tissue paper, wood-free paper, art paper, special purpose paper or toilet paper must have a good texture and excellent colorful beauty sensations.

Thus, regarding the method for producing the bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, special purpose paper or toilet paper, only the step of bleaching the pulp will be described.

In other words, in the seventh step of bleaching the pulp, which is very important in the present invention, is an ECF (elementary chlorine free) or TCF (total chlorine free) bleaching process is used in order to eliminate environmental

problems such as the generation of environmental hormone dioxin.

As bleaching stages used in this step, DED, DEDD, DEDP, DEZP, DEOP, DEOZ and PEOZ can be selectively applied. A bleaching process, the number of bleaching stages, and bleaching conditions, are determined depending on the degree of required bleaching.

In the above description of the bleaching stages, D means chlorine dioxide bleaching, E means alkaline extraction, P means peroxide bleaching, O means oxygen bleaching, and Z means ozone bleaching.

If the content of metal ions in the pulp is high, the metal ions will be inactivated by treating the pulp with a chelating agent (EDTA, DTPA, DTPMPA, etc.) to increase bleaching efficiency before conducting the bleaching of the pulp.

Herein, the chelating agent is a chemical for making the reactivity of metal ions impotent, and if large amounts the metal ions are present in the pulp, they will remarkably deteriorate the performance of a bleaching chemical used for bleaching.

For this reason, if the content of the metal ions is large so that it reduces bleaching efficiency, the pulp is treated with the chelating agent before conducting the bleaching of the pulp.

As an example of a bleaching method using the bleaching stages, the bleaching stages of DEDD indicate that bleaching is conducted in four sequential steps of: (1) chlorine dioxide bleaching, (2) alkaline extraction, (3) chlorine dioxide bleaching, and (4) chlorine dioxide bleaching.

In other words, various bleaching stages listed above indicate that a pulp producer may selectively the bleaching stages depending on the brightness or chemical purity required in the pulp to be produced, or the preference of a worker.

Regarding the purpose for increasing the number of the bleaching stages, when the brightness or chemical purity is greatly required, the number of the bleaching stages may be increased or the amount of chemicals used may be increased. Also, even if the same level is required, a method of reducing the amount of a chemical used in each stage and increasing the number of the stages can be used in order to minimize adverse effects on pulp (pulp damage and decomposition, etc).

Accordingly, even if the quality of the same level is required, it is possible to control the number of the bleaching stages or the amount of chemicals used, and it is difficult to express this control as an absolute numerical value, because the state of pulp supplied into the bleaching process varies depending the degrees of pulping or cooking conducted in the above-described steps.

However, when the pulp is bleached, it is preferable that the content of lignin in the pulp produced in the digester be first measured and, based on the measured content, the amount of addition of bleaching chemicals be calculated so as to increase or decrease the amount depending on the required quality.

Thus, the present invention can prevent the generation of dioxin, an environmental pollutant, using said bleaching agent, and has excellent bleaching effects.

In the most embodiment of the present invention, the method for producing the bleached chemical pulp for the production of wood-free paper, art paper, non-woven fabric, special purpose paper or tissue paper comprises conducting the cooking process in the following conditions and the ECF or TCF bleaching process: the content of active alkali: 16 - 20%; the content of AQ 0.01-1%; liquor ratio: 3.5-6.0; cooking temperature: 150-180 ℃; and cooking time: 120 - 200 minutes.

Also, the yield of the produced papermaking pulp, the characteristics of the fibers, the papermaking characteristics, etc., are controlled through the combination of cooking conditions, bleaching conditions and methods.

In addition to the method for producing the unbleached and semi-chemical pulp for the production of industrial paper or corrugated board liner paper and the method for producing the bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, non-woven fabric, special purpose paper or toilet paper, the present invention also provides a method for producing refiner mechanical pulps for the production of newsprint paper or medium-quality paper.

Thus, the steps of the method for producing refiner mechanical pulp for the production of newsprint paper or medium-quality paper will be sequentially described in detail. This method comprises: a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo; and a second step of screening the cut bamboo chips to filter out small fragments or impurities from the chips and washing the chips with water to remove contaminants from the chips.

Also, the method comprises: a third step of primarily

refining the washed bamboo chips, in which the bamboo chips are ground in a disc refiner; and a fourth step of screening the refined bamboo chips, in which contaminants are removed from the bamboo chips using a pressure screen, and an incompletely defibrated portion of the chips is fed back into the disc refiner.

Also, the method comprises: a fifth step of secondarily refining the defibrated pulp, in which the defibrated pulp is further ground; and a sixth step of screening the refined pulp, in which contaminants are removed from the pulp using a pressure screen, and an incompletely defibrated portion of the pulp is fed back into the disc refiner.

In addition, the method comprises: a seventh step of cleaning the defibrated pulp, in which contaminants introduced together with the bamboo are removed using a centrifugal cleaner; and an eighth step of forming the cleaned pulp into a sheet and drying the sheet.

In other words, the sequence of the steps of this method is substantially the same as that of the above-described method for producing unbleached chemical and semi-chemical pulp for the production of industrial paper or corrugated board liner paper and as that of the above-described method for producing bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, non-woven fabric, special purpose paper or toilet paper, however, it is different in that the cooking step is not carried out and the two refining steps are additionally conducted.

Thus, only the refining steps will be additionally described herein.

As used herein, the term "refining step" refers to a

step of producing refiner mechanical pulp, in which the bamboo chips resulting from the previous washing step are ground in the disc refiner to produce the pulp.

This refining step in the present invention is repeated two times to grind the chips into very fine pieces.

Accordingly, in this method, the prepared, screened and washed bamboo chips are defibrated using the refiner so as to prepare refiner mechanical pulp for the production of newsprint paper and medium-quality paper.

In this case, if the high brightness is required in the pulp, single-stage or two-stage peroxide bleaching is preferably carried out.

Also, the present invention also provides articles produced according to all the above-described pulp production methods, i.e., pulps produced using a bamboo.

Also, the pulps are made into the form of a sheet or roll, in which the sheet pulp has a thickness of 0.1-3 mm, and the roll pulp is obtained by winding a web having a thickness of 0.1-1.5 mm.

In other words, the sheet or roll pulp is an intermediate product, which will be introduced into a papermaking process to produce paper as described above.

Thus, if a pulp production factory and a papermaking factory are far away from each other, the pulp must be transported in a state in which it was packed in the form of a sheet or roll as described above. However, if the factories are integrated factories, the pulp needs not to be specially packed.

Methods for producing paper products from the intermediate products produced as described above will now be

described in a manner classified according to the kind of the paper products.

First, a method for producing industrial papers or corrugated board liner paper using said unbleached chemical and semi-chemical bamboo pulp will be described.

Specifically, the method for producing the industrial paper or corrugated board liner paper comprises: a step of disintegrating the unbleached chemical and semi-chemical bamboo pulp; and a step of refining the disintegrated pulp.

Also, the method comprises: a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp; and a step of screening the pulp.

Also, the method comprises: a sheet forming step of making the screened pulp into a product (web) in the form of a paper or paperboard; and a pressing step of pressing the web obtained in the sheet forming step to remove water from the web.

Also, the method comprises: a drying step of further removing water from the pressed web; and a calendering step of making the thickness of the paper or paperboard uniform.

In addition, the method comprises a step of slitting and cutting the dried and calendered paper into a sheet or roll and packing the sheet or roll.

Hereinafter, each of said steps will be described in further detail.

First, in the step of disintegrating the unbleached chemical and semi-chemical bamboo pulp, the pulp sheet is repulped or disintegrated into individual fibers using a pulper or hydrapulper.

This repulping or disintegration step may also be omitted, if the pulp is not made into the sheet in the pulp production process and is immediately fed to a papermaking process through pipe lines and the like.

In the step of refining the disintegrated pulp, wood pulp and bamboo pulp are refined using a disc refiner or cone refiner according to conditions required for the desired paper in order to control the structural, physical and optical properties of the paper.

Chemical pulp of broadleaf trees is usually refined at an SEL of about 0.1-5.0 Ws/m.

However, bamboo pulp needs to be treated in a manner different from wood pulp, because it has a relatively low lignin content, and its fiber is thin.

Thus, the bamboo pulp is either refined at a weak SEL (specific edge load; index indicative of the intensity of energy applied from the refiner to the pulp) of 0.01-2.5 Ws/m depending on the required properties of paper to be produced, or treated using a deflaker.

Refiners suitable for refining the bamboo pulp at low SEL include multidisk refiner, Conflo and the like.

On the other hand, if more refining is required, the refining of the pulp is conducted at a higher SEL.

In the step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp, the addition of wet chemicals and additives is performed to adjust a process and to satisfy the properties of paper according to the kind and intended use thereof.

In the case of industrial paper, liner base paper,

toilet paper and thin wrapping paper, any filler is not used, and the addition of chemicals is adjusted only depending on required size degree, wet strength or dry strength.

Examples of a chemical, which can be used for the adjustment of sizing degree, include rosin emulsion, AKD, ASA and the like, and examples of a wet strength agent, which can be used in the present invention, include urea resin, melamine resin, polyamide epichlorohydrin, acrylamide glyoxal and the like. This chemical is added in an amount of 0.1-3% depending on required wet strength or dry strength.

In the case of wood-free paper, coated base paper, newsprint paper and medium-quality paper, a filler is used in an amount of 10-30% for the improvement of printing quality. Examples of the filler, which can be used in the present invention, include calcium carbonate, activated clay, and titanium dioxide.

Examples of the sizing agent, which can be used in the present invention, include rosin emulsion, AKD, ASA and the like.

For the retention of the sizing agent and the filler, microparticle systems (e.g., cationic starch, PAM, bentonite, colloidal silica, organic microparticles, etc.) are used.

Also, the screening step is performed to break aggregates formed in a paper stock preparation process or pipe lines for supplying the paper stock to a papermaking machine and to remove lumps, which are not disintegrated, before supplying the paper stock to the papermaking machine. This screening step is usually performed just before the papermaking machine so as to pass the paper stock.

Then, the sheet forming step for producing the paper-

or board-like product is a process in which the raw material subjected to the paper stock preparation process is made into the form of a web.

Then, the pressing step of pressing the web formed in the sheet forming step to remove water from the web is performed and will now be described in detail.

Specifically, the pressing step serves to remove water from the web formed in the sheet forming step, make the web more compact and facilitate the bonding between the fibers.

In this step, it is preferable to remove water as much as large within the range in which the quality of the product is not deteriorated. This reduces the use of steam in a drying section to increase economy.

However, the pressure used in this pressing step greatly varies depending on the kind of paper.

In the case of paperboard, toilet paper and the like, a pressure lower than that in other printing and writing papers or industrial papers is applied, because a bulk property is important.

Then, the drying step of further removing water from the web passed through the pressing step is carried out, in which water in the web passed through the sheet forming step and pressing step is further removed to impart the inherent property of paper or paperboard.

Then, in the inventive method, the calendering step of making the thickness of the paper or paperboard uniform is carried out.

The calendering step serves to make the thickness of the paper or paperboard uniform and to smoothen the surface of the paper or paperboard.

In addition, the step of slitting and cutting the dried and calendered paper into a sheet or roll and packing the sheet or roll is finally performed, thereby producing industrial paper or corrugated board liner paper.

In other words, in the slitting, cutting and packing step, the dried and calendered paper or paperboard is finally slit and cut into a sheet or roll according to the demand of consumers, and the sheet or roll is packed.

The above paper production method has been described with respect to the method for producing the industrial paper and corrugated board liner paper.

However, the paper production method according to the present invention is not limited only to said industrial paper and corrugated board liner paper.

Thus, a method for producing wood-free paper and art paper will now be described in detail.

Specifically, the method for producing wood-free paper and art paper comprises a step of disintegrating the chemical bamboo pulp produced according to the above-described inventive method and a step of refining the disintegrated pulp.

Then, a step of blending the refined pulp with wood pulp (bleached chemical pulp of broadleaf trees) and a step of adding chemicals (sizing agent, filler, retention agent, dehydrating agent and other additives) to the blended pulp are carried out.

Also, the method comprises a step of screening the chemical-added pulp and a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard.

Also, the method comprises a pressing step of pressing the web obtained in the sheet forming step to remove water from the web, and a drying step of further removing water from the pressed web.

Also, the method comprises a step of sizing the surface of the dried web, a step of drying the sized web, and a calendering step of making the thickness of the paper or paperboard uniform.

In addition, the method comprises a step of coating the paper or paperboard with a pigment, a step of drying the coated paper or paperboard, and a super-calendering step of imparting surface smoothness and gloss to the paper or paperboard.

Finally, the dried and super-calendered paper is slit and cut into a sheet or roll shape which is then packed, thus producing wood-free paper and art paper.

Most of the steps of this method, including the step of disintegrating the bleached chemical bamboo pulp and the step of refining the disintegrated pulp, are the same as those of the above-described method for producing the industrial papers and corrugated board liners.

However, this method is different in that it comprises the step of blending the refined pulp with wood pulp (board-leaved tree bleached chemical pulp, etc.), the step of sizing the surface of the dried web, the step of coating the paper, and the step of super-calendering the paper.

Thus, only the different steps of this method will now be described in detail.

Specifically, in the step of blending the refined pulp with wood pulp (bleached chemical pulp of broadleaf trees),

the blending of the pulps is performed to adjust the various properties of paper to be produced, by blending the refined pulp with the bleached craft pulp, thermal mechanical pulp, chemical thermal mechanical pulp or bleached chemical thermal mechanical pulp of broadleaf trees at a suitable ratio according to the required properties of the paper.

In the production of wood-free paper such as writing and printing paper, coated base paper and the like, the bleached craft pulp of broadleaf trees is blended in an amount of about 50-80% to achieve the excellent smoothness and formation of paper so as to provide good printing quality.

Also, in the production of newsprint paper and medium-quality paper, in order to provide sufficient strength properties, the bleached craft pulp of needle-leaf trees, the bleached chemical pulp of bamboos, white ledger or CPO (computer printout) deinked pulp is blended in an amount of 10-25%.

In the case of industrial paper, toilet paper and tissue paper, bamboo pulp can be used alone, and in some cases, it can be used in a mixture with wastepaper.

Also, in the step of sizing the surface of the dried web, the surface sizing is performed to control the impregnation of fluid into paper and improve the surface characteristics of paper so as to improve the surface strength and printing quality of the paper.

In this step, oxidized starch is usually used, but in some cases, the web can be treated with a coating pigment in a sizing press, such that the print quality of the paper can be further improved without a need for a coating process.

Also, the method comprises the pigment coating step and

the super-calendering step. The super-calendering step is performed to impart surface smoothness and gloss to the coated base paper.

Thus, using the inventive method for producing wood-free paper or art paper, the intermediate product pulp produced in the above-described method for producing the bleached chemical pulp for the production of tissue paper, wood-free paper, art paper or toilet paper is produced into wood-free paper or art paper as a final product.

Furthermore, an embodiment of the method for producing printing and writing paper such as wood-free paper or coated base paper will now be described in further detail. Depending on the required print quality of paper, the bleached chemical bamboo pulp is blended with wood pulp such as the bleached chemical pulp or bleached chemical thermal mechanical pulp of broadleaf trees.

Also, papermaking chemicals such as 10-30% of filler (calcium carbonate, clay, talc, titanium dioxide, etc.), 0.1-3% of a sizing agent (rosin emulsion, AKD or ASA) and/or a retention agent (cationic starch, PAM, bentonite, colloidal silica, organic microparticles, etc.) can be added to the pulp.

Also, to improve the surface strength and print quality of paper, the surface of paper is sized with oxidized starch. If necessary, the surface sizing can also be performed using a coating pigment.

The bleached chemical pulp of boardleaf trees is refined at an SEL of about 0.1-5.0 Ws/m, and the chemical bamboo pulp is refined at a weak SEL of about 0.01-2.5 Ws/m depending on the required properties of paper or is simply

treated using a deflaker.

Meanwhile, according to the present invention, tissue paper and toilet paper can also be produced using the above-described method for producing the bleached chemical pulp.

Thus, the steps of this method will now be described.

Specifically, this method comprises a step of disintegrating the bleached chemical bamboo pulp and a step of refining the disintegrated pulp.

Also, the method comprises a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp and a step of screening the chemical-added pulp.

Also, the method comprises a sheet forming step of making the screened pulp into a paper- or paperboard-like product, and a pressing step of pressing the web obtained in the sheet forming step to remove water from the web.

In addition, the method comprises a drying step of further removing water from the pressed web, and a final step of slitting and cutting the dried paper into a sheet or roll which is then packed, thus producing tissue paper.

The steps of said method for producing tissue paper and toilet paper have all been described in detail in the method for producing industrial papers and corrugated board liners and the method for producing wood-free paper and art paper, and thus will no longer be described.

Also, the present invention also provides a method for producing toilet paper using the bleached chemical bamboo pulp, and the method will now be described in detail.

Specifically, this method for producing toilet paper comprises a step of disintegrating the bleached chemical

bamboo pulp produced according to the present invention, and a step of refining the disintegrated pulp.

Also, the method comprises a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp, and a step of screening the chemical-added pulp.

Also, the method comprises a sheet forming step of making the screened pulp into a paper or sheet product, and a pressing step of pressing the web obtained in the sheet forming step to remove water from the web.

In addition, the method comprises a drying step of further removing water from the pressed web, and a final step of slitting and cutting the dried paper into a sheet or roll which is then packed, thus producing toilet paper.

The tissue paper or toilet paper is dried using a Yankee dryer and prepared to have low weight and thus low strength. For this reason, in order to impart the paper with the ability capable of resisting a force applied during the use thereof, a doctor blade attached to the end of the Yankee dryer is used to form invisible wrinkles on the tissue paper or toilet paper.

The steps of said method for producing toilet paper have all been described in detail in the method for producing industrial papers and corrugated board liners and the method for producing wood-free paper and art paper, and thus will no longer be described.

Furthermore, the present invention provides a method for producing newsprint paper or medium-quality paper using the refiner mechanical pulp of bamboos. Thus, this method will now be described in detail.

First, in the method for producing newsprint paper or medium-quality paper using the refiner mechanical pulp of bamboos, a step of disintegrating the refiner mechanical pulp of bamboos is first carried out.

Also, the method comprises a step of disintegrating and refining a strengthening pulp, and a step of blending the refined strengthening pulp with said refined refiner mechanical pulp.

Also, the method comprises a step of adding chemicals (sizing agent, filler, retention agent, strengthening agent and other additives), and a sheet forming step of making the blended pulp into a paper or paperboard product.

Also, the method comprises a pressing step of pressing the web obtained in the sheet forming step to remove water from the web, and a drying step of further removing water from the pressed web.

In addition, the method comprises a step of sizing the surface of the dried web, a step of drying the sized web, and a step of slitting and cutting the dried paper into a sheet or roll which is then packed, thus producing newsprint paper or medium-quality paper.

To improve the print quality and the like of newsprint and medium-quality paper, the paper may also be coated with a coating pigment in a sizing press instead of performing the surface sizing.

The steps of said method for producing newsprint paper and medium-quality paper have all been described in detail in the method for producing industrial papers and corrugated board liners and the method for producing wood-free paper and art paper, and thus will no longer be described.

Knowledge obtained through many experiments conduced by the applicant in order to obtain the optimal quality and productivity of papers is as follows.

In the production of toilet paper or thin wrapping paper, the bleached chemical pulp of bamboos is refined at an SEL of 0.01-1.0 Ws/m, and if necessary, the sizing agent is used in an amount of 0-0.5%, and the strengthening agent is used in an amount of 0-0.5%.

If necessary, wrinkles are formed on the paper using a doctor blade in a Yankee dryer, or the paper is embossed after the drying step.

According to the present invention, using the antibacterial activity of the bleached chemical pulp of bamboo, various special purpose papers (non-woven fabric usable in various applications such as sanitary, clothing and hospital gowns and automobile inner materials, food or drug wrapping material, etc.) can be produced.

【Mode for Invention】

Example 1

A Myanmar bamboo was split to a width of about 2 mm and then cut to a length of 15-25 mm. The cut material was screened through a 60-mesh screen to remove contaminants and small bamboo fragments, followed by washing.

400 g (on an oven-dry weight basis) of the washed bamboo was placed in a digester into which water was added. Then, 16% (as $Na_2O$) active alkali and 0.1% anthraquinone were added thereto, and the ratio of the chemicals to the weight of the bamboo was adjusted to 4:1. Then, the bamboo chips were cooked in the digester at 170 ℃ for 120 minutes.

The cooked pulp was washed and subjected to a five-

stage bleaching of DED(EO)D, and the bleached pulp was refined with 400 ml of CSF, thus producing hand-made paper having a weight of 60 g/m$^2$. The properties of the resulting paper are shown in Table 1 below.

Table 1: Results of soda and soda-anthraquinon pulping tests

| Properties of pulp and paper | NaOH | NaOH + AQ |
|---|---|---|
| Screening yield of pulp before bleaching | 47.2 | 48.5 |
| Kappa number* | 13.6 | 10.8 |
| Screening yield of pulp after bleaching | 43.5 | 46.4 |
| Brightness (% ISO) | 88.4 | 92.6 |
| Breaking length (km) | 7.9 | 8.5 |
| Tensile index (mN m$^2$/g) | 8.1 | 8.6 |
| Burst index (kPa m$^2$/g) | 3.8 | 4.2 |

*Kappa number is used to indicate the amount of lignin remaining in the pulp produced in the digester, and is used as a standard for determining the amount of addition of chemicals in bleaching, and is calculated from the consumed amount of potassium permanganate through oxidation-reduction titration.

Example 2

The pretreatment of bamboo was performed in the same manner as in Example 1. Also, the amount of addition of chemical liquor in pulping was adjusted to 16%, 14% and 12%, and as an additive for promoting a reaction and protecting hemicellulose, 0.1% AQ was used.

For the evaluation of the possibility of use as industrial paper, the pulp was not bleached.

The washed pulp was refined with 400 ml of CSF, thus preparing hand-made paper having a weight of 80 g/$m^2$. The properties of the resulting paper are shown in Table 2 below.

Table 2: Test results for unbleached bamboo pulp

| Properties of activated alkali pulp (% as $Na_2O$) and paper | 12 | 14 | 16 |
|---|---|---|---|
| Pulp yield (%) | 42.7 | 46.5 | 48.5 |
| Kappa number | 14.6 | 12.6 | 10.5 |
| Brightness (% ISO) | 34.1 | 35.6 | 38.2 |
| Breaking length | 10.8 | 12.5 | 14.8 |
| Tensile index (mN $m^2$/g) | 7.6 | 8.9 | 9.6 |
| Burst index (kPa $m^2$/g) | 6.9 | 7.8 | 8.4 |

【Industrial Applicability】

As described above, according to the present invention, the split and cut bamboo chips are pulped in the cooking process using the soda-anthraquinon process using anthraquinon as a catalyst. Thus, the present invention can have great effects on delignification, the improvement in pulp quality and the increase in pulp yield.

Also, according to the present invention, the bamboo chips are made thin in the raw material treatment process to facilitate the impregnation of liquid chemicals into the chips and the cooking of the chips. Also, papermaking pulp can be produced in milder conditions by previously eliminating the factors of causing the loss of chemicals and reducing the pulp quality.

Furthermore, the soda-AQ process, in which anthraquinone is used as a catalyst in a cooking step, is applied for the pulping of bamboo, so that the present

invention can have great effects on delignification, the improvement in pulp quality and the increase in pulp yield.

Also, an environmental problem such as the generation of dioxin can be solved by applying an ECF and TCF bleaching process, and it is possible to control the quality of paper depending on the properties of paper to be produced, by controlling the cooking and bleaching conditions.

In addition, through the above-described technology for producing high-quality paper making pulp, wood pulp produced from felled trees grown over dozens of years can be replaced with pulp produced from bamboos, which rapidly grow to a usable degree only within about five months. Thus, the present invention is expected to have a very great effect on greenhouse gas emission reduction, which should be considered for the preservation of global environment.

【CLAIMS】

【Claim 1】

A method for producing pulps from a bamboo, the method comprising:

a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo to make bamboo chips;

a second step of screening the cut bamboo chips to filter out small fragments or impurities from the bamboo chips and washing the chips the bamboo chips with water to remove contaminants from the bamboo chips;

a third step of cooking the bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked at high temperature, thus softening and pulping the bamboo chips;

a fourth step of cleaning the bamboo chips using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo;

a fifth step of screening the cooked pulp, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the bamboo is fed back into the digester;

a sixth step of washing and thickening the screened pulp, in which a decker is used to wash the pulp, thus removing the chemical liquor, and to squeeze water so as to thicken the pulp; and

a seventh step of using the thickened pulp to produce unbleached chemical and semi-chemical bamboo pulps for industrial papers or corrugated board liners.

【Claim 2】

The method of Claim 1, wherein, in the third step of cooking the chips, the amount of alkali (as $Na_2O$) added to water is 10-30 % based on the oven-dry weight of the bamboo chips (i.e., mass excluding the content of moisture in the bamboo chips), and the anthraquinon (AQ) is added in an amount of 0.01-2%.

【Claim 3】

A method for producing pulps from a bamboo, the method comprising:

a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo to make bamboo chips;

a second step of screening the cut bamboo chips to filter out small fragments or impurities from the bamboo chips and washing the chips the bamboo chips with water to remove contaminants from the bamboo chips;

a third step of cooking the bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked at high temperature, thus softening and pulping the bamboo chips;

a fourth step of cleaning the bamboo chips using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo;

a fifth step of screening the cooked pulp, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the bamboo is fed back into the digester;

a sixth step of washing and thickening the screened pulp, in which a decker is used to wash the pulp, thus removing the chemical liquor, and to squeeze water so as to thicken the pulp;

a seventh step of bleaching the pulp; and

an eighth step of using the bleached pulp to produce bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, non-woven fabric, special purpose paper or toilet paper.

【Claim 4】

A method for producing pulps from a bamboo, the method comprising:

a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo to make bamboo chips;

a second step of screening the cut bamboo chips to filter out small fragments or impurities from the bamboo chips and washing the chips the bamboo chips with water to remove contaminants from the bamboo chips;

a third step of primarily refining the washed bamboo chips, in which the washed bamboo chips are ground in a disc refiner;

a fourth step of screening the refined bamboo chips, in which contaminants are removed from the ground bamboo chips using a pressure screen, and an incompletely defibrated portion of the chips is fed back into the disc refiner;

a fifth step of secondarily refining the screened pulp fiber, in which the defibrated pulp fiber is further ground;

a sixth step of screening the secondarily refined pulp, in which contaminants are removed from the refined pulp using a pressure screen, and an incompletely defibrated portion of the pulp fiber is fed back into the disc refiner;

a seventh step of cleaning the screened pulp using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo; and

an eighth step of using the cleaned pulp to produce refiner mechanical pulp for the production of newsprint paper or medium-quality paper.

【Claim 5】

The method of Claim 3, wherein the third step of bleaching the pulp is carried out using bleaching stages according to an ECF (elementary chlorine free) or TCF (total chlorine free) bleaching process.

【Claim 6】

The method of Claim 5, wherein the bleaching stages are selected from the group consisting of DED, DEDD, DEDP, DEZP, DEOP, DEOZ, PEOZ, DEDED, DED(EO)D, DEDOP and DEDZP.

【Claim 7】

Natural bamboo pulp produced using the method of any one of Claims 1 to 6.

【Claim 8】

The pulp of Claim 7, which is in the form of a sheet or roll.

【Claim 9】

The pulp of Claim 8, wherein the sheet pulp has a thickness of 0.1-3 mm.

【Claim 10】

The pulp of Claim 8, wherein the roll pulp is obtained by winding a web having a thickness of 0.1-1.5 mm.

【Claim 11】

A method for producing paper from bamboo pulp, the method comprising:

a step of disintegrating the unbleached chemical and semi-chemical bamboo pulp produced according to the method of Claim 1;

a step of refining the disintegrated pulp;

a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp;

a step of screening the chemical-added pulp;

a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard;

a pressing step of pressing the web obtained in the sheet forming step to remove water from the web;

a drying step of further drying water from the pressed web;

a calendering step of making the thickness of the paper or paperboard uniform; and

a step of slitting and cutting the dried paper into a sheet or roll and packing the sheet or roll,

thereby producing industrial paper or liner paper for corrugated boards.

【Claim 12】

A method for producing paper from bamboo pulp, the method comprising:

a step of disintegrating the bleached chemical bamboo pulp produced according to the method of Claim 3;

a step of refining the disintegrated pulp;

a step of blending the refined pulp with wood pulp (bleached chemical pulp of broadleaf trees);

a step of adding chemicals (sizing agent, filler, retention agent, dehydrating agent and other additives) to the blended pulp;

a step of screening the pulp having the chemicals added thereto;

a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard;

a pressing step of pressing the web obtained in the sheet forming step to remove water from the web;

a drying step of further removing water from the pressed web;

a step of sizing the surface of the dried web;

a step of drying the sized web;

a calendering step of making the thickness of the paper or paperboard uniform;

a step of coating the calendered paper or paperboard with a pigment;

a step of drying the coated paper or paperboard;

a super-calendering step of imparting smoothness and gloss to the surface of the dried paper or paperboard; and

a step of slitting and cutting the calendered paper into a sheet or roll and packing the sheet or roll,

thereby producing wood-free paper and art paper.

【Claim 13】

A method for producing paper from bamboo pulp, the method comprising:

a step of disintegrating the bleached chemical bamboo pulp produced according to the method of Claim 3;

a step of refining the disintegrated pulp;

a step of adding chemicals (sizing agent, retention agent and other additives) to the blended pulp;

a step of screening the pulp having the chemicals added thereto;

a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard;

a pressing step of pressing the web obtained in the sheet forming step to remove water from the web;

a drying step of further removing water from the pressed web; and

a step of slitting and cutting the dried paper into a sheet or roll and packing the sheet or roll,

thereby producing tissue paper.

【Claim 14】

A method for producing paper from bamboo pulp, the method comprising:

a step of disintegrating the bleached chemical bamboo pulp produced according to the method of Claim 3;

a step of refining the disintegrated pulp;

a step of adding chemicals (sizing agent, retention agent and other additives) to the blended pulp;

a step of screening the pulp having the chemicals added thereto;

a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard;

slitting and cutting the calendered paper into a sheet or roll and packing the sheet or roll,

thereby producing toilet paper.

【Claim 15】

A method for producing paper from bamboo pulp, the method comprises:

a step of disintegrating the refiner mechanical pulp produced according to the method of Claim 4;

a step of disintegrating and refining a reinforcing pulp;

a step of blending the disintegrated refiner mechanical pulp with the refined reinforcing pulp;

a step of adding chemicals (sizing agent, filler, retention agent, strengthening agent and other additives) to the blended pulp;

a sheet forming step of making the blended pulp into a product (web) in the form of paper or paperboard;

a pressing step of pressing the web obtained in the sheet forming step to remove water from the web;

a drying step of further removing water from the pressed web; and

a step of sizing the surface of the dried web;

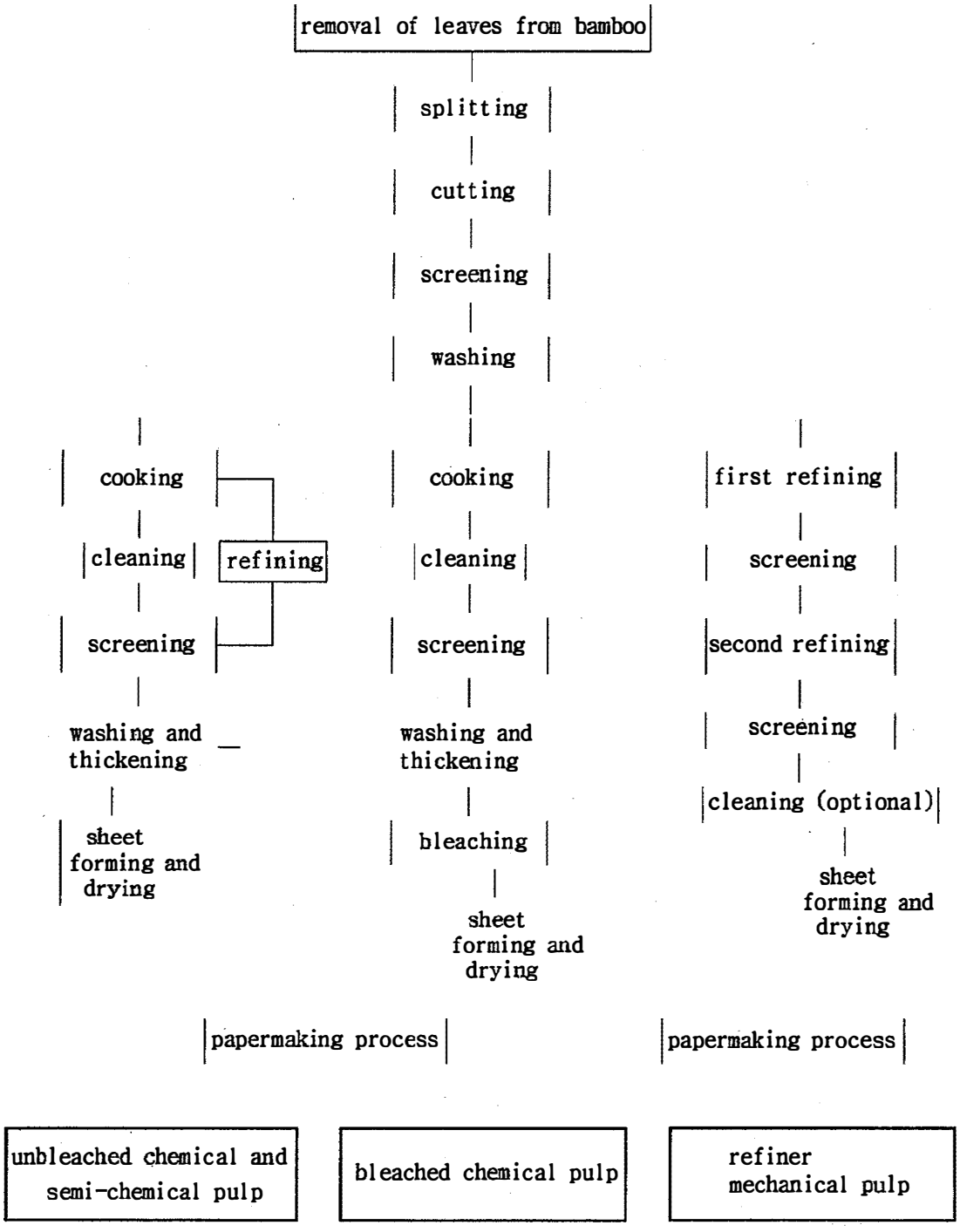
a step of drying the sized web; and

slitting and cutting the dried paper into a sheet or roll and packing the sheet or roll,

thereby producing newsprint paper or medium-quality paper.

1 / 1

FIG. 1


removal of leaves from bamboo
splitting
cutting
screening
washing
cooking
cleaning
refining
screening
washing and thickening
sheet forming and drying
cooking
cleaning
screening
washing and thickening
bleaching
sheet forming and drying
first refining
screening
second refining
screening
cleaning (optional)
sheet forming and drying
papermaking process
papermaking process
unbleached chemical and semi-chemical pulp
bleached chemical pulp
refiner mechanical pulp

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/KR2●●5/●●2118

**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)
IPC8 D21C3/●4, D21H11/12, D21H19/36

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

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
eKIPASS, INSPECT "Bamboo, Semi-chemical, Chemical, Pulp, Paper, Manufacturing"

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 4652341 A1 (Eric S. Prior) 24. Mar. 1987<br>- See the whole document. | 1-15 |
| A | JP ●5321190 A (Kikuchi Shingo) ●7. Dec. 1993<br>- See the whole document. | 1-15 |
| A | JP ●5239791 A (Tootrru Inc.) 17. Sep. 1993<br>- See the whole Document. | 1-15 |
| A | EP 1371778 A1 (Oji Paper Co., Ltd.) 17. Dec. 2●●3<br>- See the whole Document. | 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
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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

Date of the actual completion of the international search
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Information on patent family members

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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| | | JP 16068242 A | Mar. 04. 2004 |
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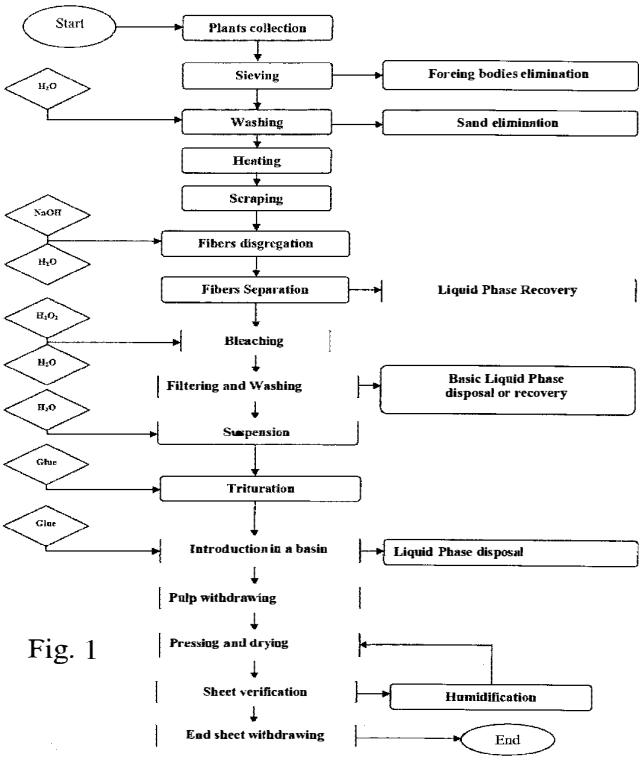



Fig. 1

(57) **Abstract**: Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives, comprising the steps of: (i). Sieving the collection product eliminating possible foreign bodies which are present in the collection product; (ii). Washing the sieved product by means of water removing possible sand which can be present; (v). Obtaining disgregated fibers by means of disgregation of the fibers by means of a treatment with a chemical disgregating agent which does not etches the cellulose fibers, possibly combined with a mechanical disgregation treatment; (vi). Separation of the fibers from the liquid phase by means of filtration recovering the corresponding liquid phase; (vii). Bleaching the fibers obtained from the previous phase by means of a treatment with a chemical bleaching agent; (viii). Filtering, w.ashing by means of water and/or pH balancing treatment.of the bleached fibers and obtainment of an essentially neutral pH; (ix). Suspension of the product obtained from the previous phase in water in a container; (xi). Triturating the suspension obtained from the previous phase obtaining a pulp with a high content of cellulose; said method being further characterised in that said collection product is a marine plants collection product.

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DESCRIPTION

# MARINE PLANTS PROCESSING METHOD FOR THE PRODUCTION OF PULP FOR THE PRODUCTION OF PAPER

## Technical field

The present invention relates to a marine plants processing method for the production of pulp for the production of paper according to the characteristics of the pre-characterizing part of claim 1. The present invention also relates to the paper obtained by the pulp obtained by means of the described method.

## Definitions

In the present description and in the appended claims the following terms must be intended according to the following definitions. The term "paper" generically indicates all of the types of paper with basic weighs up to 140 g/m$^2$, as well as paperboard with basic weighs between 140 g/m$^2$ and 400 g/m$^2$, cardboard with basic weighs higher than 400 g/m$^2$, and the corrugated board. In general it is intended as a material essentially consisting of vegetal fibers, joined together by feltration, that is by means of firm reciprocal connection of the fibers starting from a suspension to be dried, with possible addition of bonding agents, minerals, dyes and additives or superficial films. With the term "collection product" one intends the just collected product, as well as already in a partial maceration phase product, and the previously dried product which is successively re-humidified, possibly with addition of anti fermentation agents. When one indicates “a quantity of water so as to obtain the superficial covering of the matter to be treated” it is intended that the matter is placed in a container having dimensions corresponding to the volume of the matter and water is added until the matter is superficially covered. Indicatively for 4kg of matter, a quantity of about 10-20 liters is needed depending on the shape of the container and on the consistence of the matter.

## Prior art

In the field of the production of the paper the normally used manufacturing process provides, starting from the wood, a preparation phase of the fibers by means of pulping

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obtaining a mixture of fibers in a liquid suspension, a bleaching phase, a forming phase of the sheet and a relative pressing, possible phases of surface treating and a drying phase. Alternatively the process occurs directly using a cellulose pulp obtained elsewhere or deriving from the recycling of other paper. Depending on the destination of use of the paper other types of fibres can also be used, e.g. cotton, linen and hemp.

GB508671 discloses a processing method of algae marine to obtain a pulp to be used in the production process of the paper based on a digestion process of the algae in an acid aqueous solution.

GB363353 discloses a processing method of algae marine for the extraction of salts, alginic acids and cellulose that provides the use of solutions based on Calcium Chloride.

EP0488486 describes a processing method to obtain a pulp applied to particular types of algae which essentially are unicellular algae belonging to the genus of closterium and pleutotaenuim containing cellulose and having a relation between length of the body and width of the body between 10 and 200.

EP0565920 describes a treatment process of algae marine in which the algae marine are submitted to a washing phase which is followed by an anti-fermenting treatment and to a grinding phase until sizes lower than 500 micron are obtained for a successive blending with cellulose fibers which are usually used in the production of paper.

Problems of the prior art

The process to obtain paper starting from the wood presents many drawbacks, above all from the environmental point of view, both due to the need to cut trees, and due to the need to use chemical compounds for the defibration of the lignin, e.g. caustic soda and sodium sulfide, besides chemical compounds for the bleaching, e.g. chlorine or chlorine dioxide. The process has environmental disadvantages (sulphur generates smell of bad eggs, and many aqueous waste products are present) and yield disadvantages (only 50% of the wood is transformed in paper pulp, even if many waste

products are burnt obtaining energy). Also in the case of the use of different fibers, e.g. cotton, linen and hemp, a defibration phase of the lignin has to be provided, though therein the lignin content is lower.

The process disclosed in GB508671 has the disadvantage to need the use of a digestion process using strong acids, with resulting problems relative to precautions to be adopted during the process to avoid the exposure to such acids, in addition to the treatment and disposal problems of the processing residues and to the need of alkaline treatments of the obtained pulp to neutralize the acids themselves. Moreover the process described for the production of paper or cardboard anyway requires the addition of the pulp obtained by the algae to a traditional pulp, limiting the benefits coming from the use of the algae and anyway involving the problems previously described relatively to the obtainment of the pulp which is traditionally used in the production of paper.

Also the process disclosed in GB363353 presents the disadvantage of the use of chemical compounds which require a lot of care during their handling and use, and in particular it makes use of Calcium Chloride, in addition to the treatment and disposal problems of the processing residues. Moreover the described process does not describes how the following paper production occurs, but it is limited to the description of the extraction of the cellulose from the algae without specifying how it will be used, supposedly by means of addiction of the pulp obtained by the algae to a traditional pulp, limiting the benefits deriving from the use of the algae and anyway involving the problems previously described relatively to the obtainment of the pulp which is traditionally used in the production of paper.

EP0488486 describes a method which is applicable only to microalgae which live in fresh water which are very different from macroalgae marine and marine plants.

The process disclosed in EP0565920 anyway requires the addition of the pulp obtained from the algae to a traditional pulp, limiting the benefits deriving from the use of

the algae and anyway involving the problems previously described relatively to the obtainment of the pulp which is traditionally used in the production of paper.

Aim of the invention

The aim of the present invention is to supply a marine plants processing method for the production of paper which allows to obtain paper without the use of pulp derived from trees.

Concept of the invention

The aim is reached with the characteristics of the main claim. The dependent claims represent advantageous solutions.

Advantageous effects of the invention

The solution according to the present invention, by the considerable creative contribution whose effect represents an immediate and significant technical improvement, has many advantages. With the described processing method and using the indicated marine plants, paper can be obtained which is 100% obtained from the marine plants themselves, without making use of pulp coming from trees. Advantageously the method according to the present invention does not need of the use of reactors containing chlorine or its derivates for the bleaching process. This is a considerable advantage from the environmental point of view with respect to the normal paper production processes starting from the wood or in the recycling processes of the paper itself. Moreover, advantageously the use of marine plants allows to obtain also the disposal of the marine plants or parts of the marine plants which deposit on the the littoral zones and which are normally sent to garbage dump.

Description of the drawings

A practical embodiment is described hereafter with reference to the included drawings to be considered as a non-limitative example of the present invention in which Fig. 1 represents a flow diagram showing the production method of paper from marine plants according to the present invention.

Description of the invention

The processing method of marine plants for the production of paper according to the present invention preferably but not limitatively occurs by means of the use of marine plants known as fanerogame marine, which are higher plants which are very different from algae, because they are provided with roots, leaves and true flowers. Fanerogame marine live in the waters of the littoral zones and cover the sea bed forming prairies.

Among the fanerogame marine useful in the use for the present invention the following ones are present: Zostera, Posidonia, Cymodocea, Syringonium, Thalassia, Halophila, Thalassodendron.

The corresponding different species are meant to be included too. For example with reference to Cymodocea, also Cymodocea nodosa, Cymodocea rotundata, Cymodocea serrulata, etc. are intended to be included. For example with reference to Syringonium, also Syringonium filiforme, Syringonium isoetifolium, etc. are intended to be included. For example with reference to Halophila, also Halophila beccarii, Halophila decipiens, Halophila minor, Halophila ovalis, etc. are intended to be included. For example with reference to Zostera, also Zostera marina, Zostera noltii, etc. are intended to be included. For example with reference to Posidonia, also Posidonia oceanica, Posidonia australis, Posidonia sinuosa, etc. are intended to be included. For example with reference to Thalassia, also Thalassia hemprichii, Thalassia testudinum, etc. are intended to be included.

These marine plants are different from algae due to the presence of a structure comprising of roots, fust, and leaves. The leaves come off and can arrive to littoral zones constituting a source of various problems for example due to their putrefaction.

With the described processing method and using the indicated marine plants, paper can be obtained which is 100% obtained from the marine plants themselves, without making use of pulp coming from trees.

The present description will make reference to the method applied to case of marine plants which are known with the name of Posidonia oceanica because they are more

easily available on the littoral zones, but the same process can be used, in general, for all of the fanerogame marine as for tests made by the inventors.

However it is possible to to use all of the types of algae or marine plants having a high content of cellulose. As a matter of fact, a characteristic which is common to the indicated marine plants is the high content of cellulose, above all in the relative leaves, with a corresponding absence or scarceness of lignin.

Advantageously the method according to the present invention does not need of the use of reactors containing chlorine or its derivates for the bleaching process. This is a considerable advantage from the environmental point of view with respect to the normal paper production processes starting from the wood or in the recycling processes of the paper itself.

Moreover, advantageously the use of marine plants allows to obtain also the disposal of the marine plants or parts of the marine plants which deposit on the the littoral zones and which are normally sent to garbage dump.

The process according to the present invention (Fig. 1) for the production of pulp having a high cellulose content for the production of paper provides the following steps:

(0). Collection of the marine plants or algae marine, preferably fanerogame marine, even more preferably fanerogame marine selected from the group consisting of Zostera, Posidonia, Cymodocea, Syringonium, Thalassia, Halophila, Thalassodendron;

(i). Sieving the collection product eliminating possible foreign bodies which are present in the collection product itself obtaining a sieved product, preferably obtaining a sieved product with a marine plants content equal or higher to 75 % in weight of the dry total collection product after sieving, even more preferably with a marine plants content equal or higher to 95 % in weight of the dry total collection product after sieving;

(ii). Washing the sieved product by means of water removing possible sand which can be present;

(iii). Possible treatment of the humid washed product by means of a treatment in a oven at a temperature between 80 and 250 °C, for a time between 10 and 60 minutes, preferably for a time between 15 and 30 minutes, the time and the temperature being selected depending on the maceration degree of the collection product;

(iv). Possible scraping treatment of the obtained product, the scraping causing a partial grinding/breaking of the fibers and causing an increasing of the chemically etcheable surface, the scraping treatment preferably occurring by means of a passage in a mill or in cylinders;

(v). Obtaining disgregated fibers by means of disgregation of the fibers by means of a treatment with a chemical disgregating agent which does not etches the cellulose fibers, possibly combined with a mechanical disgregation treatment, the chemical disgregation preferably occurring by means of boiling the product in an aqueous solution of sodium hydroxide, obtaining disgregated fibers;

(vi). Separation of the fibers from the liquid phase by means of filtration recovering the corresponding liquid phase;

(vii). Bleaching the fibers obtained from the previous phase by means of a treatment with a chemical bleaching agent, preferably by means of a heat treatment, preferably with hydrogen peroxide in an aqueous solution;

(viii). Filtering, washing by means of water and/or pH balancing treatment of the bleached fibers and obtainment of an essentially neutral pH; preferably the pH balancing treatment being a washing by means of water of the bleached fibers until obtaining an essentially neutral pH between pH 6 and pH 8 recovering the corresponding liquid phase;

(ix). Suspension of the product obtained by the previous phase in water in a container;

(x). Possible addition of a bonding agent;

(xi). Triturating the suspension obtained from the previous phase with possible addition of a bonding agent during the triturating phase itself, obtaining a pulp with a high content of cellulose;

(xii). Possible addition of a bonding agent;

(xiii). Introducing the pulp with a high content of cellulose in a withdrawal basin;

(xiv). Withdrawing the pulp with a high content of cellulose from the withdrawal basin;

(xxiii). Pressing and drying the pulp with a high content of cellulose preferably for 6 - 8 hours obtaining a sheet of paper;

(xxiv). Verification of the paper sheet and possible re-humidification with a following further pressing and drying operation;

(xxv). Removing and withdrawing the finished paper sheet.

Surprisingly and unexpectedly the inventors found that the thus obtained sheet presents a good absorbent power of the ink also without the need to use further treatments and additives, with further benefits from the environmental point of view.

Advantageously, therefore, it is possible to obtain paper, paperboard, cardboard, substitutes and derivatives obtained by pulp having a high content of cellulose produced by means of the method according to the present invention in which 100% of the pulp is obtained from marine plants, contrarily to the teachings of the prior art which anyway provide a significant contribution of pulp obtained by the wood.

It will be however apparent that, according to the desired end quality of the paper one can anyway use the pulp obtained by marine plants with pulp obtained by wood or substitutes, obtaining paper, paperboard, cardboard, substitutes and derivatives obtained by pulp having a high content of cellulose produced by means of the method according to the present invention in which at least 50% of the pulp is obtained by marine plants.

Without entering the merits, the inventors believe that the surprising obtained results are due to the high content of cellulose of the used marine plants, in particular

the fanerogame marine and, more in detail the listed fanerogame marine and the poseidonia oceanica.

However it will be apparent that, according to the desired end quality degree, additives can be added to obtain the desired properties, e.g. starch, polymeric glossing agents e.g. vinyl polyacetate (PVA). A glossing phase can also improve the surface smoothing it.

Moreover the further use of kaolin can be provided in a smoothing phase of the paper or the use of a transparent layer, for example consisting of enamel, to give the paper a polished aspect.

While, for simplicity, the described process makes reference to a handicraft process for the production of paper in sheets, the process can be easily adapted for the industrial production of paper coils and sheets.

In this case one will adopt a continuous production process in which the solution containing cellulose obtained according to the described method is drained by a flow case with a drain of about 3% of cellulose as a dry residue. The drain occurs through a fissure onto a canvas sliding in a continuous way: the fibers concentrates and are compacted forming the initial sheet with a content of about 80% of water. A pressing phase follows which is performed in a continuous way in a dry-end with rollers which are provided with felts: the fibers are compacted to a higher extent and the sheet undergoes a rolling still losing water and reaching a concentration of about 3-4%. In conclusion the production method of paper, paperboard, cardboard, substitutes and derivatives according to the present invention provides the use of the pulp having a high content of cellulose which is obtained as previously described following the phases which are performed successively to the phases relative to the method to obtain the pulp having a high content of cellulose obtained from marine plants:

(xiii). Introduction of the pulp having a high content of cellulose in a flow-box having a draining between 2 and 5 % of cellulose as dry residue;

(xiv). Draining the pulp having a high content of cellulose on a continuously sliding conveyor for the production of paper coils;

(xv). Continuous pressing with rollers.

Advantageously the described production process of pulp does not involve the use of chlorine or derivates for the bleaching operation, obtaining satisfactory results with important advantages from the environmental point of view and from the disposal costs of the working residues.

The collection product can be a just collected product (green), as well as an already partially macerating product, as well as a product which was previoulsy dryed and successively re-humidified, possibly with addition of anti fermenting agents.

With reference to the collection phase it will be apparent that, depending on how the collection itself occurs, in the collection product also elements other than marine plants and/or algae marine can be present, e.g. sand, other vegetals, etc. To eliminate possibile foreign bodies having larger dimensions is made the following sieving phase is done, for example by means of vibrating screens or sieves, both in a humid condition and in a dry condition. The possibly present sand, instead, will be eliminated by means of washing the collection product itself, preferably after the sieving phase, but it will be apparent that the two phases also could be inverted.

Relatively to the treatment phase of the humid washing product by means of a treatment in an oven this phase is equivalent to a preliminary cooking of the product, but the inventors, during the tests which were carried out have found that this phase can also be omitted if the collection product is already partially macerated before the collection or before its use. The treatment can occur in a range of temperatures between 80°C and 250° and for a time between 10 and 60 minutes, preferably for a time between 15 and 30 minutes. The treatment temperature as well as the treatment time can change depending on to the maceration degree of the product subjected to the treatment as well as on the quantity of the product subjected to the treatment and on the arrangement of the product in the cooking chamber. For example for a product quantity

equal to 3-6 kg of collection product that substantially has not undergone a maceration the treatment can occur at a temperature of 180° - 220° for times on the order of 15-30 minutes, with most short times being preferred in the case in which the product to be treated is spread enough inside the treatment chamber, while most long times will be preferred in the case in which the product to be treated is amassed and concentrate. In a similar way most long times will be necessary for higher quantities of product to be treated. If the product is already partially macerated, then lower treatment times will be sufficient and if the product is at a greater maceration state the treatment can also be omitted.

The scraping phase is needed to increase the etcheable surface of the reactive which is used in the following phases. In the performed tests this operation has been made manually but it can be made automatic, for example by means of a passage in a mill or in cylinders; the increasing of the chemically etcheable surface of the product is obtained by means of the scraping of the product, with a partial defibration/breakage of the fibers.

Referring to the disgregation phase of the fibers by means of boiling in a solution of sodium hydroxide, it will continue until the desired maceration degree is reached. The quantities of sodium hydroxide to be used, as well as the time of the treatment can change depending on the collection product quality. Indicatively, anyway the desired maceration degree can be defined by the end average dimension of the obtained disgregated fibers. Also other disgregating agents can be used provided that they have the characteristic not to excessively disgregate the cellulose fibers. The chemical disgregation can also be coupled to a mechanical disgregation, even if it can be omitted depending on the maturation degree of the collection product and/or on the maceration degree. Referring to the quantity of sodium hydroxide, for example using 99% sodium hydroxide in a solid form, the use is provided of 100-200g of sodium hydroxide for every 4 kg of product to be submitted to disgregation in a quantity of water so as to obtain the superficial covering of the matter to be treated, about 10-20 liters. However it

will be obvious that the solution of sodium hydroxide can also be prepared starting by sodium hydroxide in solution, obtaining concentrations corresponding the indicated ones.

The successive separation phase of the fibers can occur for example by means of filtering.

By means of washing with water, as previously explained, one can act on the pH until the disappearing of the basic pH in favour of a neutral pH with a recovery of the corresponding basic liquid phase which can successively be utilized again in the process.

Referring to the bleaching phase of the fibers it occurs by means of a treatment with a chemical bleaching agent, preferably by means of a heat treatment, preferably with hydrogen peroxide in an aqueous solution. The concentrations of chemical bleaching agent can change depending on the properties of the bleaching agent itself, as well as depending on the desired bleaching degree. For example with regard to hydrogen peroxide, starting from 40 volume hydrogen peroxide, the use is provided of 150-300 ml of 40 volume hydrogen peroxide for every 4 kg of product to be submitted to bleaching in a quantity of water so as to obtain the superficial covering of the matter to be treated, about 10-20 liters. Obviously the hydrogen peroxide can also be supplied starting from starting solutions with different concentrations, e.g. 130 hydrogen peroxide diluted 1/4. In general, therefore, for every 4 kg of product to be submitted to bleaching one can use hydrogen peroxide in a quantity such as to supply concentrations corresponding to the ones which are obtained adding in water 40 volume hydrogen peroxide for every 4 kg of product to be submitted to bleaching in quantities between 150 and 300 ml of 40 volume hydrogen peroxide, in a quantity of water so as to obtain the superficial covering of the matter to be treated, which for 4 kg of product is equal to about 10-20 liters. Preferably the hydrogen peroxide will be gradually added in successive times, modulating its quantity depending on the bleaching state and on the desired end quality. The treatment preferably occurs in hot conditions

at a temperature between 60°C and the boiling-point. The treatment continues for a time between 15-60 minutes depending on the desired quality of the finished product, namely of the color, most long treatment time corresponding to a greater bleaching.

The successive suspension phase in water of the product obtained after the filtering and washing phase of the bleached fibers will preferably occur in a container in which the product which was obtained in the previous phases is placed adding water so as to obtain the superficial covering of the product itself.

The inventors found that the bonding agent addition can occur with good results first or after or during the triturating phase or also both before, after and during the triturating phase. Therefore, in general, the process according to the present invention can comprise a phase of addition of a bonding agent or glue which can occur in a phase (x) successively to the phase (ix) and previously to the phase (xi) and/or simultaneously to phase (xi) and/or in a phase (xii) following the phase (xi). Preferably this addition occurs before the triturating phase to obtain a better amalgamation of the components. Possibly the addiction of the bonding agent can occur successively in the case in which the preparation phase of the pulp is separated by the phase of its effective use for the production of the paper. As a matter of fact the present invention also allows to stop the process after the triturating phase and before the addition of the bonding agent or anyway in other intermediate stages, for example also to allow the delivery or the preservation of the product, which can possibly be filtered and/or addittivated with possible anti – fermenting agents and/or partially dried for its successive use. If the addition of the bonding agent occurs after the triturating phase, also a mixing phase to amalgamate the components will be needed. The bonding agent addition will occur in quantities in the range between 10 and 90 ml for every 4 kg of the product, even more preferably in quantities between 25 and 50 ml for every 4 kg of the product, even more preferably 35 ml for every 4 kg of the product, the bonding agent being preferably vinyl glue. For bonding agents of a different type with respect to the vinyl glue, the preferred

quantities could undergo changing depending on the properties of the bonding agent itself.

Examples will follow showing the process in a greater detail.

Example I

Following the described process Posidonia oceanica marine plants have been collected which have been preliminarily cleaned-up from fibres and undesired materials by means of sieving, e.g. foreign bodies which was possibly present.

Quantities of 4 - 4,5 Kg of sieved Posidonia oceanica marine plants have been taken.

The sieved Posidonia oceanica marine plants have been washed in water and have been left in a suspension condition for 15 minutes in water in order to let the sand decant.

The Posidonia oceanica marine plants have been heated by means of passage in a stove for 15 - 20 minutes in order to improve their workability.

The thus obtained product has been submitted to a scraping treatment in order to increase the etcheable surface of the reactive which is used in the following phases.

The thus obtained product has been boiled with 150g of 99% sodium hydroxide in solid form to in a quantity of water so as to obtain the superficial covering of the product to be treated, about 20-25 litres. The treatment has been continued until a desired disgregation degree was reached, obtaining the disgregation of the fibres. In certain tests a mechanical agitation action has been used obtaining better results and/or shorter times.

The disgregated fibers have been separated by means of filtering with a recovery of the corresponding liquid phase; the corresponding recovered liquid phase can be reutilized for successive treatments by reintegration of sodium hydroxide or it can be disposed after neutralizing the same.

A bleaching operation has been performed by means of heat treatment with 225 ml of 40 volume hydrogen peroxide in a quantity of water so as to obtain the superficial

covering of the matter to be treated, about 20-25 litres. The treatment temperature was 80°C.

Successively one have proceeded with a washing phase of the the mass of bleached fibres with a consequent pH measurement and the washing procedure has been continued until the disappearing of the basic pH in favour of a neutral pH.

A suspension in water of the obtained product has been prepared and one proceeded with a trituration of the fibres in the suspension.

Successively 30-35 ml of a bonding agent have been added, which in the disclosed example was vinylic glue and one proceeded with the mixing of the thus obtained mixture until the same was homogenized.

In this experimental phase the drawing of the obtained pulp having a high content of cellulose occurred following the following steps:

(xiv). Drawing the pulp having a high content of cellulose from the withdrawal basin by means of a screen;

(xv). Applying a rug on the screen;

(xvi). Positioning a first felt on the rug on the opposed side with respect to the side with the pulp having a high content of cellulose;

(xvii). Applying a first rigid support on the first felt, the rigid support having sizes corresponding to the sizes of the screen;

(xviii). 180 degrees overturning of the assembly consisting of first rigid support, first felt, rug, pulp having a high content of cellulose and screen;

(xix). Removing the screen;

(xx). Positioning a second felt on the pulp having a high content of cellulose in correspondence of the opposite side with respect to the side on which the rug was placed;

(xxi). Applying a second rigid support on the second felt, the rigid support having sizes corresponding to the sizes of the screen, forming a sandwich construction;

(xxii). Pressing and exsiccation of the sandwich construction obtained at the previous phase for 6 - 8 hours obtaining a sheet of paper;

(xxiii). Verification of the paper sheet and possible re-humidification with reintroduction in the press and exsiccation;

(xxiv). Removing and drawing the paper sheet.

In particular a certain quantity of fibers and bonding agent solution has been separated by a screen having A4 sheet sizes. On the screen a clean and undamaged rug has been applied in correspodence of the future paper sheet and the rug has been padded in order to let the fibers adhere to the same. A felt was then placed on the rug on the opposed side with respect to the side with the fibres and a plywood rectangle has been applied above the felt. The assembly was then overturned and the rug with the sheet was detached from the net of the screen. Another and another felt rug were then applied on the surface covered by the fibers, encompassing everything with an additional plywood rectangle, therefore obtaining a sandwich construction consisting of: plywood, felt, rug, fibers, rug, felt, plywood. The thus obtained sandwich construction has been placed in a press for 6 - 8 hours. Successively the drying of the sheets has been completed, maintaining the rug in a tensioned condition. Once the drying was completed the sheets have been detached.

With the indicated quantities a hand-crafted sheet of paper was obtained having a weight of about 6 gr., corresponding to a basic weigh of 50g/m2 having a A4 size with Havana yellow coloring.

Example II

Another test was carried out following exactly the same steps of the example I, in the same quantities, but with the addition of the bonding agent before the triturating phase. It has been observed that with this process a better amalgamation of the bonding agent with the triturated fibers is obtained, obtaining a qualitatively better end product.

Example III

Another test was carried out following exactly the same steps of the example I or in an equivalent way of the example II, in the same quantities. In the case in which the sheets, after the drying phase showed pleating, one proceeded with a re-humidification of the sheet itself with an additional successive passage in the press. In the example the additional humidification of the sheet occurred by means of a sponge. After the extraction of the sheet from the press one observed that an effective elimination of the previously present pleating was obtained.

Example IV

Proceeding as in the example I, in the disgregation phase different quantities have been tested of sodium hydroxide obtaining satisfactory results in a range between 100 and 200 gr. for every 4 kg of product, with the best results obtained for values of about 120 gr. of 99% sodium hydroxide in solid form in a water quantity so as to obtain the superficial covering of the matter to be treated, about 10-20 liters.

Example V

Proceeding as in the example I, in the bleaching phase different quantities of 40 volume hydrogen peroxide have been tested obtaining satisfactory results in a range between 150 and 300 gr. for every 4 kg of product, with the best results obtained for values of about 180 gr. of peroxide gr. of 40 volume hydrogen peroxide.

Example VI

Proceeding as in the example I, different quantities of bonding agent have been tested, in particular vinyl glue, obtaining satisfactory results in a range between 10 and 90 ml each 4 kg of triturated product, preferably in quantity included between 25 and 50 ml for every 4 kg of triturated product, with the best results obtained for values of about 35 ml for every 4 kg of triturated product.

Example VII

Proceeding as in the example I, the real content of fanerogame marine has been analyzed in relation with the available collection product, finding that the described method finds an advantageous application in the case in which the collection product

has a fanerogame marine content equal or higher than 75%, the remaining 25 % possibly consisitng of other types of algae or marine plants. Good results were obtained even with a fanerogame marine content equal or higher than 95% in weight of the dry total collection product after sieving.

Example VIII

Proceeding as in the example I, different trituration degrees of the fibers have been tested, observing that the trituration phase must not be excessively prolonged to avoid to have too much small fibers. In general good results have been found with sizes of the fibers corresponding to those obtained in the production process of the paper starting from recycled paper. It will be apparent that depending on the used trituration device and on the introduced quantities the trituration times can be different.

The description of this invention has been made with reference to the enclosed figures showing a preferred embodiment of the invention itself, but it is evident that many possible alterations, modifications and variations will be immediately apparent to those skilled in the art in light of the foregoing description. Thus, it should be understood that the invention is not limited by the foregoing description, but embraces all such alterations, modifications and variations in accordance with the spirit and scope of the appended claims.

Claims

1. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives, comprising the steps of:

(i). Sieving the collection product eliminating possible foreign bodies which are present in the collection product;

(ii). Washing the sieved product by means of water removing possible sand which can be present;

(v). Obtaining disgregated fibers by means of disgregation of the fibers by means of a treatment with a chemical disgregating agent which does not etches the cellulose fibers, possibly combined with a mechanical disgregation treatment;

(vi). Separation of the fibers from the liquid phase by means of filtration recovering the corresponding liquid phase;

(vii). Bleaching the fibers obtained from the previous phase by means of a treatment with a chemical bleaching agent;

(viii). Filtering, washing by means of water and/or pH balancing treatment of the bleached fibers and obtainment of an essentially neutral pH;

(ix). Suspension of the product obtained from the previous phase in water in a container;

(xi). Triturating the suspension obtained from the previous phase obtaining a pulp with a high content of cellulose;

said method being further characterised in that said collection product is a marine plants collection product.

2. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said collection product is a collection product of marine plants preferably with a marine plants content equal or higher to 75 % in weight

of the dry total collection product after sieving, even more preferably with a marine plants content equal or higher to 95 % in weight of the dry total collection product after sieving.

3. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 2 characterised in that said marine plants are fanerogame marine.

4. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 2 characterised in that said marine plants are selected from the group consisting of Zostera, Posidonia, Cymodocea, Syringonium, Thalassia, Halophila, Thalassodendron.

5. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 2 characterised in that said marine plants are selected from the group consisting of Cymodocea nodosa, Cymodocea rotundata, Cymodocea serrulata, Syringonium filiforme, Syringonium isoetifolium, Halophila beccarii, Halophila decipiens, Halophila minor, Halophila ovalis, Zostera marina, Zostera noltii, Posidonia oceanica, Posidonia australis, Posidonia sinuosa, Thalassia hemprichii, Thalassia testudinum.

6. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 5 characterised in that it includes a further phase (iii) following to the phase (ii), said phase (iii) providing a treatment of the washed product at a temperature between 80°C and 250° and for a time between 10 and 60 minutes, preferably for a time between 15 and 30 minutes, even more preferably at a temperature between 180° - 220° for a time between 15 and 30 minutes, the time and the temperature being selected depending on the maceration degree of the collection

product.

7. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 6 characterised in that it includes a further phase (iv) prior to the phase (v), said phase (iv) being a scraping phase providing a scraping treatment of the product..

8. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said scraping phase occurs by means of a passage of the product in a mill or in cylinders.

9. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 8 characterised in that said disgregation phase (v) of the fibres by means of said treatment with said disgregating chemical agent occurs by means of a boiling treatment in aqueous solution of sodium hydroxide.

10. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said disgregation phase (v) of the fibers by means of said treatment with said disgregating chemical agent occurs by means of a boiling treatment in aqueous solution of sodium hydroxide in concentrations corresponding to those obtained dissolving 99% sodium hydroxide in solid form in quantities between 100g and 200g of sodium hydroxide for every 4 kg of product to be submitted to disgregation in a water quantity so as to obtain the superficial covering of the matter to be treated.

11. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 10 characterised in that said phase (vii) relative to the bleaching of the fibers occurs by means of treatment with hydrogen peroxide in an

aqueous solution preferably in hot conditions at a temperature between 60°C and the boiling-point.

12. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said treatment with hydrogen peroxide in an aqueous solution occurs with hydrogen peroxide in an aqueous solution in concentrations corresponding to those obtained adding in water 40 volume hydrogen peroxide for every 4 kg of product to be submitted to bleaching in quantities between 150 and 300 ml of 40 volume hydrogen peroxide, in a water quantity so as to obtain the superficial covering of the matter to be treated.

13. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said treatment with hydrogen peroxide is continued for a time between 15 and 60 minutes depending on the end bleaching degree.

14. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 1 to 13 characterised in that it includes a further phase of bonding agent addition, said bonding agent addition phase being able to occur in a further phase (x) after the phase (ix) and before the phase (xi) and/or simultaneously with respect to the phase (xi) and/or in a further phase (xii) after the phase (xi).

15. Method to obtain pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives according to the previous claim characterised in that said bonding agent is added in quantities between 10 and 90 ml for every 4 kg of product, preferably in quantities between 25 and 50 ml for every 4 kg of product, even more preferably 35 ml for every 4 kg of product.

16. Method to obtain pulp having a high content of cellulose for the use in a process of

production of paper, paperboard, cardboard, substitutes and derivatives according to any of the previous claims 14 to 15 characterised in that said bonding agent is vinyl glue.

17. Pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives characterised in that said pulp having a high content of cellulose is obtained by means of a method to obtain pulp having a high content of cellulose according to any of the previous claims 1 to 16.

18. Paper, paperboard, cardboard, substitutes and derivatives obtained by pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives characterized in that at least 50 % of said pulp having a high content of cellulose is obtained by means of a method to obtain pulp having a high content of cellulose according to any of the previous claims from 1 to 16.

19. Paper, paperboard, cardboard, substitutes and derivatives obtained by pulp having a high content of cellulose for the use in a process of production of paper, paperboard, cardboard, substitutes and derivatives characterized in that 100 % of said pulp having a high content of cellulose is obtained by means of a method to obtain pulp having a high content of cellulose according to any of the previous claims from 1 to 16.

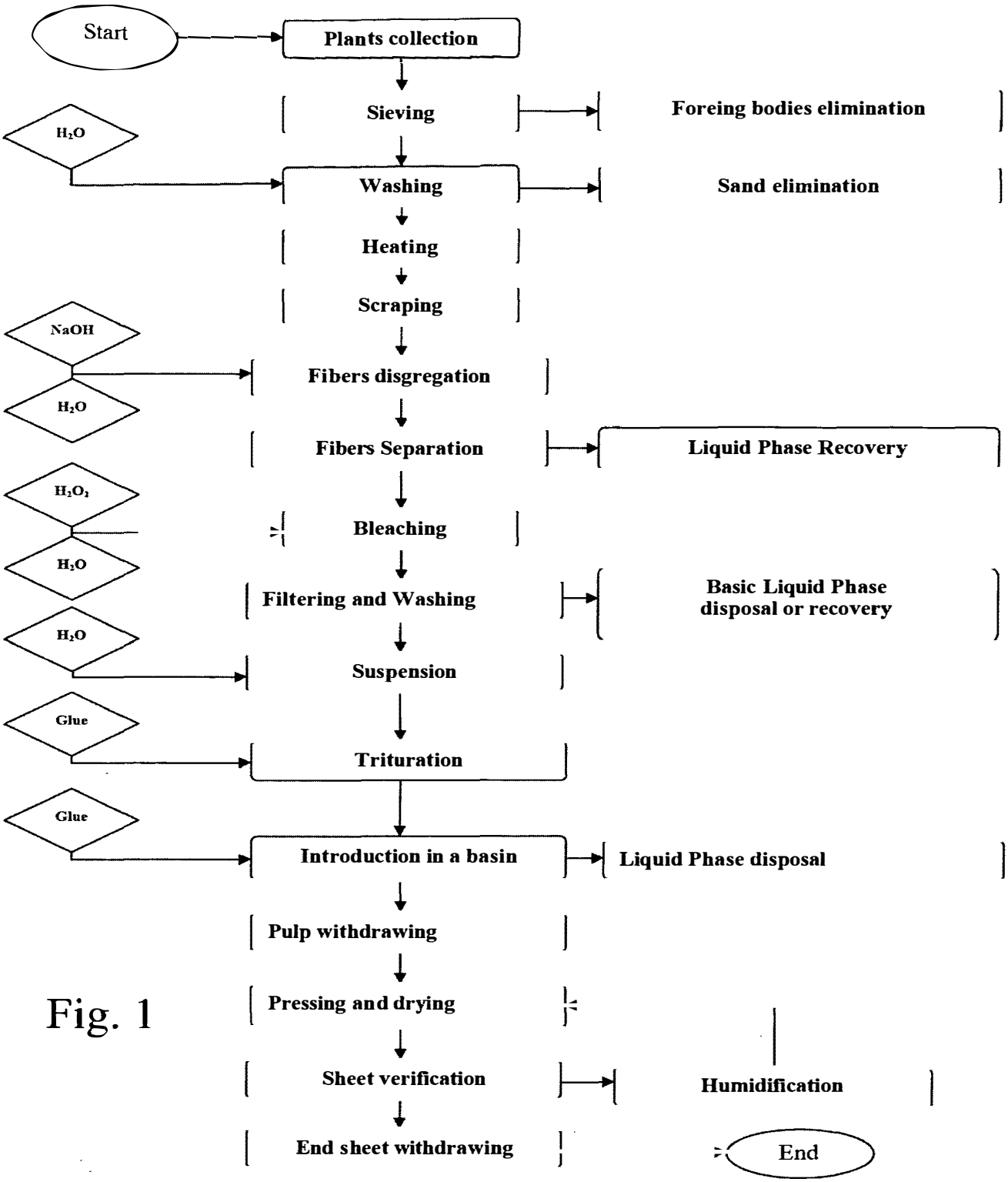

Start
Plants collection
Sieving
Foreing bodies elimination
H₂O
Washing
Sand elimination
Heating
Scraping
NaOH
Fibers disgregation
H₂O
Fibers Separation
Liquid Phase Recovery
H₂O₂
Bleaching
H₂O
Filtering and Washing
Basic Liquid Phase disposal or recovery
H₂O
Suspension
Glue
Trituration
Glue
Introduction in a basin
Liquid Phase disposal
Pulp withdrawing
Pressing and drying
Sheet verification
Humidification
End sheet withdrawing
End

Fig. 1

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International application No
PCT/EP2010/004390

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

Minimum documentation searched (classification system followed by classification symbols)
D21C D21B

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. |
|---|---|---|
| X | US 5 500 086 A (SAKAI MASAYASU [JP] ET AL) 19 March 1996 (1996-03-19) column 3, line 5 - column 4, line 21; claims 1, 3 | 1 |
| X | WO 94/04745 A1 (INT TECH MANAGEMENT ASS [US]) 3 March 1994 (1994-03-03) page 2, line 3 - page 3, line 11 page 6, line 23 - page 9, line 37 | 1 |

☐ 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

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"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

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Lanniel, Geneviève |

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

# 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 5500086 A | 19-03-1996 | NONE | |
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**(54) Title**: HIGHLY DURABLE TOWEL COMPRISING NON-WOOD FIBERS

**(57) Abstract**: The present invention relates to tissue products comprising high yield hesperaloe fiber having improved wet performance, such as improved absorbency, CD Wet/Dry Ratio and CD Wet Durability. The addition of high yield hesperaloe pulp fibers surprisingly improves the CD Wet/Dry ratio without negatively affecting the absorbency of the tissue product. For example, tissue products of the present invention generally have an Absorbent Capacity greater than about 6.0 g/g, such as from about 8.0 to 8.0 g/g. As such the tissue products are durable when wet, but are still sufficiently absorbent. This balance of absorbency and wet strength is not found in the prior art without resorting to adding latex binders or the like to the tissue product.

# HIGHLY DURABLE TOWEL COMPRISING NON-WOOD FIBERS

## BACKGROUND OF THE DISCLOSURE

In the development and manufacture of paper products, particularly paper towels for the consumer market, it is a continual objective to improve the absorbent characteristics of the product. For cleaning up some spills, the consumer needs high absorbent capacity. For some uses, consumers want a fast rate of absorbency. For other uses, a combination of high absorbent capacity and fast absorbent rate is desired. At the same time, constraints on achieving this objective include the need to maintain or reduce costs in order to provide the consumer with the highest possible value, which in part means minimizing the amount of fiber in the product.

## SUMMARY OF THE DISCLOSURE

The present inventors have successfully used hesperaloe fibers to produce a tissue that is highly absorbent while also being durable when wet. As such the tissue products of the present invention may have an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry ratio greater than about 0.30. The desirable absorbency and wet durability are achieved by forming a tissue product from wood and non-wood fibers and more specifically high yield hesperaloe pulp fibers. In achieving these properties the inventors have overcome the negative to other important properties, such as bulk and stiffness, typically associated with substituting conventional wood papermaking fibers with non-wood fibers. 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 Northern softwood kraft (NSWK) fibers.

Accordingly, in certain embodiments, the invention provides tissue products in which hesperaloe fibers replace at least about 50 percent of the NSWK, more preferably at least about 75 percent and still more preferably all NSWK while maintaining or improving absorbency and without negatively effecting stiffness and bulk.

In other embodiments the present invention provides tissue products comprising a multi-layered tissue web where one or more of the layers comprise a blend of hesperaloe fibers and softwood kraft fibers, wherein the softwood kraft fibers comprise less than about 10 weight percent of the tissue product.

In still other embodiments the present invention provides a tissue product comprising greater than about 20 weight percent high yield hesperaloe fiber, the tissue product having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.



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In yet other embodiments the present invention provides single-ply through-air dried tissue product comprising at least about 20 weight percent high yield hesperaloe pulp fibers, the tissue product having a basis weight from about 30 to about 60 gsm, a GMT from about 1500 to about 2500 g/3" and an Absorbent Capacity greater than about 7.0 g/g.

In other embodiments the present invention provides tissue product comprising at least one multi-layered through-air dried tissue web comprising a first and a second layer, the first layer being substantially free from high yield hesperaloe pulp fibers and the second layer consisting essentially of high yield hesperaloe pulp fibers, the tissue product having a Wet CD Durability from about 1.75 to about 2.0 and a Stiffness Index less than about 6.0.

## 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.



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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 10 cc/g, more preferably greater than about 11 cc/g and still more preferably greater than about 12 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



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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 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. GM Slope generally is expressed in units of kg.

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. While the GMT may vary tissue products prepared according to the present disclosure generally have a GMT greater than about 1,400 g/3", such as from about 1,400 to about 2,500 g/3".

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 (typically having units of kg), divided by the geometric mean tensile strength (typically having units of grams per three inches).

$$Stiffness\ Index = \frac{\sqrt{MD\ Tensile\ Slope\ (kg) x\ CD\ Tensile\ Slope(kg)}}{GMT\ (g/3")} \cdot x\ 1{,}000$$

While the Stiffness Index may vary tissue products prepared according to the present disclosure generally have a Stiffness Index less than about 8.0 and more preferably less than about 6.0.

As used herein, the term "Absorbent Capacity" is a measure of the amount of water absorbed by the paper towel product in the vertical orientation and is expressed as grams of water absorbed per gram of fiber (dry weight). Absorbent Capacity is measured as described in the Test Methods section and generally has units of grams per gram (g/g). While the Absorbent Capacity may vary tissue products prepared according to the present disclosure generally have an Absorbent Capacity greater than about 6.0 g/g and more preferably greater than about 7.0 g/g.

As used herein the term "CD Wet/Dry Ratio," refers to the ratio of the wet CD tensile strength to the dry CD tensile strength, measured as described in the Test Methods Section, below. While the

CD Wet/Dry Ratio may vary, tissue products prepared as described herein generally have a CD Wet/Dry Ratio greater than about 0.28 and more preferably greater than about 0.30, such as from about 0.28 to about 0.32. Generally the foregoing ratios are achieved at Wet CD Tensile greater than about 400 g/3", more preferably greater than about 425 g/3" and still more preferably greater than about 450 g/3".

As used herein the term "Wet CD Durability," refers to the CD Wet Stretch multiplied by 100, divided by the CD Wet Tensile (having units of g/3") and is a measurement of the wet CD extensibility of a product at a given wet tensile strength. At CD Wet Tensile strengths greater than about 400 g/3" the inventive tissue products of the present invention generally have Wet CD Durability greater than about 1.75 and more preferably greater than about 2.0.

As used herein the term "Wet Strength Efficiency," refers to the CD Wet/Dry Ratio divided by the add-on amount of wet strength resin (measured in kilograms per dry metric ton of fiber) multiplied by 100 and is a measure of the amount of wet strength generated relative to dry strength normalized by the amount of wet strength added.

## DETAILED DESCRIPTION OF THE DISLOSURE

Generally, the present invention provides tissue product having a CD Wet/Dry ratio that meets or exceeds satisfactory levels without the excess use of a wet strength resin. The satisfactory level of CD Wet/Dry ratio is generally greater than about 0.30. The satisfactory level of CD Wet/Dry ratio is surprisingly achieved by forming a tissue product from wood and non-wood fibers and more specifically high yield hesperaloe pulp fibers. Generally CD Wet/Dry ratios may be achieved with the addition of at least about 5 percent, by weight of the tissue product, such as from about 5 to about 50 percent and more preferably from about 15 to about 45 percent high yield hesperaloe pulp fibers.

The addition of high yield hesperaloe pulp fibers surprisingly improves the CD Wet/Dry ratio without negatively affecting the absorbency of the tissue product. For example, tissue products of the present invention generally have an Absorbent Capacity greater than about 6.0 g/g, such as from about 6.0 to 8.0 g/g. As such the tissue products are durable when wet, but are still sufficiently absorbent. This balance of absorbency and wet strength is not found in the prior art without resorting to adding latex binders or the like to the tissue product.

Further, the aforementioned wet-strength properties may be achieved with only modest additions of conventional wet-strength resin. For example, in certain embodiments the tissue products comprise less than about 15 kg of wet-strength resin per metric ton of furnish, such as from about 3 to about 15 kg, and more preferably from about 3 to about 10 kg. Rather than employ an excessive

amount of wet-strength resin, the improved wet-strength properties are achieved by the addition of high yield hesperaloe pulp fibers during the manufacture of the tissue product, such as from about 5 to about 50 percent, by weight of the product, and more preferably from about 20 to about 40 percent, by weight.

Accordingly, in certain embodiments the tissue products generally comprise high yield hesperaloe pulp fibers derived from non-woody plants in the genus Hesperaloe in the family Agavaceae. Suitable species within the genus Hesperaloe 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 process 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 amount of SSWK, by weight of the tissue product, is less than about 10 percent and more preferably less than about 5 percent.

In addition to the use of high yield hesperaloe pulp fiber the tissue products of the present invention are preferably prepared without the addition of binders, particularly latex binders and more specifically carboxyl-functional latex emulsion polymers, such as those described in US Patent Nos. 6,187,140 and 7,462,258. Latex binders, such as those disclosed in the foregoing references, have been used previously in the manufacture of tissue products to improve wet performance. These binders, however, add manufacturing complexity and cost. Therefore, it is desirable to produce a tissue product, such as the inventive tissues, without the use of binders and more specifically latex binders.

Further, tissues prepared according to the present disclosure are not treated with a sizing agent, such as alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA), either during the tissue manufacturing process or after formation and drying of the tissue web. Rather, the tissue webs are prepared by adding hesperaloe fibers and in certain embodiments a wet strength resin, to the papermaking furnish prior to formation of the web, to enhance the wet-strength properties of the finished web. Unlike conventional sizing agents, which reduce the adsorption rate of water into the sheet, hesperaloe fibers and conventional wet-strength resins allow the sheet to adsorb water as intended during the end use but maintain sheet integrity and strength when wetted.

Rather than employ latex binders or sizing agents, the tissue products typically comprise a conventional wet-strength resin. Useful conventional wet strength resins include diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), epichlorhydrin resin(s), polyamide-epichlorohydrin (PAE), or any combinations thereof, or any resins to be considered in these families of resins. Particularly preferred wet strength resins are polyamide-epichlorohydrin (PAE) resins. Commonly PAE resins are formed by first reacting a polyalkylene polyamine and an aliphatic dicarboxylic acid or dicarboxylic acid derivative. A polyaminoamide made from diethylenetriamine and adipic acid or esters of dicarboxylic acid derivatives is most common. The resulting polyaminoamide is

then reacted with epichlorohydrin. Useful PAE resins are sold under the tradename Kymene® (commercially available from Ashland, Inc., Covington, KY).

Generally the conventional wet-strength resin is added to the fiber furnish prior to formation of the tissue web. The amount of the wet-strength resin can be less than about 10 kg per ton of furnish, more preferably less than about 8 kg per ton of furnish and still more preferably less than about 5 kg per ton of furnish. Generally the add-on level of wet-strength resin will be from about 1 to about 10 kg per ton of furnish and more preferably from about 3 to about 8 kg per ton of furnish and still more preferably from about 3 to about 5 kg per ton of furnish.

Although such low add on levels of wet strength are generally not considered to be suitable for achieving exceptional wet performance, such as a CD Wet/Dry Ratio greater than about 0.30, it has now been discovered that the use of high yield hesperaloe pulp fibers yields tissue products having a CD Wet/Dry Ratio greater than about 0.30 and in certain embodiments greater than about 0.32, such as from about 0.30 to about 0.35. The combination of conventional wet strength resin, such as PAE resins, and hesperaloe fiber have a synergistic effect. Accordingly, when the CD Wet/Dry Ratio and Wet CD Durability are concerned, the combination of wet-strength resin addition and hesperaloe fiber according to the invention provides a synergistic effect which has not been disclosed previously. This synergistic effect is valuable, since it makes it possible to achieve a higher wet-strength level without the excessive use of wet-strength resin.

Table 1 illustrates the desirable increase in wet-strength properties that can be achieved via the combination of high yield hesperaloe fiber (HYH) and a conventional wet-strength resin. The samples have a basis weight of about 36 gsm and comprised a single through-air dried ply. The samples comprised either a blend of NSWK (40 wt%) and EHWK (60 wt%) or HYH (40 wt%) and EHWK (60 wt%). As the table illustrates, at a constant level of wet-strength addition, a higher wet/dry tensile level can be achieved via the addition of HYH.

TABLE 1

| HYH (wt%) | Wet Strength (kg/MT) | CD Wet/Dry Ratio | Delta CD Wet/Dry Ratio (%) | Wet Strength Efficiency |
|---|---|---|---|---|
| - | 9 | 0.22 | - | 2.4 |
| 40 | 9 | 0.3 | 36 | 3.3 |
| - | 14 | 0.24 | - | 1.7 |
| 40 | 14 | 0.31 | 29 | 2.2 |

The improvement in wet tensile properties is further evident when the inventive tissue products are compared to commercially available tissue products. As illustrated in the table below, the inventive tissue products display both wet durability, such as a CD Wet/Dry Ratio greater than about 0.30 and

good absorbency, such as an Absorbent Capacity greater than about 6.0 g/g and more preferably greater than about 7.0 g/g, such as from about 6.0 to about 7.5 g/g. In certain aspects the inventive tissue products also have improved Wet CD Durability relative to commercially available tissue products, such as a Wet CD Durability greater than about 1.5 and more preferably greater than about 1.75, such as from about 1.5 to about 2.0.

TABLE 2

| Product | Plies | Wet CD Tensile (g/3") | Wet CD Stretch (%) | CD Wet/Dry Ratio | Wet CD Durability | Absorbent Capacity (g/g) |
|---|---|---|---|---|---|---|
| Invention | 1 | 418 | 8.2 | 0.32 | 1.96 | 7.1 |
| Scott | 1 | 855 | 7.5 | 0.34 | 0.88 | 5.5 |
| Scott Naturals | 1 | 811 | 11.3 | 0.33 | 1.39 | 4.7 |
| Viva Vantage | 1 | 969 | 8.2 | 0.34 | 0.85 | 3.9 |
| Bounty Basic | 1 | 1040 | 7.2 | 0.47 | 0.69 | 4.9 |

Accordingly, in one embodiment tissue products comprise at least one multi-layered tissue web, the tissue product having a CD Wet/Dry Ratio greater than about 0.30 an Absorbent Capacity greater than about 6.0 g/g and still more preferably greater than about 6.5 g/g. Preferably the web comprises two layers, and more preferably three layers, wherein the hesperaloe fiber is selectively disposed in only one of the layers and the other layers are substantially free from hesperaloe fiber. In other embodiments, the web comprises two outer layers and a middle layer, where the hesperaloe fiber is selectively disposed in the middle layer. While in one embodiment it is preferred that the tissue web comprise a three-layered tissue having hesperaloe fiber selectively incorporated into the middle layer, it should be understood that tissue products made from the foregoing multi-layered web can include any number of plies and the plies may be made from various combinations of single- and multi-layered tissue webs. Further, tissue webs prepared according to the present invention 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.

As noted previously, the instant tissue products have a high degree of absorbent capacity such as an Absorbent Capacity greater than about 6.0 g/g, such as from about 6.0 to about 7.0 g/g and more preferably from about 6.5 to about 7.0 g/g, while also having a CD Wet/Dry Ratio greater than about 0.30, such as from about 0.30 to about 0.40. Generally the foregoing absorbent capacities and wet strengths are achieved at basis weights from about 30 to about 60 grams per square meter (gsm) and more preferably from about 35 to about 50 gsm and still more preferably from about 40 to about 50 gsm.

In addition to having satisfactory absorbent properties, the tissue products generally have improved wet CD performance. For example, in certain embodiments the tissue products have a Wet CD Durability greater than about 1.75, such as from about 1.75 to about 2.5 and more preferably from about 2.0 to about 2.5. At the foregoing Wet CD Durability levels the tissue products may have a Wet CD Stretch greater than about 8.0 percent, such as from about 8.0 percent to about 10.0 percent and more preferably from about 9.0 to about 10.0 percent.

While having improved properties, the tissue products prepared according to the present disclosure continue to be strong enough to withstand use by a consumer. For example, inventive tissue products generally have a geometric mean tensile (GMT) greater than about 1200 g/3", such as from about 1200 to about 3000 g/3", more preferably from about 1200 to about 2500 g/3" and still more preferably from about 1600 to about 2400 g/3".

Not only are the instant tissue products absorbent and strong enough to withstand use, they are generally flexible and have good hand feel. As such the tissue products may have a GM Slope less than about 10.0 kg, such as from about 4.0 to about 10.0 kg and more preferably from about 4.0 to about 8.0 kg. The foregoing GM Slopes are generally achieved at relatively modest GMT, such as from about 1200 to about 2500 g/3", and more preferably from about 1200 to about 2200 g/3". At these GM Slopes and GMT, the tissue products may have a Stiffness Index less than about 8.0, such as from about 4.0 to about 8.0 and more preferably from about 4.0 to about 6.0.

In one particularly preferred embodiment the inventive tissue product comprises a single-ply, multi-layered, through-air-dried web, wherein a first layer comprises wood pulp fibers and a second layer comprises high yield hesperaloe pulp fibers, the first layer being substantially free of hesperaloe fibers and the product comprising from about 20 to about 50 percent, by weight, hesperaloe fibers. The foregoing tissue product generally has a CD Wet/Dry Ratio greater than about 0.30 an Absorbent Capacity greater than about 6.0, while having a Stiffness Index less than about 6.0, such as from about 4.0 to about 6.0.

Webs useful in preparing tissue products according to the present disclosure can vary depending upon the particular application. In general, in addition to hesperaloe fibers, the webs can be made from any suitable type of fiber. For instance, the base web can be made from cellulosic fibers, and more preferably cellulosic pulp fibers. Suitable cellulosic fibers for use in connection with this invention include secondary (recycled) papermaking fibers and virgin papermaking fibers in all proportions. Such fibers include, without limitation, hardwood and softwood fibers.

Tissue webs made in accordance with the present disclosure can be made with a homogeneous fiber furnish or can be formed from a stratified fiber furnish producing layers within the

single- or multi-ply product. Stratified base webs can be formed using equipment known in the art, such as a multi-layered headbox. Both strength and softness of the base web can be adjusted as desired through layered tissues, such as those produced from stratified headboxes.

When constructing a web from a stratified fiber furnish, the relative weight of each layer can vary depending upon the particular application. For example, in one embodiment, when constructing a web containing three layers, each layer can be from about 15 to about 40 percent of the total weight of the web, such as from about 25 to about 35 percent of the weight of the web. Generally the hesperaloe fibers will comprise from about 5 to about 50 percent, by weight, of the web.

The tissue products 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.

In a particularly preferred 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.

In one embodiment the web is formed using a twin wire former having a papermaking headbox that injects or deposits a furnish of an aqueous suspension of papermaking fibers onto a plurality of forming fabrics, such as the outer forming fabric and the inner forming fabric, thereby forming a wet tissue web. 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 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 greater than 20 percent, more specifically between about 20 to about 40 percent, and more specifically between 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 30 to about 70 percent and more preferably from about 40 to about 60 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. Such molding to the contours of the surface of the transfer fabric 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 through-air drying fabric. Typically, the transfer fabric travels at approximately the same speed as the through-air drying fabric.

However, a second rush transfer may be performed as the web is transferred from the transfer fabric to the through-air drying fabric. This rush transfer is referred to as occurring at the second position and is achieved by operating the through-air drying fabric at a slower speed than the transfer fabric.

In addition to rush transferring the wet tissue web from the transfer fabric to the through-air drying fabric, the wet tissue web may be macroscopically rearranged to conform to the surface of the through-air drying fabric with the aid of a vacuum transfer roll or a vacuum transfer shoe. If desired, the through-air drying fabric can be run at a speed slower than the speed of the transfer fabric 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 to the topography of the through-air drying fabric.

While supported by a through-air drying fabric, the wet tissue web is dried to a final consistency of about 94 percent or greater by a through-air dryer. The web then passes through the winding nip between the reel drum and the reel and is wound into a roll of tissue for subsequent converting.

## TEST METHODS

Wet and Dry Tensile

Samples for tensile strength testing are prepared by cutting a 3 inches (76.2 mm) by 5 inches (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 4 ± 0.04 inches. The jaws are operated using pneumatic-action and are rubber coated. The minimum grip face width is 3 inches (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.

Wet tensile strength measurements are measured in the same manner, but after the center portion of the previously conditioned sample strip has been saturated with distilled water immediately prior to loading the specimen into the tensile test equipment. More specifically, prior to performing a wet CD tensile test, the sample must be aged to ensure the wet strength resin has cured. Two types of aging were practiced: natural and artificial. Natural aging was used for older samples that had already aged. Artificial aging was used for samples that were to be tested immediately after or within days of manufacture. For natural aging, the samples were held at 73°F, 50 percent relative humidity for a period of 12 days prior to testing. Following this natural aging step, the strips are then wetted individually and tested. For artificially aged samples, the 3-inch wide sample strips were heated for 4 minutes at 105 ± 2°C. Following this artificial aging step, the strips are then wetted individually and tested. Sample wetting is performed by first laying a single test strip onto a piece of blotter paper (Fiber Mark, Reliance Basis 120). A pad is then used to wet the sample strip prior to testing. The pad is a green, Scotch-Brite brand (3M) general purpose commercial scrubbing pad. To prepare the pad for testing, a full-size pad is cut approximately 2.5 inches long by 4 inches wide. A piece of masking tape is wrapped around one of the 4-inch long edges. The taped side then becomes the "top" edge of the wetting pad. To wet a tensile strip, the tester holds the top edge of the pad and dips the bottom edge in approximately 0.25 inches of distilled water located in a wetting pan. After the end of the pad has been saturated with water, the pad is then taken from the wetting pan and the excess water is removed from the pad by lightly tapping the wet edge three times across a wire mesh screen. The wet edge of the pad is then gently placed across the sample, parallel to the width of the sample, in the approximate center of the sample strip. The pad is held in place for approximately one second and then removed and placed back into the wetting pan. The wet sample is then immediately inserted into the tensile grips so the wetted area is approximately centered between the upper and lower grips. The test strip should be centered both horizontally and vertically between the grips. (It should be noted that if any of the wetted portion comes into contact with the grip faces, the specimen must be discarded and the jaws dried off before resuming testing.) The tensile test is then performed and the peak load recorded as the CD wet tensile strength of this specimen. As with the dry CD tensile test, the characterization of a product is determined by the average of at least six, but in the case of the examples disclosed, twenty representative sample measurements.



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Absorbency

As used herein, "vertical absorbent capacity" is a measure of the amount of water absorbed by a paper product (single-ply or multi-ply) or a sheet, expressed as grams of water absorbed per gram of fiber (dry weight). In particular, the vertical absorbent capacity is determined by cutting a sheet of the product to be tested (which may contain one or more plies) into a square measuring 100 millimeters by 100 millimeters (± 1 mm.) The resulting test specimen is weighed to the nearest 0.01 gram and the value is recorded as the "dry weight." The specimen is attached to a 3-point clamping device and hung from one corner in a 3-point clamping device such that the opposite corner is lower than the rest of the specimen, then the sample and the clamp are placed into a dish of water and soaked in the water for 3 minutes (± 5 seconds). The water should be distilled or de-ionized water at a temperature of 23 ± 3°C. At the end of the soaking time, the specimen and the clamp are removed from the water. The clamping device should be such that the clamp area and pressure have minimal effect on the test result. Specifically, the clamp area should be only large enough to hold the sample and the pressure should also just be sufficient for holding the sample, while minimizing the amount of water removed from the sample during clamping. The sample specimen is allowed to drain for 3 minutes (± 5 seconds). At the end of the draining time, the specimen is removed by holding a weighing dish under the specimen and releasing it from the clamping device. The wet specimen is then weighed to the nearest 0.01 gram and the value recorded as the "wet weight". The vertical absorbent capacity in grams per gram = [(wet weight - dry weight)/dry weight]. At least five (5) replicate measurements are made on representative samples from the same roll or box of product to yield an average vertical absorbent capacity value.

## EXAMPLE

Base sheets were made using a through-air dried papermaking process commonly referred to as "uncreped through-air dried" ("UCTAD") and generally described in US Patent No. 5,607,551, the contents of which are incorporated herein in a manner consistent with the present invention. Inventive base sheets were produced from a furnish comprising northern softwood kraft (NSWK), eucalyptus kraft (EHWK) and high yield hesperaloe fiber (HYH) using a layered headbox fed by three stock chests such that the webs having three layers (two outer layers and a middle layer) were formed. The outer layers comprised 100 percent EHWK for both the control and inventive samples. The center layer was 100 percent NSWK for the control sample; for the inventive sample, the center layer was 100 percent HYH. The layer splits, by weight of the web, are detailed in Table 3, below.

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 tissue web was formed on a Voith Fabrics TissueForm V forming fabric, vacuum dewatered to approximately 25 percent consistency and then subjected to rush transfer when transferred to the transfer fabric. The layer splits, by weight of the web, are detailed in Table 4, below. The transfer fabric was the fabric described as t1207-11 (commercially available from Voith Fabrics, Appleton, WI). The web was then transferred to a through-air drying fabric. Transfer to the through-drying fabric was done using vacuum levels of greater than 10 inches of mercury at the transfer. The web was then dried to approximately 98 percent solids before winding.

TABLE 3

| Sample | Layer Split (Air/Middle/Fabric wt%) | HYH (wt%) | Wet Strength (kg/MT) |
|---|---|---|---|
| Control | 30/40/30 | - | 8 |
| Inventive 1 | 30/40/30 | 40 | 8 |

The base sheet webs were converted into rolled towel products by calendering using a conventional polyurethane/steel calender comprising a 4 P&J polyurethane roll on the air side of the sheet and a standard steel roll on the fabric side. The finished product comprised a single ply of base sheet. The finished products were subjected to physical testing, the results of which are summarized in Table 4.

TABLE 4

| | Control 1 | Inventive 1 |
|---|---|---|
| BW (gsm) | 39.3 | 39.0 |
| Wet CDT (g/3") | 515 | 418 |
| Wet CDS (%) | 10.7 | 8.2 |
| Wet CD Durability | 2.08 | 1.96 |
| CD Wet/Dry | 0.31 | 0.31 |
| Absorbent Capacity (g/g) | 6.2 | 7.1 |
| Wet Strength Efficiency | 3.89 | 3.89 |
| Dry GMT (g/3") | 2217 | 1821 |
| Dry CDT (g/3") | 1655 | 1340 |
| Dry GM Slope (kg) | 7.2 | 7.7 |
| Stiffness Index | 3.25 | 4.23 |

The foregoing is one example of an inventive tissue product prepared according to the present disclosure. In a first embodiment the invention provides a tissue product comprising greater than about

20 weight percent high yield hesperaloe fiber having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.

In a second embodiment the invention provides the tissue product of the first embodiment having a Wet CD Durability of greater than about 1.75.

In a third embodiment the invention provides the tissue product of the first embodiment having an Absorbent Capacity from about 7.0 to about 7.5 g/g, a CD Wet/Dry Ratio from about 0.30 to about 0.35.

In a third embodiment the present invention provides the tissue product of the first or the second embodiments having a GMT from about 1200 to about 2600 g/3".

In a fourth embodiment the present invention provides the tissue product of any one of the first through the third embodiments having a Stiffness Index from about 4.0 to about 6.0.

In a fifth embodiment the present invention provides the tissue product of any one of the first through the fourth embodiments having a basis weight from about 34 to about 60 gsm.

In a sixth embodiment the present invention provides the tissue product of any one of the first through the fifth embodiments having wet CD stretch greater than about 8 percent, such as from about 8 to about 10 percent.

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 comprises a single-ply multi-layered web having a first, a second and a third layer.

In an eighth embodiment the present invention provides the tissue product of any one of the first through the seventh embodiments wherein the tissue product comprises from about 20 to about 50 weight percent high yield hesperaloe fiber.

In a ninth embodiment the present invention provides the tissue product of any one of the first through the eighth embodiments wherein the tissue product comprises at least one through-air dried tissue web.

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 comprises at least one multi-layered through-air dried tissue web.

In still other embodiments the disclosure provides a tissue product of any one of the foregoing embodiments wherein the tissue product comprises at least one multi-layered through-air dried tissue web comprising a first fibrous layer and a second fibrous layer, the first fibrous layer comprising wood

pulp fibers and the second fibrous layer consisting essentially of high yield hesperaloe fibers and wherein the hesperaloe fibers comprise from about 20 to about 40 weight percent of the through-air dried web.



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**WHAT IS CLAIMED IS:**

1. A tissue product comprising greater than about 20 weight percent high yield hesperaloe fiber having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.

2. The tissue product of claim 1 having a Wet CD Durability of greater than about 1.75.

3. The tissue product of claim 1 having a GMT from about 1500 to about 3000 g/3".

4. The tissue product of claim 1 having a Stiffness Index from about 4.0 to about 6.0.

5. The tissue product of claim 1 having a basis weight from about 30 to about 60 gsm.

6. The tissue product of claim 1 having a wet CD stretch greater than about 8.0 percent.

7. The tissue product of claim 1 wherein the tissue product comprises a single-ply multi-layered web having a first layer comprising conventional wood pulp fibers and a second layer consisting essentially of high yield hesperaloe pulp fiber.

8. The tissue product of claim 1 wherein the tissue product comprises at least one through-air dried tissue web.

9. A tissue product comprising at least one multi-layered through-air dried tissue web comprising a first and a second layer, the first layer being substantially free from high yield hesperaloe pulp fibers and the second layer consisting essentially of high yield hesperaloe pulp fibers, the tissue product having a Wet CD Durability from about 1.75 to about 2.0 and a Stiffness Index less than about 6.0.

10. The tissue product of claim 9 having CD Wet/Dry Ratio from about 0.28 to about 0.32.

11. The tissue product of claim 9 having an Absorbent Capacity from about 6.5 to about 7.5.

12. The tissue product of claim 9 having a GM Slope less than about 8.0 kg.

13. The tissue product of claim 9 having a basis weight from about 30 to about 60 gsm and a GMT from about 1500 to about 2500 g/3".

14. The tissue product of claim 9 wherein the tissue product is substantially free from softwood kraft pulp fibers.



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15. The tissue product of claim 9 wherein the high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.

16. A single-ply through-air dried tissue product comprising at least about 20 weight percent high yield hesperaloe pulp fibers, the tissue product having a basis weight from about 30 to about 60 gsm, a GMT from about 1500 to about 2500 g/3" and an Absorbent Capacity greater than about 7.0 g/g.

17. The single-ply through-air dried tissue product of claim 16 having a Wet CD Durability from about 1.75 to about 2.0.

18. The single-ply through-air dried tissue product of claim 16 having a Stiffness Index less than about 6.0.

19. The single-ply through-air dried tissue product of claim 16 wherein the tissue product comprises from about 20 to about 40 weight percent high yield hesperaloe fiber and is substantially free from softwood kraft pulp fibers.

20. The single-ply through-air dried tissue product of claim 16 wherein high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.



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**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/US2015/033175**

**A. CLASSIFICATION OF SUBJECT MATTER**

**A47K 7/00(2006.01)i, 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)
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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, web, hesperaloe fiber, non-woody, pulp, absorbent

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | US 5320710 A (REEVES, R. H. et al.) 14 June 1994<br>See abstract; claims 1-7. | 1-20 |
| Y | US 2013-0269892 A1 (KIMBERLY-CLARK WORLDWIDE, INC.) 17 October 2013<br>See claims 1, 3; paragraphs [0013], [0038], [0045]. | 1-20 |
| A | US 2014-0093704 A1 (SHI, B. et al.) 03 April 2014<br>See abstract; claims 1-9. | 1-20 |
| A | US 2015-0129143 A1 (CARGILL, INCORPORATED) 14 May 2015<br>See claims 1, 2, 9. | 1-20 |
| A | US 2003-0192662 A1 (HEATH, M. S. et al.) 16 October 2003<br>See abstract; claim 1. | 1-20 |

☐ 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
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"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
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"&" document member of the same patent family

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**INTERNATIONAL SEARCH REPORT**

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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



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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.



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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:

$$CD\ Durability = \frac{CD\ TEA\ (\mathrm{g} \bullet \mathrm{cm/cm2})}{CD\ Tensile\ (g/3")} \cdot x\ 1{,}000$$

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:

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



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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.



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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.



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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



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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

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, 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 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



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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).



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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.



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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.



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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. |
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| Y | US 5320710 A (REEVES et al.) 14 June 1994<br>See column 2, lines 54-68; claims 1-2 and figure 2. | 1-20 |
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☐ 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
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"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
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"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

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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(54) Title: TISSUE PAPER COMPRISING PULP FIBERS ORIGINATING FROM MISCANTHUS AND METHOD FOR MANUFACTURING THE SAME

(57) Abstract: The present invention relates to a tissue paper web composed of one or more layers wherein at least one layer comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus wherein the pulp fibers are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof. The use of Miscanthus pulp fibers according to the present invention can lead to a major absolute increase in tensile strength along with good softness values.

# Tissue paper comprising pulp fibers originating from Miscanthus and method for manufacturing the same

## DESCRIPTION

The present invention relates to a soft and strong tissue paper comprising fibers originating from a plant belonging to the genus Miscanthus, in particular from *Miscanthus Gigantheus.* The present invention also pertains to a process for the manufacture of said tissue paper as well as to products, e.g. toilet paper, hand towels, household towels etc., obtained by this process.

## BACKGROUND OF THE INVENTION

Tissue paper-based materials find extensive use in modern society. Toilet paper, paper towels such as hand towels or household (kitchen) towels, facial tissues and tissue handkerchiefs are staple items of commerce. These products are typically made from papermaking pulp comprising fibers of both hardwood and softwood types.

Among the most important physical properties of these products are their strength, their softness, their absorbency, primarily for aqueous systems, and their lint and dust resistance. These physical properties are generally tuned for addressing common consumer demand.

Tissue paper products are often exposed to extremely varied strength requirements in the wet and the dry state, respectively. For instance, it must be ensured, in the case of household paper (paper towels) that they retain their strength at least for a specific period of time when exposed to aqueous liquids or moisture-containing food. On the other hand, toilet paper should dissolve in water, sometime after use, in order to prevent the sewage systems from clogging up. Furthermore, toilet paper must not immediately lose its strength properties during use for apparent reasons.

At the same time, tactile properties such as softness are extremely important as tissue paper-based products are intended to come in intimate contact with the

body and skin. Therefore, tissue paper-based products must exhibit sufficient softness in order to ensure consumer's comfort.

However, strength and softness are generally conflicting properties. If strength rises, the softness of the tissue paper will decline due to the increase of fiber to fiber bonds. Conversely, if softness increases, the strength is decayed due to limited fiber to fiber bonds.

The prior art describes many processes for achieving a good balance between strength and softness, or increasing one property without detrimentally affecting another.

EP 0 029 269 A1 discloses a multi-layered tissue paper, and tissue paper-based products made thereof, such as toilet tissue and facial tissues, having a smooth and soft top surface. The tissue paper comprises a velutinous top layer being the outwardly facing surface formed from at least 60% by weight of short hardwood fibers, such as Northern Hardwood Sulfite and/or Eucalyptus Hardwood, united to a furnish comprising long softwood fibers. The short papermaking fibers disposed on the outer layer exhibit sufficient free end portions to achieve softness, whereas the long-fiber furnish ensures strength. However, for some applications this tissue paper does not exhibit sufficient strength, primarily in the dry state.

Another common measure for modifying the strength and softness properties of tissue papers consists in adding strengthening and/or softening compositions to tissue-based materials. In this regard, the prior art describes strengthening resins, such as polyamidoamine-epichlorine resins. However, the isolated use of strengthening resins generally provides a tissue paper which is fairly stiff and has almost the haptic properties of normal paper. Consequently, strengthening resins are often used in combination with softening compositions which, in turn, reduce strength since softeners also interact with inter-fiber hydrogen bonds.

WO 94/10381 A1 discloses soft and strong tissue paper webs which can be used in toweling, napkin, facial tissue, and toilet tissue products. The tissue paper webs generally comprise a cellulose-based furnish, such as a mixture of Northern softwood kraft and eucalyptus fibers, and a chemical softening composition comprising a cationic surfactant as softener. However, surfactants weaken the bonds between fibers in the tissue webs. As a result, the tissue paper webs do not

exhibit sufficient strength. The loss of strength due to the surfactant is hence compensated by the addition of a binding resin, such as a polyamidoamine-epichlorohydrin resin.

Likewise, US 5,397,435 and US 5,312,522 disclose tissue paper-based products such as paper towels, facial tissues and toilet tissues, comprising a combination of a chemical softening composition containing a surfactant such as a quaternary ammonium compound, and a strengthening resin such as a polyamide-epichlorohydrin resin. However, as outlined above, the use of softening and strengthening chemical compositions in combination generally does not provide a significant improvement, because the effect of one composition (e.g. softening or strengthening) is often compromised by the opposite effect caused by the other.

In addition, it can be desirable to reduce the amount of chemicals such as softening and/or strengthening chemical compositions in tissue paper. This applies primarily to cases where these chemical compositions tend to irritate the skin or trigger allergic reactions in some users. Furthermore, the biological degradability of some softening and/or strengthening chemical compositions in the environment has raised concerns.

WO 96/06223 A1 proposes a tissue sheet composed of northern softwood kraft and eucalyptus hardwood kraft, comprising a combination of "debonding" agents and strengthening agents added in a layer-wise fashion, in order to maximize the effectiveness of each additive while minimizing the interaction of the additives with each other. However, the addition of different chemical compositions in a layer-wise fashion significantly increases the complexity of the manufacturing process.

These are typical examples for the generally occurring problem in the art of tissue paper making that the above-mentioned properties conflict with each other in so far as attempts to improve one property is detrimental for another.

Further, it has been noted that, in tissue paper making processes, the primary (embryonic) fibrous webs containing eucalyptus pulp fibers sometimes do not show the desired strong adhesion to the Yankee cylinder when the web is subjected to the final drying and creping steps.

Starting from commonly used tissue paper products using mixtures of softwood and eucalyptus pulps, it is an object of the present invention to provide tissue paper webs and products having improved properties, in particular improved strength and good softness.

It is a further object of the present invention to provide a process for manufacturing such tissue paper webs. According to one aspect of the present invention, a process is provided which involves an improved adhesion of the "primary" fibrous webs to the Yankee cylinder during the final drying and creping steps of the process.

## SUMMARY OF THE PRESENT INVENTION

The present invention relates to a soft and strong tissue paper web composed of one or more layers wherein at least one of these layers comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus, in particular from *Miscanthus Gigantheus*. The present invention also relates to tissue paper products such as toilet paper, hand towels, household towels, handkerchiefs, napkins and facial tissues manufactured from said tissue paper web.

The present invention also relates to a process for the manufacture of a tissue paper web comprising the steps of

(a) providing pulp fibers comprising fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*;
(b) forming an aqueous suspension of the fibers;
(c) feeding the suspension to a tissue-making headbox;
(d) depositing the suspension onto a wire to form a wet web;
(e) dewatering the wet web; and
(f) drying and creping the web,

The pulp fibers are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment, and mixtures thereof.

The tissue paper web and tissue paper products of the present invention are distinguished by their excellent strength and good softness.

The present invention includes the following embodiments ("Items"):

1. Tissue paper web composed of one or more layers wherein at least one layer comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus wherein the pulp fibers are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof.

2. Tissue paper web according to Item 1 wherein the pulp fibers originate from *Miscanthus Giganteus*, *Miscanthus Sinensis*, or *Miscanthus Sacchariflorus*, and preferably from *Miscanthus Giganteus.*

3. Tissue paper web according to Item 1 or 2 wherein the pulp fibers, which originate from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Giganteus,* are present in an amount of at least 5 wt.-%, preferably in an amount of from 10 wt.-% to 90 wt.-%, more preferably in an amount of from 15 wt.-% to 80 wt.-%, even more preferably 20 wt.-% to 70 wt.-%, based on the total weight of the tissue paper web.

4. Tissue paper web according to any of Items 1, 2 or 3 wherein the web is composed of two or three layers made from different pulps wherein at least one of these layers is made from pulp comprising the pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Giganteus.*

5. Tissue paper web according to any of Items 1, 2, 3 or 4 wherein the remaining fibers present in said tissue paper web are selected from pulp fibers comprising hardwood fibers, such as eucalyptus, beech, aspen, acacia or birch fibers; softwood fibers such as pine, spruce, red cedar, hemlock, and larch fibers; and non-wood fibers such as cotton, bagasse, hemp, linen, sisal, straw or flax fibers.

6. Tissue paper web according to Item 4 or 5, wherein the web is composed of two layers wherein
(i) the first layer is made from pulp fibers (i-a) consisting of fibers originating from at least one plant belonging to the genus Miscanthus, preferably from

*Miscanthus Gigantheus,* and optionally hardwood fibers, or from pulp fibers (i-b) comprising, or consisting of, fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* softwood fibers, and optionally hardwood fibers, and

(ii) a second layer is made from pulp fibers comprising or consisting of softwood fibers.

7. Tissue paper web according to Item 6, wherein

(i) the first layer is made from pulp fibers (i-a), wherein the weight ratio of fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* to hardwood fibers, if present, is 100/0 to 10/90, preferably 100/0 to 20/80, and

(ii) the second layer is made from pulp comprising, or consisting of, softwood fibers,

and wherein the weight proportion of pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* based on the total weight of the tissue paper web is preferably 10 to 90 wt.-%, more preferably 10 to 80 wt.-%, in particular 25 to 75 wt.-%, such as 40 to 70 wt.-%.

8. Tissue paper web according to Item 6, wherein

(i) the first layer is made from pulp fibers (i-b) consisting of fibers originating from at least one plant belonging to the genus Miscanthus and preferably from *Miscanthus Gigantheus* (MG), softwood fibers (SW), and optionally hardwood fibers (HW), wherein the weight ratio MG / HW / SW in %, based on the total weight of pulp fibers (i-b), is 10 to 90 / 0 to 50 / 10 to 90, preferably 20 to 80 / 0 to 50 / 20 to 80, and

(ii) the second layer is made from pulp fibers comprising, or consisting of, softwood fibers, and wherein the weight proportion of pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* based on the total weight of the tissue paper web is preferably 10 to 50 wt.-% , such as 10 to 30 wt.-%.

9. Tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7 or 8, wherein the pulp fibers originating from *Miscanthus Gigantheus* are obtained in a chemical, chemo-mechanical or high yield chemical pulping process,

preferably the soda process or the CTMP process (Chemo-Thermo-Mechanical Pulping).

10. Tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7, 8 or 9, wherein the hardwood pulp fibers originate from eucalyptus and/or the softwood pulp fibers are Northern Bleached Softwood Kraft (NBSK) fibers, wherein the NBSK fibers are preferably refined to a degree of fineness of 19 to 35°SR.

11. Tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10, wherein (i) all fibers present in the web are primary pulp fibers, or (ii) a mixture of primary and secondary (recycled) pulp fibers wherein the proportion of secondary (recycled) pulp fibers does not exceed 90 wt.-% based on the tissue paper web.

12. Tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 which is composed of one or more layers wherein the pulp fibers originating from at least one plant belonging to the genus Miscanthus fulfill the following requirements:

(i) average fiber length of from 0.5 to 1.2 mm, preferably from 0.8 to 1.0 mm;

(ii) average fiber diameter of from 10 to 25 µm; and

(iii) average fiber wall thickness of from 3.0 to 5.0 µm.

13. Tissue paper product comprising at least one ply made from the tissue paper web according to any of Item 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12.

14. Tissue paper product according to Item 13, wherein the tissue paper product is selected from toilet paper, hand towel, household towel, handkerchiefs, napkins and facial tissues.

15. Tissue paper product according to Item 13 or 14 wherein the tissue paper product is a toilet paper composed of 2 to 4 plies, wherein preferably at least one outer ply, more preferably both outer plies, is/are made from the tissue paper web of Item 7, and the outer ply/plies is/are arranged such that, in the toilet paper, the first layer thereof (i), which comprises the pulp fibers originating from at least one plant belonging to the genus Miscanthus,

preferably from *Miscanthus Gigantheus*, is located on the outer surface of the toilet paper.

16. Tissue paper product according to Item 13 or 14 wherein the tissue paper product is a hand towel or household towel composed of 2 to 4 plies, wherein preferably at least one ply, optionally all plies, is/are made from the tissue paper web of Item 7 or the tissue paper web of Item 8.

17. Tissue paper product according to any of Items 13, 14, 15 or 16 wherein the tissue paper product is free of a softener and/or is free of a strengthening resin.

18. Process for the manufacture of a tissue paper web according to any of Items 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12, comprising the steps of:

(a) providing chemical pulp fibers comprising fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*;
(b) forming an aqueous suspension of said pulp fibers;
(c) feeding the suspension to a tissue-making headbox;
(d) depositing the suspension onto a wire to form a wet web;
(e) dewatering the wet web; and
(f) drying and creping the web.

Where the present description refers to "preferred" embodiments/features, combinations of these "preferred" embodiments/features shall also be deemed as disclosed as long as this combination of "preferred" embodiments/features is technically meaningful.

Hereinafter, the use of the term "comprising" should be understood as disclosing, as a more restricted embodiment, the term "consisting of" as well.

## FIGURES

Figure 1 - Schematic drawing showing the creping process on a Yankee cylinder with a creping blade. Figure 1 gives a survey on the terminology used for the

various angles influencing the creping process. In Figure 1 the following reference numbers represent:

(1) Yankee cylinder,
(2) Crepe pocket angle,
(3) Bevel angle,
(4) Blade holder angle,
(5) Sheet take-off angle,
(6) Creped sheet, and
(7) Stick out.

## DETAILED DESCRIPTION OF THE PRESENT INVENTION

### 1. Tissue paper web

The tissue paper web of the present invention is composed of one or more layers wherein at least one layer comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus.

The term "tissue paper" as used herein covers the "base (raw) tissue paper" ("**tissue paper web**") as obtained from the tissue paper machine as well as one-ply or multi-ply final products ("**tissue paper products**") made of base tissue, and tailored to the end user's needs by further converting steps.

As "**tissue paper web**" we understand the one-ply base tissue as obtained from the tissue machine. The tissue paper web is a sheet of paper made by a process comprising the steps of: forming an aqueous suspension of pulp fibers i.e. the so-called "furnish", depositing said aqueous suspension onto a wire to form a wet web, dewatering, drying and creping the web.

The tissue paper web has a basis weight of 8 to 50 g/m$^2$, in particular 10 to 30 g/m$^2$, especially 12 to 25 g/m$^2$.

The tissue paper web of the present invention is composed of one or more layers (i.e. single-layered web or multi-layered web). The term "**layer**" refers to a stratum within the web having a defined fiber 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. This technique is well-known to those skilled in the art. It renders possible the use of different kinds of fibers in each layer of the web. The "multi-layered" tissue paper web of the present invention may have 2 to 5, typically 2 or 3 layers.

The term "**ply**" as used herein refers to the one or more plies of tissue paper in the final tissue paper product as are obtained after processing ("converting") one or more base tissue paper webs. Each individual ply consists of a tissue paper web comprising one or more layers, e.g. one, two, three or four layers.

Based on the underlying compatibility of the production processes (wet forming), "tissue" production is counted among the papermaking techniques. The production of tissue is distinguished from paper production by its extremely low 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 crepe doctor or in the latter instance as a result of 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 imparting to the tissue a 3D structure by means of 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 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, properties which are frequently referred to as bulk softness, a high surface softness, 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. These properties allow tissue paper to be used, for example, as cleaning cloths (e.g. household towels), sanitary products (*e.g.* toilet paper, hand towels), paper handkerchiefs, cosmetic wipes (facial tissues) or as serviettes/napkins.

The tissue paper web of the invention and the tissue paper products made therefrom are characterized by their content of pulp fibers originating from at least one plant belonging to the genus Miscanthus.

The "**Miscanthus**" genus includes about 15 perennial rhizomatous grasses. Miscanthus grasses are usually found throughout a wide climatic range, from the tropics and subtropics to the temperate regions of Northern Asia and Europe. According to the present invention, the fibers can be selected from fibers originating from the species *Miscanthus Floridulus*, *Miscanthus Sacchariflorus*, *Miscanthus Sinensis*, *Miscanthus Gigantheus*, *Miscanthus Tinctorius*, and *Miscanthus Transmorrisonensis*.

It is preferred that the pulp fibers originate from *Miscanthus Sacchariflorus*, *Miscanthus Sinensis*, and *Miscanthus Gigantheus*. It is even more preferred that the pulp fibers originate from *Miscanthus Gigantheus*.

When the aforementioned pulp fibers originating from at least one plant belonging to the genus Miscanthus are used to form the tissue paper web of the present invention, the resulting tissue paper web/product exhibits improved properties, in particular improved strength and good softness. When pulp fibers originating from *Miscanthus Gigantheus* are used, the improvement of strength is even more pronounced while good softness is maintained.

Further, when the aforementioned pulp fibers originating from at least one plant belonging to the genus Miscanthus are used to form the tissue paper web of the present invention, the resulting tissue paper web/product exhibits excellent absorption for aqueous systems.

It is furthermore believed that the tissue paper web/product of the present invention, comprising pulp fibers originating from at least one plant belonging to

the genus Miscanthus, can exhibit **antimicrobial / antibacterial properties** which are natural attributes of plants belonging to the genus Miscanthus.

The tissue paper web of the present invention contains the aforementioned pulp fibers originating from at least one plant belonging to the genus Miscanthus in an amount of at least 5 wt.-%, preferably in an amount of 10 wt.-%, more preferably in an amount of from 10 wt.-% to 80 wt.-%, and even more preferably 20 wt.-% to 70 wt.-%, based on the total weight of the tissue paper web.

The "**pulp fibers**" used in the present invention are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof.

"**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.

In the present invention, use can also be made of **mechanical pulps subjected to chemical pre-treatment**, such as chemo-mechanical pulp (CMP pulp), or chemo-thermo- mechanical pulp (CTMP pulp).

According to one embodiment of the invention, the claimed tissue paper web and tissue paper products do not include fibrous material made from wood entirely by mechanical means, i.e. purely mechanical pulps such as groundwood pulp and refined mechanical pulp.

The pulp fibers originating from at least one plant belonging to the genus Miscanthus are preferably obtained in a chemical, chemo-mechanical (CMP) or high yield chemical pulping process. The use of alkaline chemical pulping or pretreatment processes is preferred. The pulp fibers are preferably obtained by employing the soda pulping process or the CTMP process (Chemo-Thermo-Mechanical Pulping) as described e.g. by P. Cappelletto et al. in *Industrial Crops and Products,* 11 (2000) 205-210. The pulp fibers are more preferably obtained by the soda pulping process. Kraft cooking could be used as well.

Further, the pulp fibers originating from at least one plant belonging to the genus Miscanthus can be prepared and/or treated by common techniques. For instance,

said pulp fibers can be bleached by using chlorine-free bleaching steps in view of the production of environmentally sound products and process steps.

According to one embodiment, the pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*, have a length of from 0.5 to 1.2 mm, preferably from 0.8 to 1.0 mm, a diameter of from 10 to 25 µm, e.g. 13 to 21 µm, preferably 13 to 15 µm, and a wall thickness of from 3.0 to 5.0 µm. The fiber dimensions are mean (average) values, which can be determined by techniques well-known in the art such as described by C. Ververis et al. in *Industrial Crops and Products 19 (2004) 245-254*.

In the following, for the sake of brevity, we will refer to pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*", and being selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof as "***MG pulp fibers***".

According to one embodiment, the tissue paper web is composed of two or three layers made from different pulps wherein at least one of these layers is made from pulp comprising MG pulp fibers.

According to one further embodiment, the remaining fibers present in the tissue paper web of the invention, i.e. the fibers being not MG pulp fibers, are selected from pulp fibers comprising **hardwood fibers**, such as eucalyptus, beech, aspen, acacia or birch fibers; **softwood fibers** such as pine, spruce, red cedar, douglas fir, hemlock, and larch fibers; and **non-wood fibers** such as cotton, bagasse, hemp, linen, sisal, straw or flax fibers.

As "**hardwood fibers**" we understand fibrous pulp derived from the woody substance of deciduous trees (angiosperms). Typically, hardwood fibers are "short" fibers having a length of from 1 to 2 mm, a diameter of from 15 to 30 µm, and a wall thickness of from 2 to 3 µm. Hardwood such as Eucalyptus is normally pulped by the Kraft process.

The hardwood fibers usable in the present invention preferably originate from eucalyptus, beech, aspen, acacia and birch, more preferably from eucalyptus.

As "**softwood fibers**" we understand fibrous pulp derived from the woody substance of coniferous trees (gymnosperms). Typically, softwood fibers are "long" fibers having a length of from 3 to 4 mm, a diameter of from 30 to 40 µm, and a wall thickness of from 3 to 4 µm. They are normally pulped by the Kraft process.

The softwood fibers usable in the present invention preferably originate from pine, spruce, red cedar, douglas fir, hemlock, and larch. More preferably, the softwood fibers usable in the present invention are Northern Bleached Softwood Kraft (NBSK) fibers. Preferably, at least part of the NBSK fibers to be used is refined, more preferably to a degree of fineness of 19 to 35°SR, e.g. 19 to 26°SR.

As "**non-wood fibers**" we understand fibrous pulp derived from the non-woody substance of plants such cotton, bagasse, hemp, linen, sisal, straw or flax.

According to one preferred embodiment, the tissue paper web is composed of two layers wherein

(i) the first layer is made from

(i-a) pulp fibers consisting of MG pulp fibers, and optionally hardwood fibers, or

(i-b) from pulp fibers comprising, or consisting of, MG pulp fibers, softwood fibers, and optionally hardwood fibers, and

(ii) a second layer is made from pulp fibers comprising, or consisting, of softwood fibers.

Although it is frequently preferred that the second layer is made from pulp fibers consisting (only) of softwood ("SW") fibers the present invention also extends to embodiments in which this layer is made from pulp fibers comprising softwood fibers and other pulp fibers such as MG pulp fibers and/or hardwood fibers and/or non-wood fibers such as bagasse fibers or the other fibers mentioned hereinbefore. These other pulp fibers are then preferably used in an amount of up to 60 wt.-% based on the total weight of pulp fibers being present in the second layer.

Considering an exemplary case of 80% MG pulp fibers in total, one may for instance split the furnish for technical reasons in 50% MG pulp fibers in the first layer while the second layer consists of 30% MG pulp fibers plus 20% SW pulp fibers, each based on the total weight of the tissue paper web. In an alternative embodiment 50% MG pulp fibers are used in first layer and 30% Eucalyptus plus 20% SW pulp fibers in the second layer.

The above also applies to the following embodiments where the second layer is made from pulp comprising, or consisting of, softwood fibers.

According to one further preferred embodiment, especially suitable for the manufacture of toilet tissue paper, the tissue paper web is composed of two layers wherein

(i) the first layer is made from pulp fibers consisting of MG pulp fibers, and optionally hardwood fibers,

(i-a) wherein the weight ratio of MG pulp fibers to hardwood fibers, if present, is 100/0 to 20/80, and

(ii) the second layer is made from pulp comprising, or consisting of, softwood fibers,

and wherein the weight proportion of MG pulp fibers based on the total weight of the tissue paper web is preferably 10 to 80 wt.-%, in particular 25 to 75 wt.-%, such as 40 to 70 wt.-%.

According to one further preferred embodiment, especially suitable for the manufacture of household towel and hand towel, the tissue paper web is composed of two layers wherein

(i) the first layer is made from

(i-b) pulp fibers consisting of MG pulp fibers, softwood fibers (SW), and optionally hardwood fibers (HW), wherein the weight ratio MG / HW / SW in %, based on the total weight of pulp fibers (i-b), is 10 to 90 / 0 to 50 / 10 to 90, preferably 20 to 80 / 0 to 50 / 20 to 80, e.g. 20 to 70 / 10 to 50 / 20 to 70, or 20 to 80 / 0 / 20 to 80 or 20 to 50 / 0 to 30 / 40 to 60, and

(ii) the second layer is made from pulp fibers comprising, or consisting of, softwood fibers,

and wherein the weight proportion of MG pulp fibers based on the total weight of the tissue paper web is preferably 10 to 50 wt.-%, such as 10 to 30 wt.-%.

The MG pulp fibers used in the present invention can be refined fibers and are preferably unrefined. The remaining fibers present in the tissue paper web of the invention (i.e. the fibers being not MG pulp fibers) can be **unrefined fibers, refined fibers** and mixtures thereof. Preferably, at least a part of the softwood fibers (i.e. long fibers) to be used, optionally all softwood fibers, are refined. Preferably, the hardwood fibers (i.e. short fibers) to be used are unrefined.

According to one embodiment, the hardwood pulp fibers originate from eucalyptus and/or the softwood pulp fibers are Northern Bleached Softwood Kraft (NBSK) fibers, wherein the NBSK fibers are preferably refined to a degree of fineness of 19 to 35°SR, in particular 19 to 26°SR, e.g. 19 to 24°SR.

As "**unrefined fibers**" we understand fibers as naturally occurring or being obtained by their respective preparation process (chemical or mechanical pulping, recycling etc.). Although being dependent on the fiber source, unrefined hardwood and softwood pulp fibers typically have a freeness value of about 12 to 15°SR. By contrast, unrefined MG pulp fibers (as coming from the pulp mill) can have a SR value in the range of 34 to 36°SR, typically about 35°SR. The unrefined fibers used in the tissue paper web and product of the invention usually stem from hardwood. Also MG pulp fibers are typically used as they come from the paper mill without further refining. However, the unrefined fibers to be used can also stem from softwood, e.g. softwood like spruce digested by sulfite processes.

As "**refined fibers**" we understand fibers which have been subjected to refining processes. Such processes are well known to those skilled in the art. Refined fibers typically have a freeness value of more than 15 to less than 35°SR. In the present invention, the softwood fibers are preferably refined to a degree of fineness of 19 to 35°SR, in particular 19 to 26°SR, such as 19 to 24°SR. The refined fibers usually stem from softwood.

If long refined fibers and unrefined fibers are to be combined, be it in a single-layered ply as a true mixture or in multi-layered plies based on separate pulp streams, they are preferably used in a ratio of from 90/10 to 10/90, more preferably 80/20 to 20/80, most preferably from 75/25 to 40/60.

Further, the pulp fibers present in the tissue paper web of the invention can be a primary fibrous material, a secondary fibrous material (recycled pulp) and mixtures thereof.

According to one embodiment, (i) all fibers present in the tissue paper web are primary pulp fibers, or (ii) a mixture of primary and secondary (recycled) pulp fibers. Preferably, the proportion of secondary (recycled) pulp fibers, if present, does not exceed 90 wt.-%, based on the total weight of the tissue paper web. It is more preferred that the proportion thereof is 70 wt.-% or less, e.g. 50 wt.-% or less.

As "**primary pulp fibers**" we understand fibers as obtained from the pulping process of woody substances (e.g. hardwood, softwood) and non-woody substances (e.g. cotton, bagasse, hemp, Miscanthus etc.) which have not previously been used in a manufacturing process.

As "**secondary pulp fibers**" we understand fibers that have previously been used in a manufacturing process (e.g. paper- or tissue-making), and have been reclaimed (recycled) as raw material for the process of the present invention. Secondary pulp fibers can be recycled from e.g. waste paper by common techniques in the art.

The tissue paper web of the present invention may include **softening and/or strengthening chemical compositions**.

In one embodiment, the tissue paper web of the present invention is free of softener (debonder). In one further embodiment, the tissue paper web of the present invention is free of strengthening chemical additives, such as strength resins, for instance free of the water-soluble cationic or anionic polymers described below. The tissue paper web of the present invention can also be free of both softener (debonder) and strengthening chemical additives.

When the tissue paper web includes a softener and/or a strengthening resin, a water-soluble cationic polymer, a water soluble anionic polymer and/or a cationic surfactant-based softener as described, e.g. in European patent EP 1 583 869 B1 can be used.

1.a Water-Soluble Cationic Polymer

When a water-soluble cationic polymer is used, it is possible to add the same to the pulp fibers in such an amount that 0.01 to 5 wt.-%, in particular 0.01 to 3 wt.-%, such as 0.5 to 2 wt.-% (e.g. 0.5 to 1.5 wt.-%), based on the total amount of fibers (dry weight, EN 20638:1993) is retained.

The cationic polymer to be used contains cationic groups, such as positively charged quaternary nitrogen atoms in sufficient amounts to impart the molecule water solubility. The term "water-soluble" means solubility in water (at 20°C) of at least 1 g/l, in particular at least 10 g/l, more particularly at least 20 g/l.

Preferably, the cationic water-soluble polymer is a wet strength agent. It 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. Suitable materials are described in further detail in US 3,998,690 and EP 1 583 869 B1.

The most preferred types of cationic polymer are 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. Examples of these are the well-known Kymene ® resins available from Ashland.

1.b Water-Soluble Anionic Polymer

When a water soluble anionic polymer is used, it can be added to the cellulosic fibers in such an amount that 0.01 to 3 wt.-%, in particular 0.1 to 2 wt.-%, such as

0.2 to 1 wt.-%, based on the total amount of untreated cellulosic fibers (dry weight according to DIN EN 20638) is retained by the fibers.

As "water-soluble anionic polymers" we understand those polymers having a sufficient amount of anionic groups, such as carboxy groups to be water soluble. As "water-soluble" we understand solubility in water (at 20°C) of at least 1 g/l, in particular at least 10 g/l, and more particularly at least 20 g/l.

The water soluble anionic polymer can be selected among known anionic dry strength agents. Suitable dry strength agents are described in European patent EP 1 583 869 B1.

The water soluble anionic polymer can be 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. Starch-based polymers, vinyl copolymers of carboxylic acids and cellulose-based polymers are preferred. 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.

The above anionic polymers also include anionic polymers of acrylamide. These can be made by hydrolysis of an acrylamide polymer or copolymer by means known to the art, or by copolymerizing acrylamide with acrylic acid or sodium acrylate and optionally another monomer under radical initiation, again by means known to the art. Also operable are poly(acrylic acid) or its salts such as sodium polyacrylate or ammonium poylacrylate. Other operable polymers in this group are poly(acrylic acid) and its salts, and poly(sodium acrylate).

Use can be made of commercially available anionic polymers, having carboxyl (or carboxylate salt) contents of about 0.5 to about 14 millequivalents per gram such as CMC.

The above-explained water soluble cationic polymer is used in higher amounts than the water soluble anionic polymer. Preferably the weight ratio cationic polymer/anionic polymer is from 1/1 to 10/1, more preferably 2/1 to 7/1, most preferably 3/1 to 5/1.

1.c Cationic Surfactant-Based Softener

According to one embodiment, the tissue paper web/product of the present invention is free of softening chemical additives (e.g. softener / debonder).

When a softener is used, a cationic surfactant-based softener (in the prior art sometimes referred to as "debonder") can be added to the cellulosic fibers in such an amount that 0.005 to 3 wt.-%, in particular 0.01 to 2.5 wt.-%, such as 0.5 to 2 wt.-%, based on the total amount of untreated cellulosic fibers (dry weight according DIN EN 20638) are retained by the fibers.

The softener may be selected from quaternary ammonium compounds (e.g. quaternized protein compounds, silicone quaternaries or quatemized protein compounds) or cationic phospholipids of the type as described in WO 97/04171. All suitable surfactant-based softeners have the presence of a cationic unit (preferably quaternary ammonium unit) and a long chain aliphatic group having preferably 8 to 24, more preferably 14 to 22 carbon atoms in common. The long chain aliphatic group is preferably directly linked to the cationic group.

The quaternary ammonium compounds can also be selected from those conforming to Formula I, II, III, IV or V disclosed in [0079] to [0091] of EP 1 583 869 B1.

**2. Tissue paper product**

The present invention also relates to a tissue paper product comprising at least one ply made from the tissue paper web.

To achieve the desired finished products such as toilet tissues and hand towels, the one ply base tissues with typical basis weights from 12 g/m² to 38 g/m² are

combined in a subsequent converting step to the final ply count which may be 2 to 5 depending on the targeted properties of the final tissue paper product.

The total basis weight of multiple-ply tissue products preferably does not exceed 75 g/m$^2$ and more preferably is lower than 65 g/m$^2$, e.g. lower than 55 g/m$^2$.

In order to optimally use its strength and softness properties, it is desirable to employ the tissue paper web of the invention, i.e. one comprising MG pulp fibers, in one or both outer plies of the final tissue product, since these come in contact with the body and skin of the user.

When the tissue paper web of the invention is multi-layered, it is desirable that the outer layer(s) of the outer ply/plies, i.e. the layers which come into contact with the user's body and skin, comprise MG pulp fibers. A tissue paper product distinguished by its excellent strength and good softness is thus produced.

The tissue paper product of the present invention is preferably selected from toilet paper, hand towel, household towel, handkerchiefs, serviettes/napkins and facial tissues.

According to one preferred embodiment, the tissue paper product is a **toilet paper** composed of 2 to 5 plies, e.g. 2 to 4 plies, wherein preferably at least one outer ply, more preferably both outer plies, is/are made from the tissue paper web of the invention.

More preferably, this applies to the previously described "further preferred embodiment" of a tissue paper web having a first layer (i) and a second layer (ii), which was stated to be especially suitable for the manufacture of toilet tissue paper and can be used in least one outer ply, more preferably both outer plies of a toilet paper having e.g. 2, 3, 4 or 5 plies.

In this product, it is preferred that the outer ply/plies is/are arranged such that, in the toilet paper, the first layer thereof (i), which comprises the MG pulp fibers is located on the outer surface of the toilet paper. As a result, improved strength and soft feeling when applied on the user's skin can be achieved.

According to one further preferred embodiment, the tissue paper product is a **hand towel** or **household towel** composed of 2 to 5, e.g. 2 to 4 plies. Preferably, at least one ply, optionally all plies, is/are made from the tissue paper web of the present invention.

More preferably, this applies to the previously described "further preferred embodiment" of a tissue paper web having a first layer (i) and a second layer (ii), which was stated to be especially suitable for the manufacture of hand towel or household towel and can be used in least one outer ply, more preferably both outer plies of a hand towel having e.g. 2, 3, or 4 plies or household towel having e.g. 2, 3, 4 or 5 plies.

According to one further preferred embodiment, the tissue paper product of the present invention (e.g. toilet paper, hand towel and household towel) is free of a softener and/or is free of a strengthening additive, e.g. resin.

**3. Process for the manufacture of tissue paper webs and tissue paper products**

The present invention also relates to a process for the manufacture of a **tissue paper web** as described before and below, the process comprising the steps of:

(a) providing pulp fibers comprising fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus* i.e. MG pulp fibers;

(b) forming an aqueous suspension of said pulp fibers;

(c) feeding the suspension to a tissue-making headbox;

(d) depositing the suspension onto a wire to form a wet web;

(e) dewatering the wet web; and

(f) drying and creping the web.

(a) The pulp fibers to be used in the aforementioned process can be prepared by common techniques known in the art, for instance, fractionating, sorting, washing, floating, cleaning, thickening and/or fiberizing.

When refined pulp fibers are to be used in the aforementioned process, said fibers can be refined by using techniques well-known in the art. Typically, the fibrous material to be refined is transported to a refiner unit. Fibrillation of fibers during refinement (beating) occurs either by the fibers themselves or by the refining bars. During refinement, the fibers are subjected to a variety of physical loads. Axial and tangential shearing and compressive forces acting upon the fiber play a particular role as regards fiber refining. The associate change in fiber morphology involves, but is not limited to, tearing open and removing the fibrous materials' outer wall layer (primary wall) and/or exposing the fibers and fibrillation out of the wall layers and/or partially shorting the total fiber unit and/or shearing off fibrils.

(b) After providing the pulp fibers comprising MG pulp fibers, an aqueous suspension is produced therefrom. The aqueous suspension preferably contains the pulp fibers in an amount of from 3 to 4 wt.-%, based on the water content. The aqueous suspension is then diluted to consistencies in the order of 0.5 to 1.5 wt.-%, preferably of 0.8 to 1.2 wt.-%.

In one embodiment of the invention, the aqueous suspension can be treated with the anionic and cationic water soluble polymer described before. Preferably, aqueous solutions are used for adding these chemicals but it is also possible to add them in substance.

Generally, it is preferred to add the anionic polymer first (prior to the cationic polymer) in order to ensure an optimal interaction with the cellulosic fibers, if these chemicals are to be added. After a period of time of preferably 30 seconds to 24 hours, in particular 1 to 30 minutes, the cationic polymer is also given to the aqueous slurry. Again, it is preferred to let a certain period of time pass (preferably from 1 to 30 minutes) before the aqueous slurry is conducted to the headbox and dewatered. A different order of addition can also be used as described in EP 1 583 869 B1.

(c) In step (c) the suspension is fed to a tissue-making headbox in line with methods known in the art. In a typical process, a low consistency pulp furnish is provided in a pressurized (e.g. multi-layered) headbox. The headbox has an opening for delivering a thin deposit of pulp furnish onto the Fourdrinier wire to form a wet web in the following step (d) in which the suspension is deposited onto a wire to form a wet web. According to one preferred embodiment of the invention,

softness and strength of the base tissue are influenced by producing a multi-layer tissue paper web if a specifically constructed headbox (i.e. multi-layered headbox) is used to form the primary fibrous web having physically different layers of fibrous material.

(d) The wet laying step and the further production steps are also performed in line with methods known in the art. Tissue paper can be formed by placing the fibers on one or between the two continuously revolving wires of the paper-making machine while simultaneously removing the main quantity of water of dilution until dry-solids contents of 8 to 35% are obtained.

The forming wire is often referred to in the art as a Fourdrinier wire. Once the furnish is deposited on the forming wire, it is referred to as a web. The particular techniques and equipment for making webs according to the process just described are well-known to those skilled in the art.

(e) The web is then typically dewatered to a fiber consistency of between about 8% and about 35% (total web weight basis) by gravity or vacuum dewatering, and further dewatering the web by pressing operations wherein the web is subjected to pressure developed by opposing mechanical members, for example cylindrical rolls. A shoe press such as the NipcoFlex-T available from Voith can be used for the pressing operations.

(f) In conventional tissue making processes, the formed primary fibrous web is dried in one or more steps by mechanical and thermal means until a final dry-solids content of usually about 93 to 97% is obtained. The drying is followed by the crepe process which crucially influences the properties of the finished tissue product. The creping step involves creping on a usually 4.5 to 6 m diameter drying cylinder, the so-called Yankee cylinder, by means of a crepe doctor with the aforementioned final dry-solids content of the base tissue paper (wet creping can be used if lower demands are made of the tissue quality). The creped, finally dry base tissue paper (base tissue) is then available for further processing into the tissue paper product according to the invention.

When the tissue paper is creped on the Yankee cylinder, the blade holder angle (reference number (4) in Figure 1) is preferably determined to be from 10 to 35°. In conventional tissue making processes, values of from 11 to 13° are typically

employed. If through-air-drying (TAD) technology as explained below is used, the blade holder angle preferably ranges from 20 to 35°, in particular 22 to 30°.

When practising the present invention, the geometry of the doctor blade relative to the tissue surface may also have an impact on the properties of the product obtained. Thus, thickness and relative wet strength may increase, when the bevel angle is increased from 20° over 25° to 30°. As "level angle" we understand the angle (3) given in Figure 1.

The inventors of the present invention have surprisingly found that in the present tissue paper making processes, the primary (embryonic) fibrous webs containing MG pulp fibers strongly adheres to the Yankee cylinder in the final drying and creping steps. Furthermore, the inventors have observed that due to the strong adhesion of the web to the Yankee cylinder, finer creping is achieved and a smoother tissue surface is obtained. The strong and controlled adhesion of the web to the Yankee cylinder generally facilitates the tissue paper making process.

Instead of the conventional tissue making process described above, the invention can also make use of a modified technique in which an improvement in specific volume is achieved through wet-shaping of the still wet primary (embryonic) fibrous web by means of a 3D-structured fabric or plastic belt and/or by a special kind of drying as in TAD processes. In this way an improvement in the bulk softness of the thus made tissue paper is achieved as well. The TAD (through-air-drying) technique 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 80%, before final contact drying on the Yankee cylinder, by blowing hot air through the fibrous web. Pressing the "primary" fibrous web is hence not required for TAD processes. 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 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.

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 base 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 "internal" nor external 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.

When processing ("converting") the base fibrous web or base 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, laminating, folding, imprinting, perforating, application of lotions, smoothing, stacking, rolling up. Chemical ply adhesion can be performed by using an adhesive such as Kappasil and Kappaflex adhesives available from Kapp-Chemie GmbH.

To produce multi-ply tissue paper products, such as handkerchiefs, toilet paper, hand towels, household towels etc., 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, which has already been optionally wound up in several plies, to the finished 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 packages 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.

These converting techniques are known in the art.

The present invention is now further illustrated by the following examples.

## 4. Examples

The following test methods were used to evaluate the tissue papers produced. The test samples were conditioned for at least 12 hours at 50% relative humidity and 23 °C prior to testing.

### 4.1. Basis weight

The basis weight was determined according to EN ISO 12625-6:2005, Tissue Paper and Tissue Products, Part 6: Determination of grammage.

### 4.2. Caliper

The measurement is made by a precision micrometer (precision 0.001 mm) according to a modified method based on EN ISO 12625-3:2014, 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 SE050 (available from Lorentzen & Wettre, Europe).

The **base tissue** (web) to be measured is cut into pieces of 20 x 25 cm and conditioned in an atmosphere of 23°C, 50 % RH (Relative Humidity) for at least 12 hours. For the measurement, a stack of 10 base tissue paper sheets is prepared and placed beneath the pressure plate, which is then lowered. The thickness value for the stack is then read off 5 seconds after the pressure has been stabilized. The

thickness measurement is then repeated nine times with further samples treated and prepared in the same manner.

The mean value of the 10 values is taken as thickness of 10 base tissue sheets measured (in the following referred to as "**10-ply caliper**").

The **finished product** to be measured (i.e. a one-ply or multi-ply tissue paper product) is cut into pieces of 20 x 25 cm and conditioned in an atmosphere of 23°C, 50 % RH for at least 12 hours.

For the measurement one sheet is placed beneath the pressure plate which is then lowered. The thickness value for the sheet is then read off 5 seconds after the pressure has been stabilized. The thickness measurement is then repeated nine times with further samples treated in the same manner.

The mean value of the 10 values obtained is taken as thickness of one sheet ("**one-sheet caliper**") of the finished product (e.g. a two-ply hand towel) measured.

### 4.3. Bulk in $cm^3/g$

The bulk of the tissue paper was calculated with the following formula:

$X = t / w$

$X$ = bulk ($cm^3/g$)
$t$ = mean thickness of a sheet (µm)
$w$ = basis weight of the sheets ($g/m^2$)

### 4.4 Dry tensile strength in N/m (MD + CD)

The dry strength was determined according to EN ISO 12625-4: 2005, Tissue Paper and Tissue Products, Part 4: Determination of width-related breaking strength, elongation at break and tensile energy absorption.

The tensile tester used for the measurement featured two clamps of 50 mm width. Each clamp can grip the test piece firmly, but without damage, along a straight line

across the full width of the test piece (the clamping line). The distance between the clamping lines was set at 100 mm. For special tests, the distance is reduced if the available length of the sample is lower than 100 mm (e.g. toilet tissue in cross direction).

The tissue paper product to be measured, i.e. two sheets of a single-ply or multi-ply product, was cut into test pieces of 50 mm wide with parallel edges. Each sheet was cut into two different types of test pieces by cutting in the machine direction and in the cross direction. The obtained test pieces were then conditioned in an atmosphere of 23°C, 50 % RH (Relative Humidity) for at least 12 hours.

The test piece to be measured was placed between the clamps without any strain, and such that any observable slack is eliminated. At the beginning, a pre-tensile force of 25 cN is applied (zero of stretch) then the elongation rate between the clamps was kept constant at 5 cm/min. The maximum tensile force required to break the test piece was obtained. The measurement was repeated with six test pieces and the values obtained were averaged.

The dry tensile strength was calculated by means of the following formula:

Mean dry tensile strength [N/m] = (mean maximum tensile force [N] / initial width of the test piece [mm]) x $10^3$

Results were reported separately for the machine direction (MD) and the cross direction (CD).

### 4.5. Wet tensile strength in N/50mm (MD + CD)

The wet strength was determined according to EN ISO 12625-5:2005 Tissue Paper and Tissue Products, Part 5: Determination of wet tensile strength.

The apparatus used for the measurement was a vertical tensile strength tester featuring one clamp of 50 mm width, capable of gripping the test piece firmly without slippage. Below the clamp a thin metal bar and further below a vertically movable Finch Cup soaking device filled with water was arranged as is well known in the art.

To prepare the test pieces two sheets of a single-ply or multi-ply paper were each cut into test "strips" of 5 x 15 cm with parallel edges. From each sheet two types of test pieces were prepared by cutting in the machine direction (MD) and in the cross direction (CD).

To ensure that the wet strength of the samples had fully developed, the samples to be tested were artificially aged before conducting the tensile test measurement. Aging was achieved by heating the samples in an air-circulating drying cabinet to 80°C for a period of 30 min according to the ISO standard.

For the test the strip-shaped test piece was wound once around the metal bar in the Finch Cup soaking device in order to form a loop followed by fixing both ends of the test piece loop in the clamp arranged above the soaking device. The two ends of the test piece were fixed in the clamp without any strain, and such that the test span was set at 4.5 cm. To start the measurement the Finch cup filled with water was raised so that the bar and the strip are fully immersed in the water. After that the test piece was soaked for 15 seconds followed by immediately initiating the tensile test. The wet tensile force required to break the immersed test piece was determined at an elongation rate of 5 cm/min. The measurement was repeated with six test pieces and the values obtained were averaged.

The wet tensile strength was then calculated with the following formula:

Mean wet tensile strength [N/m] = (mean maximum tensile force [N] / initial width of the test piece [mm]) x $10^3$

Results were reported separately for the machine direction (MD) and the cross direction (CD).

### 4.6. Geometrical Mean Tensile Index (dry)

The geometrical mean tensile index was calculated in accordance with EN ISO 12625-4:2005 by the following formula:

Geometrical Mean Tensile Index [Nm/g] = SQRT ((Tensile Strength MD [N/m] x Tensile Strength CD [N/m]) / (Basis Weight [$g/m^2$])$^2$)

The basis weight of the tissue paper was determined in accordance with EN ISO 12625-6, Tissue Paper and Tissue Products, Part 6: Determination of grammage, as set forth in item 4.1 above.

### 4.7. Freeness value

The freeness value (in °SR) was measured according to DIN-ISO 5267/1; March 1999.

### 4.8. Softness

Softness was rated by a panel composed of at least five qualified persons.

The final tissue paper product (i.e. three-ply toilet paper, two-ply hand towel or two-ply household towel) is compared against softness standards. The evaluation procedure consists in assessing surface and bulk softness, grip and drapability. By judgment of the panelist the tested products are ranked against standards with a known softness value. The results of the individual panelists are averaged into a final softness value for the respective finished product.

Very slight differences in tissue softness can thus be quantified by comparison with tissue references to which softness values ranging from 1.5 to 4.0 had been previously allocated. Softness ratings were averaged across all panelists.

### 4.9. Absorption

The absorption (in g/g) was determined in accordance with PrENV 12625-8 Tissue Paper and Tissue Products, Part 8: *Determination of water-absorption time and water-absorption capacity*, in accordance with the basket-immersion test method described in EP 1 362 143 B1, item 5 - test method and Figur 1).

### 4.10. Starting materials, chemicals and tissue machine

**Pulp**

Three different types of pulp fibers were used as follows:

• Northern Bleached Softwood Kraft (NBSK) Pulp from Canfor Pulp Ltd., ECF 90 pulp grade ("SW pulp")

• Chemical pulp made from Eucalyptus hardwood fibers from Suzano Pulp and Paper, Brazil; Extra Prime Bleached Eucalyptus Kraft Pulp ECF grade ("HW pulp")

• Chemical pulp produced by SCA Hygiene Products from *Miscanthus Giganteus* ("MG pulp").

The "MG pulp" was produced using the soda pulping process. Soda pulping uses NaOH as the active cooking chemical to achieve the delignification which occurs at elevated temperatures. After the cooking the pulp was bleached using conventional bleaching agents and dried.

**Chemicals**

The chemicals used in the following examples are listed below:

• For the Yankee coating:

> Adhesive 2624 from Buckman;

> Plasticizer 2616 from Buckman;

> Release agent 2098e from Buckman

• Wet strength resin Kymene™ 557 H from Ashland (12,5% solids).

• Adhesives: Kappasil 260-4410, Kappaflex binder 72-0004. and Kappaflex grau 65-0012 were each purchased from Kapp-Chemie GmbH, Germany.

Hereinafter weight proportions ("kg/t") always refer to the amount of treated cellulosic fibers (dry weight).

**Tissue machine**

A conventional tissue paper making machine was adapted to make a three-ply toilet paper (Example 1), a two-ply hand towel (Example 2) and a two-ply household towel (Example 3). The machine was equipped with a Dry Crepe configuration and involved a two-layer headbox; a Crescent Former; a Suction Turning Roll; a NipcoFlex-T shoe press; a Yankee dryer with a drying hood; and a reel section to wind up the tissue paper.

The machine settings were kept throughout the trials in the following range(s):

| | |
|---|---|
| Yankee speed: | 1000 m/min |
| Shoe press line load: | 90 kN/m |
| Creping factor: | 13% |
| Dryness before Yankee: | 42 to 48% |
| Hood temperature: | 190 – 330 °C |
| Final tissue dryness: | 94 – 97% |

**Example 1-1 (Reference toilet paper)**

To achieve the desired finished toilet tissue paper one-ply base tissue was combined in a subsequent converting step to the final ply count (3). All three plies were produced in the same manner as described below:

The first furnish stream was prepared from unrefined HW pulp.

Then, SW pulp was refined to a freeness value of 21°SR to prepare a second furnish stream.

These two furnishes were supplied to the two chambers of a two-layer headbox. The furnish streams were kept separate through the headbox and deposited between a forming wire and a felt to form a two layer embryonic web containing 40 wt.-% of the refined SW pulp and 60 wt.-% of the unrefined HW pulp, respectively.

The embryonic web was dewatered in the shoe press to a dryness of about 42 to 48% and then led over the Yankee cylinder such that the HW pulp layer was in contact with the surface of the Yankee cylinder ("Y") and the SW pulp layer was opposite the Hood ("H").

After drying and creping, three two-layer base tissue paper webs having each a basis weight of about 17 g/m$^2$ and a 10-ply caliper of about 1,25 mm were obtained.

These three paper webs were bonded to each other by decor laminating / embossing and cut to size.

In the decor laminating / embossing step the three webs were fed through the nip of an embossing station including an embossing roll with protrusions forming a micro background and design elements (feathers) and a rubber roll arranged opposite thereto. Technical solutions where décor and background embossing are created by separate rolls / nips may be utilized too. Before the middle ply reached the nip, and after being superimposed with one outer web (ply), adhesive was selectively applied to those areas of the middle web (ply) that are joined together in the nip with the corresponding areas of the two outer webs (plies) by means of the protruding design elements of the embossing roll.

The adhesive used for bonding the three paper webs together was composed of 49 wt.-% water (452.16 kg), 46 wt.-% Kappasil (260-4410) (422.40 kg), 4.5 wt.-% Kappaflex binder (72-0004) (43.20 kg), and 0.5 wt.-% Kappaflex grau (65-0012) (4.42 kg), based on the total weight (922.18 kg) of the adhesive.

The three webs were fed to the embossing station and bonded in such a manner that the HW pulp layers (produced from the first furnish) of the two outer webs (plies) were located each on the outside of the three-ply toilet paper.

**Example 1-2 (Toilet paper with 12% MG pulp)**

A three-ply toilet paper was produced in the same manner as set forth in Example 1-1 apart from the following differences.

- The first furnish stream was a 1/4 mixture of unrefined MG pulp and unrefined HW pulp, respectively.
- The SW pulp used for the second furnish stream was refined to a slightly higher freeness value of 22°SR.

In the manufacture of the resulting two-layer webs, the SW pulp layer (40%) was located on the hood side, while the layer on the Yankee side included 12%MG pulp and 48%HW pulp, each based on the total weight of the web.

These three paper webs were bonded to each other by decor laminating / embossing and cut to size in the same manner as described in Example 1-1. They were bonded in such a manner that the MG pulp-containing layers (produced from

the first furnish stream) of the two outer webs (plies) were located each on the outside of the three-ply toilet paper.

**Example 1-3 (Toilet paper with 60% MG pulp)**

A three ply toilet paper was produced in the same manner as set forth in Example 1-1 apart from the following difference:

- The first furnish stream contained only unrefined MG pulp.

In the manufacture of the resulting two-layer webs, the SW pulp layer (40%) was located on the Hood side ("H"), while the layer on the Yankee side ("Y") included 60% MG pulp, each based on the total weight of the web.

These three paper webs were bonded to each other by decor laminating / embossing and cut to size size in the same manner as described in Example 1-1. They were bonded in such a manner that the MG pulp-containing layers of the two outer webs (plies) were located each on the outside of the three-ply toilet paper.

The properties of the toilet papers obtained in examples 1-1, 1-2 and 1-3 were evaluated according to the procedures explained hereinbefore. The results were as shown in table 1 below.

**Table 1**

| | Example 1-1 (Reference) | Example 1-2 | Example 1-3 |
|---|---|---|---|
| Pulp composition of plies (Y/H) | 60%HW/40%SW | (12%MG+48%HW)/ 40%SW | 60%MG/40%SW |
| Total basis weight ($g/m^2$) | 51.9 | 49.0 | 48.6 |
| Caliper /sheet[1] (µm) | 480 | 460 | 460 |
| Bulk ($cm^3/g$) | 9.25 | 9.39 | 9.47 |
| Dry MD tensile (N/m) | 238 | 236 | 274 |
| Dry CD tensile (N/m) | 124 | 128 | 136 |
| Geometrical Mean Tensile Index (Nm/g) | 3.3 | 3.5 | 4.0 |
| Softness | 2.2 | 2.2 | 2.1 |
| Absorption | 8.4 | 8.6 | 8.5 |

[1] "one sheet caliper" as described before

These test data show that the use of MG chemical pulp fibers according to the present invention can lead to a major absolute increase in tensile strength without concomitant loss of softness, or with only a minor loss of softness.

Further, it was surprisingly observed that, during the final drying and creping steps of the process, the embryonic fibrous webs of Examples 1-2 and 1-3, which contained MG pulp fibers, showed a better adhesion to the Yankee cylinder than the web of Reference Example 1-1, which contained eucalyptus pulp fibers instead.

**Example 2-1 (Reference hand towel)**

Two tissue paper plies were produced as described below.

SW pulp was refined to a freeness value of 21°SR and two different pulp slurries (furnishes) were prepared:

- The first furnish stream was a 1/1 mixture of refined SW pulp and unrefined HW pulp, respectively.
- The second furnish stream contained only refined SW pulp.
- 5.0 kg/t of Kymene™ 557H, based on the total pulp amount, was added to the first and second furnish streams.

These two furnish streams were supplied to the two-layer headbox. The furnish streams were kept separate through the headbox and deposited onto a Fourdrinier wire to form a two-layer embryonic web containing 50 wt.-% of refined SW pulp, and 50 wt.-% of the aforementioned 1/1 mixture of refined SW pulp and unrefined HW pulp.

The embryonic web was dewatered in the shoe press to a dryness of about 42 to 48% and then led over the Yankee cylinder such that the first furnish was in contact with the surface of the Yankee cylinder and the second furnish (SW pulp only) opposite the Hood.

Two two-layer base tissue paper webs having each a basis weight of about 21 g/m$^2$ and a 10-ply caliper of about 1.37 mm were obtained and wound up on jumbo rolls.

These two paper webs were bonded together by decor laminating / embossing, cut to size and reeled-up to a dispenser hand towel dispenser.

In the decor laminating / embossing step the two webs were fed through the nip of an embossing station including an embossing roll with protrusions forming a micro background and design elements (leaf and Tork® logo) and a rubber roll arranged opposite thereto. Before one web (ply) reached the nip, adhesive was selectively applied to those areas thereof that are joined together in the nip with the

corresponding areas of the other web (ply) by means of the protruding design elements of the embossing roll.

The adhesive used for bonding the two paper webs together was the same as used in Example 1-1.

In the bonding step the webs were superimposed and fed to the embossing station in such a manner that the layers containing only softwood pulp contacted each other and were located inside the two-ply hand towel (as shown in the table below).

| | layer | Pulp composition | Kymene |
|---|---|---|---|
| 1st ply | Outer 1) | 25%SW+25%HW | Yes |
| | Inner 2) | 50%SW | Yes |
| 2nd ply | Inner 2) | 50%SW | Yes |
| | Outer 1) | 25%SW+25%HW | Yes |

1) produced from 1st furnish / 2) produced from 2nd furnish

**Example 2-2 (Hand towel with 10% MG pulp)**

A two-ply hand towel was produced in the same manner as set forth in Example 2-1 apart from the following difference:

- The first furnish stream contained a 2/3/5 mixture of unrefined MG pulp, unrefined HW pulp and refined SW pulp, respectively.

Further, in accordance with the procedure of Example 2-1,

- the second furnish stream contained only refined SW pulp.
- 5.0 kg/t of Kymene™ 557H, based on the total pulp amount, was added to the first and second furnish streams.

In the manufacture of the resulting two-layer webs, the SW layer (50%) was on the hood side, while the layer on the Yankee side included 10% MG, 15% HW and 25% SW pulp, each based on the total weight of the ply.

Two two-layer base tissue paper webs having each a basis weight of about 21 g/m$^2$ and a 10-ply caliper of about 1,20 mm were obtained and wound up on jumbo rolls.

These two paper webs were bonded together by decor lamination / embossing, cut to size and reeled-up in the same manner as described in in Example 2-1. Correspondingly, in the final two-ply hand towel, the layers containing only softwood pulp contacted each other and the MG pulp-containing layers (produced from the first furnish) were located on the outside (as shown in the table below).

| | layer | Pulp composition | Kymene |
|---|---|---|---|
| 1$^{st}$ ply | Outer 1) | 10%MG+15%HW+25%SW | Yes |
| | Inner 2) | 50%SW | Yes |
| 2$^{nd}$ ply | Inner 2) | 50%SW | Yes |
| | Outer 1) | 10%MG+15%HW+25%SW | Yes |

1) produced from 1$^{st}$ furnish / 2) produced from 2$^{nd}$ furnish

**Example 2-3 (Hand towel with 25% MG pulp)**

The two webs constituting the two plies of a two ply hand towel were produced as described below.

A first web and a second web were produced in the same manner as explained in Example 2-1 apart from the following differences:

- The first furnish stream was a 1/1 mixture of refined SW pulp and unrefined MG pulp, respectively.

Further, in accordance with the procedure of Example 2-1,

- the second furnish stream contained only refined SW pulp.
- 5.0 kg/t of Kymene$^{TM}$ 557H, based on the total pulp amount, was added to the first and second furnish streams.

The two furnish streams were kept separate through the headbox and deposited onto a Fourdrinier wire in such a ratio so as to form a two-layer embryonic web

containing 75 wt.-% of refined SW pulp and 25 wt.-% of MG pulp, each based on the total amount of pulp (= total weight of the web).

In the manufacture of the resulting webs, the SW pulp layer (50%) was on the Hood side, while the layer on the Yankee side included 25% SW + 25% MG, each based on the total weight of the web.

The first and second base tissue paper web each had a basis weight of about 21 $g/m^2$ and a 10-ply caliper of about 1.20 mm and were wound up separately on jumbo rolls.

The first paper web and the second paper web were bonded together by decor lamination / embossing, cut to size and wound on a dispenser hand towel reel in the same manner as described in in Example 2-1.

In the final two-ply hand towel, the layers containing only softwood pulp contacted each other and the MG pulp-containing layers were located on the outside (as shown in the table below).

| | layer | Pulp composition | Kymene |
|---|---|---|---|
| 1st ply | Outer 1) | 25%SW+25%MG | Yes |
| | Inner 2) | 50%SW | Yes |
| 2nd ply | Inner 2) | 50%SW | Yes |
| | Outer 1) | 25%SW+25%MG | Yes |

1) produced from first furnish / 2) produced from 2nd furnish

The properties of the hand towels obtained in examples 2-1, 2-2 and 2-3 were evaluated according to the procedures explained hereinbefore. The results were as shown in table 2 below.

**Table 2**

| | Example 2-1 (Reference) | Example 2-2 | Example 2-3 |
|---|---|---|---|
| Pulp composition of plies (Y/H) | (25%SW+25%HW)/ 50%SW | (10%MG+15%HW +25%SW)/50%SW | (25%SW+25%MG)/ 50%SW |
| Total basis weight ($g/m^2$) | 42.8 | 40.0 | 41.4 |
| Caliper /sheet[1] (µm) | 250 | 260 | 260 |
| Bulk ($cm^3/g$) | 5.84 | 6.,50 | 6.28 |
| Dry MD tensile (N/m) | 615 | 759 | 751 |
| Dry CD tensile (N/m) | 321 | 323 | 349 |
| Geometrical Mean Tensile Index (Nm/g) | 10.4 | 12.4 | 12.4 |
| Absorption (g/g) | 6.4 | 6.2 | 6.5 |

[1] "one sheet caliper" as described before

These test data show that the use of MG chemical pulp fibers according to the present invention can lead to an absolute increase in tensile strength, when compared to HW pulp fibers, e.g. Eucalyptus.

Further, it was also surprisingly observed that, during the final drying and creping steps of the process, the embryonic fibrous webs of Examples 2-2 and 2-3 which contained MG pulp fibers showed a better adhesion to the Yankee cylinder than the web of Reference Example 2-1 which contained eucalyptus pulp fibers instead.

**Example 3-1 (Reference household towel)**

The same tissue paper webs as produced in Example 2-1 were used for manufacturing a two-ply household towel. The two tissue paper webs were superimposed and bonded (laminated) to each other by embossing in a nested configuration.

In the laminating / embossing step the two webs were fed through the nip of an embossing station including an embossing roll with protrusions forming a graphical pattern and a rubber roll arranged opposite thereto. Before one web (ply) reached the nip, the same adhesive as described in Example 1-1 was selectively applied to those areas of the web that are joined together in the nip with the corresponding areas of the other web (ply) by means of the protruding elements of the embossing roll.

**Example 3-2 (Household towel with 10% MG pulp)**

The same tissue paper webs as produced in Example 2-2 were used for manufacturing a two-ply household towel. The two tissue paper webs were laminated and embossed in the same manner as described in Example 3-1.

**Example 3-3 (Household towel with 25% MG pulp)**

The same tissue paper webs as produced in Example 2-3 were used for manufacturing a two-ply household towel. The two tissue paper webs were laminated and embossed in the same manner as described in Example 3-1.

The properties of the household towels obtained in examples 3-1, 3-2 and 3-3 were evaluated according to the procedures explained hereinbefore. The results were as shown in table 3 below.

**Table 3**

| | Example 3-1 (Reference) | Example 3-2 | Example 3-3 |
|---|---|---|---|
| Pulp composition of plies (Y/H) | (25%SW+25%HW)/ 50%SW | (10%MG+15%HW +25%SW)/50%SW | (25%SW+25%MG)/ 50%SW |
| Total basis weight ($g/m^2$) | 41.4 | 39.3 | 42.1 |
| Caliper /sheet[1] (µm) | 710 | 720 | 720 |
| Bulk ($cm^3/g$) | 17.15 | 18.32 | 17.10 |
| Dry MD tensile (N/m) | 453 | 577 | 612 |
| Dry CD tensile (N/m) | 190 | 191 | 237 |
| Geometrical Mean Tensile Index (Nm/g) | 7.1 | 8.4 | 9.0 |
| Softness | 5.,5 | 5,4 | 4.9 |
| Absorption (g/g) | 10.5 | 10.6 | 9.7 |

[1] "one sheet caliper" as described before

These test data show that the use of MG pulp fibers according to the present invention can lead to an absolute increase in tensile strength without significant loss of softness.

Further, it was surprisingly observed that, during the final drying and creping steps of the process, the embryonic fibrous webs of Examples 3-2 and 3-3 which contained MG pulp fibers showed a better adhesion to the Yankee cylinder than the web of Reference Example 3-1 which contained eucalyptus pulp fibers instead.

## CLAIMS

1. Tissue paper web composed of one or more layers wherein at least one layer comprises pulp fibers originating from at least one plant belonging to the genus Miscanthus wherein the pulp fibers are selected from chemical pulp fibers, mechanical pulp fibers subjected to a chemical pretreatment and mixtures thereof.

2. Tissue paper web according to Claim 1 wherein the pulp fibers originate from *Miscanthus Gigantheus*, *Miscanthus Sinensis*, or *Miscanthus Sacchariflorus*, and preferably from *Miscanthus Gigantheus*.

3. Tissue paper web according to Claim 1 or 2 wherein the pulp fibers, which originate from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*, are present in an amount of at least 5 wt.-%, preferably in an amount of 10 wt.-% to 90 wt.-%, more preferably 15 wt.-% to 80 wt.-%, even more preferably 20 wt.-% to 70 wt.-%, based on the total weight of the tissue paper web.

4. Tissue paper web according to any of Claims 1 to 3 wherein the web is composed of two or three layers made from different pulps wherein at least one of these layers is made from pulp comprising the pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus*.

5. Tissue paper web according to any of claims 1 to 4 wherein the remaining fibers present in said tissue paper web are selected from pulp fibers comprising hardwood fibers, such as eucalyptus, beech, aspen, acacia or birch fibers; softwood fibers such as pine, spruce, red cedar, douglas fir, hemlock, and larch fibers; and non-wood fibers such as cotton, bagasse, hemp, linen, sisal, straw or flax fibers.

6. Tissue paper web according to Claim 4 or 5, wherein the web is composed of two layers wherein
(i) the first layer is made from pulp fibers (i-a) consisting of fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* and optionally hardwood fibers, or from pulp fibers

(i-b) comprising, or consisting of, fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* softwood fibers, and optionally hardwood fibers, and
(ii) a second layer is made from pulp fibers comprising, or consisting, of softwood fibers.

7. Tissue paper web according to Claim 6, wherein
(i) the first layer is made from pulp fibers (i-a), wherein the weight ratio of fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* to hardwood fibers, if present, is 100/0 to 10/90, preferably 100/0 to 20/80, and
(ii) the second layer is made from pulp comprising, or consisting of, softwood fibers,
and wherein the weight proportion of pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* based on the total weight of the tissue paper web is preferably 10 to 90 wt.%, more preferably 10 to 80 wt.-%, in particular 25 to 75 wt.-%, such as 40 to 70 wt.-%.

8. Tissue paper web according to Claim 6, wherein
(i) the first layer is made from pulp fibers (i-b) consisting of fibers originating from at least one plant belonging to the genus Miscanthus and preferably from *Miscanthus Gigantheus* (MG), softwood fibers (SW), and optionally hardwood fibers (HW), wherein the weight ratio MG / HW / SW in %, based on the total weight of pulp fibers (i-b), is 10 to 90 / 0 to 50 / 10 to 90, preferably 20 to 80 / 0 to 50 /20 to 80, and
(ii) the second layer is made from pulp fibers comprising, or consisting of, softwood fibers, and wherein the weight proportion of pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Gigantheus,* based on the total weight of the tissue paper web is preferably 10 to 50 wt-%, such as 10 to 30 wt.-%.

9. Tissue paper web according to any of claims 1 to 8, wherein the pulp fibers originating from *Miscanthus Gigantheus* are obtained in a chemical, chemo-mechanical or high yield chemical pulping process, preferably the soda process or the CTMP process (Chemo-Thermo-mechanical pulping).

10. Tissue paper web according to any of claims 1 to 9, wherein the hardwood pulp fibers originate from eucalyptus and/or the softwood pulp fibers are Northern Bleached Softwood Kraft (NBSK) fibers, wherein the NBSK fibers are preferably refined to a degree of fineness of 19 to 35°SR.

11. Tissue paper web according to any of claims 1 to 10, wherein (i) all fibers present in the web are primary pulp fibers, or (ii) a mixture of primary and secondary (recycled) pulp fibers wherein the proportion of secondary (recycled) pulp fibers does not exceed 90 wt.-% based on the tissue paper web.

12. Tissue paper web according to any of claims 1 to 11 which is composed of one or more layers wherein the pulp fibers originating from at least one plant belonging to the genus Miscanthus fulfill the following requirements:
(i) average fiber length of from 0.5 to 1.2 mm, preferably from 0.8 to 1.0 mm;
(ii) average fiber diameter of from 10 to 25 µm; and
(iii) average fiber wall thickness of from 3.0 to 5.0 µm.

13. Tissue paper product comprising at least one ply made from the tissue paper web according to any of claim 1 to 12.

14. Tissue paper product according to claim 13, wherein the tissue paper product is selected from toilet paper, hand towel, household towel, handkerchiefs, napkins and facial tissues.

15. Tissue paper product according to claim 13 or 14 wherein the tissue paper product is a toilet paper composed of 2 to 5 plies, wherein preferably at least one outer ply, more preferably both outer plies, is/are made from the tissue paper web of claim 7, and the outer ply/plies is/are arranged such that, in the toilet paper, the first layer thereof (i), which comprises the pulp fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Giganteus*, is located on the outer surface of the toilet paper.

16. Tissue paper product according to claim 13 or 14 wherein the tissue paper product is a hand towel or household towel composed of 2 to 5 plies,

wherein preferably at least one ply, optionally all plies, is/are made from the tissue paper web of claim 7 or the tissue paper web of claim 8.

17. Tissue paper product according to any of claims 13 to 16 wherein the tissue paper product is free of a softener and/or is free of a strengthening resin.

18. Process for the manufacture of a tissue paper web according to any of Claims 1 to 12, comprising the steps of:

(a) providing chemical pulp fibers comprising fibers originating from at least one plant belonging to the genus Miscanthus, preferably from *Miscanthus Giganteus*;

(b) forming an aqueous suspension of said pulp fibers;

(c) feeding the suspension to a tissue-making headbox;

(d) depositing the suspension onto a wire to form a wet web;

(e) dewatering the wet web; and

(f) drying and creping the web.

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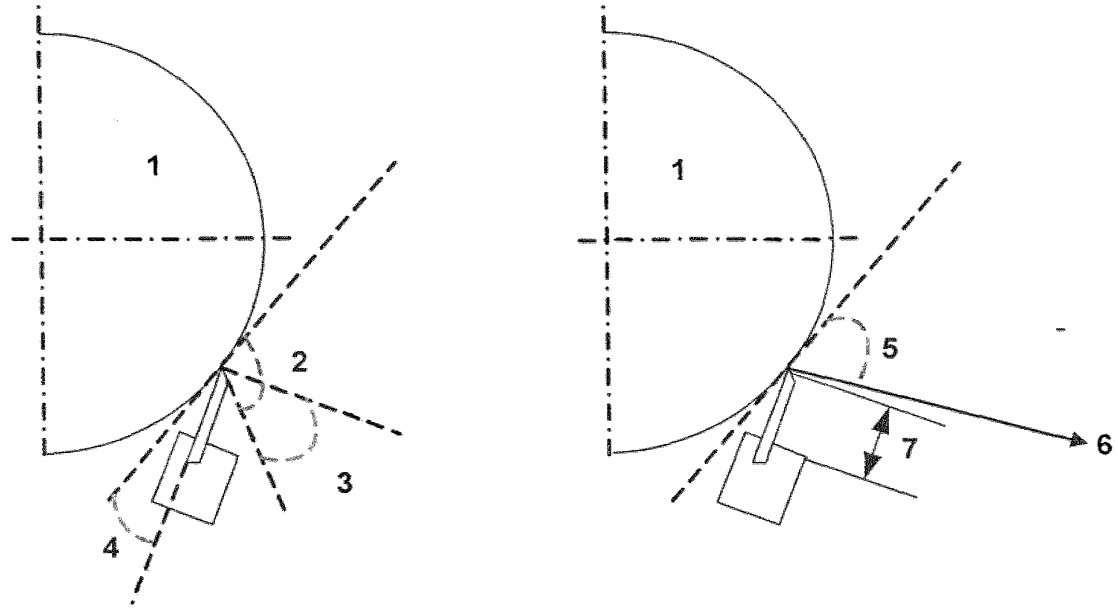



Figure 1

# INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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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 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. |
|---|---|---|
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| Y | paragraphs [0014], [0015], [0022], [0042]; claims | 1-18 |
| Y | EP 1 583 869 A1 (SCA HYGIENE PROD GMBH [DE]) 12 October 2005 (2005-10-12) the whole document | 1-18 |

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

☒ See patent family annex.

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



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Information on patent family members

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(54) **Title**: SOFT CREPED TISSUE

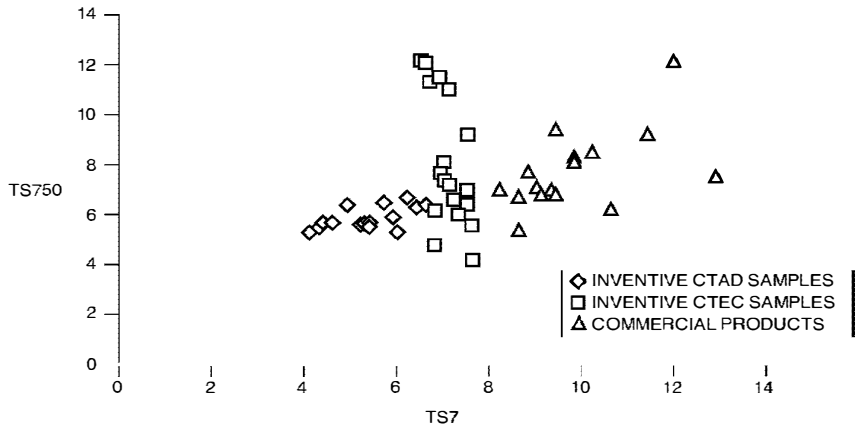



FIG. 1

(57) **Abstract**: The present disclosure is directed to creped tissue webs, and products produced therefrom. The creped tissue webs and tissue products made therefrom are soft and strong, such as having a TS7 value less than about 8.0. Moreover, the tissue of the present disclosure also preferably has low TS750 values such as less than about 7.0. Further, while webs prepared according to the present disclosure have low TS7, and in certain embodiments low TS750 values, they are also strong enough to withstand use.

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# SOFT CREPED TISSUE

## BACKGROUND

In the manufacture of paper products, such as facial tissues, bath tissues, napkins, wipes, paper towels, etc., it is often desired to optimize various properties of the products. For example, the products should have good bulk, a soft feel, and should have good strength. Unfortunately, however, when steps are taken to increase one property of the product, other characteristics of the product are often adversely affected.

For instance, it is very difficult to produce a high strength paper product that is also soft. In particular, strength is typically increased by the addition of certain strength or bonding agents to the product. Although the strength of the paper product is increased, various methods are often used to soften the product that can result in decreased fiber bonding. For example, chemical debonders can be utilized to reduce fiber bonding and thereby increase softness. Moreover, mechanical forces, such as creping or calendering, can also be utilized to increase softness.

However, reducing fiber bonding with a chemical debonder or through mechanical forces can adversely affect the strength of the paper product. For example, hydrogen bonds between adjacent fibers can be broken by such chemical debonders, as well as by mechanical forces of a papermaking process. Consequently, such debonding results in loosely bound fibers that extend from the surface of the tissue product. During processing and/or use, these loosely bound fibers can be freed from the tissue product, thereby creating lint, which is defined as individual airborne fibers and fiber fragments. Moreover, papermaking processes may also create zones of fibers that are poorly bound to each other but not to adjacent zones of fibers. As a result, during use, certain shear forces can liberate the weakly bound zones from the remaining fibers, thereby resulting in slough, i.e., bundles or pills on surfaces, such as skin or fabric. As such, the use of such debonders can often result in a much weaker paper product during use that exhibits substantial amounts of lint and slough. As such, a need currently exists for a paper product that is soft, yet strong enough to prevent sloughing. Moreover, there is a need for a product that can be produced without the excessive use of debonders.



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## SUMMARY

Typically to achieve a soft tissue the strength of the web is decreased and short, low coarseness fibers, treated with a chemical debonder, are disposed on the skin-contacting surface of the web. The softness levels achievable using such techniques, however, are limited by the user's desire to have a tissue that is strong enough to withstand use and to avoid large amounts of fibers sloughing from the tissue surface in-use. The present invention, however, overcomes these limitations to yield novel tissue webs that have improved softness, while maintaining sufficient strength.

Accordingly, in one aspect the disclosure provides a creped tissue web having a TS7 value less than about 8.0 dB $V^2$ rms.

In other aspects the disclosure provides a creped tissue web having a TS7 value less than about 8.0 dB $V^2$ rms and a TS750 value less than about 7.0 dB $V^2$ rms.

In yet other aspects the disclosure provides a creped tissue product comprising one or more plies, the tissue product having a geometric mean tensile (GMT) from greater than about 600 g/3" and a TS7 value of less than about 8 dB $V^2$ rms.

In still other aspects the disclosure provides a creped tissue web having a GMT from about 300 about 1000 g/3" and a TS7 value of less than about 8.0 dB $V^2$ rms.

In other aspects the disclosure provides a creped tissue web having a basis weight of greater than about 10 gsm and a TS7 value from about 4.0 to about 8.0 dB $V^2$ rms.

In still other aspects the present disclosure provides a multi-ply tissue product comprising two multi-layered creped tissue webs, the tissue webs having three superposed layers, an inner layer consisting essentially of softwood fibers and two outer layers consisting essentially of hardwood fibers, the inner layer being located between the two outer layers, wherein each web has a GMT greater than about 300 g/3" and a TS7 value of less than about 8.0 dB $V^2$ rms.

These and other features and aspects of the present disclosure are discussed in greater detail below.

## DEFINITIONS

As used herein, the terms "TS7" and "TS7 value" refer to an output of an EMTEC Tissue Softness Analyzer ("TSA") (Emtec Electronic GmbH, Leipzig, Germany) as described in the Test Methods section. The units of the TS7 value are dB $V^2$ rms, however, TS7 values are often referred to herein without reference to units.

As used herein, the terms "TS750" and "TS750 value" refer to another output of the TSA as described in the Test Methods section. The units of the TS750 value are dB $V^2$ rms, however, TS750 values are often referred to herein without reference to units.

As used herein, the term "geometric mean tensile" (GMT) refers to the square root of the product of the machine direction tensile and the cross-machine direction tensile of the web, which are determined as described in the Test Method section.

As used herein, the term "tissue product" refers to products made from tissue webs and includes, bath tissues, facial tissues, paper towels, industrial wipers, foodservice wipers, napkins, medical pads, and other similar products.

As used herein, the terms "tissue web" and "tissue sheet" refer to a fibrous sheet material suitable for use as a tissue product.

As used herein, the term "caliper" is the representative thickness of a single 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" with Note 3 for stacked sheets. 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. Caliper may be expressed in mils (0.001 inches) or microns.

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

## DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of TS7 values (x-axis) versus TS750 values (y-axis) for various inventive and commercial tissue samples;



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FIG. 2 is a plot of TS750 values (x-axis) versus GMT (y-axis) for various inventive and commercial tissue samples; and

FIG. 3 is a plot of TS7 values (x-axis) versus GMT (y-axis) for various inventive and commercial tissue samples.

## DETAILED DESCRIPTION

In general, the present disclosure is directed to creped tissue webs, and products produced therefrom. The creped tissue webs and tissue products made therefrom are soft and strong and as such generally have TS7 values less than about 8.0 and a geometric mean tensile ("GMT") greater than about 300 g/3" for single-ply tissue webs and greater than about 500 g/3" for multi-ply tissue products. In particularly preferred embodiments tissue produced according to the present disclosure also has a low TS750 value such as less than about 7.0. Further, while tissue prepared according to the present disclosure has low TS7, and in certain embodiments low TS750, it is also strong enough to withstand use. As such single-ply tissue webs prepared as disclosed herein preferably have a GMT greater than about 300 g/3", such as from about 400 to about 500 g/3".

Tissue webs and products having low TS7 and/or TS750 values may be prepared using a number of creped tissue making processes, such as conventional wet pressed (also referred to herein as "CTEC") and through-air dried (also referred to herein as "TAD"). Further, products having low TS7 and/or TS750 values may be prepared by post-treating the web by calendering or application of a topical additive such as a polysiloxane that makes a tissue product feel softer to the skin of a user. Suitable polysiloxanes that can be used in the present invention include amine, aldehyde, carboxylic acid, hydroxyl, alkoxyl, polyether, polyethylene oxide, and polypropylene oxide derivatized silicones, such as aminopolydialkylsiloxanes. When using an aminopolydialkysiloxane, the two alkyl radicals can be methyl groups, ethyl groups, and/or a straight, branched or cyclic carbon chain containing from about 3 to about 8 carbon atoms. Some commercially available examples of polysiloxanes include Y-14128, Y-14344, Y-14461 and FTS-226 (commercially available from Momentive Performance Materials, Albany, NY), and Dow Corning 8620, 2-8182, and 2-8194 (commercially available from Dow Corning Corporation, Midland, MI).



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When used, polysiloxanes may be combined with water and surfactants, such as nonionic ethoxylated alcohols, to form emulsions and applied to tissue webs. Since the process of the present invention can accommodate higher viscosities, however, the polysiloxanes can be added directly to a tissue web without having to be combined with water, a surfactant or any other dilution agent. For example, a neat composition, such as a neat polysiloxane can be applied to a web in accordance with the present disclosure.

Additionally, tissue webs and products having low TS7 and/or TS750 values may be prepared by applying a creping composition at high addition levels, such as greater than about 30 mg of solids per square meter of the creping surface, such as a Yankee Dryer. Still more preferably the creping composition is added to the creping surface at solids greater than about 50 mg/m$^2$, and even more preferably greater than about 100 mg/m$^2$, such as from about 50 to about 300 mg/m$^2$. The level of total solids add-on is preferably several times greater than traditional creping methods, which have typically employed add-on levels from about 2 to about 30 mg/m$^2$. Even at the increased add-on levels the present disclosure provides creping compositions that balance adhesion and release of the web from the Yankee Dryer, without the build-up of deposits of organic and/or inorganic components that can have a negative impact on creping efficiency.

When applied at high add-on levels to the Yankee Dryer, the creping compositions of the present disclosure develop proper coating equilibrium and a relatively constant Z-directional thickness of the coating on the dryer surface. When transferred to the web, the creping composition may form a continuous or a discontinuous film depending upon the additive composition and amount applied to the web. In other embodiments, the creping composition may be applied to a web such that the creping composition forms discrete treated areas on the surface of the web.

The thickness of the additive composition when present on the surface of a base sheet can vary depending upon the ingredients of the additive composition and the amount applied. In general, for instance, the thickness can vary from about 0.01 microns to about 10 microns. At higher add-on levels, for instance, the thickness may be from about 3 microns to about 8 microns. At lower add-on levels, however, the thickness may be from about 0.1 microns to about 1 micron, such as from about 0.3 microns to about 0.7 microns.

The area of the base sheet covered by the additive composition may vary from about 10 to about 100 percent of the surface area of one side of the base sheet. For instance,



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the additive composition may cover from about 20 to 100 percent of the surface area of the base sheet, such as from about 20 to about 90 percent, such as from about 20 to about 75 percent.

To achieve the desired creping efficiency and tissue product properties, tissue webs may be creped using a creping composition comprising at least one, and more preferably at least two, water-soluble polymers. For purposes herein, "water-soluble" means that the polymers dissolve completely in water to give a solution as opposed to a latex, dispersion, or suspension of undissolved particles.

In one embodiment the water-soluble polymer applied to the creping surface is an aqueous solution comprising a polyether, a polyamide, or a mixture of one or both with another water-soluble polymer. Suitable polyethers include (poly)ethylene oxide, (poly)propylene oxide, ethylene oxide/propylene oxide copolymers, (poly)tetra methylene oxide, poly vinyl methyl ether, and the like. Suitable polyamides include (poly)vinylpyrrolidone, (poly)ethyl oxazoline, (poly)amidoamine, (poly)acrylamide, polyethylene imine, and the like. Number average molecular weights for these components should be from about 10,000 to about 500,000.

Other water-soluble polymers which can be mixed with either of the water-soluble polymeric components used to form the creping composition include polyvinyl alcohol (PVOH), carboxymethylcellulose, hydroxypropyl cellulose, and the like.

In certain embodiments the creping composition may further comprise a polymeric component having an affinity for the fibers making up the web, such as a cationic polymer, and more specifically a cationic starch. As used herein the term "cationic starch" refers to a starch that has been chemically modified to impart a cationic constituent moiety. Suitable cationic polymers include cationic starches having a charge density of at least about 0.1 mEq/g, such as, for example, Redibond™ 2038 (Ingredion Incorporated, Westchester, IL) which has a charge density of about 0.22 mEq/g.

Particularly preferred cationic starches for use in the creping composition of the present disclosure are the tertiary aminoalkyl ethers and quaternary ammonium alkyl ethers, which include commercial cationic starches produced by Ingredion Incorporated, Westchester, IL, under the trade names Redibond™ and Optipro™. Grades with cationic

moieties only such as Redibond 5327™, Redibond 5330A™, and Optipro™ 650 are suitable, as are grades with additional anionic functionality such as Redibond 2038™.

The cationic component can be present in the creping composition in any operative amount and will vary based on the chemical component selected, as well as on the end properties that are desired. For example, in the exemplary case of Redibond 2038™, the cationic component can be present in the creping composition in an amount of about 10 to 90 wt %, such as 20 to 80 wt % or 30 to 70 wt % based on the total weight of the creping composition, to provide improved benefits.

Other suitable cationic components include cationic debonders and/or softeners. Cationic debonders and softeners are known in the papermaking art and are generally used as wet-end additives to enhance bulk and softness. Debonders are generally hydrophobic molecules that have a cationic charge. As wet end additives debonders function typically by disrupting inter-fiber bonding thereby increasing bulk and increasing perceived softness, but at the expense of a decrease in sheet strength. Softening agents are similar in chemistry to debonders, i.e., they are generally hydrophobic molecules that have a cationic charge. Examples of debonders and softening chemistries may include the simple quaternary ammonium salts having the general formula:

$$(R^{1'})_{4-b} - N^{+} - (R^{1''})_b\ X^{-}$$

wherein $R^{1'}$ is a $C_{1-6}$ alkyl group, $R^{1''}$ is a $C_{14-22}$ alkyl group, b is an integer from 1 to 3 and $X^{-}$ is any suitable counterion. Other similar compounds may include the monoester, diester, monoamide, and diamide derivatives of the simple quaternary ammonium salts. A number of variations on these quaternary ammonium compounds should be considered to fall within the scope of the present invention. Additional softening compositions include cationic oleyl imidazoline materials such as methyl-1-oleyl amidoethyl-2-oleyl imidazo linium methylsulfate commercially available as Mackernium CD-183 (McIntyre Ltd., University Park, IL) and Prosoft TQ-1003 (Ashland, Inc., Covington, KY).

In still other embodiments the creping composition comprises a water soluble cationic polyamide-epihalohydrin, which is the reaction product of an epihalohydrin and a polyamide containing secondary amine groups or tertiary amine groups. Commercially available preferred polyamide-epihalohydrins are sold under the trade names including Kymene™, Crepetrol™ and Rezosol™ (Ashland Water Technologies, Wilmington, DE).



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Compared to commercially available tissue, tissue products prepared according to the present disclosure generally have low TS7 values, such as less than about 8.0 and more preferably less than about 7.5, even more preferably less than about 7.0, and most preferably less than about 6.5, such as from about 4.0 to about 7.0. In other embodiments tissue products have low TS750 values, such as less than about 7.0, more preferably less than about 6.0, and still more preferably less than about 5.5, such as from about 4.0 to about 6.0. In other embodiments tissue products may have both a low TS7 value, such as less than about 8.0 and a low TS750 value, such as less than about 7.0, all while maintaining sufficient strength to withstand use, such as a GMT greater than about 400 g/3", such as from about 400 to about 1000 g/3".

Without wishing to be bound by theory, tissue webs and products produced therefrom are believed to achieve low TS7 and/or low TS750 values through the beneficial combination of improved tissue making methods and materials, such as, for example, high levels of low coarseness hardwood fibers, the addition of novel creping compositions at high add-on levels, the introduction of fine crepe structure to the creped tissue web and the post-treatment of the tissue web with calendering and/or topical treatment.

To illustrate the improvement over commercially available tissue, the table below compares inventive samples prepared as described herein with commercially available tissue.

TABLE 1

| | BW (gsm) | TS7 | TS750 | E (mm/N) | D (mm/N) |
|---|---|---|---|---|---|
| Kleenex● Ultra Facial Tissue | 25.7 | 9.4 | 6.8 | 3.58 | 3.67 |
| Kleenex● Lotion Facial Tissue | 27.9 | 9.0 | 7.1 | 3.54 | 3.69 |
| Kleenex● Anti-Viral Facial Tissue | 45.5 | 9.1 | 6.8 | 3.09 | 3.27 |
| Puffs Ultra Strong and Soft● Facial Tissue | 36.9 | 8.8 | 7.7 | 3.05 | 3.18 |
| Puffs Plus● Facial Tissue | 46.4 | 8.6 | 5.4 | 3.18 | 3.33 |
| Puffs Plus Lotion● Facial Tissue | 46.5 | 9.8 | 8.1 | 3.28 | 3.44 |
| Von's Ultra● Facial Tissue | 44.8 | 8.6 | 6.7 | 2.82 | 2.98 |
| Kroger Nice & Soft with Lotion | 46.2 | 9.3 | 7.0 | 3.11 | 3.32 |
| ShopRite Ultra Facial Tissue | 46.6 | 9.4 | 9.4 | 3.08 | 3.27 |
| Up&Up™ Ultra Facial Tissue | 46.4 | 8.2 | 7.0 | 3.45 | 3.65 |

| | | | | | |
|---|---|---|---|---|---|
| Up&Up™ Facial Tissue | 31.2 | 11.4 | 9.2 | 3.22 | 3.32 |
| Scotties® Facial Tissue | 31.2 | 12.0 | 12.1 | 2.84 | 2.92 |
| Publix ® Facial Tissue | 32.2 | 12.9 | 7.5 | 3.38 | 3.47 |
| Walgreens® Facial Tissue | 27.8 | 10.2 | 8.5 | 3.23 | 3.36 |
| Puffs® Facial Tissue | 29.6 | 10.6 | 6.2 | 3.43 | 3.53 |
| Kleenex® Facial Tissue | 28.4 | 9.8 | 8.3 | 3.27 | 3.40 |
| Inventive CTEC Sample | 29.6 | 7.6 | 6.0 | 2.7 | 3.2 |
| Inventive CTAD Sample | 29.8 | 4.1 | 5.3 | 2.68 | 3.36 |

The basis weight of tissue webs made in accordance with the present disclosure can vary depending upon the final product. For example, the process may be used to produce bath tissues, facial tissues, paper towels, and the like. In general, the basis weight of such fibrous products may vary from about 5 grams per square meter (gsm) to about 110 gsm, such as from about 10 gsm to about 90 gsm. For bath tissue and facial tissues products, for instance, the basis weight of the product may range from about 10 gsm to about 40 gsm.

Likewise, tissue web basis weight may also vary, such as from about 5 gsm to about 50 gsm, more preferably from about 10 gsm to about 30 gsm and still more preferably from about 14 gsm to about 20 gsm.

In multiple-ply products, the basis weight of each web present in the product can also vary. In general, the total basis weight of a multiple ply product will generally be from about 10 gsm to about 100 gsm. Thus, the basis weight of each ply can be from about 10 gsm to about 60 gsm, such as from about 20 gsm to about 40 gsm.

Tissue webs and products produced according to the present disclosure also have good bulk characteristics. For instance, bulk may vary from about 4 to about 15 $cm^3/g$, such as from about 5 to about 12 $cm^3/g$ or from about 6 to about 10 $cm^3/g$.

In addition to having good bulk, tissue webs and products prepared according to the present disclosure have improved softness and surface smoothness. For example, tissue webs prepared according to the present disclosure have TS7 values less than about 8.0, such as from about 5.0 to about 7.0 and in certain embodiments a TS750 value less than about 7.0, such as from about 4.0 to about 6.0. In a particularly preferred embodiment the present disclosure provides a tissue product comprising at least one creped tissue web having a basis weight of at least about 12 gsm, a GMT of at least about 300 g/3" and a TS7 value from about 5.0 to about 8.0.

Moreover, the low TS7 and/or TS750 values are achieved at relatively modest geometric mean tensile strengths. For example, tissue products prepared according to the

present disclosure have geometric mean tensile strengths of less than about 1000 g/3″, and more preferably less than about 900 g/3", such as from about 400 to about 1000 g/3".

In general, any suitable tissue web may be treated in accordance with the present disclosure. The tissue webs may then be converted into various tissue products, such as bath tissue, facial tissue, paper towels, napkins, and the like. Tissue products made according to the present disclosure may include single-ply or multiple-ply tissue products. For instance, in some aspects, the product may include two plies, three plies, or more.

Fibers suitable for making tissue webs comprise any natural or synthetic fibers including both nonwoody fibers and woody or pulp fibers. Pulp fibers can be prepared in high-yield or low-yield forms and can be pulped in any known method, including kraft, sulfite, high-yield pulping methods and other known pulping methods. Fibers prepared from organosolv pulping methods can also be used, including the fibers and methods disclosed in US Patent Nos. 4,793,898, 4,594,130, and 3,585,104. Useful fibers can also be produced by anthraquinone pulping, exemplified by US Patent No. 5,595,628.

Chemically treated natural cellulosic fibers can be used, for example, mercerized pulps, chemically stiffened or crosslinked fibers, or sulfonated fibers. For good mechanical properties in using web forming fibers, it can be desirable that the fibers be relatively undamaged and largely unrefined or only lightly refined. While recycled fibers can be used, virgin fibers are generally useful for their mechanical properties and lack of contaminants. Mercerized fibers, regenerated cellulosic fibers, cellulose produced by microbes, rayon, and other cellulosic material or cellulosic derivatives can be used. Suitable web forming fibers can also include recycled fibers, virgin fibers, or mixes thereof.

In general, any process capable of forming a web can also be utilized in the present disclosure. For example, a web forming process of the present disclosure can utilize creping, wet creping, double creping, recreping, double recreping, embossing, wet pressing, air pressing, through-air drying, hydroentangling, creped through-air drying, co-forming, airlaying, as well as other processes known in the art. For hydroentangled material, the percentage of pulp is about 70 to 85 percent and the balance of fiber is synthetic.

Also suitable for articles of the present disclosure are fibrous sheets that are pattern densified or imprinted, such as the fibrous sheets disclosed in any of the following



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US Patent Nos. 4,514,345, 4,528,239, 5,098,522, 5,260,171, and 5,624,790, the disclosures of which are incorporated herein by reference to the extent they are non-contradictory herewith. Such imprinted fibrous sheets may have a network of densified regions that have been imprinted against a drum dryer by an imprinting fabric, and regions that are relatively less densified (e.g., "domes" in the fibrous sheet) corresponding to deflection conduits in the imprinting fabric, wherein the fibrous sheet superposed over the deflection conduits was deflected by an air pressure differential across the deflection conduit to form a lower-density pillow-like region or dome in the fibrous sheet.

Further, while webs having desired softness and strength may be produced without the use of chemical debonders to reduce the amount of fiber-fiber bonding within the web, in certain embodiments the fiber furnish used to form the base web may be treated with a chemical debonding agent. The debonding agent can be added to the fiber slurry during the pulping process or can be added directly to the headbox. Suitable debonding agents that may be used in the present disclosure include cationic debonding agents such as fatty dialkyl quaternary amine salts, mono fatty alkyl tertiary amine salts, primary amine salts, imidazoline quaternary salts, silicone, quaternary salt and unsaturated fatty alkyl amine salts. Other suitable debonding agents are disclosed in US Patent No. 5,529,665, which is incorporated herein by reference in a manner consistent herewith.

While the creped webs of the present disclosure achieve low TS7 values and/or TS750 values without post treatment, the webs may, in certain embodiments, be post treated to provide additional benefits. The types of chemicals that may be added to the web may include topical additive such as a polysiloxane that makes a tissue product feel softer to the skin of a user. Suitable polysiloxanes that can be used in the present invention include amine, aldehyde, carboxylic acid, hydroxyl, alkoxyl, polyether, polyethylene oxide, and polypropylene oxide derivatized silicones, such as aminopolydialkylsiloxanes. Other suitable additives may include compositions that supply skin health benefits such as mineral oil, aloe extract, vitamin-E, silicone, lotions in general, and the like. Such chemicals may be added at any point in the web forming process.

Tissue webs that may be treated in accordance with the present disclosure may include a single homogenous layer of fibers or may include a stratified or layered construction. For instance, the tissue web ply may include two or three layers of fibers. Each layer may have a different fiber composition. For example a three-layered headbox

generally includes an upper head box wall and a lower head box wall. Headbox further includes a first divider and a second divider, which separate three fiber stock layers.

Each of the fiber layers comprises a dilute aqueous suspension of papermaking fibers. The particular fibers contained in each layer generally depend upon the product being formed and the desired results. For instance, the fiber composition of each layer may vary depending upon whether a bath tissue product, facial tissue product or paper towel is being produced. In one aspect, for instance, the middle layer contains southern softwood kraft fibers either alone or in combination with other fibers such as high yield fibers. Outer layers, on the other hand, contain softwood fibers, such as northern softwood kraft. In an alternative aspect, the middle layer may contain softwood fibers for strength, while the outer layers may comprise hardwood fibers, such as eucalyptus fibers.

In general, any process capable of forming a base sheet may be utilized in the present disclosure. For example, an endless traveling forming fabric, suitably supported and driven by rolls, receives the layered papermaking stock issuing from the headbox. Once retained on the fabric, the layered fiber suspension passes water through the fabric. Water removal is achieved by combinations of gravity, centrifugal force and vacuum suction depending on the forming configuration. Forming multi-layered paper webs is also described and disclosed in US Patent No. 5,129,988, which is incorporated herein by reference in a manner that is consistent herewith.

Preferably the formed web is dried by transfer to the surface of a rotatable heated dryer drum, such as a Yankee dryer. In accordance with the present disclosure, the creping composition 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. Creping the 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 addition to applying the creping composition during formation of the tissue web, the creping composition may also be used in post-forming processes. For example, in one aspect, the creping composition may be used during a print-creping process. Specifically, once topically applied to a tissue web, the creping composition has been found well-suited to adhering the tissue web to a creping surface, such as in a print-creping operation.

Tissue webs made according to the present disclosure can be incorporated into multiple-ply products. For instance, in one aspect, a tissue web made according to the present disclosure can be attached to one or more other tissue webs for forming a wiping product having desired characteristics. The other webs laminated to the tissue web of the present disclosure can be, for instance, a wet-creped web, a calendered web, an embossed web, a through-air dried web, a creped through-air dried web, an uncreped through-air dried web, an airlaid web, and the like.

In certain embodiments, when incorporating a tissue web made according to the present disclosure into a multiple-ply product, it may be desirable to only apply the creping composition to one side of the tissue web and to thereafter crepe the treated side of the web. The creped side of the web is then used to form an exterior surface of a multiple-ply product. The untreated and uncreped side of the web, on the other hand, is attached by any suitable means to one or more plies.

## TEST METHODS

TS7 and TS750 Values

TS7 and TS750 values were measured using an EMTEC Tissue Softness Analyzer ("TSA") (Emtec Electronic GmbH, Leipzig, Germany). The TSA comprises a rotor with vertical blades which rotate on the test piece applying a defined contact pressure. Contact

between the vertical blades and the test piece creates vibrations, which are sensed by a vibration sensor. The sensor then transmits a signal to a PC for processing and display. The signal is displayed as a frequency spectrum. For measurement of TS7 and TS750 values the blades are pressed against sample with a load of 100 mN and the rotational speed of the blades is 2 revolutions per second.

To measure TS7 and TS750 values two different frequency analyses are performed. The first frequency analysis is performed in the range of approximately 200 Hz to 1000 Hz, with the amplitude of the peak occurring at 750 Hz being recorded as the TS750 value. The TS750 value represents the surface smoothness of the sample. A high amplitude peak correlates to a rougher surface. A second frequency analysis is performed in the range from 1 to 10 kHZ, with the amplitude of the peak occurring at 7 kHz being recorded as the TS7 value. The TS7 value represents the softness of sample. A lower amplitude correlates to a softer sample. Both TS750 and TS7 values have the units dB $V^2$ rms.

To measure the stiffness properties of the test sample, the rotor is initially loaded against the sample to a load of 100 mN. Then, the rotor is gradually loaded further until the load reaches 600 mN. As the sample is loaded the instrument records sample displacement (μm) versus load (mN) and outputs a curve over the range of 100 to 600 mN. The modulus value "E" is reported as the slope of the displacement versus loading curve for this first loading cycle, with units of mm displacement /N of loading force. After the first loading cycle from 100 to 600 mN is completed, the instrument reduces the load back to 100 mN and then increases the load again to 600 mN for a second loading cycle. The slope of the displacement versus loading curve from the second loading cycle is called the "D" modulus value.

Test samples were prepared by cutting a circular sample having a diameter of 112.8 mm. All samples were allowed to equilibrate at TAPPI standard temperature and humidity conditions for at least 24 hours prior to completing the TSA testing. Only one ply of tissue is tested. Multi-ply samples are separated into individual plies for testing. The sample is placed in the TSA with the softer (dryer or Yankee) side of the sample facing upward. The sample is secured and the measurements are started via the PC. The PC records, processes and stores all of the data according to standard TSA protocol. The reported values are the average of five replicates, each one with a new sample.



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Tensile

Samples for tensile strength testing are prepared by cutting a 3 inches (76.2 mm) x 5 inches (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 4±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 inches (76.2 mm), and the approximate height of a jaw is 0.5 inches (12.7 mm). The crosshead speed is 10±0.04 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.

For multiple-ply products tensile testing is done on the number of plies expected in the finished product. For example, 2-ply products are tested two plies at one time and the recorded MD and CD tensile strengths are the strengths of both plies.

## EXAMPLES

Example 1: Soft Creped Wet Pressed Tissue

Samples were made using a conventional wet pressed tissue-making process on a pilot scale tissue machine. Initially, northern softwood kraft (NSWK) pulp (Pictou Harmony Pulp, Northern Pulp, Nova Scotia, Canada) was dispersed in a pulper for 30 minutes at about 1.6 percent consistency at about 100°F. The NSWK pulp was refined in a batch refiner for about 4 minutes to a Canadian Standard Freeness (CSF) value of about 500 ml. The NSWK pulp was then transferred to a dump chest and subsequently diluted

with water to approximately 0.6 percent consistency. Softwood fibers were then pumped to a machine chest where they were further diluted with water to a consistency of about 0.3 percent and mixed with 2 kg/MT of Kymene● 920A on a dry-solids basis (Ashland Water Technologies, Wilmington, DE) prior to the headbox. The softwood fibers were added to the middle layer in the 3-layer tissue structure. The NSWK content contributed approximately 10 to 20 percent of the final sheet weight. The specific layer splits (dryer layer / middle layer / felt layer) are as set forth in Table 2.

Eucalyptus hardwood kraft (EHWK) pulp (Fibria Veracel pulp, Fibria, Sao Paulo, Brazil) was dispersed in a pulper for 30 minutes at about 1.6 percent consistency at about 100°F. The EHWK pulp was then transferred to a dump chest and diluted to about 0.6 percent consistency. The EHWK pulp was then pumped to a machine chest where they were further diluted with water to a consistency of about 0.15 percent and mixed with 2kg/MT of Kymene● 920A. These fibers were added to the dryer and felt layers of the 3-layer sheet structure and contributed approximately 80 to 90 percent of the final sheet weight. The specific layer splits (dryer layer / middle layer / felt layer) are as set forth in Table 2.

Debonder (ProSoft™ TQ-1003, Ashland, Inc., Covington, KY) was added to the machine chest supplying EHWK pulp to the dryer side of the three layered tissue structure. The amount of debonder added varied from 4 pounds per ton of fiber to 12 pounds of debonder per ton of EHWK pulp, depending on the sample (see Table 2 for details).

The pulp fibers from the machine chests were pumped to the headbox at a consistency of about 0.02 percent. Pulp fibers from each machine chest were sent through separate manifolds in the headbox to create a 3-layered tissue structure. The fibers were deposited onto a TissueForm V forming fabric (Voith Paper Fabrics, Wilson, NC) in an inclined fourdrenier type of former.

The wet sheet from the forming fabric, at about 10 to 20 percent consistency, was vacuum dewatered and then transferred to a Superfine Duramesh press felt (Albany International Corp., Rochester, NH). The wet tissue sheet, supported by the press felt, was passed through the nip of a pressure roll, in order to partially dewater the sheet to a consistency of about 40 percent. The wet sheet was then adhered the Yankee dryer by spraying the creping composition onto the dryer surface using a spray boom situated underneath the dryer.

TABLE 2

| Sample | Debonder Addition (lb/MT) | Layer Splits (%HW/%SW/%HW) |
|---|---|---|
| 1 | 0 | 50 / 20 / 30 |
| 2 | 4 | 50 / 20 / 30 |
| 3 | 0 | 50 / 20 / 30 |
| 4 | 0 | 50 / 20 / 30 |
| 5 | 4 | 50 / 20 / 30 |
| 6 | 6 | 50 / 20 / 30 |
| 7 | 12 | 50 / 20 / 30 |
| 8 | 0 | 60 / 10 / 30 |
| 9 | 8 | 60 / 10 / 30 |
| 10 | 0 | 60 / 10 / 30 |
| 11 | 12 | 60 / 10 / 30 |
| 12 | 12 | 60 / 10 / 30 |

The creping compositions generally comprised a mixture of PerForm● PC 1279 (Ashland, Inc., Covington, KY), ProSoft™ TQ-1003 (Ashland, Inc., Covington, KY) and Redibond● 2038A (Ingredion Incorporated, Westchester, IL) or a mixture of poly(ethylene oxide) (commercially available as Polyox™ N80 from Dow Chemical, Midland, MI) and polyvinyl alcohol (Celvol 523 from Celanese, Houston TX) . The creping compositions used to produce each of the samples is detailed in Table 3.

Creping compositions were prepared by dissolution of the solid polymers into water followed by stirring until the solution was homogeneous. Individual polymers were diluted depending on the desired spray coverage on the Yankee dryer. Alternatively, flow rates of the polymer solutions were varied to provide the desired amount of solids to the base web. The sheet was dried to about 98 to 99 percent consistency as it traveled on the Yankee dryer and to the creping blade. The Yankee dryer was heated with 30 to 35 psi of steam pressure to dry the sheet to a target sheet temperature of 240°F before the creping blade. The Yankee dryer was traveling at about 60 FPM, unless otherwise noted. The creping blade, an 80-Proto-HY02 Durablade● (BTG, Eclépens, Switzerland) with a 10 to 15 degree grind angle, was loaded at a pressure of 30 psig. The creping blade subsequently scraped the tissue sheet off of the Yankee dryer. The creped tissue base sheet was then wound onto a core traveling at about 47 to about 52 FPM into soft rolls for converting. The basis weight of the resulting tissue was about 14 gsm and the GMT ranged from about 300 to about 450 g/3".



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The soft rolls were then either converted directly to tissue product by rewinding and plying so that both creped sides were on the outside of a 2-ply tissue product, or subject to post treatment. In the event that soft rolls were post treated, they were either calendered or treated with silicone (see Tables 3 and 4 for details). The calendering was between two steel rolls with a nip loading of 50 psi. Silicone treatment was completed by applying 1 percent (by dry weight) of Momentive Y-14868 silicone emulsion (commercially available from Momentive Performance Materials, Albany, NY) using rotogravure printing on the outside surface of each of the two plies.



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TABLE 3

| | Creping Composition | | | | |
|---|---|---|---|---|---|
| Sample | Component 1 (wt %) | Component 2 (wt %) | Component 3 (wt %) | Creping composition Add-on ($mg/m^2$) | Post Treatment |
| 1C | Redibond 2038A (65%) | TQ-1003 (35%) | - | 300 | Calendered |
| 1S | Redibond 2038A (65%) | TQ-1003 (35%) | - | 300 | Silicone |
| 2C | Redibond 2038A (65%) | TQ-1003 (35%) | - | 300 | Calendered |
| 2S | Redibond 2038A (65%) | TQ-1003 (35%) | - | 300 | Silicone |
| 3S | Redibond 2038A (75%) | TQ-1003 (25%) | - | 300 | Silicone |
| 4S | Redibond 2038A (75%) | TQ-1003 (25%) | - | 300 | Silicone |
| 5S | PVOH (80%) | Polyox (20%) | - | 300 | Silicone |
| 6S | PVOH (80%) | Polyox (20%) | - | 300 | Silicone |
| 7S | PVOH (80%) | Polyox (20%) | - | 300 | Silicone |
| 8S | PVOH (90%) | Polyox (10%) | - | 300 | Silicone |
| 9C | Redibond (30%) | PC1279 (40%) | TQ-1003 (30%) | 300 | Calendered |
| 9S | Redibond (30%) | PC1279 (40%) | TQ-1003 (30%) | 300 | Silicone |
| 10C | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 10S | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Silicone |
| 11C | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 11 | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | - |
| 12 | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | - |
| 12S | Redibond (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Silicone |



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Table 4

| Sample | TS7 | TS750 | E (mm/N) | D (mm/N) | Single Sheet Caliper (μm) | 2-ply BW (gsm) | Bulk ($cm^3/g$) |
|---|---|---|---|---|---|---|---|
| 1C | 7.2 | 6.6 | 3.0 | 3.8 | 143 | 26.9 | 5.32 |
| 1S | 7.0 | 7.4 | 3.1 | 3.9 | 132 | 27.3 | 4.83 |
| 2C | 7.1 | 7.2 | 3.0 | 3.8 | 134 | 26.5 | 5.05 |
| 2S | 6.9 | 7.7 | 3.0 | 3.9 | 138 | 27.0 | 5.10 |
| 3S | 7.5 | 7.0 | 3.0 | 3.7 | 143 | 27.5 | 5.21 |
| 4S | 7.5 | 6.4 | 2.9 | 3.5 | 133 | 27.2 | 4.88 |
| 5S | 7.3 | 6.0 | 2.7 | 3.2 | 125 | 29.1 | 4.29 |
| 6S | 7.6 | 4.2 | 2.7 | 3.3 | 128 | 29.6 | 4.33 |
| 7S | 7.6 | 5.6 | 3.2 | 4.0 | 140 | 28.6 | 4.90 |
| 8S | 6.8 | 4.8 | 3.0 | 4.2 | 121 | 25.6 | 4.72 |
| 9C | 7.0 | 8.1 | 3.1 | 4.0 | 199 | 35.6 | 5.59 |
| 9S | 6.8 | 6.2 | 3.0 | 4.3 | 191 | 36.6 | 5.21 |
| 10C | 7.5 | 9.2 | 2.9 | 3.4 | 156 | 27.5 | 5.68 |
| 10S | 7.1 | 11.0 | 2.9 | 3.3 | 152 | 27.1 | 5.62 |
| 11C | 6.7 | 11.3 | 3.7 | 4.2 | 159 | 27.3 | 5.82 |
| 11 | 6.6 | 12.1 | 3.0 | 3.8 | 220 | 27.5 | 8.00 |
| 12 | 6.5 | 12.2 | 3.5 | 4.1 | 227 | 40.5 | 5.60 |
| 12S | 6.9 | 11.5 | 2.9 | 3.8 | 194 | 38.4 | 5.05 |

Example 2: Soft Creped Through-Air Dried Tissue

Additional inventive samples were made using a papermaking process commonly referred to as creped through-air-dried ("CTAD") in which the web is formed using a through-air dried tissue making process and creped after final drying.

Initially, northern softwood kraft (NSWK) pulp (Pictou Harmony Pulp, Northern Pulp, Nova Scotia, Canada) was dispersed in a pulper for 30 minutes at about 1.6 percent consistency at about 100°F. The NSWK pulp was refined in a batch refiner for about 4 minutes to a Canadian Standard Freeness (CSF) value of about 500 ml. The NSWK pulp was then transferred to a dump chest and subsequently diluted with water to approximately 0.6 percent consistency. Softwood fibers were then pumped to a machine chest where they were further diluted with water to a consistency of about 0.3 percent and mixed with 2 kg/MT of Kymene● 920A on a dry-solids basis (Ashland Water Technologies, Wilmington, DE) and 1 kg/MT of Baystrength 3000 (Kemira, Atlanta, GA) prior to the headbox. The softwood fibers were added to the middle layer in the 3-layer tissue structure.

The NSWK content contributed approximately 30 percent of the final sheet weight. The specific layer splits (dryer layer / middle layer / felt layer) are as set forth in Table 5.

Eucalyptus hardwood kraft (EHWK) pulp (Fibria Veracel pulp, Fibria, Sao Paulo, Brazil) was dispersed in a pulper for 30 minutes at about 2.3 percent consistency at about 100°F. The EHWK pulp was then transferred to a dump chest and diluted to about 1.0 percent consistency. The EHWK pulp was then pumped to a machine chest where they were further diluted with water to a consistency of about 0.22 percent and mixed with 2kg/MT of Kymene● 920A. These fibers were added to the dryer and felt layers of the 3-layer sheet structure and contributed to approximately 70 percent of the final sheet weight. The specific layer splits (dryer layer / middle layer / felt layer) are as set forth in Table 5.

Debonder (ProSoft™ TQ-1003, Ashland, Inc., Covington, KY) was added to the machine chest supplying EHWK pulp to the dryer side of the three layered tissue structure. The amount of debonder added varied from 4 pounds per ton of fiber to 12 pounds of debonder per ton of EHWK pulp, depending on the sample (see Table 5 for details).

The pulp fibers from the machine chests were pumped to the headbox at a consistency of about 0.02 percent. Pulp fibers from each machine chest were sent through separate manifolds in the headbox to create a 3-layered tissue structure. The web was formed on a TissueForm V forming fabric (Voith Paper fabrics, Wilson, NC), transferred to a Voith 2164 fabric (Voith Paper fabrics, Wilson, NC) and vacuum dewatered to roughly 25 percent consistency. The web was then transferred to a Voith Saturn 852 fabric (Voith Paper fabrics, Wilson, NC) for the TAD fabric. No rush transfer was utilized at the transfer to the TAD fabric. After the web was transferred to the TAD fabric, the web was dried, however the consistency was maintained low enough to allow significant molding when the web was transferred using high vacuum to the impression fabric. A vacuum level of at least 10 inches of mercury was used for the transfer to the impression fabric in order to mold the web as much as possible into the fabric. Two different impression fabrics were used, as shown in Table 5 – either a Voith Saturn 852 fabric (Voith Paper fabrics, Wilson, NC) with the long shute (LS) knuckles toward the sheet or a Voith Saturn 952 fabric (Voith Paper fabrics, Wilson, NC) with the long warp (LW) knuckles toward the sheet. The web was then transferred to a Yankee dryer and creped. Minimum pressure was used at the web



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transfer to minimize compaction of the web during the transfer to the Yankee dryer so as to maintain maximum web caliper.

TABLE 5

| Sample | Debonder (lb/MT) | Layer Splits (%HW/%SW/%HW) | Refining (min) | Impression Fabric |
|---|---|---|---|---|
| 13 | 0 | 35 / 30 /35 | 5 | Saturn 852 - LS |
| 14 | 0 | 35 / 30 /35 | 4 | Saturn 852 - LS |
| 15 | 6 | 35 / 30 /35 | 4 | Saturn 852 - LS |
| 16 | 0 | 35 / 30 /35 | 4 | Saturn 852 - LS |
| 17 | 0 | 35 / 30 /35 | 4 | Saturn 852 - LS |
| 18 | 0 | 35 / 30 /35 | 3 | Saturn 852 - LS |
| 19 | 0 | 35 / 30 /35 | 3 | Saturn 852 - LS |
| 20 | 0 | 35 / 30 /35 | 3 | Saturn 852 - LS |
| 21 | 12 | 35 / 30 /35 | 3 | Saturn 852 - LS |
| 22 | 4 | 35 / 30 /35 | 3 | Saturn 952 - LW |
| 23 | 4 | 35 / 30 /35 | 3 | Saturn 952 - LW |

The web was adhered to the Yankee dryer using one of the creping compositions specified in Table 6, below. The creping compositions were prepared by dissolution of the solid polymers into water followed by stirring until the solution was homogeneous. Individual polymers were diluted depending on the desired spray coverage on the Yankee dryer. Alternatively, flow rates of the polymer solutions were varied to provide the desired amount of solids to the base web. The sheet was dried to about 98 to 99 percent consistency as it traveled on the Yankee dryer and to the creping blade. The Yankee dryer was heated with 30 to 35 psi of steam to dry the sheet to a target sheet temperature of 240°F, as measured above the creping blade. The Yankee dryer was traveling at about 60 FPM, unless otherwise noted. The creping blade, an 80-Proto-HY02 Durablade● (BTG, Eclépens, Switzerland) with a 10 to 15 degree grind angle, was loaded at a pressure of 30 psig. The creping blade subsequently scraped the tissue sheet off of the Yankee dryer. The creped tissue basesheet was then wound onto a core traveling at about 47 to about 52 FPM into soft rolls for converting. The basis weight of the resulting tissue was about 14 gsm and the GMT ranged from about 300 to about 450 g/3".



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TABLE 6

| Sample | Component 1 (wt %) | Component 2 (wt %) | Component 3 (wt %) | Creping composition Add-on ($mg/m^2$) | Post Treatment |
|---|---|---|---|---|---|
| 13C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Calendered |
| 14C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Calendered |
| 14S | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Silicone |
| 15C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Calendered |
| 16C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 60 | Calendered |
| 17C | Redibond 2038A (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 17S | Redibond 2038A (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Silicone |
| 18C | Redibond 2038A (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 19C | Redibond 2038A (40%) | PC1279 (40%) | TQ-1003 (20%) | 300 | Calendered |
| 20C | PVOH (80%) | N80 Polyox (20%) | - | 200 | Calendered |
| 20S | PVOH (80%) | N80 Polyox (20%) | - | 200 | Silicone |
| 21C | PVOH (80%) | N80 Polyox (20%) | - | 200 | Calendered |
| 21S | PVOH (80%) | N80 Polyox (20%) | - | 200 | Silicone |
| 22C | PVOH (91.7%) | Kymene 920A (7.6%) | Rezesol 2008M (0.7%) | 40 | Calendered |
| 23C | PVOH (80%) | N80 Polyox (20%) | - | 200 | Calendered |

The soft rolls were then either converted directly to tissue product by rewinding and plying so that both creped sides were on the outside of a 2-ply tissue product, or subject to post treatment. In the event that soft rolls were post treated, they were either calendered or treated with silicone (see Tables 3 and 4 for details). The calendering was between two steel rolls with a nip loading of 50 psi. Silicone treatment was done by applying 1 percent (bone dry weight) of Momentive Y-14868 silicone emulsion (commercially available from



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Momentive Performance Materials, Albany, NY) using rotogravure printing on the outside surface of each of the two plies.

TABLE 7

| Sample | GMT (g/3") | TS7 | TS750 | E (mm/N) | D (mm/N) |
|---|---|---|---|---|---|
| 13C | 894 | 5.7 | 6.5 | 2.71 | 3.07 |
| 14C | 735 | 5.3 | 5.7 | 2.74 | 3.10 |
| 14S | 735 | 5.2 | 5.6 | 2.98 | 3.38 |
| 15C | 651 | 4.1 | 5.3 | 2.68 | 3.36 |
| 16C | 777 | 6.2 | 6.7 | 2.31 | 2.75 |
| 17C | 851 | 4.9 | 6.4 | 2.25 | 2.61 |
| 17S | 851 | 5.4 | 5.7 | 2.43 | 2.87 |
| 18C | 916 | 4.6 | 5.7 | 2.18 | 2.71 |
| 19C | 936 | 5.9 | 5.9 | 2.15 | 2.48 |
| 20C | 999 | 6.4 | 6.3 | 2.02 | 2.35 |
| 20S | 999 | 5.4 | 5.5 | 2.21 | 2.54 |
| 21C | 530 | 4.4 | 5.7 | 2.31 | 2.88 |
| 21S | 530 | 4.3 | 5.5 | 2.62 | 3.31 |
| 22C | 680 | 6.6 | 6.4 | 2.42 | 2.76 |
| 23C | 587 | 6.0 | 5.3 | 2.65 | 3.08 |

These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.



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We claim:

1. A creped tissue web having a TS7 value less than about 8.0 dB $V^2$ rms.

2. The creped tissue web of claim 1 having a TS750 value less than about 8.0 dB $V^2$ rms.

3. The creped tissue web of claims 1 or 2 having a TS750 value from about 4.0 to about 7.0 dB $V^2$ rms.

4. The creped tissue web of anyone of the foregoing claims wherein the TS7 value is less than about 7 dB $V^2$ rms.

5. The creped tissue web of anyone of the foregoing claims wherein the TS7 value is from about 4 to about 8 dB $V^2$ rms.

6. The creped tissue web of anyone of the foregoing claims wherein the basis weight of the web is at least about 10 gsm.

7. The creped tissue web of anyone of the foregoing claims wherein the basis weight is from about 10 to about 16 gsm.

8. The creped tissue web of anyone of the foregoing claims wherein the web has a GMT of at least about 300 g/3".

9. The creped tissue web of anyone of the foregoing claims wherein the web has a GMT from about 300 to about 500 g/3".

10. A creped multi-ply tissue product having a TS7 value less than about 8.0 dB $V^2$ rms.

11. The creped multi-ply tissue product of claim 10 having a TS750 value less than about 8.0 dB $V^2$ rms.

12. The creped multi-ply tissue product of claims 10 or 11 having a TS750 value from about 4.0 to about 7.0 dB $V^2$ rms.



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13. The creped multi-ply tissue product of anyone of claims 10 through 12 wherein the TS7 value is less than about 7 dB $V^2$ rms.

14. The creped multi-ply tissue product of anyone of claims 10 through 13 wherein the TS7 value is from about 4 to about 8 dB $V^2$ rms.

15. The creped multi-ply tissue product of anyone of claims 10 through 14 wherein the basis weight of the product is at least about 25 gsm.

16. The creped multi-ply tissue product of anyone of claims 10 through 15 wherein the basis weight of the product is from about 25 to about 32 gsm.

17. The creped multi-ply tissue product of anyone of claims 10 through 16 wherein the product has a GMT of at least about 600 g/3".

18. The creped multi-ply tissue product of anyone of claims 10 through 17 wherein the product has a GMT from about 600 to about 1000 g/3".

19. A creped multi-ply tissue product comprising at least one ply which comprises a creped tissue web having a first and second side, wherein a water-soluble creping composition selected from the group consisting of a polyether, a polyamide, a polyvinyl alcohol, a cationic starch, and a cationic polyamide-epihalohydrin, is disposed on at least the first or second side and the at least one ply has a TS7 value less than about 8.0 dB $V^2$ rms and a TS750 value less than about 7.0 dB $V^2$ rms.

20. The creped multi-ply tissue product of claim 19 wherein the product has a basis weight of at least about 20 gsm and GMT of at least about 600 g/3".



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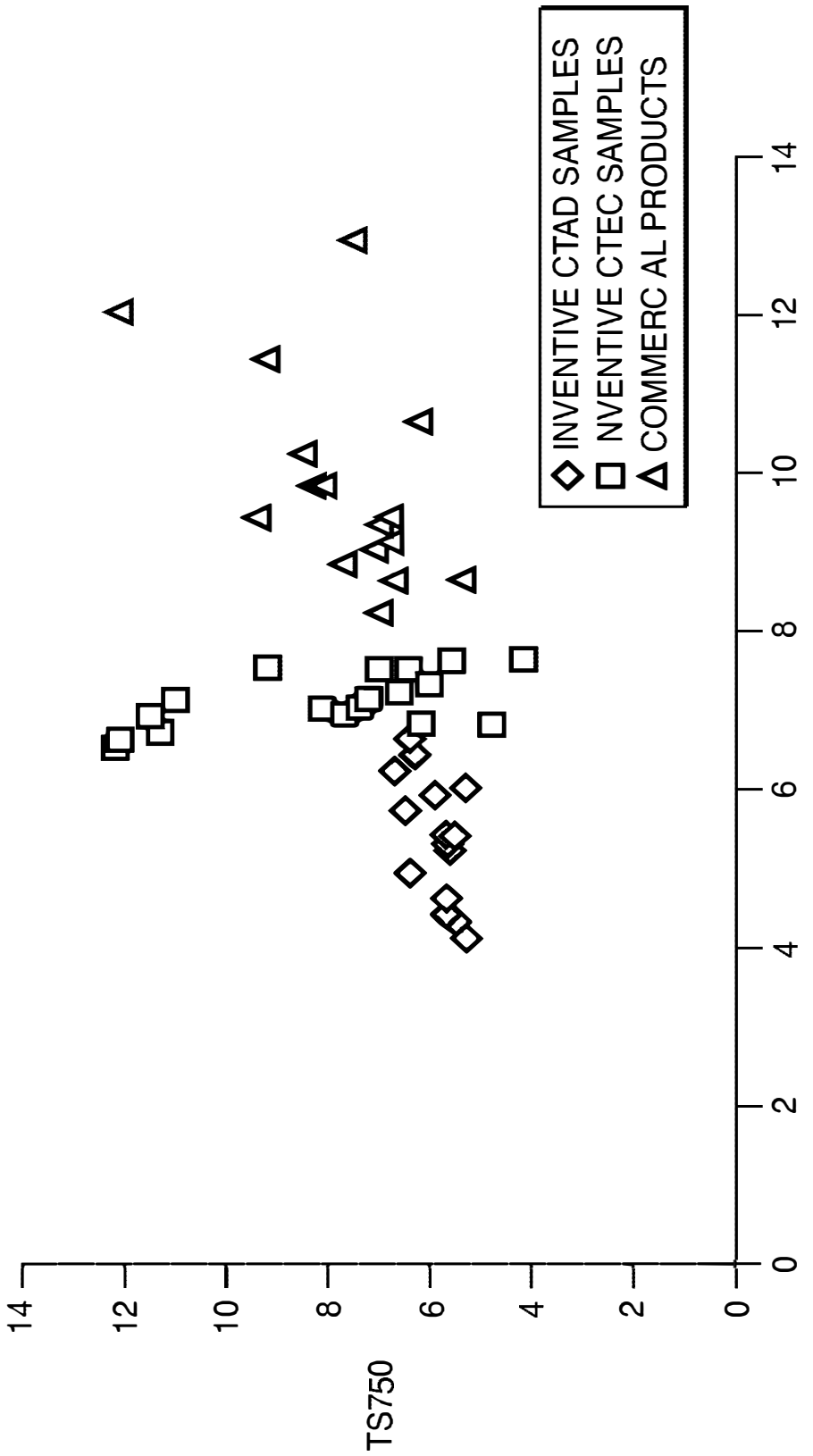

INVENTIVE CTAD SAMPLES
NVENTIVE CTEC SAMPLES
COMMERC AL PRODUCTS
TS750
TS7
0
2
4
6
8
10
12
14

FIG. 1

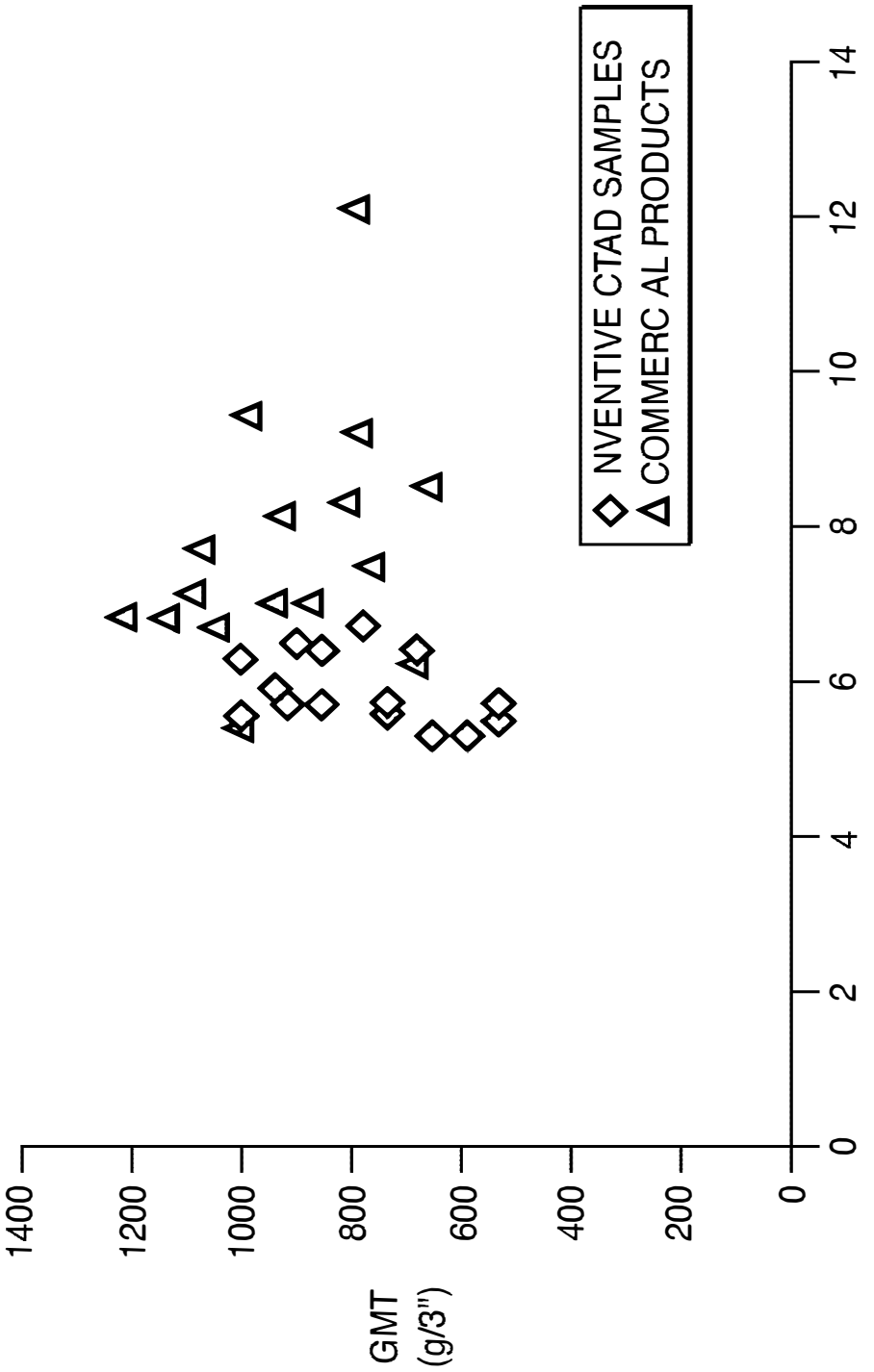

NVENTIVE CTAD SAMPLES
COMMERC AL PRODUCTS
GMT (g/3")
TS750
0
200
400
600
800
1000
1200
1400
0
2
4
6
8
10
12
14

FIG. 2

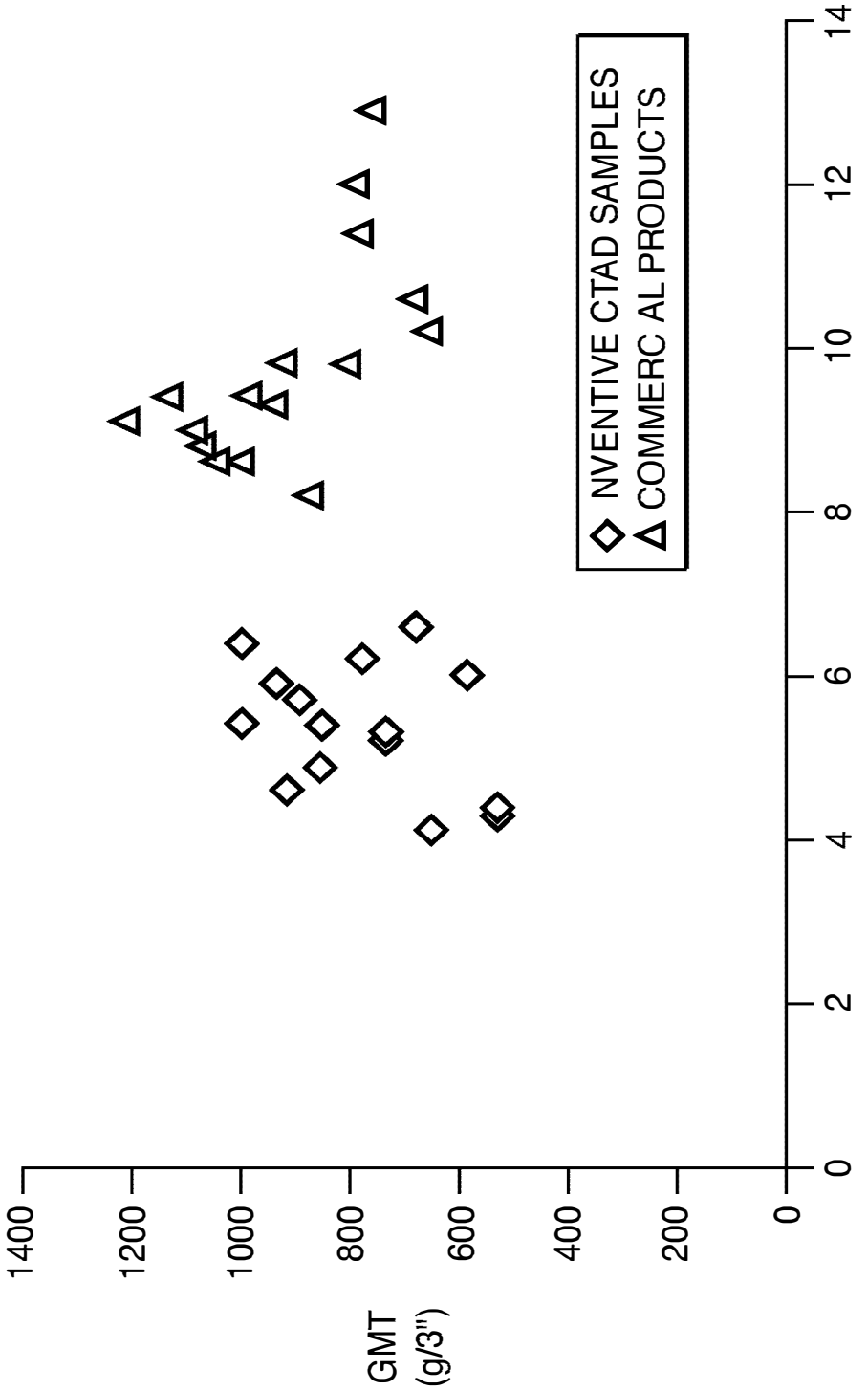

GMT (g/3")
1400
1200
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
TS7
NVENTIVE CTAD SAMPLES
COMMERC AL PRODUCTS

FIG. 3

**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/IB2013/058817**

**A. CLASSIFICATION OF SUBJECT MATTER**

**D21H 27/40(2006.01)i, D21H 27/30(2006.01)i, D21H 27/00(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)
D21H 27/40; D21F 3/00; D21F 11/00; B32B 23/04; D21H 27/02; D21H 21/18; D21H 27/00; D21H 19/00; B31F 1/12; D21H 27/30

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: creping, tissue, TS7, TS750

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 2010-0065234 A1 (KLERELID, INGVAR BERNDT ERIK et al.) 18 March 2010<br>See abstract; claims 18 and 49. | 1-3,10-12,19,20 |
| A | EP 0399522 A2 (KIMBERLY-CLARK CORPORATION) 28 November 1990<br>See abstract; claim 1. | 1-3,10-12,19,20 |
| A | US 2007-0137808 A1 (LOSTOCCO, MICHAEL R. et al.) 21 June 2007<br>See abstract; claims 12-14. | 1-3,10-12,19,20 |
| A | US 2012-0031576 A1 (GANE, PATRICK ARTHUR CHARLES et al.) 9 February 2012<br>See abstract; claims 48 and 75-86. | 1-3,10-12,19,20 |
| A | US 5409572 A (KERSHAW, THOMAS N. et al.) 25 April 1995<br>See abstract; claim 1. | 1-3,10-12,19,20 |
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☐ 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
25 February 2014 (25.02.2014)

Date of mailing of the international search report
**25 February 2014 (25.02.2014)**

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Form PCT/ISA/210 (second sheet) (July 2009)

**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/IB2013/058817**

**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.: 4-9,13-18
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.
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**Declarations under Rule 4.17**:

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

**Published**:

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WO 2016/195627 A1

(54) **Title**: HIGHLY DURABLE TOWEL COMPRISING NON-WOOD FIBERS

(57) **Abstract**: The present invention relates to tissue products comprising high yield hesperaloe fiber having improved wet performance, such as improved absorbency, CD Wet/Dry Ratio and CD Wet Durability. The addition of high yield hesperaloe pulp fibers surprisingly improves the CD Wet/Dry ratio without negatively affecting the absorbency of the tissue product. For example, tissue products of the present invention generally have an Absorbent Capacity greater than about 6.0 g/g, such as from about 8.0 to 8.0 g/g. As such the tissue products are durable when wet, but are still sufficiently absorbent. This balance of absorbency and wet strength is not found in the prior art without resorting to adding latex binders or the like to the tissue product.

# HIGHLY DURABLE TOWEL COMPRISING NON-WOOD FIBERS

## BACKGROUND OF THE DISCLOSURE

In the development and manufacture of paper products, particularly paper towels for the consumer market, it is a continual objective to improve the absorbent characteristics of the product. For cleaning up some spills, the consumer needs high absorbent capacity. For some uses, consumers want a fast rate of absorbency. For other uses, a combination of high absorbent capacity and fast absorbent rate is desired. At the same time, constraints on achieving this objective include the need to maintain or reduce costs in order to provide the consumer with the highest possible value, which in part means minimizing the amount of fiber in the product.

## SUMMARY OF THE DISCLOSURE

The present inventors have successfully used hesperaloe fibers to produce a tissue that is highly absorbent while also being durable when wet. As such the tissue products of the present invention may have an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry ratio greater than about 0.30. The desirable absorbency and wet durability are achieved by forming a tissue product from wood and non-wood fibers and more specifically high yield hesperaloe pulp fibers. In achieving these properties the inventors have overcome the negative to other important properties, such as bulk and stiffness, typically associated with substituting conventional wood papermaking fibers with non-wood fibers. 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 Northern softwood kraft (NSWK) fibers.

Accordingly, in certain embodiments, the invention provides tissue products in which hesperaloe fibers replace at least about 50 percent of the NSWK, more preferably at least about 75 percent and still more preferably all NSWK while maintaining or improving absorbency and without negatively effecting stiffness and bulk.

In other embodiments the present invention provides tissue products comprising a multi-layered tissue web where one or more of the layers comprise a blend of hesperaloe fibers and softwood kraft fibers, wherein the softwood kraft fibers comprise less than about 10 weight percent of the tissue product.

In still other embodiments the present invention provides a tissue product comprising greater than about 20 weight percent high yield hesperaloe fiber, the tissue product having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.



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In yet other embodiments the present invention provides single-ply through-air dried tissue product comprising at least about 20 weight percent high yield hesperaloe pulp fibers, the tissue product having a basis weight from about 30 to about 60 gsm, a GMT from about 1500 to about 2500 g/3" and an Absorbent Capacity greater than about 7.0 g/g.

In other embodiments the present invention provides tissue product comprising at least one multi-layered through-air dried tissue web comprising a first and a second layer, the first layer being substantially free from high yield hesperaloe pulp fibers and the second layer consisting essentially of high yield hesperaloe pulp fibers, the tissue product having a Wet CD Durability from about 1.75 to about 2.0 and a Stiffness Index less than about 6.0.

## 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.



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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 10 cc/g, more preferably greater than about 11 cc/g and still more preferably greater than about 12 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 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. GM Slope generally is expressed in units of kg.

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. While the GMT may vary tissue products prepared according to the present disclosure generally have a GMT greater than about 1,400 g/3", such as from about 1,400 to about 2,500 g/3".

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 (typically having units of kg), divided by the geometric mean tensile strength (typically having units of grams per three inches).

$$Stiffness\ Index = \frac{\sqrt{MD\ Tensile\ Slope\ (kg) x\ CD\ Tensile\ Slope(kg)}}{GMT\ (g/3")} \cdot x\ 1{,}000$$

While the Stiffness Index may vary tissue products prepared according to the present disclosure generally have a Stiffness Index less than about 8.0 and more preferably less than about 6.0.

As used herein, the term "Absorbent Capacity" is a measure of the amount of water absorbed by the paper towel product in the vertical orientation and is expressed as grams of water absorbed per gram of fiber (dry weight). Absorbent Capacity is measured as described in the Test Methods section and generally has units of grams per gram (g/g). While the Absorbent Capacity may vary tissue products prepared according to the present disclosure generally have an Absorbent Capacity greater than about 6.0 g/g and more preferably greater than about 7.0 g/g.

As used herein the term "CD Wet/Dry Ratio," refers to the ratio of the wet CD tensile strength to the dry CD tensile strength, measured as described in the Test Methods Section, below. While the



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CD Wet/Dry Ratio may vary, tissue products prepared as described herein generally have a CD Wet/Dry Ratio greater than about 0.28 and more preferably greater than about 0.30, such as from about 0.28 to about 0.32. Generally the foregoing ratios are achieved at Wet CD Tensile greater than about 400 g/3", more preferably greater than about 425 g/3" and still more preferably greater than about 450 g/3".

As used herein the term "Wet CD Durability," refers to the CD Wet Stretch multiplied by 100, divided by the CD Wet Tensile (having units of g/3") and is a measurement of the wet CD extensibility of a product at a given wet tensile strength. At CD Wet Tensile strengths greater than about 400 g/3" the inventive tissue products of the present invention generally have Wet CD Durability greater than about 1.75 and more preferably greater than about 2.0.

As used herein the term "Wet Strength Efficiency," refers to the CD Wet/Dry Ratio divided by the add-on amount of wet strength resin (measured in kilograms per dry metric ton of fiber) multiplied by 100 and is a measure of the amount of wet strength generated relative to dry strength normalized by the amount of wet strength added.

## DETAILED DESCRIPTION OF THE DISLOSURE

Generally, the present invention provides tissue product having a CD Wet/Dry ratio that meets or exceeds satisfactory levels without the excess use of a wet strength resin. The satisfactory level of CD Wet/Dry ratio is generally greater than about 0.30. The satisfactory level of CD Wet/Dry ratio is surprisingly achieved by forming a tissue product from wood and non-wood fibers and more specifically high yield hesperaloe pulp fibers. Generally CD Wet/Dry ratios may be achieved with the addition of at least about 5 percent, by weight of the tissue product, such as from about 5 to about 50 percent and more preferably from about 15 to about 45 percent high yield hesperaloe pulp fibers.

The addition of high yield hesperaloe pulp fibers surprisingly improves the CD Wet/Dry ratio without negatively affecting the absorbency of the tissue product. For example, tissue products of the present invention generally have an Absorbent Capacity greater than about 6.0 g/g, such as from about 6.0 to 8.0 g/g. As such the tissue products are durable when wet, but are still sufficiently absorbent. This balance of absorbency and wet strength is not found in the prior art without resorting to adding latex binders or the like to the tissue product.

Further, the aforementioned wet-strength properties may be achieved with only modest additions of conventional wet-strength resin. For example, in certain embodiments the tissue products comprise less than about 15 kg of wet-strength resin per metric ton of furnish, such as from about 3 to about 15 kg, and more preferably from about 3 to about 10 kg. Rather than employ an excessive



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amount of wet-strength resin, the improved wet-strength properties are achieved by the addition of high yield hesperaloe pulp fibers during the manufacture of the tissue product, such as from about 5 to about 50 percent, by weight of the product, and more preferably from about 20 to about 40 percent, by weight.

Accordingly, in certain embodiments the tissue products generally comprise high yield hesperaloe pulp fibers derived from non-woody plants in the genus Hesperaloe in the family Agavaceae. Suitable species within the genus Hesperaloe 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 process 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.



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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 amount of SSWK, by weight of the tissue product, is less than about 10 percent and more preferably less than about 5 percent.

In addition to the use of high yield hesperaloe pulp fiber the tissue products of the present invention are preferably prepared without the addition of binders, particularly latex binders and more specifically carboxyl-functional latex emulsion polymers, such as those described in US Patent Nos. 6,187,140 and 7,462,258. Latex binders, such as those disclosed in the foregoing references, have been used previously in the manufacture of tissue products to improve wet performance. These binders, however, add manufacturing complexity and cost. Therefore, it is desirable to produce a tissue product, such as the inventive tissues, without the use of binders and more specifically latex binders.

Further, tissues prepared according to the present disclosure are not treated with a sizing agent, such as alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA), either during the tissue manufacturing process or after formation and drying of the tissue web. Rather, the tissue webs are prepared by adding hesperaloe fibers and in certain embodiments a wet strength resin, to the papermaking furnish prior to formation of the web, to enhance the wet-strength properties of the finished web. Unlike conventional sizing agents, which reduce the adsorption rate of water into the sheet, hesperaloe fibers and conventional wet-strength resins allow the sheet to adsorb water as intended during the end use but maintain sheet integrity and strength when wetted.

Rather than employ latex binders or sizing agents, the tissue products typically comprise a conventional wet-strength resin. Useful conventional wet strength resins include diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), epichlorhydrin resin(s), polyamide-epichlorohydrin (PAE), or any combinations thereof, or any resins to be considered in these families of resins. Particularly preferred wet strength resins are polyamide-epichlorohydrin (PAE) resins. Commonly PAE resins are formed by first reacting a polyalkylene polyamine and an aliphatic dicarboxylic acid or dicarboxylic acid derivative. A polyaminoamide made from diethylenetriamine and adipic acid or esters of dicarboxylic acid derivatives is most common. The resulting polyaminoamide is

then reacted with epichlorohydrin. Useful PAE resins are sold under the tradename Kymene® (commercially available from Ashland, Inc., Covington, KY).

Generally the conventional wet-strength resin is added to the fiber furnish prior to formation of the tissue web. The amount of the wet-strength resin can be less than about 10 kg per ton of furnish, more preferably less than about 8 kg per ton of furnish and still more preferably less than about 5 kg per ton of furnish. Generally the add-on level of wet-strength resin will be from about 1 to about 10 kg per ton of furnish and more preferably from about 3 to about 8 kg per ton of furnish and still more preferably from about 3 to about 5 kg per ton of furnish.

Although such low add on levels of wet strength are generally not considered to be suitable for achieving exceptional wet performance, such as a CD Wet/Dry Ratio greater than about 0.30, it has now been discovered that the use of high yield hesperaloe pulp fibers yields tissue products having a CD Wet/Dry Ratio greater than about 0.30 and in certain embodiments greater than about 0.32, such as from about 0.30 to about 0.35. The combination of conventional wet strength resin, such as PAE resins, and hesperaloe fiber have a synergistic effect. Accordingly, when the CD Wet/Dry Ratio and Wet CD Durability are concerned, the combination of wet-strength resin addition and hesperaloe fiber according to the invention provides a synergistic effect which has not been disclosed previously. This synergistic effect is valuable, since it makes it possible to achieve a higher wet-strength level without the excessive use of wet-strength resin.

Table 1 illustrates the desirable increase in wet-strength properties that can be achieved via the combination of high yield hesperaloe fiber (HYH) and a conventional wet-strength resin. The samples have a basis weight of about 36 gsm and comprised a single through-air dried ply. The samples comprised either a blend of NSWK (40 wt%) and EHWK (60 wt%) or HYH (40 wt%) and EHWK (60 wt%). As the table illustrates, at a constant level of wet-strength addition, a higher wet/dry tensile level can be achieved via the addition of HYH.

TABLE 1

| HYH (wt%) | Wet Strength (kg/MT) | CD Wet/Dry Ratio | Delta CD Wet/Dry Ratio (%) | Wet Strength Efficiency |
|---|---|---|---|---|
| - | 9 | 0.22 | - | 2.4 |
| 40 | 9 | 0.3 | 36 | 3.3 |
| - | 14 | 0.24 | - | 1.7 |
| 40 | 14 | 0.31 | 29 | 2.2 |

The improvement in wet tensile properties is further evident when the inventive tissue products are compared to commercially available tissue products. As illustrated in the table below, the inventive tissue products display both wet durability, such as a CD Wet/Dry Ratio greater than about 0.30 and

good absorbency, such as an Absorbent Capacity greater than about 6.0 g/g and more preferably greater than about 7.0 g/g, such as from about 6.0 to about 7.5 g/g. In certain aspects the inventive tissue products also have improved Wet CD Durability relative to commercially available tissue products, such as a Wet CD Durability greater than about 1.5 and more preferably greater than about 1.75, such as from about 1.5 to about 2.0.

TABLE 2

| Product | Plies | Wet CD Tensile (g/3") | Wet CD Stretch (%) | CD Wet/Dry Ratio | Wet CD Durability | Absorbent Capacity (g/g) |
|---|---|---|---|---|---|---|
| Invention | 1 | 418 | 8.2 | 0.32 | 1.96 | 7.1 |
| Scott | 1 | 855 | 7.5 | 0.34 | 0.88 | 5.5 |
| Scott Naturals | 1 | 811 | 11.3 | 0.33 | 1.39 | 4.7 |
| Viva Vantage | 1 | 969 | 8.2 | 0.34 | 0.85 | 3.9 |
| Bounty Basic | 1 | 1040 | 7.2 | 0.47 | 0.69 | 4.9 |

Accordingly, in one embodiment tissue products comprise at least one multi-layered tissue web, the tissue product having a CD Wet/Dry Ratio greater than about 0.30 an Absorbent Capacity greater than about 6.0 g/g and still more preferably greater than about 6.5 g/g. Preferably the web comprises two layers, and more preferably three layers, wherein the hesperaloe fiber is selectively disposed in only one of the layers and the other layers are substantially free from hesperaloe fiber. In other embodiments, the web comprises two outer layers and a middle layer, where the hesperaloe fiber is selectively disposed in the middle layer. While in one embodiment it is preferred that the tissue web comprise a three-layered tissue having hesperaloe fiber selectively incorporated into the middle layer, it should be understood that tissue products made from the foregoing multi-layered web can include any number of plies and the plies may be made from various combinations of single- and multi-layered tissue webs. Further, tissue webs prepared according to the present invention 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.

As noted previously, the instant tissue products have a high degree of absorbent capacity such as an Absorbent Capacity greater than about 6.0 g/g, such as from about 6.0 to about 7.0 g/g and more preferably from about 6.5 to about 7.0 g/g, while also having a CD Wet/Dry Ratio greater than about 0.30, such as from about 0.30 to about 0.40. Generally the foregoing absorbent capacities and wet strengths are achieved at basis weights from about 30 to about 60 grams per square meter (gsm) and more preferably from about 35 to about 50 gsm and still more preferably from about 40 to about 50 gsm.

In addition to having satisfactory absorbent properties, the tissue products generally have improved wet CD performance. For example, in certain embodiments the tissue products have a Wet CD Durability greater than about 1.75, such as from about 1.75 to about 2.5 and more preferably from about 2.0 to about 2.5. At the foregoing Wet CD Durability levels the tissue products may have a Wet CD Stretch greater than about 8.0 percent, such as from about 8.0 percent to about 10.0 percent and more preferably from about 9.0 to about 10.0 percent.

While having improved properties, the tissue products prepared according to the present disclosure continue to be strong enough to withstand use by a consumer. For example, inventive tissue products generally have a geometric mean tensile (GMT) greater than about 1200 g/3", such as from about 1200 to about 3000 g/3", more preferably from about 1200 to about 2500 g/3" and still more preferably from about 1600 to about 2400 g/3".

Not only are the instant tissue products absorbent and strong enough to withstand use, they are generally flexible and have good hand feel. As such the tissue products may have a GM Slope less than about 10.0 kg, such as from about 4.0 to about 10.0 kg and more preferably from about 4.0 to about 8.0 kg. The foregoing GM Slopes are generally achieved at relatively modest GMT, such as from about 1200 to about 2500 g/3", and more preferably from about 1200 to about 2200 g/3". At these GM Slopes and GMT, the tissue products may have a Stiffness Index less than about 8.0, such as from about 4.0 to about 8.0 and more preferably from about 4.0 to about 6.0.

In one particularly preferred embodiment the inventive tissue product comprises a single-ply, multi-layered, through-air-dried web, wherein a first layer comprises wood pulp fibers and a second layer comprises high yield hesperaloe pulp fibers, the first layer being substantially free of hesperaloe fibers and the product comprising from about 20 to about 50 percent, by weight, hesperaloe fibers. The foregoing tissue product generally has a CD Wet/Dry Ratio greater than about 0.30 an Absorbent Capacity greater than about 6.0, while having a Stiffness Index less than about 6.0, such as from about 4.0 to about 6.0.

Webs useful in preparing tissue products according to the present disclosure can vary depending upon the particular application. In general, in addition to hesperaloe fibers, the webs can be made from any suitable type of fiber. For instance, the base web can be made from cellulosic fibers, and more preferably cellulosic pulp fibers. Suitable cellulosic fibers for use in connection with this invention include secondary (recycled) papermaking fibers and virgin papermaking fibers in all proportions. Such fibers include, without limitation, hardwood and softwood fibers.

Tissue webs made in accordance with the present disclosure can be made with a homogeneous fiber furnish or can be formed from a stratified fiber furnish producing layers within the

single- or multi-ply product. Stratified base webs can be formed using equipment known in the art, such as a multi-layered headbox. Both strength and softness of the base web can be adjusted as desired through layered tissues, such as those produced from stratified headboxes.

When constructing a web from a stratified fiber furnish, the relative weight of each layer can vary depending upon the particular application. For example, in one embodiment, when constructing a web containing three layers, each layer can be from about 15 to about 40 percent of the total weight of the web, such as from about 25 to about 35 percent of the weight of the web. Generally the hesperaloe fibers will comprise from about 5 to about 50 percent, by weight, of the web.

The tissue products 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.

In a particularly preferred 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.

In one embodiment the web is formed using a twin wire former having a papermaking headbox that injects or deposits a furnish of an aqueous suspension of papermaking fibers onto a plurality of forming fabrics, such as the outer forming fabric and the inner forming fabric, thereby forming a wet tissue web. 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 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 greater than 20 percent, more specifically between about 20 to about 40 percent, and more specifically between 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 30 to about 70 percent and more preferably from about 40 to about 60 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. Such molding to the contours of the surface of the transfer fabric 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 through-air drying fabric. Typically, the transfer fabric travels at approximately the same speed as the through-air drying fabric.

However, a second rush transfer may be performed as the web is transferred from the transfer fabric to the through-air drying fabric. This rush transfer is referred to as occurring at the second position and is achieved by operating the through-air drying fabric at a slower speed than the transfer fabric.

In addition to rush transferring the wet tissue web from the transfer fabric to the through-air drying fabric, the wet tissue web may be macroscopically rearranged to conform to the surface of the through-air drying fabric with the aid of a vacuum transfer roll or a vacuum transfer shoe. If desired, the through-air drying fabric can be run at a speed slower than the speed of the transfer fabric 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 to the topography of the through-air drying fabric.

While supported by a through-air drying fabric, the wet tissue web is dried to a final consistency of about 94 percent or greater by a through-air dryer. The web then passes through the winding nip between the reel drum and the reel and is wound into a roll of tissue for subsequent converting.

## TEST METHODS

Wet and Dry Tensile

Samples for tensile strength testing are prepared by cutting a 3 inches (76.2 mm) by 5 inches (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 4 ± 0.04 inches. The jaws are operated using pneumatic-action and are rubber coated. The minimum grip face width is 3 inches (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.

Wet tensile strength measurements are measured in the same manner, but after the center portion of the previously conditioned sample strip has been saturated with distilled water immediately prior to loading the specimen into the tensile test equipment. More specifically, prior to performing a wet CD tensile test, the sample must be aged to ensure the wet strength resin has cured. Two types of aging were practiced: natural and artificial. Natural aging was used for older samples that had already aged. Artificial aging was used for samples that were to be tested immediately after or within days of manufacture. For natural aging, the samples were held at 73°F, 50 percent relative humidity for a period of 12 days prior to testing. Following this natural aging step, the strips are then wetted individually and tested. For artificially aged samples, the 3-inch wide sample strips were heated for 4 minutes at 105 ± 2°C. Following this artificial aging step, the strips are then wetted individually and tested. Sample wetting is performed by first laying a single test strip onto a piece of blotter paper (Fiber Mark, Reliance Basis 120). A pad is then used to wet the sample strip prior to testing. The pad is a green, Scotch-Brite brand (3M) general purpose commercial scrubbing pad. To prepare the pad for testing, a full-size pad is cut approximately 2.5 inches long by 4 inches wide. A piece of masking tape is wrapped around one of the 4-inch long edges. The taped side then becomes the "top" edge of the wetting pad. To wet a tensile strip, the tester holds the top edge of the pad and dips the bottom edge in approximately 0.25 inches of distilled water located in a wetting pan. After the end of the pad has been saturated with water, the pad is then taken from the wetting pan and the excess water is removed from the pad by lightly tapping the wet edge three times across a wire mesh screen. The wet edge of the pad is then gently placed across the sample, parallel to the width of the sample, in the approximate center of the sample strip. The pad is held in place for approximately one second and then removed and placed back into the wetting pan. The wet sample is then immediately inserted into the tensile grips so the wetted area is approximately centered between the upper and lower grips. The test strip should be centered both horizontally and vertically between the grips. (It should be noted that if any of the wetted portion comes into contact with the grip faces, the specimen must be discarded and the jaws dried off before resuming testing.) The tensile test is then performed and the peak load recorded as the CD wet tensile strength of this specimen. As with the dry CD tensile test, the characterization of a product is determined by the average of at least six, but in the case of the examples disclosed, twenty representative sample measurements.



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Absorbency

As used herein, "vertical absorbent capacity" is a measure of the amount of water absorbed by a paper product (single-ply or multi-ply) or a sheet, expressed as grams of water absorbed per gram of fiber (dry weight). In particular, the vertical absorbent capacity is determined by cutting a sheet of the product to be tested (which may contain one or more plies) into a square measuring 100 millimeters by 100 millimeters (± 1 mm.) The resulting test specimen is weighed to the nearest 0.01 gram and the value is recorded as the "dry weight." The specimen is attached to a 3-point clamping device and hung from one corner in a 3-point clamping device such that the opposite comer is lower than the rest of the specimen, then the sample and the clamp are placed into a dish of water and soaked in the water for 3 minutes (± 5 seconds). The water should be distilled or de-ionized water at a temperature of 23 ± 3°C. At the end of the soaking time, the specimen and the clamp are removed from the water. The clamping device should be such that the clamp area and pressure have minimal effect on the test result. Specifically, the clamp area should be only large enough to hold the sample and the pressure should also just be sufficient for holding the sample, while minimizing the amount of water removed from the sample during clamping. The sample specimen is allowed to drain for 3 minutes (± 5 seconds). At the end of the draining time, the specimen is removed by holding a weighing dish under the specimen and releasing it from the clamping device. The wet specimen is then weighed to the nearest 0.01 gram and the value recorded as the "wet weight". The vertical absorbent capacity in grams per gram = [(wet weight - dry weight)/dry weight]. At least five (5) replicate measurements are made on representative samples from the same roll or box of product to yield an average vertical absorbent capacity value.

## EXAMPLE

Base sheets were made using a through-air dried papermaking process commonly referred to as "uncreped through-air dried" ("UCTAD") and generally described in US Patent No. 5,607,551, the contents of which are incorporated herein in a manner consistent with the present invention. Inventive base sheets were produced from a furnish comprising northern softwood kraft (NSWK), eucalyptus kraft (EHWK) and high yield hesperaloe fiber (HYH) using a layered headbox fed by three stock chests such that the webs having three layers (two outer layers and a middle layer) were formed. The outer layers comprised 100 percent EHWK for both the control and inventive samples. The center layer was 100 percent NSWK for the control sample; for the inventive sample, the center layer was 100 percent HYH. The layer splits, by weight of the web, are detailed in Table 3, below.

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 tissue web was formed on a Voith Fabrics TissueForm V forming fabric, vacuum dewatered to approximately 25 percent consistency and then subjected to rush transfer when transferred to the transfer fabric. The layer splits, by weight of the web, are detailed in Table 4, below. The transfer fabric was the fabric described as t1207-11 (commercially available from Voith Fabrics, Appleton, WI). The web was then transferred to a through-air drying fabric. Transfer to the through-drying fabric was done using vacuum levels of greater than 10 inches of mercury at the transfer. The web was then dried to approximately 98 percent solids before winding.

TABLE 3

| Sample | Layer Split (Air/Middle/Fabric wt%) | HYH (wt%) | Wet Strength (kg/MT) |
|---|---|---|---|
| Control | 30/40/30 | - | 8 |
| Inventive 1 | 30/40/30 | 40 | 8 |

The base sheet webs were converted into rolled towel products by calendering using a conventional polyurethane/steel calender comprising a 4 P&J polyurethane roll on the air side of the sheet and a standard steel roll on the fabric side. The finished product comprised a single ply of base sheet. The finished products were subjected to physical testing, the results of which are summarized in Table 4.

TABLE 4

| | Control 1 | Inventive 1 |
|---|---|---|
| BW (gsm) | 39.3 | 39.0 |
| Wet CDT (g/3") | 515 | 418 |
| Wet CDS (%) | 10.7 | 8.2 |
| Wet CD Durability | 2.08 | 1.96 |
| CD Wet/Dry | 0.31 | 0.31 |
| Absorbent Capacity (g/g) | 6.2 | 7.1 |
| Wet Strength Efficiency | 3.89 | 3.89 |
| Dry GMT (g/3") | 2217 | 1821 |
| Dry CDT (g/3") | 1655 | 1340 |
| Dry GM Slope (kg) | 7.2 | 7.7 |
| Stiffness Index | 3.25 | 4.23 |

The foregoing is one example of an inventive tissue product prepared according to the present disclosure. In a first embodiment the invention provides a tissue product comprising greater than about



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20 weight percent high yield hesperaloe fiber having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.

In a second embodiment the invention provides the tissue product of the first embodiment having a Wet CD Durability of greater than about 1.75.

In a third embodiment the invention provides the tissue product of the first embodiment having an Absorbent Capacity from about 7.0 to about 7.5 g/g, a CD Wet/Dry Ratio from about 0.30 to about 0.35.

In a third embodiment the present invention provides the tissue product of the first or the second embodiments having a GMT from about 1200 to about 2600 g/3".

In a fourth embodiment the present invention provides the tissue product of any one of the first through the third embodiments having a Stiffness Index from about 4.0 to about 6.0.

In a fifth embodiment the present invention provides the tissue product of any one of the first through the fourth embodiments having a basis weight from about 34 to about 60 gsm.

In a sixth embodiment the present invention provides the tissue product of any one of the first through the fifth embodiments having wet CD stretch greater than about 8 percent, such as from about 8 to about 10 percent.

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 comprises a single-ply multi-layered web having a first, a second and a third layer.

In an eighth embodiment the present invention provides the tissue product of any one of the first through the seventh embodiments wherein the tissue product comprises from about 20 to about 50 weight percent high yield hesperaloe fiber.

In a ninth embodiment the present invention provides the tissue product of any one of the first through the eighth embodiments wherein the tissue product comprises at least one through-air dried tissue web.

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 comprises at least one multi-layered through-air dried tissue web.

In still other embodiments the disclosure provides a tissue product of any one of the foregoing embodiments wherein the tissue product comprises at least one multi-layered through-air dried tissue web comprising a first fibrous layer and a second fibrous layer, the first fibrous layer comprising wood

pulp fibers and the second fibrous layer consisting essentially of high yield hesperaloe fibers and wherein the hesperaloe fibers comprise from about 20 to about 40 weight percent of the through-air dried web.



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**WHAT IS CLAIMED IS:**

1. A tissue product comprising greater than about 20 weight percent high yield hesperaloe fiber having an Absorbent Capacity greater than about 7.0 g/g and a CD Wet/Dry Ratio greater than about 0.30.

2. The tissue product of claim 1 having a Wet CD Durability of greater than about 1.75.

3. The tissue product of claim 1 having a GMT from about 1500 to about 3000 g/3".

4. The tissue product of claim 1 having a Stiffness Index from about 4.0 to about 6.0.

5. The tissue product of claim 1 having a basis weight from about 30 to about 60 gsm.

6. The tissue product of claim 1 having a wet CD stretch greater than about 8.0 percent.

7. The tissue product of claim 1 wherein the tissue product comprises a single-ply multi-layered web having a first layer comprising conventional wood pulp fibers and a second layer consisting essentially of high yield hesperaloe pulp fiber.

8. The tissue product of claim 1 wherein the tissue product comprises at least one through-air dried tissue web.

9. A tissue product comprising at least one multi-layered through-air dried tissue web comprising a first and a second layer, the first layer being substantially free from high yield hesperaloe pulp fibers and the second layer consisting essentially of high yield hesperaloe pulp fibers, the tissue product having a Wet CD Durability from about 1.75 to about 2.0 and a Stiffness Index less than about 6.0.

10. The tissue product of claim 9 having CD Wet/Dry Ratio from about 0.28 to about 0.32.

11. The tissue product of claim 9 having an Absorbent Capacity from about 6.5 to about 7.5.

12. The tissue product of claim 9 having a GM Slope less than about 8.0 kg.

13. The tissue product of claim 9 having a basis weight from about 30 to about 60 gsm and a GMT from about 1500 to about 2500 g/3".

14. The tissue product of claim 9 wherein the tissue product is substantially free from softwood kraft pulp fibers.



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15. The tissue product of claim 9 wherein the high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.

16. A single-ply through-air dried tissue product comprising at least about 20 weight percent high yield hesperaloe pulp fibers, the tissue product having a basis weight from about 30 to about 60 gsm, a GMT from about 1500 to about 2500 g/3" and an Absorbent Capacity greater than about 7.0 g/g.

17. The single-ply through-air dried tissue product of claim 16 having a Wet CD Durability from about 1.75 to about 2.0.

18. The single-ply through-air dried tissue product of claim 16 having a Stiffness Index less than about 6.0.

19. The single-ply through-air dried tissue product of claim 16 wherein the tissue product comprises from about 20 to about 40 weight percent high yield hesperaloe fiber and is substantially free from softwood kraft pulp fibers.

20. The single-ply through-air dried tissue product of claim 16 wherein high yield hesperaloe pulp fibers have a lignin content from about 10 to about 15 weight percent.



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**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/US2015/033175**

**A. CLASSIFICATION OF SUBJECT MATTER**

**A47K 7/00(2006.01)i, 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 7/00; D21H 11/12; D21H 17/28; D21H 17/00; D21H 27/00; B31F 1/12; A47K 10/16

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, web, hesperaloe fiber, non-woody, pulp, absorbent

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | US 5320710 A (REEVES, R. H. et al.) 14 June 1994<br>See abstract; claims 1-7. | 1-20 |
| Y | US 2013-0269892 A1 (KIMBERLY-CLARK WORDWIDE, INC.) 17 October 2013<br>See claims 1, 3; paragraphs [0013], [0038], [0045]. | 1-20 |
| A | US 2014-0093704 A1 (SHI, B. et al.) 03 April 2014<br>See abstract; claims 1-9. | 1-20 |
| A | US 2015-0129143 A1 (CARGILL, INCORPORATED) 14 May 2015<br>See claims 1, 2, 9. | 1-20 |
| A | US 2003-0192662 A1 (HEATH, M. S. et al.) 16 October 2003<br>See abstract; claim 1. | 1-20 |

☐ 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
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"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

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Information on patent family members

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**PCT/US2015/033175**

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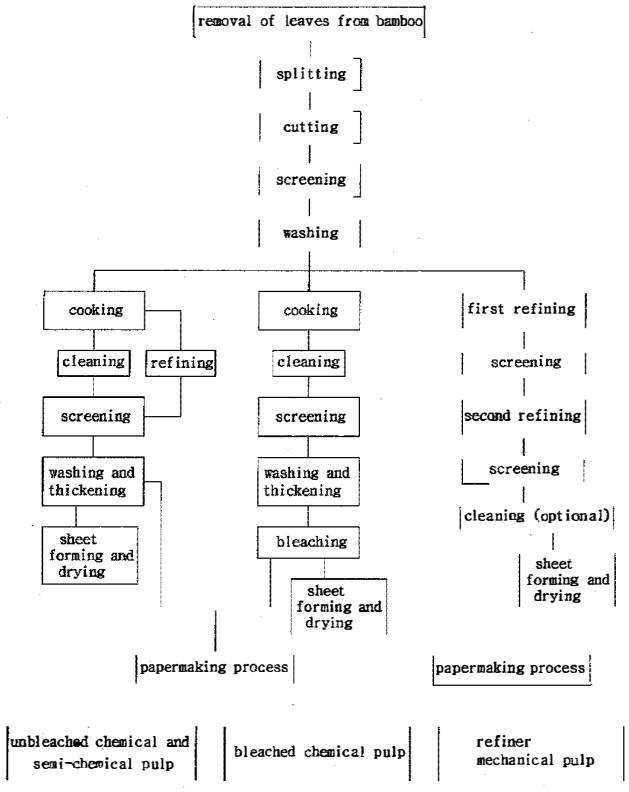
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(54) **Title:** PROCESS FOR PRODUCING PULP UTILIZING BAMBOO AND PULP AND PAPERS PRODUCED USING THE SAME




(57) **Abstract:** Disclosed are a technique for producing high quality paper-making pulp capable of replacing wood pulp, utilizing bamboo and paper products produced using the same. The present invention can be applied to techniques for producing a variety of paper-making pulps which can be used in production of industrial papers, printing and writing papers, thin wrapping papers, toilet papers and special purpose papers from bamboo, and processes for producing a variety of paper products from the same. The present invention relates to a process for producing pulp utilizing bamboo, which is capable of producing pulp under mild conditions by facilitating penetration of liquid chemicals in chemical pulp production, is capable of simplifying manufacturing processes, and is also capable of maximizing pulp yield and minimizing weakening of pulp fibers, thereby maximizing pulp quality; and pulp and papers produced using the same.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

【DESCRIPTION】

【Invention Title】

PROCESS FOR PRODUCING PULP UTILIZING BAMBOO AND PULP AND PAPERS PRODUCED USING THE SAME

【Technical Field】

The present invention relates to a technology for producing high-quality paper-making pulp capable of substituting for wood pulp, and paper products, using a bamboo, and encompasses a technology for producing various paper-making pulps usable in the production of industrial paper, printing and writing paper, thin wrapping paper, toilet paper, non-woven fabric and special purpose paper, from bamboos, as well as a method for producing various papers from said pulps. The method according to the present invention can produce chemical pulp in mild conditions by facilitating the penetration of liquid chemicals in the production of the pulp, simplify a process, maximize pulp yield, and minimize the weakening of pulp fiber to maximize pulp quality. Also, the present invention relates to pulp produced using said method.

【Background Art】

Generally, papermaking pulps are recognized to be produced using wood.

In other words, because the papermaking pulps consist mostly of wood pulps, and it has recently became a great problem to produce the papermaking pulp while conserving forests due to the lack of wood resources and maintaining the environment, effects to produce the pulps using non-woody plant fibers and the like are being conducted.

Such non-woody plants include paper mulberry bast fibers, hemps, cottons, and Manila hemps, and Korean Patent Publication Nos. 98-9651 and 93-2604 disclose a method for producing pulp using rice-straw.

All such efforts can be considered as efforts to conserve trees, which can prevent environmental pollution.

In other words, these efforts aim to conserve trees by absorbing pollutants and carbon dioxide contained in the atmosphere through photosynthetic action while producing and supplying oxygen.

The development of industry and civilization really led to a great improvement in the quality of life of mankind, but involved a rapid increase in energy use, so that the emission of greenhouse gas was also rapidly increased, and thus the contamination of the global environment and side effects thereof became very severe.

In typical examples thereof, the depletion of the ozone layer in the South Pole becomes very rapidly severe, and misfortunes caused by a rapid change in weather, global warming and ecosystem destruction occur in the whole world.

Such environment pollution phenomena very rapidly progressed to reach a state that threatens the survival of mankind, and thus the Tokyo Protocol on the reduction of greenhouse gas emissions, which has been delayed due to the noncooperation of some of highly developed countries, became effective.

Accordingly, in manufactures in various countries, efforts to reduce greenhouse gas emissions are urgently required, and in severe cases, additional expenses for purchasing greenhouse gas emission rights are expected.

One means for solving this problem, which has recently received great attention, is a non-woody plant that eliminates the need for the felling of wood.

In other words, when this non-woody plant is used to produce pulp, there will be a great advantage in that wood, which is consumed in large amounts, needs to be felled.

Among the non-woody plants, a bamboo, which has recently attracted attention and is used as a raw material in the present invention, is produced in large amounts in Southeast Asia countries such as China and Myanmar and sufficiently grows to a usable degree only within about five months.

However, the use of the bamboo has shortcomings in that, because the compact structure of the bamboo is not considered, the pulping of the bamboo is not satisfactorily achieved, large amounts of chemicals and energy are consumed, and a bleaching process is conduced in strong conditions to reduce yield and to cause the decomposition and destruction of fiber, making the fiber weak.

A chlorine bleaching process using elemental chlorine provides the cause of dioxin generation.

Also, because bleaching powder that acts as the cause of the corrosion of an apparatus is used as a bleaching chemical, the durability of the production apparatus is highly problematic.

In addition, this processing problem acts as the cause of increasing chemical amount, energy consumption and production cost per unit pulp production.

Methods for producing papermaking pulp and paper using a bamboo, like the present invention, were also developed in

the prior art, but have not been widely used, the reason for which will now be described.

Even though the bamboo has a very compact and hard structure, a bamboo chip having a thickness of 3.2 mm and a length and width of 19 mm was prepared in the prior art. Because the penetration of liquid chemical into the chip was difficult, the cooking of the chip was not sufficiently performed, thus making bleaching difficult.

The application of the prior art as described above cannot efficiently produce pulp, reduces the quality of pulp and is very disadvantageous in environmental terms.

Japanese Patent 3,184,993 invented by Kikuchi Shingo is very disadvantageous in terms of pulp yield, pulp quality and the consumption of liquid chemicals, because bamboo leaves and stalks are all used. Also, the technology of the household industrial level, which is difficult to perform mass production, is applied, because the bamboo is simply treated with an alkali solution in atmospheric conditions.

The paper making method in said Japanese Patent is a method for producing a kind of fiber mat for use in special applications such as forest bath, deodorization, air purification and wall papers using household industrial means and is entirely different from a paper production method for mass production, which is suggested in the present invention.

Also, in US Patent No. 4,857,145 invented by Eduardo J. Villavicencio, a shredder is used to prepare bamboo chips having a length of 10-25 cm or more, which are then chemically digested.

In this case, although it is possible to minimize damage to fibers as stated by the inventor, the fibers

require a wide space for the storage thereof, because their volume is very large. Also, the fibers cannot be treated in large amounts during a digestion process.

Furthermore, because the thickness of the prepared bamboo chips is large, the fibers are pre-impregnated with black liquor or digestion chemicals at high pressure to facilitate the digestion of chemicals. For this reason, additional processes, facilities and energy are required.

Also, the dissociation of the fibers is induced by treatment such as an explosion process by repeating pressurization and depressurization in a digestion process.

This pulping process is unsuitable for the mass production of papermaking pulp, because it requires much time and results in a significant reduction in pulp quality.

Also, because the pulp discharged from a digester is treated with a refiner so as to disintegrate it into a fiber state, the fibers can be significantly damaged. Also, the pulp shows properties similar to those of semi-chemical pulp, and it is optionally carried out to bleach the pulp.

Accordingly, the pulp produced in said US Patent can be used as a raw material for the production of low-grade paper and industrial paper, but is not suitable for the production of high-grade printing and writing paper, toilet paper, thin paper, newsprint paper or medium-quality paper.

【Disclosure】

【Technical Problem】

The present invention has been made to solve the problems occurring in the prior art, and it is an object of the present invention to provide a method for producing high-quality papermaking pulp capable of substituting for wood

pulp, and paper products, using a bamboo. More specifically, it is an object of the present invention to provide a method for producing various papermaking pulps using a bamboo, which makes it possible to produce the pulp in mild conditions by facilitating the impregnation of liquid chemicals into the pulp, simplify a process, maximize the pulp yield and minimize the weakening of the pulp fiber to maximize the quality of the pulp, as well as pulp prepared using said method, and a method for producing paper products from said pulp. The pulp, which is produced in the inventive method, can be used to produce various paper products, including industrial paper, printing and writing paper, thin wrapping paper, toilet paper, non-woven fabric and special purpose paper.

【Technical Solution】

To achieve the above object, the present invention provides a method for producing pulp from a bamboo, the method comprising: a step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo to make bamboo chips; a step of screening the cut bamboo chips to filter out small fragments or impurities from the chips and washing the chips with water to remove contaminants from the bamboo chips; a step of cooking the screened bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked in the digester at high temperature, thus softening and pulping the bamboo chips; a step of cleaning the cooked pulp using a centrifugal cleaner so as to remove

contaminants introduced together with the bamboo; a step of screening the cleaned pulp, in which contaminants are removed from the cleaned pulp using a pressure screen, and an incompletely cooked of the pulp is fed back into the digester; a step of washing and thickening the screened pulp, in which a decker is used to wash the pulp, thus removing the chemical liquor, and to squeeze water, thus thickening the pulp; and a step of using the thickened pulp to produce unbleached chemical and semi-chemical bamboo pulp for industrial paper or liner paper for corrugated boards.

In another embodiment, the present invention provides a method for producing bleached chemical bamboo pulp for the production of tissue paper, wood-free paper, art paper or toilet paper, and a method for producing refiner mechanical pulp for the production of newsprint paper or medium-quality paper, each of the methods having modifications of said method for producing the unbleached chemical and semi-chemical bamboo pulps for industrial paper or liner paper for corrugated boards.

In still another embodiment, the present invention provides a method for producing industrial paper or liner paper for corrugated boards, the method comprising: a step of disintegrating the unbleached chemical or semi-chemical bamboo pulp produced according to said method; a step of refining the disintegrated pulp; a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp; a step of screening the pulp having the chemicals added thereto; a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard; a pressing step of pressing the web

obtained in the sheet forming step to remove water; a drying step of further removing water from the pressed web; a calendering step of making the thickness of the paper or paperboard uniform; a step of slitting and cutting the calendered paper into a sheet or roll and packing the sheet or roll.

In addition, the present invention provides a method for producing tissue paper, wood-free paper, art paper or toilet paper from bleached chemical bamboo pulp, and a method for producing newsprint paper or medium-quality paper from refiner mechanical pulp, each of the methods having modifications of said method for producing industrial paper and liner paper for corrugated boards.

【Description of Drawings】

FIG. 1 is a flow chart showing processes for producing bamboo pulps according to the present invention.

【Best Mode】

The present invention relates to methods for producing papermaking pulps using a bamboo, as well as pulps produced using said methods, and methods for producing papers using the pulps. The production methods have great characteristics and will now be described in detail.

Among the methods for producing pulps using a bamboo, the steps of the method for producing unbleached chemical and semi-chemical pulp for industrial paper or liner paper for corrugated boards will now be sequentially described with reference to FIG. 1.

Specifically, the method for producing unbleached chemical and semi-chemical pulp for the production of industrial paper or liner paper for corrugated boards

comprises: a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo; and a second step of screening the cut bamboo chips to filter out small fragments or impurities from the bamboo chips and washing the bamboo chips with water to remove contaminants from the bamboo chips.

Also, the method comprises: a third step of cooking the washed bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked in the digester at high temperature, thus softening and pulping the bamboo chips; and a fourth step of cleaning the cooked pulp using a centrifugal cleaner to remove contaminants introduced together with the bamboo.

If semi-chemical pulp is to be produced, the third step comprises conducting the cooking process in mild conditions and then conducting refining instead of the cleaning.

Also, the method comprises: a fifth step of screening the chips, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the pulp is fed back into the digester; and a sixth step of washing and thickening the chips, in which a decker is used to wash the pulp, thus removing the chemical liquor, and to squeeze water from the pulp, thus thickening the pulp.

In addition, the method comprises: a seventh step of forming a sheet from the washed and thickened pulp and drying the sheet, thereby producing unbleached chemical and semi-

chemical pulp for industrial paper or liner paper for corrugated boards.

The above-described steps will now be described in further detail. In the third step of cooking the bamboo chips, the amount of alkali (as $Na_2O$) added to water is 10-30 % based on the oven-dry weight of the bamboo chips (i.e., mass excluding the content of moisture in the bamboo chips), and the anthraquinon (AQ) is added in an amount of 0.01-2%.

In other words, the bamboo leaf contains a large amount of extracts unnecessary to produce pulp, but has a small amount of essential fibrous material.

Thus, because the bamboo leaf is of help to prepare pulp, but rather can act as the cause of increasing the consumption of chemicals, the bamboo leaf is removed before introducing the bamboo into a process for producing the pulp.

In other words, in the inventive method for producing the bamboo pulp, the bamboo leaf is not used and only the bamboo stalk is used.

Then, a longitudinal splitting step of longitudinally splitting the bamboo to a width of 1.5-3 mm is conducted.

Due to the compact structure of the bamboo, the impregnation of chemicals into the bamboo is significantly difficult compared to wood.

Thus, the production of the pulp must be started with the crushing of the bamboo. For this purpose, the bamboo is first longitudinally split into half, and the split bamboo is additionally split to a narrower width.

In this step, the bamboo is preferably split to a width of 1.5-2.0 mm.

This longitudinal splitting is a significantly

characteristic step of the present invention, and when the bamboo is split at random without considering orientation, fibrous material will not be uniformly split, but rather the fibrous material itself can be broken.

This reduces the strength of the produced pulp to reduce the quality thereof.

For this reason, in the inventive production method, the bamboo is used after it is longitudinally split several times to have narrow width.

It is also possible to use a method of splitting the bamboo in a one-step process using a device mounted with a plurality of blades.

Then, the step of transversely cutting the longitudinally split bamboo to a length of 10-30 mm is conducted.

In other words, in order to produce small bamboo chips which are easily filled and packed in a digester, the split bamboo is transversely cut to a length of 10-30 mm using a blade cutter.

If the length of the bamboo chips is too large, they cannot be effectively packed into the digester, and if the bamboo is cut to an excessively short length, large damage to fiber can occur, resulting in the reduction in the strength of the pulp.

Then, the second step of screening the cut bamboo chips to filter out small fragments or impurities from the chips and of washing the chips with water to remove contaminants from the chips is carried out.

In other words, even if small fragments which are generated in the step of cutting the bamboo are prepared into

pulp, the pulp is in a state in which the fibrous material was broken. Thus, these small fragments can weaken the strength of the pulp, increase the consumption of chemicals, and adversely affects dehydration in a papermaking machine.

Also, contaminants introduced during the cutting step are not of any help to produce the pulp.

Accordingly, if these small fragments and contaminants are all used in the production of the pulp, they will greatly reduce the yield (production rate) of the pulp and will adversely affect the quality of the pulp. For this reason, these are removed by screening.

Also, in other words, the contaminant, dust and the like attached to the bamboo chips are removed with water.

This can reduce the consumption of unnecessary chemicals in a cooking process and allows pure pulp to be obtained, thus improving the quality of the produced pulp.

Then, the third step is carried out, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked in the digester at high temperature, thus softening and pulping the bamboo chips.

The use of a prior sulfite process for the cooking of the bamboo chips has problems in that the fiber becomes weak and the yield of the pulp is low.

Thus, in the present invention, a soda-AQ process is applied in order to promote delignification and to prevent the decomposition of hemicellulose, thus increasing the yield and quality of the pulp.

In other words, the soda-AQ process comprises adding a liquor consisting of alkali (mainly NaOH), anthraquinone and water in a liquor ratio of 3.5-6.9 : 1 with respect to the oven-dry weight of the bamboo chips.

Also, in the soda-AQ process, the amount of alkali (as $Na_2O$) added to water is preferably 10-30 % based on the oven-dry weight of the bamboo chips (i.e., mass excluding the content of moisture in the bamboo chips), and the anthraquinon (AQ) is preferably added in an amount of 0.01-1%.

The cooking temperature in this cooking step is preferably 130-210 ℃, and the cooking time is preferably controlled within the range of 90-120 minutes depending on the polymerization degree and the quality of pulp to be produced.

As used herein, the term "oven-dry weight" means the mass of the bamboo chips that excludes the content of moisture in the bamboo chips.

Then, the fourth step of cleaning the bamboo chips using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo is conducted.

In other words, the centrifugal cleaner is used to remove contaminants introduced in the process together with the bamboo.

Then, a fifth step of screening the pulp is conducted, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the pulp is fed back into the digester.

In other words, non-disintegrated fibrous portions or contaminants are removed using the pressure screen.

A portion passed through the screen is sent to a

subsequent process, whereas a rejected portion remaining on the screen is filtered through a vibrating screen, a rejected portion remaining on the vibrating screen is wasted, and a fibrous portion or an incompletely cooked portion is sent back into the digester.

A sixth step of washing and thickening the pulp is conducted, in which a decker is used to wash the pulp, thus removing the chemicals from the pulp, and to squeeze water from the pulp, thus thickening the pulp.

The decker (not shown) is a machine that serves to wash the pulp and, at the same time, to thicken the pulp by squeezing water. Using this decker, the pulp is washed and thickened to a concentration suitable for the next step.

In this step, the washing operation is repeated at least three times in order to remove the remaining chemicals, fine powders and parenchyma cells as much as possible.

Then, a seventh step of forming the washed pulp into a sheet or roll is conducted, in which the washed pulp is made into a sheet and dried, thus completing the production of unbleached chemical and semi-chemical pulp for industrial paper or liner paper for corrugated boards.

To produce unbleached pulp for the production of industrial paper and liner paper, which have a more excellent quality, the cooking step in the above-described method is preferably carried out in the following conditions milder than those for the production of bleached chemical pulp: the content of active alkali: 12-14%; the content of AQ: 0.01 - 1%; liquor ratio: 3.5-6.9; cooking temperature: 130 - 150 ℃; and cooking time: 90-120 minutes.

Such conditions were determined through many

experiments conducted by the applicant.

Furthermore, said unbleached chemical and semi-chemical pulp for the production of industrial paper or liner paper for corrugated boards, bleached chemical pulp for the production of tissue paper, wood-free paper, art paper or toilet paper, and refiner mechanical pulp for the production of newsprint paper or medium-quality paper, can undergo a slitting, cutting and packing step.

However, it is preferable that the pulps should not be subjected to this slitting, cutting and packing step and should be immediately sent to a papermaking process to make paper and paperboard products.

It is to be understood that, if a pulp production factory and a paper production factory are separately placed, the slitting, cutting and packing step must be carried out.

The pulps are generally packed in the form of rolls or sheets.

In other words, it is preferable that the pulp produced in the pulping process is immediately fed into a papermaking process for use as a papermaking raw material without undergoing a drying process.

The bamboo pulp fiber has a structure and dimension different from those of wood pulp.

Such properties can be advantages in some terms depending on the intended use of the pulps, but can also be disadvantages in other terms.

Thus, depending on the quality requirement of paper to be produced, the blending or treatment of the pulps is required.

The method for producing the unbleached chemical and

semi-chemical bamboo pulp for the production of industrial paper and liner paper has been described above. Thus, a step of completing the production of bleached chemical pulp for use in the production of tissue paper, wood-free paper, art paper, non-woven fabric, special purpose paper and toilet paper will now be described.

Specifically, the method for producing bleached chemical pulp for the production of tissue paper, wood-free paper, art paper or toilet paper, using a bamboo, comprises: a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo; and a second step of screening the cut bamboo chips to filter out small fragments or impurities from the chips and washing the chips to remove contaminants from the chips.

Also, the method comprises: a third step of cooking the washed bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked in the digester at high temperature, thus softening and pulping the bamboo chips; and a fourth step of cleaning the cooked pulp using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo.

Also, the method comprises: a fifth step of screening the cleaned pulp, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the pulp is fed back into the digester; and a sixth step of washing and thickening the pulp, in which a decker is used to wash the pulp, thus removing the chemical

liquor from the pulp, and to squeeze water from the pulp, thus thickening the pulp.

In addition, the method comprises: a seventh step of bleaching the thickened pulp; and a eighth step of forming the bleached pulp into a sheets or roll and drying the sheet or roll, thereby producing bleached chemical pulp for the production of tissue paper, wood-free paper, art paper or toilet paper.

In other words, the method for producing the bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, special purpose paper or toilet paper is the same as the above-described method for producing the unbleached chemical and semi-chemical pulp for the production of industrial paper or corrugated board liner paper with respect to the first step to the sixth step, but it performs the cooking step in conditions stronger than those of the production of the unbleached chemical and semi-chemical pulp and comprises the seventh step of bleaching the pulps.

This is because the industrial paper and corrugated boards need not to be bleached, but tissue paper, wood-free paper, art paper, special purpose paper or toilet paper must have a good texture and excellent colorful beauty sensations.

Thus, regarding the method for producing the bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, special purpose paper or toilet paper, only the step of bleaching the pulp will be described.

In other words, in the seventh step of bleaching the pulp, which is very important in the present invention, is an ECF (elementary chlorine free) or TCF (total chlorine free) bleaching process is used in order to eliminate environmental

problems such as the generation of environmental hormone dioxin.

As bleaching stages used in this step, DED, DEDD, DEDP, DEZP, DEOP, DEOZ and PEOZ can be selectively applied. A bleaching process, the number of bleaching stages, and bleaching conditions, are determined depending on the degree of required bleaching.

In the above description of the bleaching stages, D means chlorine dioxide bleaching, E means alkaline extraction, P means peroxide bleaching, O means oxygen bleaching, and Z means ozone bleaching.

If the content of metal ions in the pulp is high, the metal ions will be inactivated by treating the pulp with a chelating agent (EDTA, DTPA, DTPMPA, etc.) to increase bleaching efficiency before conducting the bleaching of the pulp.

Herein, the chelating agent is a chemical for making the reactivity of metal ions impotent, and if large amounts the metal ions are present in the pulp, they will remarkably deteriorate the performance of a bleaching chemical used for bleaching.

For this reason, if the content of the metal ions is large so that it reduces bleaching efficiency, the pulp is treated with the chelating agent before conducting the bleaching of the pulp.

As an example of a bleaching method using the bleaching stages, the bleaching stages of DEDD indicate that bleaching is conducted in four sequential steps of: (1) chlorine dioxide bleaching, (2) alkaline extraction, (3) chlorine dioxide bleaching, and (4) chlorine dioxide bleaching.

In other words, various bleaching stages listed above indicate that a pulp producer may selectively the bleaching stages depending on the brightness or chemical purity required in the pulp to be produced, or the preference of a worker.

Regarding the purpose for increasing the number of the bleaching stages, when the brightness or chemical purity is greatly required, the number of the bleaching stages may be increased or the amount of chemicals used may be increased. Also, even if the same level is required, a method of reducing the amount of a chemical used in each stage and increasing the number of the stages can be used in order to minimize adverse effects on pulp (pulp damage and decomposition, etc).

Accordingly, even if the quality of the same level is required, it is possible to control the number of the bleaching stages or the amount of chemicals used, and it is difficult to express this control as an absolute numerical value, because the state of pulp supplied into the bleaching process varies depending the degrees of pulping or cooking conducted in the above-described steps.

However, when the pulp is bleached, it is preferable that the content of lignin in the pulp produced in the digester be first measured and, based on the measured content, the amount of addition of bleaching chemicals be calculated so as to increase or decrease the amount depending on the required quality.

Thus, the present invention can prevent the generation of dioxin, an environmental pollutant, using said bleaching agent, and has excellent bleaching effects.

In the most embodiment of the present invention, the method for producing the bleached chemical pulp for the production of wood-free paper, art paper, non-woven fabric, special purpose paper or tissue paper comprises conducting the cooking process in the following conditions and the ECF or TCF bleaching process: the content of active alkali: 16 - 20%; the content of AQ 0.01-1%; liquor ratio: 3.5-6.0; cooking temperature: 150-180 ℃; and cooking time: 120 - 200 minutes.

Also, the yield of the produced papermaking pulp, the characteristics of the fibers, the papermaking characteristics, etc., are controlled through the combination of cooking conditions, bleaching conditions and methods.

In addition to the method for producing the unbleached and semi-chemical pulp for the production of industrial paper or corrugated board liner paper and the method for producing the bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, non-woven fabric, special purpose paper or toilet paper, the present invention also provides a method for producing refiner mechanical pulps for the production of newsprint paper or medium-quality paper.

Thus, the steps of the method for producing refiner mechanical pulp for the production of newsprint paper or medium-quality paper will be sequentially described in detail. This method comprises: a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo; and a second step of screening the cut bamboo chips to filter out small fragments or impurities from the chips and washing the chips with water to remove contaminants from the chips.

Also, the method comprises: a third step of primarily

refining the washed bamboo chips, in which the bamboo chips are ground in a disc refiner; and a fourth step of screening the refined bamboo chips, in which contaminants are removed from the bamboo chips using a pressure screen, and an incompletely defibrated portion of the chips is fed back into the disc refiner.

Also, the method comprises: a fifth step of secondarily refining the defibrated pulp, in which the defibrated pulp is further ground; and a sixth step of screening the refined pulp, in which contaminants are removed from the pulp using a pressure screen, and an incompletely defibrated portion of the pulp is fed back into the disc refiner.

In addition, the method comprises: a seventh step of cleaning the defibrated pulp, in which contaminants introduced together with the bamboo are removed using a centrifugal cleaner; and an eighth step of forming the cleaned pulp into a sheet and drying the sheet.

In other words, the sequence of the steps of this method is substantially the same as that of the above-described method for producing unbleached chemical and semi-chemical pulp for the production of industrial paper or corrugated board liner paper and as that of the above-described method for producing bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, non-woven fabric, special purpose paper or toilet paper, however, it is different in that the cooking step is not carried out and the two refining steps are additionally conducted.

Thus, only the refining steps will be additionally described herein.

As used herein, the term "refining step" refers to a

step of producing refiner mechanical pulp, in which the bamboo chips resulting from the previous washing step are ground in the disc refiner to produce the pulp.

This refining step in the present invention is repeated two times to grind the chips into very fine pieces.

Accordingly, in this method, the prepared, screened and washed bamboo chips are defibrated using the refiner so as to prepare refiner mechanical pulp for the production of newsprint paper and medium-quality paper.

In this case, if the high brightness is required in the pulp, single-stage or two-stage peroxide bleaching is preferably carried out.

Also, the present invention also provides articles produced according to all the above-described pulp production methods, i.e., pulps produced using a bamboo.

Also, the pulps are made into the form of a sheet or roll, in which the sheet pulp has a thickness of 0.1-3 mm, and the roll pulp is obtained by winding a web having a thickness of 0.1-1.5 mm.

In other words, the sheet or roll pulp is an intermediate product, which will be introduced into a papermaking process to produce paper as described above.

Thus, if a pulp production factory and a papermaking factory are far away from each other, the pulp must be transported in a state in which it was packed in the form of a sheet or roll as described above. However, if the factories are integrated factories, the pulp needs not to be specially packed.

Methods for producing paper products from the intermediate products produced as described above will now be

described in a manner classified according to the kind of the paper products.

First, a method for producing industrial papers or corrugated board liner paper using said unbleached chemical and semi-chemical bamboo pulp will be described.

Specifically, the method for producing the industrial paper or corrugated board liner paper comprises: a step of disintegrating the unbleached chemical and semi-chemical bamboo pulp; and a step of refining the disintegrated pulp.

Also, the method comprises: a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp; and a step of screening the pulp.

Also, the method comprises: a sheet forming step of making the screened pulp into a product (web) in the form of a paper or paperboard; and a pressing step of pressing the web obtained in the sheet forming step to remove water from the web.

Also, the method comprises: a drying step of further removing water from the pressed web; and a calendering step of making the thickness of the paper or paperboard uniform.

In addition, the method comprises a step of slitting and cutting the dried and calendered paper into a sheet or roll and packing the sheet or roll.

Hereinafter, each of said steps will be described in further detail.

First, in the step of disintegrating the unbleached chemical and semi-chemical bamboo pulp, the pulp sheet is repulped or disintegrated into individual fibers using a pulper or hydrapulper.

This repulping or disintegration step may also be omitted, if the pulp is not made into the sheet in the pulp production process and is immediately fed to a papermaking process through pipe lines and the like.

In the step of refining the disintegrated pulp, wood pulp and bamboo pulp are refined using a disc refiner or cone refiner according to conditions required for the desired paper in order to control the structural, physical and optical properties of the paper.

Chemical pulp of broadleaf trees is usually refined at an SEL of about 0.1-5.0 Ws/m.

However, bamboo pulp needs to be treated in a manner different from wood pulp, because it has a relatively low lignin content, and its fiber is thin.

Thus, the bamboo pulp is either refined at a weak SEL (specific edge load; index indicative of the intensity of energy applied from the refiner to the pulp) of 0.01-2.5 Ws/m depending on the required properties of paper to be produced, or treated using a deflaker.

Refiners suitable for refining the bamboo pulp at low SEL include multidisk refiner, Conflo and the like.

On the other hand, if more refining is required, the refining of the pulp is conducted at a higher SEL.

In the step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp, the addition of wet chemicals and additives is performed to adjust a process and to satisfy the properties of paper according to the kind and intended use thereof.

In the case of industrial paper, liner base paper,

toilet paper and thin wrapping paper, any filler is not used, and the addition of chemicals is adjusted only depending on required size degree, wet strength or dry strength.

Examples of a chemical, which can be used for the adjustment of sizing degree, include rosin emulsion, AKD, ASA and the like, and examples of a wet strength agent, which can be used in the present invention, include urea resin, melamine resin, polyamide epichlorohydrin, acrylamide glyoxal and the like. This chemical is added in an amount of 0.1-3% depending on required wet strength or dry strength.

In the case of wood-free paper, coated base paper, newsprint paper and medium-quality paper, a filler is used in an amount of 10-30% for the improvement of printing quality. Examples of the filler, which can be used in the present invention, include calcium carbonate, activated clay, and titanium dioxide.

Examples of the sizing agent, which can be used in the present invention, include rosin emulsion, AKD, ASA and the like.

For the retention of the sizing agent and the filler, microparticle systems (e.g., cationic starch, PAM, bentonite, colloidal silica, organic microparticles, etc.) are used.

Also, the screening step is performed to break aggregates formed in a paper stock preparation process or pipe lines for supplying the paper stock to a papermaking machine and to remove lumps, which are not disintegrated, before supplying the paper stock to the papermaking machine. This screening step is usually performed just before the papermaking machine so as to pass the paper stock.

Then, the sheet forming step for producing the paper-

or board-like product is a process in which the raw material subjected to the paper stock preparation process is made into the form of a web.

Then, the pressing step of pressing the web formed in the sheet forming step to remove water from the web is performed and will now be described in detail.

Specifically, the pressing step serves to remove water from the web formed in the sheet forming step, make the web more compact and facilitate the bonding between the fibers.

In this step, it is preferable to remove water as much as large within the range in which the quality of the product is not deteriorated. This reduces the use of steam in a drying section to increase economy.

However, the pressure used in this pressing step greatly varies depending on the kind of paper.

In the case of paperboard, toilet paper and the like, a pressure lower than that in other printing and writing papers or industrial papers is applied, because a bulk property is important.

Then, the drying step of further removing water from the web passed through the pressing step is carried out, in which water in the web passed through the sheet forming step and pressing step is further removed to impart the inherent property of paper or paperboard.

Then, in the inventive method, the calendering step of making the thickness of the paper or paperboard uniform is carried out.

The calendering step serves to make the thickness of the paper or paperboard uniform and to smoothen the surface of the paper or paperboard.

In addition, the step of slitting and cutting the dried and calendered paper into a sheet or roll and packing the sheet or roll is finally performed, thereby producing industrial paper or corrugated board liner paper.

In other words, in the slitting, cutting and packing step, the dried and calendered paper or paperboard is finally slit and cut into a sheet or roll according to the demand of consumers, and the sheet or roll is packed.

The above paper production method has been described with respect to the method for producing the industrial paper and corrugated board liner paper.

However, the paper production method according to the present invention is not limited only to said industrial paper and corrugated board liner paper.

Thus, a method for producing wood-free paper and art paper will now be described in detail.

Specifically, the method for producing wood-free paper and art paper comprises a step of disintegrating the chemical bamboo pulp produced according to the above-described inventive method and a step of refining the disintegrated pulp.

Then, a step of blending the refined pulp with wood pulp (bleached chemical pulp of broadleaf trees) and a step of adding chemicals (sizing agent, filler, retention agent, dehydrating agent and other additives) to the blended pulp are carried out.

Also, the method comprises a step of screening the chemical-added pulp and a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard.

Also, the method comprises a pressing step of pressing the web obtained in the sheet forming step to remove water from the web, and a drying step of further removing water from the pressed web.

Also, the method comprises a step of sizing the surface of the dried web, a step of drying the sized web, and a calendering step of making the thickness of the paper or paperboard uniform.

In addition, the method comprises a step of coating the paper or paperboard with a pigment, a step of drying the coated paper or paperboard, and a super-calendering step of imparting surface smoothness and gloss to the paper or paperboard.

Finally, the dried and super-calendered paper is slit and cut into a sheet or roll shape which is then packed, thus producing wood-free paper and art paper.

Most of the steps of this method, including the step of disintegrating the bleached chemical bamboo pulp and the step of refining the disintegrated pulp, are the same as those of the above-described method for producing the industrial papers and corrugated board liners.

However, this method is different in that it comprises the step of blending the refined pulp with wood pulp (board-leaved tree bleached chemical pulp, etc.), the step of sizing the surface of the dried web, the step of coating the paper, and the step of super-calendering the paper.

Thus, only the different steps of this method will now be described in detail.

Specifically, in the step of blending the refined pulp with wood pulp (bleached chemical pulp of broadleaf trees),

the blending of the pulps is performed to adjust the various properties of paper to be produced, by blending the refined pulp with the bleached craft pulp, thermal mechanical pulp, chemical thermal mechanical pulp or bleached chemical thermal mechanical pulp of broadleaf trees at a suitable ratio according to the required properties of the paper.

In the production of wood-free paper such as writing and printing paper, coated base paper and the like, the bleached craft pulp of broadleaf trees is blended in an amount of about 50-80% to achieve the excellent smoothness and formation of paper so as to provide good printing quality.

Also, in the production of newsprint paper and medium-quality paper, in order to provide sufficient strength properties, the bleached craft pulp of needle-leaf trees, the bleached chemical pulp of bamboos, white ledger or CPO (computer printout) deinked pulp is blended in an amount of 10-25%.

In the case of industrial paper, toilet paper and tissue paper, bamboo pulp can be used alone, and in some cases, it can be used in a mixture with wastepaper.

Also, in the step of sizing the surface of the dried web, the surface sizing is performed to control the impregnation of fluid into paper and improve the surface characteristics of paper so as to improve the surface strength and printing quality of the paper.

In this step, oxidized starch is usually used, but in some cases, the web can be treated with a coating pigment in a sizing press, such that the print quality of the paper can be further improved without a need for a coating process.

Also, the method comprises the pigment coating step and

the super-calendering step. The super-calendering step is performed to impart surface smoothness and gloss to the coated base paper.

Thus, using the inventive method for producing wood-free paper or art paper, the intermediate product pulp produced in the above-described method for producing the bleached chemical pulp for the production of tissue paper, wood-free paper, art paper or toilet paper is produced into wood-free paper or art paper as a final product.

Furthermore, an embodiment of the method for producing printing and writing paper such as wood-free paper or coated base paper will now be described in further detail. Depending on the required print quality of paper, the bleached chemical bamboo pulp is blended with wood pulp such as the bleached chemical pulp or bleached chemical thermal mechanical pulp of broadleaf trees.

Also, papermaking chemicals such as 10-30% of filler (calcium carbonate, clay, talc, titanium dioxide, etc.), 0.1-3% of a sizing agent (rosin emulsion, AKD or ASA) and/or a retention agent (cationic starch, PAM, bentonite, colloidal silica, organic microparticles, etc.) can be added to the pulp.

Also, to improve the surface strength and print quality of paper, the surface of paper is sized with oxidized starch. If necessary, the surface sizing can also be performed using a coating pigment.

The bleached chemical pulp of boardleaf trees is refined at an SEL of about 0.1-5.0 Ws/m, and the chemical bamboo pulp is refined at a weak SEL of about 0.01-2.5 Ws/m depending on the required properties of paper or is simply

treated using a deflaker.

Meanwhile, according to the present invention, tissue paper and toilet paper can also be produced using the above-described method for producing the bleached chemical pulp.

Thus, the steps of this method will now be described.

Specifically, this method comprises a step of disintegrating the bleached chemical bamboo pulp and a step of refining the disintegrated pulp.

Also, the method comprises a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp and a step of screening the chemical-added pulp.

Also, the method comprises a sheet forming step of making the screened pulp into a paper- or paperboard-like product, and a pressing step of pressing the web obtained in the sheet forming step to remove water from the web.

In addition, the method comprises a drying step of further removing water from the pressed web, and a final step of slitting and cutting the dried paper into a sheet or roll which is then packed, thus producing tissue paper.

The steps of said method for producing tissue paper and toilet paper have all been described in detail in the method for producing industrial papers and corrugated board liners and the method for producing wood-free paper and art paper, and thus will no longer be described.

Also, the present invention also provides a method for producing toilet paper using the bleached chemical bamboo pulp, and the method will now be described in detail.

Specifically, this method for producing toilet paper comprises a step of disintegrating the bleached chemical

bamboo pulp produced according to the present invention, and a step of refining the disintegrated pulp.

Also, the method comprises a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp, and a step of screening the chemical-added pulp.

Also, the method comprises a sheet forming step of making the screened pulp into a paper or sheet product, and a pressing step of pressing the web obtained in the sheet forming step to remove water from the web.

In addition, the method comprises a drying step of further removing water from the pressed web, and a final step of slitting and cutting the dried paper into a sheet or roll which is then packed, thus producing toilet paper.

The tissue paper or toilet paper is dried using a Yankee dryer and prepared to have low weight and thus low strength. For this reason, in order to impart the paper with the ability capable of resisting a force applied during the use thereof, a doctor blade attached to the end of the Yankee dryer is used to form invisible wrinkles on the tissue paper or toilet paper.

The steps of said method for producing toilet paper have all been described in detail in the method for producing industrial papers and corrugated board liners and the method for producing wood-free paper and art paper, and thus will no longer be described.

Furthermore, the present invention provides a method for producing newsprint paper or medium-quality paper using the refiner mechanical pulp of bamboos. Thus, this method will now be described in detail.

First, in the method for producing newsprint paper or medium-quality paper using the refiner mechanical pulp of bamboos, a step of disintegrating the refiner mechanical pulp of bamboos is first carried out.

Also, the method comprises a step of disintegrating and refining a strengthening pulp, and a step of blending the refined strengthening pulp with said refined refiner mechanical pulp.

Also, the method comprises a step of adding chemicals (sizing agent, filler, retention agent, strengthening agent and other additives), and a sheet forming step of making the blended pulp into a paper or paperboard product.

Also, the method comprises a pressing step of pressing the web obtained in the sheet forming step to remove water from the web, and a drying step of further removing water from the pressed web.

In addition, the method comprises a step of sizing the surface of the dried web, a step of drying the sized web, and a step of slitting and cutting the dried paper into a sheet or roll which is then packed, thus producing newsprint paper or medium-quality paper.

To improve the print quality and the like of newsprint and medium-quality paper, the paper may also be coated with a coating pigment in a sizing press instead of performing the surface sizing.

The steps of said method for producing newsprint paper and medium-quality paper have all been described in detail in the method for producing industrial papers and corrugated board liners and the method for producing wood-free paper and art paper, and thus will no longer be described.

Knowledge obtained through many experiments conduced by the applicant in order to obtain the optimal quality and productivity of papers is as follows.

In the production of toilet paper or thin wrapping paper, the bleached chemical pulp of bamboos is refined at an SEL of 0.01-1.0 Ws/m, and if necessary, the sizing agent is used in an amount of 0-0.5%, and the strengthening agent is used in an amount of 0-0.5%.

If necessary, wrinkles are formed on the paper using a doctor blade in a Yankee dryer, or the paper is embossed after the drying step.

According to the present invention, using the antibacterial activity of the bleached chemical pulp of bamboo, various special purpose papers (non-woven fabric usable in various applications such as sanitary, clothing and hospital gowns and automobile inner materials, food or drug wrapping material, etc.) can be produced.

【Mode for Invention】

Example 1

A Myanmar bamboo was split to a width of about 2 mm and then cut to a length of 15-25 mm. The cut material was screened through a 60-mesh screen to remove contaminants and small bamboo fragments, followed by washing.

400 g (on an oven-dry weight basis) of the washed bamboo was placed in a digester into which water was added. Then, 16% (as $Na_2O$) active alkali and 0.1% anthraquinone were added thereto, and the ratio of the chemicals to the weight of the bamboo was adjusted to 4:1. Then, the bamboo chips were cooked in the digester at 170 ℃ for 120 minutes.

The cooked pulp was washed and subjected to a five-

stage bleaching of DED(EO)D, and the bleached pulp was refined with 400 ml of CSF, thus producing hand-made paper having a weight of 60 g/$m^2$. The properties of the resulting paper are shown in Table 1 below.

Table 1: Results of soda and soda-anthraquinon pulping tests

| Properties of pulp and paper | NaOH | NaOH + AQ |
|---|---|---|
| Screening yield of pulp before bleaching | 47.2 | 48.5 |
| Kappa number* | 13.6 | 10.8 |
| Screening yield of pulp after bleaching | 43.5 | 46.4 |
| Brightness (% ISO) | 88.4 | 92.6 |
| Breaking length (km) | 7.9 | 8.5 |
| Tensile index (mN $m^2$/g) | 8.1 | 8.6 |
| Burst index (kPa $m^2$/g) | 3.8 | 4.2 |

*Kappa number is used to indicate the amount of lignin remaining in the pulp produced in the digester, and is used as a standard for determining the amount of addition of chemicals in bleaching, and is calculated from the consumed amount of potassium permanganate through oxidation-reduction titration.

Example 2

The pretreatment of bamboo was performed in the same manner as in Example 1. Also, the amount of addition of chemical liquor in pulping was adjusted to 16%, 14% and 12%, and as an additive for promoting a reaction and protecting hemicellulose, 0.1% AQ was used.

For the evaluation of the possibility of use as industrial paper, the pulp was not bleached.

The washed pulp was refined with 400 ml of CSF, thus preparing hand-made paper having a weight of 80 g/$m^2$. The properties of the resulting paper are shown in Table 2 below.

Table 2: Test results for unbleached bamboo pulp

| Properties of activated alkali pulp (% as $Na_2O$) and paper | 12 | 14 | 16 |
|---|---|---|---|
| Pulp yield (%) | 42.7 | 46.5 | 48.5 |
| Kappa number | 14.6 | 12.6 | 10.5 |
| Brightness (% ISO) | 34.1 | 35.6 | 38.2 |
| Breaking length | 10.8 | 12.5 | 14.8 |
| Tensile index (mN $m^2$/g) | 7.6 | 8.9 | 9.6 |
| Burst index (kPa $m^2$/g) | 6.9 | 7.8 | 8.4 |

【Industrial Applicability】

As described above, according to the present invention, the split and cut bamboo chips are pulped in the cooking process using the soda-anthraquinon process using anthraquinon as a catalyst. Thus, the present invention can have great effects on delignification, the improvement in pulp quality and the increase in pulp yield.

Also, according to the present invention, the bamboo chips are made thin in the raw material treatment process to facilitate the impregnation of liquid chemicals into the chips and the cooking of the chips. Also, papermaking pulp can be produced in milder conditions by previously eliminating the factors of causing the loss of chemicals and reducing the pulp quality.

Furthermore, the soda-AQ process, in which anthraquinone is used as a catalyst in a cooking step, is applied for the pulping of bamboo, so that the present

invention can have great effects on delignification, the improvement in pulp quality and the increase in pulp yield.

Also, an environmental problem such as the generation of dioxin can be solved by applying an ECF and TCF bleaching process, and it is possible to control the quality of paper depending on the properties of paper to be produced, by controlling the cooking and bleaching conditions.

In addition, through the above-described technology for producing high-quality paper making pulp, wood pulp produced from felled trees grown over dozens of years can be replaced with pulp produced from bamboos, which rapidly grow to a usable degree only within about five months. Thus, the present invention is expected to have a very great effect on greenhouse gas emission reduction, which should be considered for the preservation of global environment.

【CLAIMS】

【Claim 1】

A method for producing pulps from a bamboo, the method comprising:

a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo to make bamboo chips;

a second step of screening the cut bamboo chips to filter out small fragments or impurities from the bamboo chips and washing the chips the bamboo chips with water to remove contaminants from the bamboo chips;

a third step of cooking the bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked at high temperature, thus softening and pulping the bamboo chips;

a fourth step of cleaning the bamboo chips using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo;

a fifth step of screening the cooked pulp, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the bamboo is fed back into the digester;

a sixth step of washing and thickening the screened pulp, in which a decker is used to wash the pulp, thus removing the chemical liquor, and to squeeze water so as to thicken the pulp; and

a seventh step of using the thickened pulp to produce unbleached chemical and semi-chemical bamboo pulps for industrial papers or corrugated board liners.

【Claim 2】

The method of Claim 1, wherein, in the third step of cooking the chips, the amount of alkali (as $Na_2O$) added to water is 10-30 % based on the oven-dry weight of the bamboo chips (i.e., mass excluding the content of moisture in the bamboo chips), and the anthraquinon (AQ) is added in an amount of 0.01-2%.

【Claim 3】

A method for producing pulps from a bamboo, the method comprising:

a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo to make bamboo chips;

a second step of screening the cut bamboo chips to filter out small fragments or impurities from the bamboo chips and washing the chips the bamboo chips with water to remove contaminants from the bamboo chips;

a third step of cooking the bamboo chips, in which the bamboo chips are introduced into a digester, the ratio of a chemical liquor consisting of water, alkali and anthraquinone to the weight of the bamboo chips is adjusted to 1:3.5-6.0 (bamboo: chemical liquor), and the bamboo chips are cooked at high temperature, thus softening and pulping the bamboo chips;

a fourth step of cleaning the bamboo chips using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo;

a fifth step of screening the cooked pulp, in which contaminants are removed from the cooked pulp using a pressure screen, and an incompletely cooked portion of the bamboo is fed back into the digester;

a sixth step of washing and thickening the screened pulp, in which a decker is used to wash the pulp, thus removing the chemical liquor, and to squeeze water so as to thicken the pulp;

a seventh step of bleaching the pulp; and

an eighth step of using the bleached pulp to produce bleached chemical pulp for the production of tissue paper, wood-free paper, art paper, non-woven fabric, special purpose paper or toilet paper.

【Claim 4】

A method for producing pulps from a bamboo, the method comprising:

a first step of removing a leaf from a bamboo and splitting and cutting the leaf-removed bamboo to make bamboo chips;

a second step of screening the cut bamboo chips to filter out small fragments or impurities from the bamboo chips and washing the chips the bamboo chips with water to remove contaminants from the bamboo chips;

a third step of primarily refining the washed bamboo chips, in which the washed bamboo chips are ground in a disc refiner;

a fourth step of screening the refined bamboo chips, in which contaminants are removed from the ground bamboo chips using a pressure screen, and an incompletely defibrated portion of the chips is fed back into the disc refiner;

a fifth step of secondarily refining the screened pulp fiber, in which the defibrated pulp fiber is further ground;

a sixth step of screening the secondarily refined pulp, in which contaminants are removed from the refined pulp using a pressure screen, and an incompletely defibrated portion of the pulp fiber is fed back into the disc refiner;

a seventh step of cleaning the screened pulp using a centrifugal cleaner so as to remove contaminants introduced together with the bamboo; and

an eighth step of using the cleaned pulp to produce refiner mechanical pulp for the production of newsprint paper or medium-quality paper.

【Claim 5】

The method of Claim 3, wherein the third step of bleaching the pulp is carried out using bleaching stages according to an ECF (elementary chlorine free) or TCF (total chlorine free) bleaching process.

【Claim 6】

The method of Claim 5, wherein the bleaching stages are selected from the group consisting of DED, DEDD, DEDP, DEZP, DEOP, DEOZ, PEOZ, DEDED, DED(EO)D, DEDOP and DEDZP.

【Claim 7】

Natural bamboo pulp produced using the method of any one of Claims 1 to 6.

【Claim 8】

The pulp of Claim 7, which is in the form of a sheet or roll.

【Claim 9】

The pulp of Claim 8, wherein the sheet pulp has a thickness of 0.1-3 mm.

【Claim 10】

The pulp of Claim 8, wherein the roll pulp is obtained by winding a web having a thickness of 0.1-1.5 mm.

【Claim 11】

A method for producing paper from bamboo pulp, the method comprising:

a step of disintegrating the unbleached chemical and semi-chemical bamboo pulp produced according to the method of Claim 1;

a step of refining the disintegrated pulp;

a step of adding chemicals (sizing agent, retention agent, strengthening agent and other additives) to the refined pulp;

a step of screening the chemical-added pulp;

a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard;

a pressing step of pressing the web obtained in the sheet forming step to remove water from the web;

a drying step of further drying water from the pressed web;

a calendering step of making the thickness of the paper or paperboard uniform; and

a step of slitting and cutting the dried paper into a sheet or roll and packing the sheet or roll,

thereby producing industrial paper or liner paper for corrugated boards.

【Claim 12】

A method for producing paper from bamboo pulp, the method comprising:

a step of disintegrating the bleached chemical bamboo pulp produced according to the method of Claim 3;

a step of refining the disintegrated pulp;

a step of blending the refined pulp with wood pulp (bleached chemical pulp of broadleaf trees);

a step of adding chemicals (sizing agent, filler, retention agent, dehydrating agent and other additives) to the blended pulp;

a step of screening the pulp having the chemicals added thereto;

a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard;

a pressing step of pressing the web obtained in the sheet forming step to remove water from the web;

a drying step of further removing water from the pressed web;

a step of sizing the surface of the dried web;

a step of drying the sized web;

a calendering step of making the thickness of the paper or paperboard uniform;

a step of coating the calendered paper or paperboard with a pigment;

a step of drying the coated paper or paperboard;

a super-calendering step of imparting smoothness and gloss to the surface of the dried paper or paperboard; and

a step of slitting and cutting the calendered paper into a sheet or roll and packing the sheet or roll,

thereby producing wood-free paper and art paper.

【Claim 13】

A method for producing paper from bamboo pulp, the method comprising:

a step of disintegrating the bleached chemical bamboo pulp produced according to the method of Claim 3;

a step of refining the disintegrated pulp;

a step of adding chemicals (sizing agent, retention agent and other additives) to the blended pulp;

a step of screening the pulp having the chemicals added thereto;

a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard;

a pressing step of pressing the web obtained in the sheet forming step to remove water from the web;

a drying step of further removing water from the pressed web; and

a step of slitting and cutting the dried paper into a sheet or roll and packing the sheet or roll,

thereby producing tissue paper.

【Claim 14】

A method for producing paper from bamboo pulp, the method comprising:

a step of disintegrating the bleached chemical bamboo pulp produced according to the method of Claim 3;

a step of refining the disintegrated pulp;

a step of adding chemicals (sizing agent, retention agent and other additives) to the blended pulp;

a step of screening the pulp having the chemicals added thereto;

a sheet forming step of making the screened pulp into a product (web) in the form of paper or paperboard;

slitting and cutting the calendered paper into a sheet or roll and packing the sheet or roll,

thereby producing toilet paper.

【Claim 15】

A method for producing paper from bamboo pulp, the method comprises:

a step of disintegrating the refiner mechanical pulp produced according to the method of Claim 4;

a step of disintegrating and refining a reinforcing pulp;

a step of blending the disintegrated refiner mechanical pulp with the refined reinforcing pulp;

a step of adding chemicals (sizing agent, filler, retention agent, strengthening agent and other additives) to the blended pulp;

a sheet forming step of making the blended pulp into a product (web) in the form of paper or paperboard;

a pressing step of pressing the web obtained in the sheet forming step to remove water from the web;

a drying step of further removing water from the pressed web; and

a step of sizing the surface of the dried web;

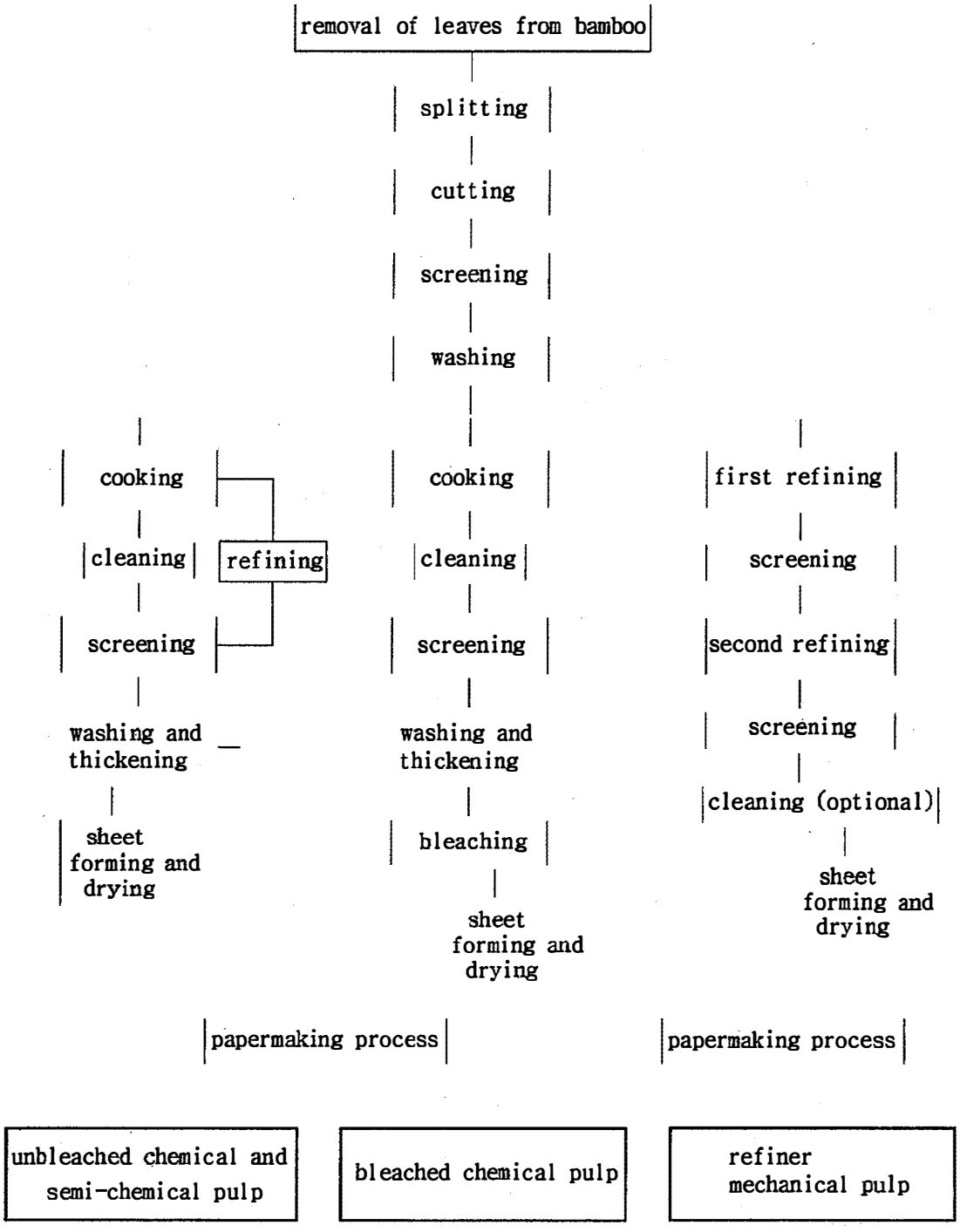
a step of drying the sized web; and

slitting and cutting the dried paper into a sheet or roll and packing the sheet or roll,

thereby producing newsprint paper or medium-quality paper.

1 / 1

FIG. 1


removal of leaves from bamboo
splitting
cutting
screening
washing
cooking
cleaning
refining
screening
washing and thickening
sheet forming and drying
cooking
cleaning
screening
washing and thickening
bleaching
sheet forming and drying
first refining
screening
second refining
screening
cleaning (optional)
sheet forming and drying
papermaking process
papermaking process
unbleached chemical and semi-chemical pulp
bleached chemical pulp
refiner mechanical pulp

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/KR2●●5/●●2118

**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**

Minimum documentation searched (classification system followed by classification symbols)
IPC8 D21C3/●4, D21H11/12, D21H19/36

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

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
eKIPASS, INSPECT "Bamboo, Semi-chemical, Chemical, Pulp, Paper, Manufacturing"

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 4652341 A1 (Eric S. Prior) 24. Mar. 1987<br>- See the whole document. | 1-15 |
| A | JP ●5321190 A (Kikuchi Shingo) ●7. Dec. 1993<br>- See the whole document. | 1-15 |
| A | JP ●5239791 A (Tootrru Inc.) 17. Sep. 1993<br>- See the whole Document. | 1-15 |
| A | EP 1371778 A1 (Oji Paper Co., Ltd.) 17. Dec. 2●●3<br>- See the whole Document. | 1-15 |

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

☒ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

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| US 4652341 A1 | Mar. 24. 1987 | NONE | |
| JP 05321190 A | Dec. 07. 1993 | JP 03184993 B2 | Jul. 09. 2001 |
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| EP 1371778 A1 | Dec. 17. 2003 | CN 1480789 A | Mar. 10. 2004 |
| | | JP 16068242 A | Mar. 04. 2004 |
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(54) Title: SANITARY TISSUE PRODUCTS

(57) Abstract: Sanitary tissue products employing fibrous structures that exhibit novel combination of average TS7 values and slip stick coefficient of friction and/or compressibility properties and methods for making same.

# SANITARY TISSUE PRODUCTS

## FIELD OF THE INVENTION

The present invention relates to sanitary tissue products comprising fibrous structures that exhibit a novel combination of surface feel (surface mobility) as evidenced by average TS7 Emtec values of the sanitary tissue products and surface smoothness (glide vs. grip) as evidenced by slip stick coefficient of friction of the sanitary tissue product and/or a novel combination of surface feel (surface mobility) as evidenced by average TS7 Emtec values of the sanitary tissue products and cushiness as evidenced by compressibility of the sanitary tissue products and methods for making same.

## BACKGROUND OF THE INVENTION

Surface feel (surface mobility) and surface smoothness and/or cushiness are attributes that consumers desire in their sanitary tissue products, for example bath tissue products. However, there has been a surface feel and/or surface smoothness and/or cushiness dichotomy. Historically when the surface feel and/or surface smoothness of a sanitary tissue product, such as bath tissue product, have been increased, the cushiness of the sanitary tissue product has decreased and vice versa. A technical measure of surface feel is average TS7 Emtec values of the sanitary tissue product, which is measured by the Emtec Test Method described herein. A technical measure of surface smoothness is slip stick coefficient of friction values of the sanitary tissue product, which is measured by the Slip Stick Coefficient of Friction Test Method described herein. A technical measure of cushiness is compressibility values of the sanitary tissue product which is measured by the Stack Compressibility and Resilient Bulk Test Method described herein. Current sanitary tissue products fall short of consumers' expectations for surface feel and surface smoothness and cushiness, with and more importantly without surface softening agents.

Emtec TS7 values, as outlined in the Emtec Paper Testing Technology user manual, are "dependent on the softness/hardness of the fibers (stiffness of the individual fibers) and structure of the material (bulk, binding of the fibers). The height of this peak TS7 correlates with the real material softness". "Excitation of horizontal vibrations of the blades itself (in resonance frequency at approximately 6,500 Hz), caused by momentary blocking and swinging back of the blades by the fibers when moving over the surface." In order to achieve low average Emtec TS7 values as measured according to the Emtec Test Method described herein and thus good surface mobility/real material softness, it has in the past been necessary for the sanitary tissue product to exhibit low Slipstick Coefficient of Friction values as well.

It is also desired for the sanitary tissue product to have a high level of compressibility to give the consumer the "cushiness" that is desired. Historically, as compressibility is increased, surface mobility (as represented by average Emtec TS7 values) becomes worse, thus resulting in higher average TS7 values as measured according to the Emtec Test Method described herein.

Formulators in the past believed that a creped surface of a fibrous structure, such as by creping the fibrous structure off a dryer or Yankee and/or by other means of foreshortening the fibrous structure, such as rush transfer steps in making the fibrous structure, was needed to achieve improved softness of fibrous structure and to achieve low average TS7 values. Such formulators have tried to utilize the EMTEC Tissue Softness Analyzer from Emtec Electronic GmbH of Leipzig, Germany to measure the softness (TS7) of creped fibrous structures and/or surface smoothness (TS750) of the creped surfaces of the sanitary tissue products. In the past, the formulators of sanitary tissue products apparently believed that creped surfaces of wood pulp fiber-containing fibrous structures were needed in order to attempt to measure softness of the creped fibrous structures using the EMTEC Tissue Softness Analyzer. It has been unexpectedly found that uncreped surfaces of fibrous structures can be measured using the EMTEC Tissue Softness Analyzer to measure softness of such fibrous structures, which is contrary to the teachings of the past.

Another problem with the past formulators' measurements using the EMTEC Tissue Softness Analyzer is that the measurements are very dependent upon which of two calibration methods is used in calibrating the EMTEC Tissue Softness Analyzer. Apparently, the past formulators failed to appreciate this fact and didn't indicate which of the two calibration methods were used or even if the EMTEC Tissue Softness Analyzer was calibrated at all. As a result the values the past formulators reported for TS7 and TS750 and other EMTEC Tissue Softness Analyzer values obtained from the EMTEC Tissue Softness Analyzer on creped surfaces of wood pulp fiber-containing fibrous structures are suspect at best, if not worthless from an absolute value point of view. At most, the values obtained by past formulators for creped fibrous structures may have value internally to the formulator from a relative perspective to show which versions of the same creped surface, wood pulp-containing fibrous structures differ in softness.

Accordingly, one problem faced by sanitary tissue product manufacturers is how to improve (i.e., decrease) the average TS7 Emtec values and/or the slip stick coefficient of friction

properties, with and more importantly without surface softening agents, and improve (i.e., increase) the compressibility of sanitary tissue products, for example bath tissue products, to make such sanitary tissue products smoother and cushier to better meet consumers' expectations for more clothlike, luxurious, and plush sanitary tissue products since the actions historically used to make a sanitary tissue product smoother negatively impact the cushiness of the sanitary tissue product and vice versa.

Accordingly, there exists a need for sanitary tissue products, for example bath tissue products, that exhibit improved average TS7 Emtec values and slip stick coefficient of friction properties and improved compressibility properties, to provide consumers with sanitary tissue products that fulfill their desires and expectations for more comfortable and/or luxurious sanitary tissue products, and methods for making such sanitary tissue products.

## SUMMARY OF THE INVENTION

The present invention fulfills the need described above by providing sanitary tissue products, for example bath tissue products, that are smoother and cushier than known sanitary tissue products, for example bath tissue products, as evidenced by improved average TS7 Emtec values as measured according to the Emtec Test Method described herein and/or improved slip stick coefficient of friction values as measured according to the Slip Stick Coefficient of Friction Test Method described herein and improved compressibility values as measured according to the Stack Compressibility and Resilient Bulk Test Method described herein, and methods for making such sanitary tissue products.

It has been unexpectedly found that the following variables improve surface mobility (lower average TS7 values) without Slipstick Coefficient of Friction being as much of a factor and while providing good "cushiness" (increased Compressibility): 3D patterned fibrous structure (semi-continuous and/or discrete knuckles), angle of the semi-continuous and discrete knuckles (straight and greater than 45° from machine direction), and orientation of fibrous structure (uncreped surface forming an exterior surface of the fibrous structure and/or sanitary tissue product comprising the fibrous structure).

It has been unexpectedly found that discrete knuckle and/or semi-continuous knuckle fibrous structures improve surface mobility (lower average TS7 values) without Slipstick Coefficient of Friction being as much of a factor while still providing good "cushiness" (higher Compressibility). Not wishing to be bound by theory, it is believed that one of the reasons for the improved surface mobility without Slipstick Coefficient of Friction being as much of a factor and still providing good "cushiness" of the discrete and/or semi-continuous knuckle fibrous

structures is the continuous or semi-continuous pillow network being available for surface feel and compression. The pillows are lower density regions which have higher stretch and are more flexible than the higher density knuckles. As a result, 3D patterned fibrous structures with a continuous and/or semi-continuous pillow portion will have better "cushiness" because under compressive load, the 3D patterned fibrous structures will be more likely to compress due to the higher flexibility/lower density of the semi-continuous and/or continuous pillow network. Further, the semi-continuous and/or continuous pillow network will also have better surface mobility, because the strain imparted on the surface of the 3D patterned fibrous structure will move through the pillow more easily than through a knuckle, providing less stress on the surface of the 3D patterned fibrous structure due to the lower density of the pillow structure. This will result in an improved surface mobility performance (lower average TS7 values).

It has also unexpectedly been found that the angle of the semi-continuous and/or discrete knuckles being greater than 45° (with respect to the cross-machine direction) and straight rather than curved improves surface mobility without Slipstick Coefficient of Friction being as much of a factor while providing good "cushiness". Not wishing to be bound by theory, it is believed that one of the reasons for the improved surface mobility without Slipstick Coefficient of Friction being as much of a factor and good "cushiness" when the angle of the semi-continuous and/or discrete knuckles is greater than 45° (with respect to the cross-machine direction) and straight is the better molding that is possible when the orientation of the knuckle is greater than 45° (with respect to the cross-machine direction). Because the majority of fibers in the 3D patterned fibrous structure are substantially machine direction oriented, when the angle of the discrete and/or semi-continuous knuckles is greater than 45° (with respect to the machine direction) better molding into the pillows occurs. This better molding into the pillows creates a better continuous and/or semi-continuous pillow region. This more robust low density pillow region creates a better low density network which will lead to good "cushiness" and good surface mobility.

It has also unexpectedly been found that the orientation of the fibrous structure, specifically converting the fibrous structure such that its uncreped surface (the surface that has not contacted the dryer and/or Yankee and thus has not been creped off the dryer and/or Yankee) (low density pillow side out rather than high density knuckle side out) improves surface mobility without Slipstick Coefficient of Friction being as much of a factor while still providing good "cushiness". Not wishing to be bound by theory, it is believed that one of the reasons for the improved surface mobility without Slipstick Coefficient of Friction being as much of a factor and good "cushiness" when the orientation of the fibrous structure is uncreped surface (low density pillow surface) side out is the fact that the lower density pillows are on the surface of the fibrous

structure. When the fibrous structure undergoes compressive force with the lower density pillows on the surface of the fibrous structure, the fibrous structure will have increased "cushiness". At the same time, having the low density pillows on the surface of the fibrous structure creates better surface mobility, because a strain imparted on the surface of the fibrous structure will move through the pillow more easily than through a knuckle, providing less stress on the surface of the 3D patterned fibrous structure due to the lower density of the pillow structure.

The combination of either a semi-continuous and/or discrete knuckle structure creating a continuous and/or semi-continuous low density pillow network, the angle of the discrete or semi-continuous knuckles allowing for the best possible molding into the pillows, and the uncreped side out orientation leading to the low density pillow network being on the surface of the fibrous structure leads to the best possible scenario for the best possible surface mobility due to the best possible low density pillow network allowing the strain imparted on the surface of the fibrous structure to move through the pillow most easily, providing less stress on the surface of the fibrous structure due to the lower density of the best possible low density pillow structure. In addition, this best possible low density pillow network will have better "cushiness" because under compressive load, the fibrous structure will be most likely to compress due to the higher flexibility/lower density of the best possible low density pillow structure.

Accordingly, one solution to the problem set forth above is achieved by making the sanitary tissue products or at least one fibrous structure ply employed in the sanitary tissue products on patterned molding members that impart three-dimensional (3D) patterns to the sanitary tissue products and/or fibrous structure plies made thereon, wherein the patterned molding members are designed such that the resulting sanitary tissue products, for example bath tissue products, made using the patterned molding members and/or the process conditions used during the making process, for example vacuum settings during the sanitary tissue product making process, are smoother and cushier than known sanitary tissue products as evidenced by the sanitary tissue products, for example bath tissue products, with or without surface softening agents, that exhibit average TS7 values as measured according to the Emtec Test Method described herein and slip stick coefficient of friction values as measured according to the Slip Stick Coefficient of Friction Test Method described herein such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values and/or as evidenced by the sanitary tissue products, for example bath tissue products, with or without surface softening

agents, that exhibit average TS7 values less than 7.5 dB $V^2$ rms as measured according to the Emtec Test Method described herein and Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Compressibility and Resilient Bulk Test Method described herein. Non-limiting examples of such patterned molding members include patterned felts, patterned forming wires, patterned rolls, patterned fabrics, and patterned belts utilized in conventional wet-pressed papermaking processes, air-laid papermaking processes, and/or wet-laid papermaking processes that produce 3D patterned sanitary tissue products and/or 3D patterned fibrous structure plies employed in sanitary tissue products. Other non-limiting examples of such patterned molding members include through-air-drying fabrics and through-air-drying belts utilized in through-air-drying papermaking processes that produce through-air-dried sanitary tissue products, for example 3D patterned through-air dried sanitary tissue products, and/or through-air-dried fibrous structure plies, for example 3D patterned through-air-dried fibrous structure plies, employed in sanitary tissue products. Non-limiting examples of such patterned molding members include patterned felts, patterned forming wires, patterned rolls, patterned fabrics, and patterned belts utilized in conventional wet-pressed papermaking processes, air-laid papermaking processes, and/or wet-laid papermaking processes that produce 3D patterned sanitary tissue products and/or 3D patterned fibrous structure plies employed in sanitary tissue products. Other non-limiting examples of such patterned molding members include through-air-drying fabrics and through-air-drying belts utilized in through-air-drying papermaking processes that produce through-air-dried sanitary tissue products, for example 3D patterned through-air dried sanitary tissue products, and/or through-air-dried fibrous structure plies, for example 3D patterned through-air-dried fibrous structure plies, employed in sanitary tissue products.

Unlike in the past, it has unexpectedly been found that a 3D patterned fibrous structure with its uncreped surface (the surface of the fibrous structure that has not been in contact with the dryer or Yankee and thus has not been creped off the dryer and/or Yankee) forming an exterior surface, for example a consumer-contacting surface, of the fibrous structure exhibits lower average TS7 values than non-3D patterned fibrous structures and even 3D patterned fibrous structures that have their creped surface (the surface of the fibrous structure that has been in contact with a dryer and/or Yankee and thus has been creped off the dryer and/or Yankee).

Further, it has unexpectedly been found that the 3D patterned fibrous structures of the present invention exhibit good surface mobility performance (low average TS7 values) without needing as low of a Slipstick Coefficient of Friction as has been needed in the past to achieve the same performance.

In addition, it has unexpectedly been found that the 3D patterned fibrous structures of the present invention exhibit both good surface mobility (low average TS7 values) and good "cushiness" (high compressibility).

In addition to the impact of the patterned molding members, the fibers utilized to make the sanitary tissue products of the present invention also may influence the average TS7 values and/or slip stick coefficient of friction values of the sanitary tissue products. It has unexpectedly been found that the use of non-wood pulp fibers, for example trichomes, positively impact the surface smoothness of the sanitary tissue products, for example when they form at least part of an exterior surface of the sanitary tissue products, as evidenced by a decrease in the slip stick coefficient of frictions compared to sanitary tissue products containing only wood pulp fibers, without negatively impacting the compressibility of the sanitary tissue products.

In one example of the present invention, a sanitary tissue product comprising a plurality of pulp fibers, wherein the sanitary tissue product exhibits an average TS7 value (dB $V^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction value as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values as shown in Fig. 1A, is provided.

In another example of the present invention, a sanitary tissue product comprising a plurality of pulp fibers, wherein the sanitary tissue product exhibits an average TS7 value of less than 7.5 dB $V^2$ rms as measured according to the Emtec Test Method and a Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method as shown in Fig. 1B, is provided.

In another example of the present invention, a through-air-dried sanitary tissue product, such as a 3D patterned through-air-dried sanitary tissue product, for example bath tissue product, comprising a plurality of pulp fibers, wherein the through-air-dried sanitary tissue product exhibits an average TS7 value (dB $V^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction value as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values as shown in Fig. 1A, is provided.

In yet another example of the present invention, a sanitary tissue product, for example bath tissue product, comprising at least one through-air-dried fibrous structure ply comprising a plurality of pulp fibers, wherein the sanitary tissue product exhibits an average TS7 value of less than 7.5 db $V^2$ rms as measured according to the Emtec Test Method and a Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method as shown in Fig. 1B, is provided.

In still another example of the present invention, a sanitary tissue product, for example bath tissue product, comprising at least one 3D patterned through-air-dried fibrous structure ply comprising a plurality of pulp fibers, wherein the sanitary tissue product exhibits an average TS7 value (dB $V^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction value as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values as shown in Fig. 1A, is provided.

In even another example of the present invention, a multi-ply, for example two-ply, sanitary tissue product, for example bath tissue product, comprising a plurality of pulp fibers, wherein the multi-ply sanitary tissue product exhibits an average TS7 value of less than 7.5 dB $V^2$ rms as measured according to the Emtec Test Method and a Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method as shown in Fig. 1B, is provided.

In even yet another example of the present invention, a multi-ply, for example two-ply, sanitary tissue product, for example bath tissue product, comprising at least one 3D patterned fibrous structure ply, for example a 3D patterned through-air-dried fibrous structure ply, comprising a plurality of pulp fibers, wherein the multi-ply sanitary tissue product exhibits an average TS7 value (dB $V^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction value as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values as shown in Fig. 1A, is provided.

In another example of the present invention, a creped sanitary tissue product comprising a plurality of pulp fibers, wherein the creped sanitary tissue product exhibits an average TS7 value of less than 7.5 dB V rms as measured according to the Emtec Test Method and a

Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method as shown in Fig. 1B, is provided.

In another example of the present invention, a creped sanitary tissue product comprising a at least one 3D patterned creped fibrous structure ply comprising a plurality of pulp fibers, wherein the creped sanitary tissue product exhibits an average TS7 value (dB V$^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction value as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.92981$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values as shown in Fig. 1A, is provided.

In another example of the present invention, a creped through-air-dried sanitary tissue product, such as a 3D patterned creped through-air-dried sanitary tissue product, for example bath tissue product, comprising a plurality of pulp fibers, wherein the creped through-air-dried sanitary tissue product exhibits an average TS7 value of less than 7.5 dB V$^2$ rms as measured according to the Emtec Test Method and a Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method as shown in Fig. 1B, is provided.

In yet another example of the present invention, a creped sanitary tissue product, for example bath tissue product, comprising at least one creped through-air-dried fibrous structure ply comprising a plurality of pulp fibers, wherein the creped sanitary tissue product exhibits an average TS7 value (dB V$^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction value as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values as shown in Fig. 1A, is provided.

In still another example of the present invention, a creped sanitary tissue product, for example bath tissue product, comprising at least one 3D patterned creped through-air-dried fibrous structure ply comprising a plurality of pulp fibers, wherein the creped sanitary tissue product exhibits an average TS7 value of less than 7.5 dB V$^2$ rms as measured according to the Emtec Test Method and a Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method as shown in Fig. 1B, is provided.

In even another example of the present invention, a creped multi-ply, for example two-ply, sanitary tissue product, for example bath tissue product, comprising a plurality of pulp fibers, wherein the creped multi-ply sanitary tissue product exhibits an average TS7 value (dB $V^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction value as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values as shown in Fig. 1A, is provided.

In even yet another example of the present invention, a creped multi-ply, for example two-ply, sanitary tissue product, for example bath tissue product, comprising at least one 3D patterned creped fibrous structure ply, for example a 3D patterned creped through-air-dried fibrous structure ply, comprising a plurality of pulp fibers, wherein the creped multi-ply sanitary tissue product exhibits an average TS7 value of less than 7.5 dB $V^2$ rms as measured according to the Emtec Test Method and a Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method as shown in Fig. 1B, is provided.

In still yet another example of the present invention, a method for making a single- or multi-ply sanitary tissue product according to the present invention, wherein the method comprises the steps of:

a. contacting a patterned molding member with a fibrous structure comprising a plurality of pulp fibers such that a 3D patterned fibrous structure ply is formed; and

b. making a single- or multi-ply sanitary tissue product according to the present invention comprising the 3D patterned fibrous structure ply such that the sanitary tissue product exhibits an average TS7 value (dB $V^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction value as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of Average TS7 values to Slip Stick Coefficient of Friction values where the x-axis is Slip Stick Coefficient of Friction values and the y-axis is Average TS7 values as shown in Fig. 1A and/or the sanitary tissue product exhibits an average TS7 value of less than 7.5 dB $V^2$ rms as measured according to the Emtec Test Method and a Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as

measured according to the Stack Compressibility and Resilient Bulk Test Method as shown in Fig. 1B, is provided.

Accordingly, the present invention provides sanitary tissue products, for example bath tissue products, that are smoother and cushier than known sanitary tissue products, for example bath tissue products, and methods for making same.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a plot of Average TS7 values (dB $V^2$ rms) to Slip Stick Coefficient of Friction values (COF*10000) for sanitary tissue products of the present invention and prior art sanitary tissue products, both single-ply and multi-ply sanitary tissue products, illustrating the low level of average TS7 values in combination with the mid-level of Slip Stick Coefficient of Friction values exhibited by the sanitary tissue products, for example bath tissue products, of the present invention;

Fig. 1B is a plot of Average TS7 values (dB $V^2$ rms) to Compressibility values [mils/(log(g/in$^2$))] for sanitary tissue products of the present invention and prior art sanitary tissue products, both single-ply and multi-ply sanitary tissue products, illustrating the low level of average TS7 values in combination with the mid-level of Compressibility values exhibited by the sanitary tissue products, for example bath tissue products, of the present invention;

Fig. 2 is a schematic representation of an example of a molding member according to the present invention;

Fig. 3 is an image of a sanitary tissue product made using the molding member of Fig. 2;

Fig. 4A is a schematic representation of a portion of another example of a molding member according to the present invention;

Fig. 4B is a cross-sectional view of Fig. 4A taken along line 4B-4B;

Fig. 5A is a schematic representation of a sanitary tissue product made using the molding member of Figs. 4A and 4B;

Fig. 5B is a cross-sectional view of Fig. 5A taken along line 5B-5B;

Fig. 6 is a schematic representation of an example of a through-air-drying papermaking process for making a sanitary tissue product according to the present invention;

Fig. 7 is a schematic representation of an example of an uncreped through-air-drying papermaking process for making a sanitary tissue product according to the present invention;

Fig. 8 is a schematic representation of an example of fabric creped papermaking process for making a sanitary tissue product according to the present invention;

Fig. 9 is a schematic representation of another example of a fabric creped papermaking process for making a sanitary tissue product according to the present invention;

Fig. 10 is a schematic representation of an example of belt creped papermaking process for making a sanitary tissue product according to the present invention;

Fig. 11 is a schematic representation of another example of a molding member according to the present invention;

Fig. 12 is an image of a sanitary tissue product made using the molding member of Fig. 11;

Fig. 13 is a schematic representation of another example of a molding member according to the present invention;

Fig. 14 is a schematic representation of another example of a molding member according to the present invention;

Fig. 15 is an image of a sanitary tissue product made using the molding member of Fig. 14;

Fig. 16 is a schematic representation of a prior art example of a molding member according to the present invention;

Fig. 17 is a schematic representation of a sanitary tissue product made using the molding member of Fig. 16;

Fig. 18 is a schematic representation of a prior art example of a molding member according to the present invention;

Fig. 19 is a schematic representation of a prior art example of a molding member according to the present invention;

Fig. 20 is an image of a sanitary tissue product made using the molding member of Fig. 19;

Fig. 21 is a schematic representation of a prior art example of a molding member according to the present invention;

Fig. 22 is an image of a sanitary tissue product made using the molding member of Fig. 21;

Fig. 23 is a schematic top view representation of a Slip Stick Coefficient of Friction Test Method set-up;

Fig. 24 is an image of a friction sled for use in the Slip Stick Coefficient of Friction Test Method; and

Fig. 25 is a schematic side view representation of a Slip Stick Coefficient of Friction Test Method set-up.

## DETAILED DESCRIPTION OF THE INVENTION

Definitions

"Sanitary tissue product" as used herein means a soft, low density (i.e. < about 0.15 $g/cm^3$) article comprising one or more fibrous structure plies according to the present invention, wherein the sanitary tissue product is useful as a wiping implement for post-urinary and post-bowel movement cleaning (toilet tissue), for otorhinolaryngological discharges (facial tissue), and multi-functional absorbent and cleaning uses (absorbent towels). The sanitary tissue product may be convolutedly wound upon itself about a core or without a core to form a sanitary tissue product roll.

The sanitary tissue products and/or fibrous structures of the present invention may exhibit a basis weight of greater than 15 $g/m^2$ to about 120 $g/m^2$ and/or from about 15 $g/m^2$ to about 110 $g/m^2$ and/or from about 20 $g/m^2$ to about 100 $g/m^2$ and/or from about 30 to 90 $g/m^2$. In addition, the sanitary tissue products and/or fibrous structures of the present invention may exhibit a basis weight between about 40 $g/m^2$ to about 120 $g/m^2$ and/or from about 50 $g/m^2$ to about 110 $g/m^2$ and/or from about 55 $g/m^2$ to about 105 $g/m^2$ and/or from about 60 to 100 $g/m^2$.

The sanitary tissue products of the present invention may exhibit a sum of MD and CD dry tensile strength of greater than about 59 g/cm (150 g/in) and/or from about 78 g/cm to about 394 g/cm and/or from about 98 g/cm to about 335 g/cm. In addition, the sanitary tissue product of the present invention may exhibit a sum of MD and CD dry tensile strength of greater than about 196 g/cm and/or from about 196 g/cm to about 394 g/cm and/or from about 216 g/cm to about 335 g/cm and/or from about 236 g/cm to about 315 g/cm. In one example, the sanitary tissue product exhibits a sum of MD and CD dry tensile strength of less than about 394 g/cm and/or less than about 335 g/cm.

In another example, the sanitary tissue products of the present invention may exhibit a sum of MD and CD dry tensile strength of greater than about 196 g/cm and/or greater than about 236 g/cm and/or greater than about 276 g/cm and/or greater than about 315 g/cm and/or greater than about 354 g/cm and/or greater than about 394 g/cm and/or from about 315 g/cm to about 1968 g/cm and/or from about 354 g/cm to about 1181 g/cm and/or from about 354 g/cm to about 984 g/cm and/or from about 394 g/cm to about 787 g/cm.

The sanitary tissue products of the present invention may exhibit an initial sum of MD and CD wet tensile strength of less than about 78 g/cm and/or less than about 59 g/cm and/or less than about 39 g/cm and/or less than about 29 g/cm.

The sanitary tissue products of the present invention may exhibit an initial sum of MD and CD wet tensile strength of greater than about 118 g/cm and/or greater than about 157 g/cm and/or greater than about 196 g/cm and/or greater than about 236 g/cm and/or greater than about 276 g/cm and/or greater than about 315 g/cm and/or greater than about 354 g/cm and/or greater than about 394 g/cm and/or from about 118 g/cm to about 1968 g/cm and/or from about 157 g/cm to about 1181 g/cm and/or from about 196 g/cm to about 984 g/cm and/or from about 196 g/cm to about 787 g/cm and/or from about 196 g/cm to about 591 g/cm.

The sanitary tissue products of the present invention may exhibit a density (based on measuring caliper at 95 $g/in^2$) of less than about 0.60 $g/cm^3$ and/or less than about 0.30 $g/cm^3$ and/or less than about 0.20 $g/cm^3$ and/or less than about 0.10 $g/cm^3$ and/or less than about 0.07 $g/cm^3$ and/or less than about 0.05 $g/cm^3$ and/or from about 0.01 $g/cm^3$ to about 0.20 $g/cm^3$ and/or from about 0.02 $g/cm^3$ to about 0.10 $g/cm^3$.

The sanitary tissue products of the present invention may be in the form of sanitary tissue product rolls. Such sanitary tissue product rolls may comprise a plurality of connected, but perforated sheets of fibrous structure, that are separably dispensable from adjacent sheets.

In another example, the sanitary tissue products may be in the form of discrete sheets that are stacked within and dispensed from a container, such as a box.

The fibrous structures and/or sanitary tissue products of the present invention may comprise additives such as surface softening agents, for example silicones, quaternary ammonium compounds, aminosilicones, lotions, and mixtures thereof, temporary wet strength agents, permanent wet strength agents, bulk softening agents, wetting agents, latexes, especially surface-pattern-applied latexes, dry strength agents such as carboxymethylcellulose and starch, and other types of additives suitable for inclusion in and/or on sanitary tissue products.

"Fibrous structure" as used herein means a structure that comprises a plurality of pulp fibers. In one example, the fibrous structure may comprise a plurality of wood pulp fibers. In another example, the fibrous structure may comprise a plurality of non-wood pulp fibers, for example plant fibers, synthetic staple fibers, and mixtures thereof. In still another example, in addition to pulp fibers, the fibrous structure may comprise a plurality of filaments, such as polymeric filaments, for example thermoplastic filaments such as polyolefin filaments (i.e., polypropylene filaments) and/or hydroxyl polymer filaments, for example polyvinyl alcohol filaments and/or polysaccharide filaments such as starch filaments. In one example, a fibrous structure according to the present invention means an orderly arrangement of fibers alone and with filaments within a structure in order to perform a function. Non-limiting examples of fibrous structures of the present invention include paper.

Non-limiting examples of processes for making fibrous structures include known wet-laid papermaking processes, for example conventional wet-pressed papermaking processes and through-air-dried 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, fabric, or belt such that an embryonic fibrous structure is formed, after which drying and/or bonding the fibers together results in a fibrous structure. Further processing the fibrous structure may be carried out such that a finished fibrous structure is formed. For example, in typical papermaking processes, the finished fibrous structure is the fibrous structure that is wound on the reel at the end of papermaking, often referred to as a parent roll, and may subsequently be converted into a finished product, e.g. a single- or multi-ply sanitary tissue product.

The fibrous structures of the present invention may be homogeneous or may be layered. If layered, the fibrous structures may comprise at least two and/or at least three and/or at least four and/or at least five layers of fiber and/or filament compositions.

In one example, the fibrous structure of the present invention consists essentially of fibers, for example pulp fibers, such as cellulosic pulp fibers and more particularly wood pulp fibers.

In another example, the fibrous structure of the present invention comprises fibers and is void of filaments.

In still another example, the fibrous structures of the present invention comprises filaments and fibers, such as a co-formed fibrous structure.

"Co-formed fibrous structure" as used herein means that the fibrous structure comprises a mixture of at least two different materials wherein at least one of the materials comprises a filament, such as a polypropylene filament, and at least one other material, different from the first material, comprises a solid additive, such as a fiber and/or a particulate. In one example, a co-formed fibrous structure comprises solid additives, such as fibers, such as wood pulp fibers, and filaments, such as polypropylene filaments.

"Fiber" and/or "Filament" as used herein means an elongate particulate having an apparent length greatly exceeding its apparent width, i.e. a length to diameter ratio of at least about 10. In one example, a "fiber" is an elongate particulate as described above that exhibits a length of less than 5.08 cm (2 in.) and a "filament" is an elongate particulate as described above that exhibits a length of greater than or equal to 5.08 cm (2 in.).

Fibers are typically considered discontinuous in nature. Non-limiting examples of fibers include pulp fibers, such as wood pulp fibers, and synthetic staple fibers such as polyester fibers.

Filaments are typically considered continuous or substantially continuous in nature. Filaments are relatively longer than fibers. Non-limiting examples of filaments include meltblown and/or spunbond filaments. Non-limiting examples of materials that can be spun into filaments include natural polymers, such as starch, starch derivatives, cellulose and cellulose derivatives, hemicellulose, hemicellulose derivatives, and synthetic polymers including, but not limited to polyvinyl alcohol filaments and/or polyvinyl alcohol derivative filaments, and thermoplastic polymer filaments, such as polyesters, nylons, polyolefins such as polypropylene filaments, polyethylene filaments, and biodegradable or compostable thermoplastic fibers such as polylactic acid filaments, polyhydroxyalkanoate filaments and polycaprolactone filaments. The filaments may be monocomponent or multicomponent, such as bicomponent filaments.

In one example of the present invention, “fiber” refers to papermaking fibers. Papermaking fibers useful in the present invention include cellulosic fibers commonly known as wood pulp fibers. Applicable wood pulps include chemical pulps, such as Kraft, sulfite, and sulfate pulps, as well as mechanical pulps including, for example, groundwood, thermomechanical pulp and chemically modified thermomechanical pulp. Chemical pulps, however, may be preferred since they impart a superior tactile sense of softness to tissue sheets made therefrom. Pulps derived from both deciduous trees (hereinafter, also referred to as "hardwood") and coniferous trees (hereinafter, also referred to as "softwood") may be utilized. The hardwood and softwood fibers can be blended, or alternatively, can be deposited in layers to provide a stratified fibrous structure. U.S. Pat. No. 4,300,981 and U.S. Pat. No. 3,994,771 are incorporated herein by reference for the purpose of disclosing layering of hardwood and softwood fibers. Also applicable to the present invention are fibers derived from recycled paper, which may contain any or all of the above categories as well as other non-fibrous materials such as fillers and adhesives used to facilitate the original papermaking.

In one example, the wood pulp fibers are selected from the group consisting of hardwood pulp fibers, softwood pulp fibers, and mixtures thereof. The hardwood pulp fibers may be selected from the group consisting of: tropical hardwood pulp fibers, northern hardwood pulp fibers, and mixtures thereof. The tropical hardwood pulp fibers may be selected from the group consisting of: eucalyptus fibers, acacia fibers, and mixtures thereof. The northern hardwood pulp fibers may be selected from the group consisting of: cedar fibers, maple fibers, and mixtures thereof.

In addition to the various wood pulp fibers, other cellulosic fibers such as cotton linters, rayon, lyocell, trichomes, seed hairs, and bagasse can be used in this invention. Other sources of cellulose in the form of fibers or capable of being spun into fibers include grasses and grain sources.

"Trichome" or "trichome fiber" as used herein means an epidermal attachment of a varying shape, structure and/or function of a non-seed portion of a plant. In one example, a trichome is an outgrowth of the epidermis of a non-seed portion of a plant. The outgrowth may extend from an epidermal cell. In one embodiment, the outgrowth is a trichome fiber. The outgrowth may be a hairlike or bristlelike outgrowth from the epidermis of a plant.

Trichome fibers are different from seed hair fibers in that they are not attached to seed portions of a plant. For example, trichome fibers, unlike seed hair fibers, are not attached to a seed or a seed pod epidermis. Cotton, kapok, milkweed, and coconut coir are non-limiting examples of seed hair fibers.

Further, trichome fibers are different from nonwood bast and/or core fibers in that they are not attached to the bast, also known as phloem, or the core, also known as xylem portions of a nonwood dicotyledonous plant stem. Non-limiting examples of plants which have been used to yield nonwood bast fibers and/or nonwood core fibers include kenaf, jute, flax, ramie and hemp.

Further trichome fibers are different from monocotyledonous plant derived fibers such as those derived from cereal straws (wheat, rye, barley, oat, etc), stalks (corn, cotton, sorghum, *Hesperaloe funifera*, etc.), canes (bamboo, bagasse, etc.), grasses (esparto, lemon, sabai, switchgrass, etc), since such monocotyledonous plant derived fibers are not attached to an epidermis of a plant.

Further, trichome fibers are different from leaf fibers in that they do not originate from within the leaf structure. Sisal and abaca are sometimes liberated as leaf fibers.

Finally, trichome fibers are different from wood pulp fibers since wood pulp fibers are not outgrowths from the epidermis of a plant; namely, a tree. Wood pulp fibers rather originate from the secondary xylem portion of the tree stem.

"Basis Weight" as used herein is the weight per unit area of a sample reported in lbs/3000 $ft^2$ or $g/m^2$ (gsm) and is measured according to the Basis Weight Test Method described herein.

"Machine Direction" or "MD" as used herein means the direction parallel to the flow of the fibrous structure through the fibrous structure making machine and/or sanitary tissue product manufacturing equipment.

"Cross Machine Direction" or "CD" as used herein means the direction parallel to the width of the fibrous structure making machine and/or sanitary tissue product manufacturing equipment and perpendicular to the machine direction.

"Ply" as used herein means an individual, integral fibrous structure.

"Plies" as used herein means two or more individual, integral fibrous structures disposed in a substantially contiguous, face-to-face relationship with one another, forming a multi-ply fibrous structure and/or multi-ply sanitary tissue product. It is also contemplated that an individual, integral fibrous structure can effectively form a multi-ply fibrous structure, for example, by being folded on itself.

"Embossed" as used herein with respect to a fibrous structure and/or sanitary tissue product means that a fibrous structure and/or sanitary tissue product has been subjected to a process which converts a smooth surfaced fibrous structure and/or sanitary tissue product to a decorative surface by replicating a design on one or more emboss rolls, which form a nip through which the fibrous structure and/or sanitary tissue product passes. Embossed does not include creping, microcreping, printing or other processes that may also impart a texture and/or decorative pattern to a fibrous structure and/or sanitary tissue product.

"Differential density", as used herein, means a fibrous structure and/or sanitary tissue product that comprises one or more regions of relatively low fiber density, which are referred to as pillow regions, and one or more regions of relatively high fiber density, which are referred to as knuckle regions.

"Densified", as used herein means a portion of a fibrous structure and/or sanitary tissue product that is characterized by regions of relatively high fiber density (knuckle regions).

"Non-densified", as used herein, means a portion of a fibrous structure and/or sanitary tissue product that exhibits a lesser density (one or more regions of relatively lower fiber density) (pillow regions) than another portion (for example a knuckle region) of the fibrous structure and/or sanitary tissue product.

"Non-rolled" as used herein with respect to a fibrous structure and/or sanitary tissue product of the present invention means that the fibrous structure and/or sanitary tissue product is an individual sheet (for example not connected to adjacent sheets by perforation lines. However, two or more individual sheets may be interleaved with one another) that is not convolutedly wound about a core or itself. For example, a non-rolled product comprises a facial tissue.

"Stack Compressibility and Resilient Bulk Test Method" as used herein means the Stack Compressibility and Resilient Bulk Test Method described herein.

"Slip Stick Coefficient of Friction Test Method" as used herein means the Slip Stick Coefficient of Friction Test Method described herein.

"Creped" as used herein means creped off of a Yankee dryer or other similar roll and/or fabric creped and/or belt creped. Rush transfer of a fibrous structure alone does not result in a "creped" fibrous structure or "creped" sanitary tissue product for purposes of the present invention.

Sanitary Tissue Product

The sanitary tissue products of the present invention may be single-ply or multi-ply sanitary tissue products. In other words, the sanitary tissue products of the present invention may comprise one or more fibrous structures. The fibrous structures and/or sanitary tissue products of the present invention are made from a plurality of pulp fibers, for example wood pulp fibers and/or other cellulosic pulp fibers, for example trichomes. In addition to the pulp fibers, the fibrous structures and/or sanitary tissue products of the present invention may comprise synthetic fibers and/or filaments.

As shown in Figs. 1A and 1B and Table 1 below, which contains a portion of the data values represented in Figs. 1A and 1B, the sanitary tissue products of the present invention exhibit a combination (Fig. 1A) of average TS7 values as measured according to the Emtec Test Method described herein and Slip Stick Coefficient of Friction values as measured according to the Slip Stick Coefficient of Friction Test Method described herein and a combination (Fig. 1B) of TS7 values as measured according to the Emtec Test Method described herein and Compressibility values as measured according to the Stack Compressibility and Resilient Bulk Test Method described herein that are novel over known sanitary tissue products.

| Sample | Knuckle (Discrete, Continuous, Semi-Continuous) | FSO (Uncreped Surface out) vs WSO (Creped Surface out) Converting | Angle of Knuckle (relative to CD) | Slip Stick Coefficient of Friction [ COF*10000 ] | Compressibility [mils/(log(g/in$^2$))] | Avg TS7 |
|---|---|---|---|---|---|---|
| Prior Art | | | | 708 | 68.4 | 14.3 |
| Prior Art | | | | 675 | 66.8 | 13.5 |
| Prior Art | | | | 408 | 36.4 | 5.9 |
| Prior Art | | | | 335 | 35.7 | 5.3 |
| Prior Art | | | | 392 | 40.8 | 7.8 |

| | | | | |
|---|---|---|---|---|
| Prior Art | | 321 | 35.0 | 6.2 |
| Prior Art | | 745 | 56.3 | 10.3 |
| Prior Art | | 643 | 52.3 | 9.5 |
| Prior Art | | 511 | 55.2 | 8.9 |
| Great Value® Ultra Soft | | 366 | 28.8 | 9.5 |
| Great Value® Ultra Strong | | 423 | 29.7 | 9.7 |
| Kirkland® Ultra Soft | | 393 | 20.2 | 10.6 |
| Kroger® Ultra Soft | | 428 | 24.5 | 11.0 |
| Kroger® Ultra Strong | | 558 | 24.6 | 13.0 |
| Quilted Northern® Ultra Plush | | 456 | 31.8 | 10.0 |
| Quilted Northern® Ultra Plush | | 501 | 30.7 | 10.4 |
| Scott 1000 | | 692 | 7.2 | 20.4 |
| White Cloud® Luxuriously Soft | | 396 | 25.0 | 9.8 |
| White Cloud® Ultra | | 772 | 26.5 | 15.5 |
| Kleenex® Viva | | 851 | 27.7 | 23.8 |
| Kleenex® Lotion | | 287 | 7.6 | 9.2 |
| Kleenex® Regular | | 354 | 8.7 | 11.2 |
| Kleenex® Ultra | | 268 | 9.1 | 8.9 |
| Puffs® Lotion | | 332 | 21.6 | 9.8 |
| Puffs® Ultra | | 308 | 13.3 | 8.5 |
| Kirkland® Signature Ultra Soft | | 359 | 19.4 | 9.0 |
| Charmin® Ultra Soft | WSO | 350 | 26.9 | 7.9 |
| Charmin® Ultra Soft | WSO | 363 | 30.1 | 7.9 |
| Charmin® Ultra Soft | WSO | 358 | 24.8 | 8.1 |
| Charmin® Ultra Soft | WSO | 334 | 27.2 | 8.1 |
| Charmin® Ultra Soft | WSO | 364 | 21.4 | 8.3 |
| Charmin® Ultra Soft | WSO | 357 | 27.9 | 8.1 |
| Charmin® Ultra Soft | WSO | 368 | 20.8 | 9.1 |
| Charmin® Ultra Soft | WSO | 372 | 26.8 | 9.5 |
| Charmin® Ultra Soft | WSO | 350 | 21.7 | 8.3 |
| Charmin® Ultra Soft | WSO | 361 | 22.9 | 8.2 |
| Charmin® Ultra Soft | WSO | 350 | 20.7 | 8.2 |
| Charmin® Ultra Soft | WSO | 360 | 27.3 | 8.4 |
| Charmin® Ultra Soft | WSO | 378 | 22.1 | 8.5 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Charmin® Ultra Soft | | WSO | | 368 | 26.2 | 7.5 |
| Charmin® Ultra Soft | | WSO | | 309 | 27.1 | 6.9 |
| Charmin® Ultra Strong | | WSO | | 414 | 31.3 | 8.2 |
| Charmin® Sensitive | | FSO | | 437 | 26.0 | 9.6 |
| Charmin® Ultra Strong | | WSO | | 475 | 26.5 | 10.4 |
| Prior Art | | | | 326 | 35.0 | 6.9 |
| Prior Art | | | | 327 | 33.6 | 6.3 |
| Comparative Example 1 - Semi-continuous CD Knuckle POINT OF COMPARISON | Semi-Continuous | FSO | variable (average = 0) | 343 | 37.1 | 6.3 |
| Comparative Example 4 – POINT OF COMPARISON | Discrete | FSO | Variable (average = 45) | 318 | 36.0 | 5.7 |
| Comparative Exmaple 5 - POINT OF COMPARISON | Discrete AND Semi-Continuous (Dual-Cast) | FSO | Variable | 732 | 43.1 | 9.1 |
| Comparative Example 3 - Charmin® Ultra Soft POINT OF COMPARISON | Semi-Continuous | WSO | 85 | 329 | 32.5 | 7.7 |
| Comparative Example 2 - POINT OF COMPARISON | Continuous | FSO | Variable | 510 | 42.7 | 7.7 |
| Invention | Semi-Continuous | FSO | 85 | 541 | 41.1 | 6.6 |
| Invention | Semi-Continuous | FSO | 85 | 522 | 39.2 | 6.4 |
| Invention (Example 1) | Semi-Continuous | FSO | 85 | 697 | 41.8 | 7.3 |
| Invnetion (Example 4) | Discrete | FSO | 45 | 409 | 40.6 | 5.6 |
| Invention | Discrete | FSO | 45 | 423 | 40.1 | 5.9 |
| Invention | Discrete | FSO | 45 | 448 | 40.7 | 5.9 |
| Invention | Discrete | FSO | 45 | 409 | 40.7 | 5.6 |
| Invention | Discrete | FSO | 75 | 448 | 40.3 | 6.1 |
| Invention (Example 3) | Discrete AND Semi-Continuous | FSO | 75 | 495 | 38.2 | 6.1 |
| Invention | Discrete | FSO | 75 | 386 | 41 | 5.5 |
| Invention (Example 2) | Discrete | FSO | 75 | 415 | 40.6 | 5.5 |
| Invention | Discrete | FSO | 75 | 457 | 42.2 | 6.0 |
| Invention | Discrete | FSO | 75 | 427 | 42 | 5.9 |
| Invention | Semi-Continuous | FSO | 85 | 407 | 38.2 | 5.3 |
| Invention | Semi-Continuous | FSO | 85 | 383 | 39.1 | 5.2 |

Table 1

The sanitary tissue products of the present invention may exhibit an average TS7 value of less than 10 and/or less than 9 and/or less than 8 and/or less than 7 and/or less than 6 and/or less than 5.5 and/or greater than 4 and/or greater than 4.5 and/or greater than 5 dB $V^2$ rms as measured according to the Emtec Test Method described herein.

The sanitary tissue products of the present invention may exhibit a Slip Stick Coefficient of Friction value (COF*10000) of greater than 230 and/or greater than 300 and/or greater than 350 and/or greater than 400 and/or greater than 425 and/or greater than 475 and/or greater than 500 and/or greater than 530 and/or greater than 600 and/or greater than 675 and/or less than 730

and/or less than 700 as measured according to the Slip Stick Coefficient of Friction Test Method described herein.

The sanitary tissue products of the present invention may exhibit a Compressibility of greater than 38.0 and/or greater than 40.0 and/or greater than 41.0 and/or greater than 42.0 and/or less than 60.0 and/or less than 55.0 and/or less than 50.0 and/or less than 45.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method described herein.

The fibrous structures and/or sanitary tissue products of the present invention may be creped or uncreped.

The fibrous structures and/or sanitary tissue products of the present invention may be wet-laid or air-laid.

The fibrous structures and/or sanitary tissue products of the present invention may be embossed.

The fibrous structures and/or sanitary tissue products of the present invention may comprise a surface softening agent or be void of a surface softening agent. In one example, the sanitary tissue product is a non-lotioned sanitary tissue product, such as a sanitary tissue product comprising a non-lotioned fibrous structure ply, for example a non-lotioned through-air-dried fibrous structure ply, for example a non-lotioned creped through-air-dried fibrous structure ply and/or a non-lotioned uncreped through-air-dried fibrous structure ply. In yet another example, the sanitary tissue product may comprise a non-lotioned fabric creped fibrous structure ply and/or a non-lotioned belt creped fibrous structure ply.

The fibrous structures and/or sanitary tissue products of the present invention may comprise trichome fibers and/or may be void of trichome fibers.

The fibrous structures and/or sanitary tissue products of the present invention may exhibit the compressibility values alone or in combination with the slip stick coefficient of friction values with or without the aid of surface softening agents. In other words, the sanitary tissue products of the present invention may exhibit the compressibility values described above alone or in combination with the slip stick coefficient of friction values when surface softening agents are not present on and/or in the sanitary tissue products, in other words the sanitary tissue product is void of surface softening agents. This does not mean that the sanitary tissue products themselves cannot include surface softening agents. It simply means that when the sanitary tissue product is made without adding the surface softening agents, the sanitary tissue product exhibits the compressibility and slip stick coefficient of friction values of the present invention. Addition of a surface softening agent to such a sanitary tissue product within the scope of the present invention

(without the need of a surface softening agent or other chemistry) may enhance the sanitary tissue product's compressibility and/or slip stick coefficient of friction to an extent. However, sanitary tissue products that need the inclusion of surface softening agents on and/or in them to be within the scope of the present invention, in other words to achieve the compressibility and slip stick coefficient of friction values of the present invention, are outside the scope of the present invention.

Patterned Molding Members

The sanitary tissue products of the present invention and/or fibrous structure plies employed in the sanitary tissue products of the present invention are formed on patterned molding members that result in the sanitary tissue products of the present invention. In one example, the pattern molding member comprises a non-random repeating pattern. In another example, the pattern molding member comprises a resinous pattern.

A "reinforcing element" may be a desirable (but not necessary) element in some examples of the molding member, serving primarily to provide or facilitate integrity, stability, and durability of the molding member comprising, for example, a resinous material. The reinforcing element can be fluid-permeable or partially fluid-permeable, may have a variety of embodiments and weave patterns, and may comprise a variety of materials, such as, for example, a plurality of interwoven yarns (including Jacquard-type and the like woven patterns), a felt, a plastic, other suitable synthetic material, or any combination thereof.

As shown in Fig. 2, a non-limiting example of a patterned molding member suitable for use in the present invention comprises a through-air-drying belt 10. The through-air-drying belt 10 comprises a plurality of discrete knuckles 12 (white in the drawing) formed by line segments of resin 14 (white in drawing) arranged in a non-random, repeating pattern, such as a woven pattern, for example a herringbone pattern. The discrete knuckles 12 are dispersed within a continuous pillow network 16 (black in drawing), which constitute a deflection conduit into which portions of a fibrous structure ply being made on the through-air-drying belt 10 of Fig. 2 deflect. Fig. 3 is an image of a resulting sanitary tissue product 18 being made on the through-air-drying belt 10. The sanitary tissue product 18 comprises a continuous pillow region (low density region) imparted by the continuous pillow network 16 of the through-air-drying belt 10 of Fig. 2. The sanitary tissue product 18 further comprises discrete knuckle regions (high density regions) imparted by the discrete knuckles 12 of the through-air-drying belt 10 of Fig. 2. The continuous pillow region and discrete knuckle regions may exhibit different densities, for

example, one or more of the discrete knuckle regions may exhibit a density that is greater than the density of the continuous pillow region.

As shown in Figs. 4A-4B, a non-limiting example of another patterned molding member suitable for use in the present invention comprises a through-air-drying belt 10. The through-air-drying belt 10 comprises a plurality of semi-continuous knuckles 24 formed by semi-continuous line segments of resin 26 arranged in a non-random, repeating pattern, for example a substantially machine direction repeating pattern of semi-continuous lines (at angle of from about 85° to about 90° with respect to the cross-machine direction) supported on a support fabric comprising filaments 27. The semi-continuous knuckles 24 are spaced from adjacent semi-continuous knuckles 24 by semi-continuous pillows 28, which constitute deflection conduits into which portions of a fibrous structure ply being made on the through-air-drying belt 10 of Figs. 4A-4B deflect. As shown in Figs. 5A-5B, a resulting sanitary tissue product 18 being made on the through-air-drying belt 10 of Figs. 4A-4B comprises semi-continuous pillow regions 30 (low density regions) imparted by the semi-continuous pillows 28 of the through-air-drying belt 10 of Figs. 4A-4B. The sanitary tissue product 18 further comprises semi-continuous knuckle regions 32 (high density regions) imparted by the semi-continuous knuckles 24 of the through-air-drying belt 10 of Figs. 4A-4B. The semi-continuous pillow regions 30 and semi-continuous knuckle regions 32 may exhibit different densities, for example, one or more of the semi-continuous knuckle regions 32 may exhibit a density that is greater than the density of one or more of the semi-continuous pillow regions 30.

Without wishing to be bound by theory, foreshortening (dry & wet crepe, fabric crepe, rush transfer, etc) is an integral part of fibrous structure and/or sanitary tissue paper making, helping to produce the desired balance of strength, stretch, softness, absorbency, etc. Fibrous structure support, transport and molding members used in the papermaking process, such as rolls, wires, felts, fabrics, belts, etc. have been variously engineered to interact with foreshortening to further control the fibrous structure and/or sanitary tissue product properties.

Non-limiting Examples of Making Sanitary Tissue Products

The sanitary tissue products of the present invention may be made by any suitable papermaking process so long as a molding member of the present invention is used to make the sanitary tissue product or at least one fibrous structure ply of the sanitary tissue product and that the sanitary tissue product exhibits an average TS7 value and slip stick coefficient of friction value and/or compressibility value of the present invention. The method may be a sanitary tissue product making process that uses a cylindrical dryer such as a Yankee (a Yankee-process) or it

may be a Yankeeless process as is used to make substantially uniform density and/or uncreped fibrous structures and/or sanitary tissue products. Alternatively, the fibrous structures and/or sanitary tissue products may be made by an air-laid process and/or meltblown and/or spunbond processes and any combinations thereof so long as the fibrous structures and/or sanitary tissue products of the present invention are made thereby.

As shown in Fig. 6, one example of a process and equipment, represented as 36 for making a sanitary tissue product according to the present invention comprises supplying an aqueous dispersion of fibers (a fibrous furnish or fiber slurry) to a headbox 38 which can be of any convenient design. From headbox 38 the aqueous dispersion of fibers is delivered to a first foraminous member 40 which is typically a Fourdrinier wire, to produce an embryonic fibrous structure 42.

The first foraminous member 40 may be supported by a breast roll 44 and a plurality of return rolls 46 of which only two are shown. The first foraminous member 40 can be propelled in the direction indicated by directional arrow 48 by a drive means, not shown. Optional auxiliary units and/or devices commonly associated fibrous structure making machines and with the first foraminous member 40, but not shown, include forming boards, hydrofoils, vacuum boxes, tension rolls, support rolls, wire cleaning showers, and the like.

After the aqueous dispersion of fibers is deposited onto the first foraminous member 40, embryonic fibrous structure 42 is formed, typically by the removal of a portion of the aqueous dispersing medium by techniques well known to those skilled in the art. Vacuum boxes, forming boards, hydrofoils, and the like are useful in effecting water removal. The embryonic fibrous structure 42 may travel with the first foraminous member 40 about return roll 46 and is brought into contact with a patterned molding member 50, such as a 3D patterned through-air-drying belt. While in contact with the patterned molding member 50, the embryonic fibrous structure 42 will be deflected, rearranged, and/or further dewatered.

The patterned molding member 50 may be in the form of an endless belt. In this simplified representation, the patterned molding member 50 passes around and about patterned molding member return rolls 52 and impression nip roll 54 and may travel in the direction indicated by directional arrow 56. Associated with patterned molding member 50, but not shown, may be various support rolls, other return rolls, cleaning means, drive means, and the like well known to those skilled in the art that may be commonly used in fibrous structure making machines.

After the embryonic fibrous structure 42 has been associated with the patterned molding member 50, fibers within the embryonic fibrous structure 42 are deflected into pillows and/or

pillow network ("deflection conduits") present in the patterned molding member 50. In one example of this process step, there is essentially no water removal from the embryonic fibrous structure 42 through the deflection conduits after the embryonic fibrous structure 42 has been associated with the patterned molding member 50 but prior to the deflecting of the fibers into the deflection conduits. Further water removal from the embryonic fibrous structure 42 can occur during and/or after the time the fibers are being deflected into the deflection conduits. Water removal from the embryonic fibrous structure 42 may continue until the consistency of the embryonic fibrous structure 42 associated with patterned molding member 50 is increased to from about 25% to about 35%. Once this consistency of the embryonic fibrous structure 42 is achieved, then the embryonic fibrous structure 42 can be referred to as an intermediate fibrous structure 58. During the process of forming the embryonic fibrous structure 42, sufficient water may be removed, such as by a noncompressive process, from the embryonic fibrous structure 42 before it becomes associated with the patterned molding member 50 so that the consistency of the embryonic fibrous structure 42 may be from about 10% to about 30%.

While applicants decline to be bound by any particular theory of operation, it appears that the deflection of the fibers in the embryonic fibrous structure and water removal from the embryonic fibrous structure begin essentially simultaneously. Embodiments can, however, be envisioned wherein deflection and water removal are sequential operations. Under the influence of the applied differential fluid pressure, for example, the fibers may be deflected into the deflection conduit with an attendant rearrangement of the fibers. Water removal may occur with a continued rearrangement of fibers. Deflection of the fibers, and of the embryonic fibrous structure, may cause an apparent increase in surface area of the embryonic fibrous structure. Further, the rearrangement of fibers may appear to cause a rearrangement in the spaces or capillaries existing between and/or among fibers.

It is believed that the rearrangement of the fibers can take one of two modes dependent on a number of factors such as, for example, fiber length. The free ends of longer fibers can be merely bent in the space defined by the deflection conduit while the opposite ends are restrained in the region of the ridges. Shorter fibers, on the other hand, can actually be transported from the region of the ridges into the deflection conduit (The fibers in the deflection conduits will also be rearranged relative to one another). Naturally, it is possible for both modes of rearrangement to occur simultaneously.

As noted, water removal occurs both during and after deflection; this water removal may result in a decrease in fiber mobility in the embryonic fibrous structure. This decrease in fiber mobility may tend to fix and/or freeze the fibers in place after they have been deflected and

rearranged. Of course, the drying of the fibrous structure in a later step in the process of this invention serves to more firmly fix and/or freeze the fibers in position.

Any convenient means conventionally known in the papermaking art can be used to dry the intermediate fibrous structure 58. Examples of such suitable drying process include subjecting the intermediate fibrous structure 58 to conventional and/or flow-through dryers and/or Yankee dryers.

In one example of a drying process, the intermediate fibrous structure 58 in association with the patterned molding member 50 passes around the patterned molding member return roll 52 and travels in the direction indicated by directional arrow 56. The intermediate fibrous structure 58 may first pass through an optional predryer 60. This predryer 60 can be a conventional flow-through dryer (hot air dryer) well known to those skilled in the art. Optionally, the predryer 60 can be a so-called capillary dewatering apparatus. In such an apparatus, the intermediate fibrous structure 58 passes over a sector of a cylinder having preferential-capillary-size pores through its cylindrical-shaped porous cover. Optionally, the predryer 60 can be a combination capillary dewatering apparatus and flow-through dryer. The quantity of water removed in the predryer 60 may be controlled so that a predried fibrous structure 62 exiting the predryer 60 has a consistency of from about 30% to about 98%. The predried fibrous structure 62, which may still be associated with patterned molding member 50, may pass around another patterned molding member return roll 52 and as it travels to an impression nip roll 54. As the predried fibrous structure 62 passes through the nip formed between impression nip roll 54 and a surface of a Yankee dryer 64, the pattern formed by the top surface 66 of patterned molding member 50 is impressed into the predried fibrous structure 62 to form a 3D patterned fibrous structure 68. The imprinted fibrous structure 68 can then be adhered to the surface of the Yankee dryer 64 where it can be dried to a consistency of at least about 95%.

The 3D patterned fibrous structure 68 can then be foreshortened by creping the 3D patterned fibrous structure 68 with a creping blade 70 to remove the 3D patterned fibrous structure 68 from the surface of the Yankee dryer 64 resulting in the production of a 3D patterned creped fibrous structure 72 in accordance with the present invention. As used herein, foreshortening refers to the reduction in length of a dry (having a consistency of at least about 90% and/or at least about 95%) fibrous structure which occurs when energy is applied to the dry fibrous structure in such a way that the length of the fibrous structure is reduced and the fibers in the fibrous structure are rearranged with an accompanying disruption of fiber-fiber bonds. Foreshortening can be accomplished in any of several well-known ways. One common method of foreshortening is creping. The 3D patterned creped fibrous structure 72 may be subjected to

post processing steps such as calendaring, tuft generating operations, and/or embossing and/or converting.

Another example of a papermaking process for making the sanitary tissue products of the present invention is illustrated in Fig. 7. Fig. 7 illustrates an uncreped through-air-drying process. In this example, a multi-layered headbox 74 deposits an aqueous suspension of papermaking fibers between forming wires 76 and 78 to form an embryonic fibrous structure 80. The embryonic fibrous structure 80 is transferred to a slower moving transfer fabric 82 with the aid of at least one vacuum box 84. The level of vacuum used for the fibrous structure transfers can be from about 3 to about 15 inches of mercury (76 to about 381 millimeters of mercury). The vacuum box 84 (negative pressure) can be supplemented or replaced by the use of positive pressure from the opposite side of the embryonic fibrous structure 80 to blow the embryonic fibrous structure 80 onto the next fabric in addition to or as a replacement for sucking it onto the next fabric with vacuum. Also, a vacuum roll or rolls can be used to replace the vacuum box(es) 84.

The embryonic fibrous structure 80 is then transferred to a molding member 50 of the present invention, such as a through-air-drying fabric, and passed over through-air-dryers 86 and 88 to dry the embryonic fibrous structure 80 to form a 3D patterned fibrous structure 90. While supported by the molding member 50, the 3D patterned fibrous structure 90 is finally dried to a consistency of about 94% percent or greater. After drying, the 3D patterned fibrous structure 90 is transferred from the molding member 50 to fabric 92 and thereafter briefly sandwiched between fabrics 92 and 94. The dried 3D patterned fibrous structure 90 remains with fabric 94 until it is wound up at the reel 96 ("parent roll") as a finished fibrous structure. Thereafter, the finished 3D patterned fibrous structure 90 can be unwound, calendered and converted into the sanitary tissue product of the present invention, such as a roll of bath tissue, in any suitable manner.

Yet another example of a papermaking process for making the sanitary tissue products of the present invention is illustrated in Fig. 8. Fig. 8 illustrates a papermaking machine 98 having a conventional twin wire forming section 100, a felt run section 102, a shoe press section 104, a molding member section 106, in this case a creping fabric section, and a Yankee dryer section 108 suitable for practicing the present invention. Forming section 100 includes a pair of forming fabrics 110 and 112 supported by a plurality of rolls 114 and a forming roll 116. A headbox 118 provides papermaking furnish to a nip 120 between forming roll 116 and roll 114 and the fabrics 110 and 112. The furnish forms an embryonic fibrous structure 122 which is dewatered on the fabrics 110 and 112 with the assistance of vacuum, for example, by way of vacuum box 124.

The embryonic fibrous structure 122 is advanced to a papermaking felt 126 which is supported by a plurality of rolls 114 and the felt 126 is in contact with a shoe press roll 128. The embryonic fibrous structure 122 is of low consistency as it is transferred to the felt 126. Transfer may be assisted by vacuum; such as by a vacuum roll if so desired or a pickup or vacuum shoe as is known in the art. As the embryonic fibrous structure 122 reaches the shoe press roll 128 it may have a consistency of 10-25% as it enters the shoe press nip 130 between shoe press roll 128 and transfer roll 132. Transfer roll 132 may be a heated roll if so desired. Instead of a shoe press roll 128, it could be a conventional suction pressure roll. If a shoe press roll 128 is employed it is desirable that roll 114 immediately prior to the shoe press roll 128 is a vacuum roll effective to remove water from the felt 126 prior to the felt 126 entering the shoe press nip 130 since water from the furnish will be pressed into the felt 126 in the shoe press nip 130. In any case, using a vacuum roll at the roll 114 is typically desirable to ensure the embryonic fibrous structure 122 remains in contact with the felt 126 during the direction change as one of skill in the art will appreciate from the diagram.

The embryonic fibrous structure 122 is wet-pressed on the felt 126 in the shoe press nip 130 with the assistance of pressure shoe 134. The embryonic fibrous structure 122 is thus compactively dewatered at the shoe press nip 130, typically by increasing the consistency by 15 or more points at this stage of the process. The configuration shown at shoe press nip 130 is generally termed a shoe press; in connection with the present invention transfer roll 132 is operative as a transfer cylinder which operates to convey embryonic fibrous structure 122 at high speed, typically 1000 feet/minute (fpm) to 6000 fpm to the patterned molding member section 106 of the present invention, for example a through-air-drying fabric section, also referred to in this process as a creping fabric section.

Transfer roll 132 has a smooth transfer roll surface 136 which may be provided with adhesive and/or release agents if needed. Embryonic fibrous structure 122 is adhered to transfer roll surface 136 which is rotating at a high angular velocity as the embryonic fibrous structure 122 continues to advance in the machine-direction indicated by arrows 138. On the transfer roll 132, embryonic fibrous structure 122 has a generally random apparent distribution of fiber.

Embryonic fibrous structure 122 enters shoe press nip 130 typically at consistencies of 10-25% and is dewatered and dried to consistencies of from about 25 to about 70% by the time it is transferred to the molding member 140 according to the present invention, which in this case is a patterned creping fabric, as shown in the diagram.

Molding member 140 is supported on a plurality of rolls 114 and a press nip roll 142 and forms a molding member nip 144, for example fabric crepe nip, with transfer roll 132 as shown.

The molding member 140 defines a creping nip over the distance in which molding member 140 is adapted to contact transfer roll 132; that is, applies significant pressure to the embryonic fibrous structure 122 against the transfer roll 132. To this end, backing (or creping) press nip roll 142 may be provided with a soft deformable surface which will increase the length of the creping nip and increase the fabric creping angle between the molding member 140 and the embryonic fibrous structure 122 and the point of contact or a shoe press roll could be used as press nip roll 142 to increase effective contact with the embryonic fibrous structure 122 in high impact molding member nip 144 where embryonic fibrous structure 122 is transferred to molding member 140 and advanced in the machine-direction 138. By using different equipment at the molding member nip 144, it is possible to adjust the fabric creping angle or the takeaway angle from the molding member nip 144. Thus, it is possible to influence the nature and amount of redistribution of fiber, delamination/debonding which may occur at molding member nip 144 by adjusting these nip parameters. In some embodiments it may by desirable to restructure the z-direction interfiber characteristics while in other cases it may be desired to influence properties only in the plane of the fibrous structure. The molding member nip parameters can influence the distribution of fiber in the fibrous structure in a variety of directions, including inducing changes in the z-direction as well as the MD and CD. In any case, the transfer from the transfer roll to the molding member is high impact in that the fabric is traveling slower than the fibrous structure and a significant velocity change occurs. Typically, the fibrous structure is creped anywhere from 10-60% and even higher during transfer from the transfer roll to the molding member.

Molding member nip 144 generally extends over a molding member nip distance of anywhere from about 1/8" to about 2", typically 1/2" to 2". For a molding member 140, for example creping fabric, with 32 CD strands per inch, embryonic fibrous structure 122 thus will encounter anywhere from about 4 to 64 weft filaments in the molding member nip 144.

The nip pressure in molding member nip 144, that is, the loading between roll 142 and transfer roll 132 is suitably 20-100 pounds per linear inch (PLI).

After passing through the molding member nip 144, and for example fabric creping the embryonic fibrous structure 122, a 3D patterned fibrous structure 146 continues to advance along MD 138 where it is wet-pressed onto Yankee cylinder (dryer) 148 in transfer nip 150. Transfer at nip 150 occurs at a 3D patterned fibrous structure 146 consistency of generally from about 25 to about 70%. At these consistencies, it is difficult to adhere the 3D patterned fibrous structure 146 to the Yankee cylinder surface 152 firmly enough to remove the 3D patterned fibrous structure 146 from the molding member 140 thoroughly. This aspect of the process is important,

particularly when it is desired to use a high velocity drying hood as well as maintain high impact creping conditions.

In this connection, it is noted that conventional TAD processes do not employ high velocity hoods since sufficient adhesion to the Yankee dryer is not achieved.

It has been found in accordance with the present invention that the use of particular adhesives cooperate with a moderately moist fibrous structure (25-70% consistency) to adhere it to the Yankee dryer sufficiently to allow for high velocity operation of the system and high jet velocity impingement air drying. In this connection, a poly(vinyl alcohol)/polyamide adhesive composition as noted above is applied at 154 as needed.

The 3D patterned fibrous structure is dried on Yankee cylinder 148 which is a heated cylinder and by high jet velocity impingement air in Yankee hood 156. As the Yankee cylinder 148 rotates, 3D patterned fibrous structure 146 is creped from the Yankee cylinder 148 by creping doctor blade 158 and wound on a take-up roll 160. Creping of the paper from a Yankee dryer may be carried out using an undulatory creping blade, such as that disclosed in U.S. Pat. No. 5,690,788, the disclosure of which is incorporated by reference. Use of the undulatory crepe blade has been shown to impart several advantages when used in production of tissue products. In general, tissue products creped using an undulatory blade have higher caliper (thickness), increased CD stretch, and a higher void volume than do comparable tissue products produced using conventional crepe blades. All of these changes effected by use of the undulatory blade tend to correlate with improved softness perception of the tissue products.

When a wet-crepe process is employed, an impingement air dryer, a through-air dryer, or a plurality of can dryers can be used instead of a Yankee. Impingement air dryers are disclosed in the following patents and applications, the disclosure of which is incorporated herein by reference: U.S. Pat. No. 5,865,955 of Ilvespaaet et al. U.S. Pat. No. 5,968,590 of Ahonen et al. U.S. Pat. No. 6,001,421 of Ahonen et al. U.S. Pat. No. 6,119,362 of Sundqvist et al. U.S. patent application Ser. No. 09/733,172, entitled Wet Crepe, Impingement-Air Dry Process for Making Absorbent Sheet, now U.S. Pat. No. 6,432,267. A throughdrying unit as is well known in the art and described in U.S. Pat. No. 3,432,936 to Cole et al., the disclosure of which is incorporated herein by reference as is U.S. Pat. No. 5,851,353 which discloses a can-drying system.

There is shown in Fig. 9 a papermaking machine 98, similar to Fig. 8, for use in connection with the present invention. Papermaking machine 98 is a three fabric loop machine having a forming section 100 generally referred to in the art as a crescent former. Forming section 100 includes a forming wire 162 supported by a plurality of rolls such as rolls 114. The forming section 100 also includes a forming roll 166 which supports paper making felt 126 such

that embryonic fibrous structure 122 is formed directly on the felt 126. Felt run 102 extends to a shoe press section 104 wherein the moist embryonic fibrous structure 122 is deposited on a transfer roll 132 (also referred to sometimes as a backing roll) as described above. Thereafter, embryonic fibrous structure 122 is creped onto molding member 140, such as a crepe fabric, in molding member nip 144 before being deposited on Yankee dryer 148 in another press nip 150. The papermaking machine 98 may include a vacuum turning roll, in some embodiments; however, the three loop system may be configured in a variety of ways wherein a turning roll is not necessary. This feature is particularly important in connection with the rebuild of a papermachine inasmuch as the expense of relocating associated equipment i.e. pulping or fiber processing equipment and/or the large and expensive drying equipment such as the Yankee dryer or plurality of can dryers would make a rebuild prohibitively expensive unless the improvements could be configured to be compatible with the existing facility.

Fig. 10 shows another example of a papermaking process to make the sanitary tissue products of the present invention. Fig. 10 illustrates a papermaking machine 98 for use in connection with the present invention. Papermaking machine 98 is a three fabric loop machine having a forming section 100, generally referred to in the art as a crescent former. Forming section 100 includes headbox 118 depositing a furnish on forming wire 110 supported by a plurality of rolls 114. The forming section 100 also includes a forming roll 166, which supports papermaking felt 126, such that embryonic fibrous structure 122 is formed directly on felt 126. Felt run 102 extends to a shoe press section 104 wherein the moist embryonic fibrous structure 122 is deposited on a transfer roll 132 and wet-pressed concurrently with the transfer. Thereafter, embryonic fibrous structure 122 is transferred to the molding member section 106, by being transferred to and/or creped onto molding member 140 of the present invention, for example a through-air-drying belt, in molding member nip 144, for example belt crepe nip, before being optionally vacuum drawn by suction box 168 and then deposited on Yankee dryer 148 in another press nip 150 using a creping adhesive, as noted above. Transfer to a Yankee dryer from the creping belt differs from conventional transfers in a conventional wet press (CWP) from a felt to a Yankee. In a CWP process, pressures in the transfer nip may be 500 PLI (87.6 kN/meter) or so, and the pressured contact area between the Yankee surface and the fibrous structure is close to or at 100%. The press roll may be a suction roll which may have a P&J hardness of 25-30. On the other hand, a belt crepe process of the present invention typically involves transfer to a Yankee with 4-40% pressured contact area between the fibrous structure and the Yankee surface at a pressure of 250-350 PLI (43.8-61.3 kN/meter). No suction is applied in the transfer nip, and a softer pressure roll is used, P&J hardness 35-45. The papermaking machine may include a

suction roll, in some embodiments; however, the three loop system may be configured in a variety of ways wherein a turning roll is not necessary. This feature is particularly important in connection with the rebuild of a papermachine inasmuch as the expense of relocating associated equipment, i.e., the headbox, pulping or fiber processing equipment and/or the large and expensive drying equipment, such as the Yankee dryer or plurality of can dryers, would make a rebuild prohibitively expensive, unless the improvements could be configured to be compatible with the existing facility.

Non-limiting Examples of Methods for Making Sanitary Tissue Products and Paper Toweling Products

Example 1 - Through-Air-Drying Belt (Semi-continuous Knuckle, Fabric Side Out (FSO), 85 Degree angle knuckles relative to CD)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a fibrous structure according to the present invention on a pilot-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and equally distributed in the top and bottom chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is then directed to the NSK fan pump where the NSK slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% NSK slurry is then directed and distributed to the center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the NSK fiber stock pipe at a rate sufficient to deliver 0.28% temporary wet strengthening additive based on the dry weight of the NSK fibers. The

absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber and bottom headbox chamber. The NSK fiber slurry is directed to the center headbox chamber. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 34% of the top side is made up of the eucalyptus fibers, about 34% is made of the eucalyptus fibers on the bottom side and about 32% is made up of the NSK fibers in the center. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and wire table vacuum boxes. The Fourdrinier wire is an 84M (84 by 76 5A, Albany International). The speed of the Fourdrinier wire is about 763 feet per minute (fpm).

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 18-22% at the point of transfer, to a 3D patterned, semi-continuous knuckle, through-air-drying belt as shown in Fig. 11 (white areas impart knuckles and black areas impart pillow regions in the fibrous structure). The speed of the 3D patterned through-air-drying belt is 650 feet per minute (fpm), which is 14.8% slower than the speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure as shown in Fig. 12 comprising a pattern of semi-continuous high density knuckle regions substantially oriented in the machine direction. Each semi-continuous high density knuckle region substantially oriented in the machine direction is separated by a low density pillow region substantially oriented in the machine direction. This 3D patterned through-air-drying belt is formed by casting a layer of an impervious resin surface of semi-continuous knuckles onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the resin cast is about 12 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 50-65% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 80% polyvinyl alcohol

(PVA 88-44), about 20% UNICREPE® 457T20. UNICREPE® 457T20 is commercially available from GP Chemicals. The creping adhesive is delivered to the Yankee surface at a rate of about 0.10-0.20% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 96-99% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 45° and is positioned with respect to the Yankee dryer to provide an impact angle of about 101°. The Yankee dryer is operated at a temperature of about 275°F and a speed of about 650 fpm. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 583 fpm.

Two parent rolls of the fibrous structure are then converted into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The two parent rolls are converted with the low density pillow side out, the uncreped surface (the surface that doesn't contact the dryer and/or Yankee). The line speed is 650 ft/min. One parent roll of the fibrous structure is unwound and transported to an emboss stand where the fibrous structure is strained to form the emboss pattern in the fibrous structure via a 0.50" Pressure Roll Nip and then combined with the fibrous structure from the other parent roll to make a multi-ply (2-ply) sanitary tissue product. Approximately 0.5% of a softening agent is added to the top side only of the multi-ply sanitary tissue product. The multi-ply sanitary tissue product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above.

Example 2 - Through-Air-Drying Belt (Discrete Knuckle, Fabric Side Out (FSO), 75 Degree knuckles relative to CD)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a fibrous structure according to the present invention on a pilot-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to a hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and distributed in the top and bottom chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 1.5% fiber by weight using a conventional repulper, then transferred to a hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe and mixed with the aqueous slurry of Northern Softwood Kraft (NSK), described in the next paragraph, to a fan pump where the slurry consistency is reduced from about 1.5% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus/NSK slurry is then pumped and distributed in the center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is then mixed with the 1.5% aqueous slurry of Eucalyptus fibers (described in the preceding paragraph) and directed to a fan pump where the NSK slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% Eucalyptus/NSK slurry is then directed and distributed to the center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the NSK fiber stock pipe at a rate sufficient to deliver 0.25% temporary wet strengthening additive based on the dry weight of the NSK fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber and bottom headbox chamber. The NSK/Eucalyptus fiber slurry is directed to the center headbox chamber. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 40% of the top side is made up of the eucalyptus fibers, about 15% is made of the eucalyptus fibers on the bottom side, about 40% is made up of the NSK fibers in the center, and about 5% is made up of the eucalyptus fiber in the center. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and wire table vacuum boxes. The Fourdrinier

wire is a Legent 866A Dual Layer (0.11 mm x 0.18 mm, Asten Johnson). The speed of the Fourdrinier wire is about 800 feet per minute (fpm).

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 18-22% at the point of transfer, to a 3D patterned, discrete knuckle, through-air-drying belt as shown in Fig. 2. The speed of the 3D patterned through-air-drying belt is 800 feet per minute (fpm), which is the same speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure as shown in Fig. 3 comprising a pattern of discrete high density knuckle regions oriented approximately 75 Degrees relative to the cross direction. Each discrete high density knuckle region oriented approximately 75° relative to the cross direction is separated by a low density continuous pillow region oriented approximately 75° relative to the cross direction. This 3D patterned through-air-drying belt is formed by casting a layer of an impervious resin surface of discrete knuckles onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the resin cast is about 12.5 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 50-65% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 78% polyvinyl alcohol (PVA 88-44), about 22% UNICREPE® 457T20. UNICREPE® 457T20 is commercially available from GP Chemicals. The creping adhesive is delivered to the Yankee surface at a rate of about 0.10-0.20% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 96-98% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25° and is positioned with respect to the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer is operated at a temperature of about 275°F and a speed of about 800 fpm. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 640 fpm.

Two parent rolls of the fibrous structure are then converted into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The two parent rolls are converted with the low density pillow side out, the uncreped surface (the surface that doesn't contact the

dryer and/or Yankee). The line speed is 550 ft/min. One parent roll of the fibrous structure is unwound and transported to an emboss stand where the fibrous structure is strained to form the emboss pattern in the fibrous structure via a 0.56" Pressure Roll Nip and then combined with the fibrous structure from the other parent roll to make a multi-ply (2-ply) sanitary tissue product. Approximately 0.75% of a softening agent is added to the top side only of the multi-ply sanitary tissue product. The multi-ply sanitary tissue product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above.

Example 3 - Through-Air-Drying Belt (Discrete AND Semi-continuous Knuckles, Fabric Side Out (FSO), 75 Degree knuckles relative to CD)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a fibrous structure according to the present invention on a pilot-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to a hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and distributed in the top and bottom chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is then directed to a fan pump where the NSK slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% NSK slurry is then directed and distributed to the center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the NSK fiber stock pipe at a rate sufficient to deliver 0.17% temporary wet strengthening additive based on the dry weight of the NSK fibers. The

absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the top layer Euc fiber stock pipe at a rate sufficient to deliver 0.14% temporary wet strengthening additive based on the dry weight of the top layer Euc fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber and bottom headbox chamber. The NSK fiber slurry is directed to the center headbox chamber. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 35% of the top side is made up of the eucalyptus fibers, about 19% is made of the eucalyptus fibers on the bottom side, and about 46% is made up of the NSK fibers in the center. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and wire table vacuum boxes. The Fourdrinier wire is a Legent 866A Dual Layer (0.11 mm x 0.18 mm, Asten Johnson). The speed of the Fourdrinier wire is about 800 feet per minute (fpm).

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 18-22% at the point of transfer, to a 3D patterned, discrete knuckle, through-air-drying belt as shown in Fig. 13 (white areas impart knuckles and black areas impart pillow regions in the fibrous structure). The speed of the 3D patterned through-air-drying belt is 800 feet per minute (fpm), which is the same speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure comprising a pattern of discrete and semi-continuous high density knuckle regions oriented approximately 75 Degrees relative to the cross direction. Each discrete and semi-continuous high density knuckle region oriented approximately 75 Degrees relative to the cross direction is separated by a low density continuous and semi-continuous pillow region oriented approximately 75 Degrees relative to the cross direction. This 3D patterned through-air-drying belt is formed by casting a layer of an impervious resin surface of discrete knuckles onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the resin cast is about 12.6 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 40-65% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 78% polyvinyl alcohol (PVA 88-44), about 22% UNICREPE® 457T20. UNICREPE® 457T20 is commercially available from GP Chemicals. The creping adhesive is delivered to the Yankee surface at a rate of about 0.10-0.20% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 96-98% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25° and is positioned with respect to the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer is operated at a temperature of about 275°F and a speed of about 800 fpm. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 644 fpm.

Two parent rolls of the fibrous structure are then converted into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The two parent rolls are converted with the low density pillow side out, the uncreped surface (the surface that doesn't contact the dryer and/or Yankee). The line speed is 750 ft/min. One parent roll of the fibrous structure is unwound and transported to an emboss stand where the fibrous structure is strained to form the emboss pattern in the fibrous structure via a 0.51" Pressure Roll Nip and then combined with the fibrous structure from the other parent roll to make a multi-ply (2-ply) sanitary tissue product. Approximately 0.5% of a proprietary quaternary amine softener is added to the top side only of the multi-ply sanitary tissue product. The multi-ply sanitary tissue product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above.

Example 4 - Through-Air-Drying Belt (Discrete Knuckle, Fabric Side Out (FSO), 45 Degree knuckles relative to CD)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a fibrous structure according to the present invention on a pilot-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to a hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and distributed in the top and bottom chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is then directed to a fan pump where the NSK slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% NSK slurry is then directed and distributed to the center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the NSK fiber stock pipe at a rate sufficient to deliver 0.17% temporary wet strengthening additive based on the dry weight of the NSK fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the top headbox Euc layer fiber stock pipe at a rate sufficient to deliver 0.14% temporary wet strengthening additive based on the dry weight of the top layer Euc fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber and bottom headbox chamber. The NSK fiber slurry is directed to the center

headbox chamber. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 36% of the top side is made up of the eucalyptus fibers, about 17% is made of the eucalyptus fibers on the bottom side, and about 47 is made up of the NSK fibers in the center. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and wire table vacuum boxes. The Fourdrinier wire is a Legent 866A Dual Layer (0.11 mm x 0.18 mm, Asten Johnson). The speed of the Fourdrinier wire is about 800 feet per minute (fpm).

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 18-22% at the point of transfer, to a 3D patterned, discrete knuckle, through-air-drying belt as shown in Fig. 14 (white areas impart knuckles and black area imparts pillow region in the fibrous structure). The speed of the 3D patterned through-air-drying belt is 800 feet per minute (fpm), which is the same speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure as shown in Fig. 15 comprising a pattern of discrete high density knuckle regions oriented approximately 45 Degrees relative to the cross direction. Each discrete high density knuckle region oriented approximately 45 Degrees relative to the cross direction is separated by a low density continuous pillow region oriented approximately 45 Degrees relative to the cross direction. This 3D patterned through-air-drying belt is formed by casting a layer of an impervious resin surface of discrete knuckles onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the resin cast is about 12.2 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 50-65% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 78% polyvinyl alcohol (PVA 88-44), about 22% UNICREPE® 457T20. UNICREPE® 457T20 is commercially available from GP Chemicals. The creping adhesive is delivered to the Yankee surface at a rate of about 0.10-0.20% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 95-98% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25° and is positioned with respect to the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer is operated at a temperature of about 275°F and a speed of about 800 fpm. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 640 fpm.

Two parent rolls of the fibrous structure are then converted into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The two parent rolls are converted with the low density pillow side out, the uncreped surface (the surface that doesn't contact the dryer and/or Yankee). The line speed is 750 ft/min. One parent roll of the fibrous structure is unwound and transported to an emboss stand where the fibrous structure is strained to form the emboss pattern in the fibrous structure via a 0.5" Pressure Roll Nip and then combined with the fibrous structure from the other parent roll to make a multi-ply (2-ply) sanitary tissue product. Approximately 0.5% of a proprietary quaternary amine softener is added to the top side only of the multi-ply sanitary tissue product. The multi-ply sanitary tissue product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above.

Comparative Examples

Comparative Example 1 (Semi-continuous Knuckle, Fabric Side Out (FSO), variable angle (with average 0 Degree) knuckles relative to CD)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a Semi-Continuous Knuckle, Fabric Side Out, variable angle (with average 0 Degree) Knuckle relative to CD fibrous structure according to the Points of Comparison in the Data Table on a pilot-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to a hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and distributed in the top and bottom chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the

softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is then mixed with the 1.5% aqueous slurry of Eucalyptus fibers (described in the preceding paragraph) and directed to a fan pump where the NSK slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% NSK slurry is then directed and distributed to center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the NSK fiber stock pipe at a rate sufficient to deliver 0.41% temporary wet strengthening additive based on the dry weight of the NSK fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the bottom layer Euc fiber stock pipe at a rate sufficient to deliver 0.06% temporary wet strengthening additive based on the dry weight of the bottom layer Euc fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the top layer Euc fiber stock pipe at a rate sufficient to deliver 0.06% temporary wet strengthening additive based on the dry weight of the top layer Euc fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber and bottom headbox chamber. The NSK fiber slurry is directed to the center headbox chamber. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 39.5% of the sheet is made up of the eucalyptus fibers in the bottom headbox chamber, about 21.0% is made of the NSK fibers in the center layer, and about 39.5% is made up of the Euc fibers in the top layer. Dewatering occurs through the Fourdrinier wire and is assisted by a

deflector and wire table vacuum boxes. The Fourdrinier wire is an 84M (84 by 76 5A, Albany International). The speed of the Fourdrinier wire is about 800 feet per minute (fpm).

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 14-25% at the point of transfer, to a 3D patterned, semi-continuous knuckle, through-air-drying belt as shown in Prior Art Fig. 16 (white areas impart knuckles and black areas impart pillow regions in the fibrous structure). The speed of the 3D patterned through-air-drying belt is 800 feet per minute (fpm), which is the same speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure as shown in Prior Art Fig. 17 comprising a pattern of semi-continuous high density knuckle regions oriented at varying angles (with an average of approximately 0 Degrees) relative to the cross direction. Each semi-continuous high density knuckle region oriented approximately 0 Degrees relative to the cross direction is separated by a low density semi-continuous pillow region oriented approximately 0 Degrees relative to the cross direction. This 3D patterned through-air-drying belt is formed by casting a layer of an impervious resin surface of discrete knuckles onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the resin cast is about 13.5 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 50-70% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 60% polyvinyl alcohol (PVA 88-44), about 40% UNICREPE® 457T20. UNICREPE® 457T20 is commercially available from GP Chemicals. The creping adhesive is delivered to the Yankee surface at a rate of about 0.10-0.20% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 96-98% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25° and is positioned with respect to the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer is operated at a temperature of about 325°F and a speed of about 800 fpm. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 703 fpm.

Two parent rolls of the fibrous structure are then converted into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The two parent rolls are converted with the low density pillow side out, the uncreped surface (the surface that doesn't contact the dryer and/or Yankee). The line speed is 550-600 ft/min. One parent roll of the fibrous structure is unwound and transported to an emboss stand where the fibrous structure is strained to form the emboss pattern in the fibrous structure via a 0.5" Pressure Roll Nip and then combined with the fibrous structure from the other parent roll to make a multi-ply (2-ply) sanitary tissue product. Approximately 0.5% of a proprietary quaternary amine softener is added to the top side only of the multi-ply sanitary tissue product. The multi-ply sanitary tissue product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above, under the "Points of Comparison" Label.

Comparative Example 2 (Continuous Knuckle, Fabric Side Out (FSO), knuckles various relative to CD)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a Continuous Knuckle, Fabric Side Out, various angle Knuckle relative to CD fibrous structure according to the Points of Comparison in the Data Table on a full-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3-6% fiber by weight using a conventional repulper, then transferred to a hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to an additional Hardwood stock check and then to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and distributed in the Fabric-side chamber and Wire-Side chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3-6% fiber by weight using a conventional repulper, then transferred to the softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is directed to a Mix Tank, where it is mixed with a Broke stream (described in the paragraph below). The refined NSK fiber slurry is directed to a fan pump where the NSK slurry

consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% NSK slurry is then directed and distributed to the center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of a mixture of Eucalyptus and NSK fibers that have been reprocessed from scrap Charmin is prepared at about 3-6% fiber by weight using a conventional repulper, then transferred to a Broke storage chest. The Broke fiber slurry is then directed to a Mix Tank where it is mixed with the refined NSK referenced in the paragraph above. The Broke fiber slurry is directed to a fan pump where the Broke slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% Broke slurry is then directed and distributed to the center chamber of a multi-layered three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Parez® 750C commercially available from Kemira) is prepared and is added to the combined NSK/Broke fiber stock pipe coming out of the Mix Tank referenced in the preceding two paragraphs at a rate sufficient to deliver 0.8%-2.5 temporary wet strengthening additive based on the dry weight of the NSK fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber and bottom headbox chamber. The NSK fiber and Broke fiber slurry is directed to the center headbox chamber. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 20-40% of the sheet is made up of the eucalyptus fibers in the fabric-layer headbox chamber, about 20-40% is made of the NSK fibers in the center layer, and about 20-40% is made up of the Euc fibers in the wire layer. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and wire table vacuum boxes. The Fourdrinier wire is a 84M (84 by 76 5A, Albany International). The speed of the Fourdrinier wire is about 2800-4000 feet per minute (fpm).

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 14-25% at the point of transfer, to a 3D patterned, discrete knuckle, through-air-drying belt as shown in Prior Art Fig. 18 (white area imparts knuckle and black areas impart pillow regions in the fibrous structure). The speed of the 3D patterned through-air-drying

belt is 2800-4000 feet per minute (fpm), which is the same speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure comprising a pattern of continuous high density knuckle regions that vary in their angle relative to the cross direction. Each continuous high density knuckle region that vary in their angle relative to the cross direction is separated by a low density discrete pillow region oriented that vary in their angle relative to the cross direction. This 3D patterned through-air-drying belt is formed by casting a layer of an impervious resin surface of discrete knuckles onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the resin cast is about 12.0 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 50-70% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 90% polyvinyl alcohol (PVA 88-44), about 10% Crepertrol® 6115. Crepetrol® 6115 is commercially available from Hercules Inc. The creping adhesive is delivered to the Yankee surface at a rate of about 0.10-0.20% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 94-98% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25° and is positioned with respect to the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer is operated at a temperature of about 275°F and a speed of about 2800-4000 fpm. Approximately 1.0% of a proprietary quaternary amine softener is sprayed onto the sheet, therefore being added to both sides of a 2 ply sheet. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 2200-3400 fpm.

Two parent rolls of the fibrous structure are then converted into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The two parent rolls are converted with the low density pillow side out, the uncreped surface (the surface that doesn't contact the dryer and/or Yankee). The line speed is 750-1500 ft/min. Both parent roll of the fibrous structure are unwound and transported to a combiner where the fibrous structure is combined with a hot-melt adhesive to make a multi-ply (2-ply) sanitary tissue product. The multi-ply sanitary tissue

product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above, under the "Points of Comparison" Label.

Comparative Example 3 (Semi-continuous Knuckle, Wire Side Out (WSO), 85 Degree knuckles relative to CD)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a Semi-Continuous Knuckle, Wire Side Out, 85 Degree Knuckle relative to CD fibrous structure according to the Points of Comparison in the Data Table on a pilot-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to a hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and distributed in the top, center, and bottom chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is then mixed with the 1.5% aqueous slurry of Eucalyptus fibers (described in the preceding paragraph) and directed to a fan pump where the NSK slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% NSK slurry is then directed and distributed to the top and center chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the NSK fiber stock pipe at a rate sufficient to deliver 0.17% temporary wet strengthening additive based on the dry weight of the NSK fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the Euc fiber stock pipe at a rate sufficient to deliver 0.14% temporary wet strengthening additive based on the dry weight of the Euc fibers in the bottom chamber of the headbox. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber, center headbox chamber, and bottom headbox chamber. The NSK fiber slurry is directed to the center and top headbox chambers. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 35% of the sheet is made up of the eucalyptus fibers in the bottom headbox chamber, about 21.5% is made of the NSK fibers in the center layer, about 11% is made up of the Euc fibers in the center layer, about 21.5% is made up of the NSK fibers in the top layer, and about 11% is made up of the Euc fibers in the top layer. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and wire table vacuum boxes. The Fourdrinier wire is a Legent 866A Dual Layer (0.11 mm x 0.18 mm, Asten Johnson). The speed of the Fourdrinier wire is about 800 feet per minute (fpm).

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 14-25% at the point of transfer, to a 3D patterned, discrete knuckle, through-air-drying belt as shown in Fig. 11 (white areas impart knuckles and black areas impart pillow regions in the fibrous structure). The speed of the 3D patterned through-air-drying belt is 800 feet per minute (fpm), which is the same speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure as shown in Fig. 12 comprising a pattern of semi-continuous high density knuckle regions oriented approximately 85 Degrees relative to the cross direction. Each discrete high density knuckle region oriented approximately 85 Degrees relative to the cross direction is separated by a low density semi-continuous pillow region oriented approximately 85 Degrees relative to the cross direction. This 3D patterned through-air-drying belt is formed by casting a layer of an impervious resin surface of discrete knuckles onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the resin cast is about 12.0 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 50-70% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 78% polyvinyl alcohol (PVA 88-44), about 22% UNICREPE® 457T20. UNICREPE® 457T20 is commercially available from GP Chemicals. The creping adhesive is delivered to the Yankee surface at a rate of about 0.10-0.20% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 96-98% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25° and is positioned with respect to the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer is operated at a temperature of about 275°F and a speed of about 800 fpm. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 632 fpm.

Two parent rolls of the fibrous structure are then converted into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The two parent rolls are converted with the high density knuckle side out, the creped surface (the surface that contacts the dryer and/or Yankee). The line speed is 550-600 ft/min. One parent roll of the fibrous structure is unwound and transported to an emboss stand where the fibrous structure is strained to form the emboss pattern in the fibrous structure via a 0.56" Pressure Roll Nip and then combined with the fibrous structure from the other parent roll to make a multi-ply (2-ply) sanitary tissue product. Approximately 0.25% of a proprietary quaternary amine softener is added to the top side only of the multi-ply sanitary tissue product. The multi-ply sanitary tissue product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above, under the "Points of Comparison" Label.

Comparative Example 4 (Discrete Knuckle, Fabric Side Out (FSO), knuckles various angles with average of 45 degrees relative to CD)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a Discrete Knuckle, Fabric Side Out, various angle Knuckle with average of 45 degrees relative to CD fibrous structure according to the Points of Comparison in the Data Table on a pilot-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and equally distributed in the top and bottom chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is then directed to the NSK fan pump where the NSK slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then directed and distributed to the center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Parez® commercially available from Kemira) is prepared and is added to the NSK fiber stock pipe at a rate sufficient to deliver 0.3% temporary wet strengthening additive based on the dry weight of the NSK fibers. The absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber and bottom headbox chamber. The NSK fiber slurry is directed to the center headbox chamber. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 50% of the top side is made up of the eucalyptus fibers, about 20% is made of the eucalyptus fibers on the bottom side and about 30% is made up of the NSK fibers in the center. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and wire table

vacuum boxes. The Fourdrinier wire is an 84M (84 by 76 5A, Albany International). The speed of the Fourdrinier wire is about 800 feet per minute (fpm).

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 16-20% at the point of transfer, to a 3D patterned through-air-drying belt as shown in Prior Art Fig. 19 (white areas impart knuckles and black area imparts pillow region in the fibrous structure). The speed of the 3D patterned through-air-drying belt is the same as the speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure as shown in Prior Art Fig. 20 comprising a pattern of discrete high density knuckle regions dispersed throughout a continuous low density pillow region. This 3D patterned through-air-drying belt is formed by casting an impervious resin surface onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the resin cast is about 12 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 50-65% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 80% polyvinyl alcohol (PVA 88-50), about 20% CREPETROL® 457T20. CREPETROL® 457T20 is commercially available from Ashland (formerly Hercules Incorporated of Wilmington, DE). The creping adhesive is delivered to the Yankee surface at a rate of about 0.15% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 97% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25° and is positioned with respect to the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer is operated at a temperature of about 275°F and a speed of about 800 fpm. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 680 fpm.

Two parent rolls of the fibrous structure are then converted with the low density pillow side out, the uncreped surface (the surface that doesn't contact the dryer and/or Yankee) into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The line speed is 400 ft/min. One parent roll of the fibrous structure is unwound and transported to an

emboss stand where the fibrous structure is strained to form the emboss pattern in the fibrous structure and then combined with the fibrous structure from the other parent roll to make a multi-ply (2-ply) sanitary tissue product. The multi-ply sanitary tissue product is then transported over a slot extruder through which a surface chemistry may be applied. The multi-ply sanitary tissue product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above.

Comparative Example 5 (Discrete and Semi-continuous Knuckle Dual-Cast, Fabric Side Out (FSO) Fibrous Structure)

The following Example illustrates a non-limiting example for a preparation of a sanitary tissue product comprising a discrete and semi-continuous Knuckle Dual-Cast, Fabric Side Out, fibrous structure according to the Points of Comparison in the Data Table on a pilot-scale Fourdrinier fibrous structure making (papermaking) machine.

An aqueous slurry of eucalyptus (Fibria Brazilian bleached hardwood kraft pulp) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the hardwood fiber stock chest. The eucalyptus fiber slurry of the hardwood stock chest is pumped through a stock pipe to a hardwood fan pump where the slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% eucalyptus slurry is then pumped and equally distributed in the top and bottom chambers of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

Additionally, an aqueous slurry of NSK (Northern Softwood Kraft) pulp fibers is prepared at about 3% fiber by weight using a conventional repulper, then transferred to the softwood fiber stock chest. The NSK fiber slurry of the softwood stock chest is pumped through a stock pipe to be refined to a Canadian Standard Freeness (CSF) of about 630. The refined NSK fiber slurry is then directed to the NSK fan pump where the NSK slurry consistency is reduced from about 3% by fiber weight to about 0.15% by fiber weight. The 0.15% NSK slurry is then directed and distributed to the center chamber of a multi-layered, three-chambered headbox of a Fourdrinier wet-laid papermaking machine.

In order to impart temporary wet strength to the finished fibrous structure, a 1% dispersion of temporary wet strengthening additive (e.g., Fennorez® 91 commercially available from Kemira) is prepared and is added to the NSK fiber stock pipe at a rate sufficient to deliver 0.23% temporary wet strengthening additive based on the dry weight of the NSK fibers. The

absorption of the temporary wet strengthening additive is enhanced by passing the treated slurry through an in-line mixer.

The wet-laid papermaking machine has a layered headbox having a top chamber, a center chamber, and a bottom chamber where the chambers feed directly onto the forming wire (Fourdrinier wire). The eucalyptus fiber slurry of 0.15% consistency is directed to the top headbox chamber and bottom headbox chamber. The NSK fiber slurry is directed to the center headbox chamber. All three fiber layers are delivered simultaneously in superposed relation onto the Fourdrinier wire to form thereon a three-layer embryonic fibrous structure (web), of which about 26% of the top side is made up of the eucalyptus fibers, about 26% is made of the eucalyptus fibers on the bottom side and about 48% is made up of the NSK fibers in the center. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and wire table vacuum boxes. The Fourdrinier wire is an 84M (84 by 76 5A, Albany International). The speed of the Fourdrinier wire is about 800 feet per minute (fpm). The one-ply Basis Weight for this condition was 11.3 pounds per 3000 square feet. The one-ply caliper (at 95 gsi) was 10.65 mils.

The embryonic wet fibrous structure is transferred from the Fourdrinier wire, at a fiber consistency of about 18-22% at the point of transfer, to a 3D patterned through-air-drying belt as shown in Prior Art Fig. 21 (black areas impart knuckles and white areas impart pillow regions in the fibrous structure). The speed of the 3D patterned through-air-drying belt is the same as the speed of the Fourdrinier wire. The 3D patterned through-air-drying belt is designed to yield a fibrous structure as shown in Prior Art Fig. 22 comprising a pattern of high density knuckle regions dispersed throughout a multi-elevational continuous pillow region. The multi-elevational continuous pillow region comprises an intermediate density pillow region (density between the high density knuckles and the low density other pillow region) and a low density pillow region formed by the deflection conduits created by the semi-continuous knuckle layer substantially oriented in the machine direction. This 3D patterned through-air-drying belt is formed by casting a first layer of an impervious resin surface of semi-continuous knuckles onto a fiber mesh supporting fabric similar to that shown in Figs. 4A and 4B and then casting a second layer of impervious resin surface of discrete knuckles. The supporting fabric is a 98 x 52 filament, dual layer fine mesh. The thickness of the first layer resin cast is about 6 mils above the supporting fabric and the thickness of the second layer resin cast is about 13 mils above the supporting fabric.

Further de-watering of the fibrous structure is accomplished by vacuum assisted drainage until the fibrous structure has a fiber consistency of about 20% to 30%.

While remaining in contact with the 3D patterned through-air-drying belt, the fibrous structure is pre-dried by air blow-through pre-dryers to a fiber consistency of about 50-65% by weight.

After the pre-dryers, the semi-dry fibrous structure is transferred to a Yankee dryer and adhered to the surface of the Yankee dryer with a sprayed creping adhesive. The creping adhesive is an aqueous dispersion with the actives consisting of about 80% polyvinyl alcohol (PVA 88-44), about 20% UNICREPE® 457T20. UNICREPE® 457T20 is commercially available from GP Chemicals. The creping adhesive is delivered to the Yankee surface at a rate of about 0.15% adhesive solids based on the dry weight of the fibrous structure. The fiber consistency is increased to about 96-98% before the fibrous structure is dry-creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25° and is positioned with respect to the Yankee dryer to provide an impact angle of about 81°. The Yankee dryer is operated at a temperature of about 300°F and a speed of about 800 fpm. The fibrous structure is wound in a roll (parent roll) using a surface driven reel drum having a surface speed of about 655 fpm.

Two parent rolls of the fibrous structure are then converted into a sanitary tissue product by loading the roll of fibrous structure into an unwind stand. The line speed is 400 ft/min. One parent roll of the fibrous structure is unwound and transported to an emboss stand where the fibrous structure is strained to form the emboss pattern in the fibrous structure via a 0.75" Pressure Roll Nip and then combined with the fibrous structure from the other parent roll to make a multi-ply (2-ply) sanitary tissue product.. The multi-ply sanitary tissue product is then transported to a winder where it is wound onto a core to form a log. The log of multi-ply sanitary tissue product is then transported to a log saw where the log is cut into finished multi-ply sanitary tissue product rolls. The multi-ply sanitary tissue product of this example exhibits the properties shown in Table 1, above.

Test Methods

Unless otherwise specified, all tests described herein including those described under the Definitions section and the following test methods are conducted on samples that have been conditioned in a conditioned room at a temperature of 23°C ± 1.0°C and a relative humidity of 50% ± 2% for a minimum of 2 hours prior to the test. The samples tested are "usable units." "Usable units" as used herein means sheets, flats from roll stock, pre-converted flats, and/or single or multi-ply products. All tests are conducted in such conditioned room. Do not test

samples that have defects such as wrinkles, tears, holes, and like. All instruments are calibrated according to manufacturer's specifications.

Emtec Test Method

TS7 and TS750 values are measured using an EMTEC Tissue Softness Analyzer ("Emtec TSA") (Emtec Electronic GmbH, Leipzig, Germany) interfaced with a computer running Emtec TSA software (version 3.19 or equivalent). According to Emtec, the TS7 value correlates with the real material softness, while the TS750 value correlates with the felt smoothness/roughness of the material. The Emtec TSA comprises a rotor with vertical blades which rotate on the test sample at a defined and calibrated rotational speed (set by manufacturer) and contact force of 100 mN. Contact between the vertical blades and the test piece creates vibrations, which create sound that is recorded by a microphone within the instrument. The recorded sound file is then analyzed by the Emtec TSA software. The sample preparation, instrument operation and testing procedures are performed according the instrument manufacture's specifications.

Sample Preparation

Test samples are prepared by cutting square or circular samples from a finished product. Test samples are cut to a length and width (or diameter if circular) of no less than about 90 mm, and no greater than about 120 mm, in any of these dimensions, to ensure the sample can be clamped into the TSA instrument properly. Test samples are selected to avoid perforations, creases or folds within the testing region. Prepare 8 substantially similar replicate samples for testing. Equilibrate all samples at TAPPI standard temperature and relative humidity conditions (23 °C ± 2 C° and 50 % ± 2 %) for at least 1 hour prior to conducting the TSA testing, which is also conducted under TAPPI conditions.

Testing Procedure

Calibrate the instrument according to the manufacturer's instructions using the 1-point calibration method with Emtec reference standards ("ref.2 samples"). If these reference samples are no longer available, use the appropriate reference samples provided by the manufacturer. Calibrate the instrument according to the manufacturer's recommendation and instruction, so that the results will be comparable to those obtained when using the 1-point calibration method with Emtec reference standards ("ref.2 samples").

Mount the test sample into the instrument, and perform the test according to the manufacturer's instructions. When complete, the software displays values for TS7 and TS750. Record each of these values to the nearest 0.01 dB $V^2$ rms. The test piece is then removed from

the instrument and discarded. This testing is performed individually on the top surface (outer facing surface of a rolled product) of four of the replicate samples, and on the bottom surface (inner facing surface of a rolled product) of the other four replicate samples.

The four test result values for TS7 and TS750 from the top surface are averaged (using a simple numerical average); the same is done for the four test result values for TS7 and TS750 from the bottom surface. Report the individual average values of TS7 and TS750 for both the top and bottom surfaces on a particular test sample to the nearest 0.01 dB $V^2$ rms. Additionally, average together all eight test value results for TS7 and TS750, and report the overall average values for TS7 and TS750 on a particular test sample to the nearest 0.01 dB $V^2$ rms.

Basis Weight Test Method

Basis weight of a fibrous structure and/or sanitary tissue product is measured on stacks of twelve usable units using a top loading analytical balance with a resolution of ± 0.001 g. The balance is protected from air drafts and other disturbances using a draft shield. A precision cutting die, measuring 3.500 in ± 0.0035 in by 3.500 in ± 0.0035 in is used to prepare all samples.

With a precision cutting die, cut the samples into squares. Combine the cut squares to form a stack twelve samples thick. Measure the mass of the sample stack and record the result to the nearest 0.001 g.

The Basis Weight is calculated in lbs/3000 $ft^2$ or $g/m^2$ as follows:

Basis Weight = (Mass of stack) / [(Area of 1 square in stack) x (No. of squares in stack)]

For example,

Basis Weight (lbs/3000 $ft^2$) = [[Mass of stack (g) / 453.6 (g/lbs)] / [12.25 ($in^2$) / 144 ($in^2/ft^2$) x 12]] x 3000

or,

Basis Weight ($g/m^2$) = Mass of stack (g) / [79.032 ($cm^2$) / 10,000 ($cm^2/m^2$) x 12]

Report result to the nearest 0.1 lbs/3000 $ft^2$ or 0.1 $g/m^2$. Sample dimensions can be changed or varied using a similar precision cutter as mentioned above, so as at least 100 square inches of sample area in stack.

Caliper Test Method

Caliper of a fibrous structure and/or sanitary tissue product is measured using a ProGage Thickness Tester (Thwing-Albert Instrument Company, West Berlin, NJ) with a pressure foot diameter of 2.00 inches (area of 3.14 $in^2$) at a pressure of 95 $g/in^2$. Four (4) samples are prepared by cutting of a usable unit such that each cut sample is at least 2.5 inches per side, avoiding

creases, folds, and obvious defects. An individual specimen is placed on the anvil with the specimen centered underneath the pressure foot. The foot is lowered at 0.03 in/sec to an applied pressure of 95 g/in$^2$. The reading is taken after 3 sec dwell time, and the foot is raised. The measure is repeated in like fashion for the remaining 3 specimens. The caliper is calculated as the average caliper of the four specimens and is reported in mils (0.001 in) to the nearest 0.1 mils.

Density Test Method

The density of a fibrous structure and/or sanitary tissue product is calculated as the quotient of the Basis Weight of a fibrous structure or sanitary tissue product expressed in lbs/3000 ft$^2$ divided by the Caliper (at 95 g/in$^2$) of the fibrous structure or sanitary tissue product expressed in mils. The final Density value is calculated in lbs/ft$^3$ and/or g/cm$^3$, by using the appropriate converting factors.

Stack Compressibility and Resilient Bulk Test Method

Stack thickness (measured in mils, 0.001 inch) is measured as a function of confining pressure (g/in$^2$) using a Thwing-Albert (14 W. Collings Ave., West Berlin, NJ) Vantage Compression/Softness Tester (model 1750-2005 or similar) or equivalent instrument, equipped with a 2500 g load cell (force accuracy is +/- 0.25% when measuring value is between 10%-100% of load cell capacity, and 0.025% when measuring value is less than 10% of load cell capacity), a 1.128 inch diameter steel pressure foot (one square inch cross sectional area) which is aligned parallel to the steel anvil (2.5 inch diameter). The pressure foot and anvil surfaces must be clean and dust free, particularly when performing the steel-to-steel test. Thwing-Albert software (MAP) controls the motion and data acquisition of the instrument.

The instrument and software is set-up to acquire crosshead position and force data at a rate of 50 points/sec. The crosshead speed (which moves the pressure foot) for testing samples is set to 0.20 inches/min (the steel-to-steel test speed is set to 0.05 inches/min). Crosshead position and force data are recorded between the load cell range of approximately 5 and 1500 grams during compression. The crosshead is programmed to stop immediately after surpassing 1500 grams, record the thickness at this pressure (termed $T_{max}$), and immediately reverse direction at the same speed as performed in compression. Data is collected during this decompression portion of the test (also termed recovery) between approximately 1500 and 5 grams. Since the foot area is one square inch, the force data recorded corresponds to pressure in units of g/in$^2$. The MAP software is programmed to the select 15 crosshead position values (for both compression

and recovery) at specific pressure trap points of 10, 25, 50, 75, 100, 125, 150, 200, 300, 400, 500, 600, 750, 1000, and 1250 g/in$^2$ (i.e., recording the crosshead position of very next acquired data point after the each pressure point trap is surpassed). In addition to these 30 collected trap points, $T_{max}$ is also recorded, which is the thickness at the maximum pressure applied during the test (approximately 1500 g/in$^2$).

Since the overall test system, including the load cell, is not perfectly rigid, a steel-to-steel test is performed (i.e., nothing in between the pressure foot and anvil) at least twice for each batch of testing, to obtain an average set of steel-to-steel crosshead positions at each of the 31 trap points described above. This steel-to-steel crosshead position data is subtracted from the corresponding crosshead position data at each trap point for each tested stacked sample, thereby resulting in the stack thickness (mils) at each pressure trap point during the compression, maximum pressure, and recovery portions of the test.

StackT (trap) = StackCP (trap) – SteelCP (trap)

Where:

trap = trap point pressure at either compression, recovery, or max

StackT = Thickness of Stack (at trap pressure)

StackCP = Crosshead position of Stack in test (at trap pressure)

SteelCP = Crosshead position of steel-to-steel test (at trap pressure)

A stack of five (5) usable units thick is prepared for testing as follows. The minimum usable unit size is 2.5 inch by 2.5 inch; however a larger sheet size is preferable for testing, since it allows for easier handling without touching the central region where compression testing takes place. For typical perforated rolled bath tissue, this consists of removing five (5) sets of 3 connected usable units. In this case, testing is performed on the middle usable unit, and the outer 2 usable units are used for handling while removing from the roll and stacking. For other product formats, it is advisable, when possible, to create a test sheet size (each one usable unit thick) that is large enough such that the inner testing region of the created 5 usable unit thick stack is never physically touched, stretched, or strained, but with dimensions that do not exceed 14 inches by 6 inches.

The 5 sheets (one usable unit thick each) of the same approximate dimensions, are placed one on top the other, with their MD aligned in the same direction, their outer face all pointing in the same direction, and their edges aligned +/- 3 mm of each other. The central portion of the stack, where compression testing will take place, is never to be physically touched, stretched,

and/or strained (this includes never to 'smooth out' the surface with a hand or other apparatus prior to testing).

The 5 sheet stack is placed on the anvil, positioning it such that the pressure foot will contact the central region of the stack (for the first compression test) in a physically untouched spot, leaving space for a subsequent (second) compression test, also in the central region of the stack, but separated by ¼ inch or more from the first compression test, such that both tests are in untouched, and separated spots in the central region of the stack. From these two tests, an average crosshead position of the stack at each trap pressure (i.e., StackCP(trap)) is calculated for compression, maximum pressure, and recovery portions of the tests. Then, using the average steel-to-steel crosshead trap points (i.e., SteelCP(trap)), the average stack thickness at each trap (i.e., StackT(trap) is calculated (mils).

Stack Compressibility is defined here as the absolute value of the linear slope of the stack thickness (mils) as a function of the log(10) of the confining pressure (grams/in$^2$), by using the 15 compression trap points discussed previously (i.e., compression from 10 to 1250 g/in$^2$), in a least squares regression. The units for Stack Compressibility are [mils/(log(g/in$^2$))], and is reported to the nearest 0.1 [mils/(log(g/in$^2$))].

Resilient Bulk is calculated from the stack weight per unit area and the sum of 8 StackT(trap) thickness values from the maximum pressure and recovery portion of the tests: i.e., at maximum pressure ($T_{max}$) and recovery trap points at R1250, R1000, R750, R500, R300, R100, and R10 g/in$^2$ (a prefix of "R" denotes these traps come from recovery portion of the test). Stack weight per unit area is measured from the same region of the stack contacted by the compression foot, after the compression testing is complete, by cutting a 3.50 inch square (typically) with a precision die cutter, and weighing on a calibrated 3-place balance, to the nearest 0.001 gram. The weight of the precisely cut stack, along with the StackT(trap) data at each required trap pressure (each point being an average from the two compression/recovery tests discussed previously), are used in the following equation to calculate Resilient Bulk, reported in units of cm$^3$/g, to the nearest 0.1 cm$^3$/g.

$$\text{Resilient Bulk} = \frac{\text{SUM}\left(\text{StackT}(T_{max}, \text{R1250}, \text{R1000}, \text{R750}, \text{R500}, \text{R300}, \text{R100}, \text{R10})\right) * 0.00254}{\text{M/A}}$$

Where:

StackT = Thickness of Stack (at trap pressures of $T_{max}$ and recovery pressures listed above), (mils)

M = weight of precisely cut stack, (grams)

A = area of the precisely cut stack, (cm$^2$)

Slip Stick Coefficient of Friction Test Method

Background

Friction is the force resisting the relative motion of solid surfaces, fluid layers, and material elements sliding against each other. Of particular interest here, 'dry' friction resists relative lateral motion of two solid surfaces in contact. Dry friction is subdivided into static friction between non-moving surfaces, and kinetic friction between moving surfaces. "Slip Stick", as applied here, is the term used to describe the dynamic variation in kinetic friction.

Friction is not itself a fundamental force but arises from fundamental electromagnetic forces between the charged particles constituting the two contacting surfaces. Textured surfaces also involve mechanical interactions, as is the case when sandpaper drags against a fibrous substrate. The complexity of these interactions makes the calculation of friction from first principles impossible and necessitates the use of empirical methods for analysis and the development of theory. As such, a specific sled material and test method was identified, and has shown correlation to human perception of surface feel.

This Slip Stick Coefficient of Friction Test Method measures the interaction of a diamond file (120-140 grit) against a surface of a test sample, in this case a fibrous structure and/or sanitary tissue product, at a pressure of about 32 $g/in^2$ as shown in Figs. 23-25. The friction measurements are highly dependent on the exactness of the sled material surface properties, and since each sled has no 'standard' reference, sled-to-sled surface property variation is accounted for by testing a test sample with multiple sleds, according to the equipment and procedure described below.

Equipment and Set-up

A Thwing-Albert (14 W. Collings Ave., West Berlin, NJ) friction/peel test instrument (model 225-1) or equivalent if no longer available, is used, equipped with data acquisition software and a calibrated 2000 gram load cell that moves horizontally across the platform. Attached to the load cell is a small metal fitting (defined here as the "load cell arm") which has a small hole near its end, such that a sled string can be attached (for this method, however, no string will be used). Into this load cell arm hole, insert a cap screw (¾ inch #8-32) by partially screwing it into the opening, so that it is rigid (not loose) and pointing vertically, perpendicular to the load cell arm.

After turning instrument on, set instrument test speed to 2 inches/min, test time to 10 seconds, and wait at least 5 minutes for instrument to warm up before re-zeroing the load cell

(with nothing touching it) and testing. Force data from the load cell is acquired at a rate of 52 points per second, reported to the nearest 0.1 gram force. Press the 'Return' button to move crosshead 201 to its home position.

A smooth surfaced metal test platform 200, with dimensions of 5 inches by 4 inches by ¾ inch thick, is placed on top of the test instrument platen surface, on the left hand side of the load cell 203, with one of its 4 inch by ¾ inch sides facing towards the load cell 203, positioned 1.125 inches d from the left most tip of the load cell arm 202 as shown in Figs. 23 and 25.

Sixteen test sleds 204 are required to perform this test (32 different sled surface faces). Each is made using a dual sided, wide faced diamond file 206 (25mm x 25mm, 120/140 grit, 1.2mm thick, McMaster-Carr part number 8142A14) with 2 flat metal washers 208 (approximately 11/16th inch outer diameter and about 11/32nd inch inner diameter). The combined weight of the diamond file 206 and 2 washers 208 is 11.7 grams +/-0.2 grams (choose different washers until weight is within this range). Using a metal bonding adhesive (Loctite 430, or similar), adhere the 2 washers 208 to the c-shaped end 210 of the diamond file 206 (one each on either face), aligned and positioned such that the opening 212 is large enough for the cap screw 214 to easily fit into, and to make the total length of sled 204 to approximately 3 inches long. Clean sled 204 by dipping it, diamond face end 216 only, into an acetone bath, while at the same time gently brushing with soft bristled toothbrush 3-6 times on both sides of the diamond file 206. Remove from acetone and pat dry each side with Kimwipe tissue (do not rub tissue on diamond surface, since this could break tissue pieces onto sled surface). Wait at least 15 minutes before using sled 204 in a test. Label each side of the sled 204 (on the arm or washer, not on the diamond face) with a unique identifier (i.e., the first sled is labeled "1a" on one side, and "1b" on its other side). When all 16 sleds 204 are created and labeled, there are then 32 different diamond face surfaces for available for testing, labeled 1a and 1b through 16a and 16b. These sleds 204 must be treated as fragile (particularly the diamond surfaces) and handled carefully; thus, they are stored in a slide box holder, or similar protective container.

Sample Prep

If sample to be tested is bath tissue, in perforated roll form, then gently remove 8 sets of 2 connected sheets from the roll, touching only the corners (not the regions where the test sled will contact). Use scissors or other sample cutter if needed. If sample is in another form, cut 8 sets of sample approximately 8 inches long in the MD, by approximately 4 inches long in the CD, one usable unit thick each. Make note and/or a mark that differentiates both face sides of each sample (e.g., fabric side or wire side, top or bottom, etc.). When sample prep is complete, there

are 8 sheets prepared with appropriate marking that differentiates one side from the other. These will be referred to hereinafter as: sheets #1 through #8, each with a top side and a bottom side.

Test Operation

Press the 'Return' button to ensure crosshead 201 is in its home position.

Without touching test area of sample, place sheet #1 218 on test platform 200, top side facing up, aligning one of the sheet's CD edges (i.e. edge that is parallel to the CD) along the platform 218 edge closest to the load cell 202 (+/- 1 mm). This first test (pull), of 32 total, will be in the MD direction on the top side of the sheet 218. Place a brass bar weight or equivalent 220 (1 inch diameter, 3.75 inches long) on the sheet 218, near its center, aligned perpendicular to the sled pull direction, to prevent sheet 218 from moving during the test. Place test sled "1a" 204 over cap screw head 214 (i.e., sled washer opening 212 over cap screw head 214, and sled side 1a is facing down) such that the diamond file 206 surface is laying flat and parallel on the sheet 218 surface and the cap screw 214 is touching the inside edge of the washers 208.

Gently place a cylindrically shaped brass 20 gram (+/- 0.01 grams) weight 222 on top of the sled 204, with its edge aligned and centered with the sled's back end. Initiate the sled movement m and data acquisition by pressing the 'Test' button on the instrument. The test set up is shown in Fig. 25. The computer collects the force (grams) data and, after approximately 10 seconds of test time, this first of 32 test pulls of the overall test is complete.

If the test pull was set-up correctly, the diamond file 206 face (25mm by 25mm square) stays in contact with the sheet 218 during the entire 10 second test time (i.e., does not overhang over the sheet 218 or test platform 200 edge). Also, if at any time during the test the sheet 218 moves, the test is invalid, and must be rerun on another untouched portion of the sheet 218, using a heavier brass bar weight or equivalent 220 to hold sheet 218 down. If the sheet 218 rips or tears, rerun the test on another untouched portion of the sheet 218 (or create a new sheet 218 from the sample). If it rips again, then replace the sled 204 with a different one (giving it the same sled name as the one it replaced). These statements apply to all 32 test pulls.

For the second of 32 test pulls (also an MD pull, but in the opposite direction on the sheet), first remove the 20 gram weight 222, the sled 204, and the brass bar weight or equivalent 220 from the sheet 218. Press the 'Return' button on the instrument to reset the crosshead 201 to its home position. Rotate the sheet 218 180° (with top side still facing up), and replace the brass bar weight or equivalent 220 onto the sheet 218 (in the same position described previously). Place test sled "1b" 204 over the cap screw head 214 (i.e., sled washer opening 212 over cap screw head 214, and sled side 1b is facing down) and the 20 gram weight 222 on the sled 204, in

the same manner as described previously. Press the 'Test' button to collect the data for the second test pull.

The third test pull will be in the CD direction. After removing the sled 204, weights 220, 222, and returning the crosshead 201, the sheet 218 is rotated 90° from its previous position (with top side still facing up), and positioned so that its MD edge is aligned with the test platform 200 edge (+/- 1mm). Position the sheet 218 such that the sled 204 will not touch any perforation, if present, or touch the area where the brass bar weight or equivalent 220 rested in previous test pulls. Place the brass bar weight or equivalent 220 onto the sheet 218 near its center, aligned perpendicular to the sled pull direction m. Place test sled "2a" 204 over the cap screw head 214 (i.e., sled washer opening 212 over cap screw head 214, and sled side 2a is facing down) and the 20 gram weight 222 on the sled 204, in the same manner as described previously. Press the 'Test' button to collect the data for the third test pull.

The fourth test pull will also be in the CD, but in the opposite direction and on the opposite half section of the sheet 218. After removing the sled 204, weights 220, 222, and returning the crosshead 201, the sheet 218 is rotated 180° from its previous position (with top side still facing up), and positioned so that its MD edge is again aligned with the test platform 200 edge (+/- 1mm). Position the sheet 218 such that the sled 204 will not touch any perforation, if present, or touch the area where the brass bar weight or equivalent 220 rested in previous test pulls. Place the brass bar weight or equivalent 220 onto the sheet 218 near its center, aligned perpendicular to the sled pull direction m. Place test sled "2b" 204 over the cap screw head 214 (i.e., sled washer opening 212 over cap screw head 214, and sled side 2b is facing down) and the 20 gram weight 222 on the sled 204, in the same manner as described previously. Press the 'Test' button to collect the data for the fourth test pull.

After the fourth test pull is complete, remove the sled 204, weights 220, 222, and return the crosshead 201 to the home position. Sheet #1 218 is discarded.

Test pulls 5-8 are performed in the same manner as 1-4, except that sheet #2 218 has its bottom side now facing upward, and sleds 3a, 3b, 4a, and 4b are used.

Test pulls 9-12 are performed in the same manner as 1-4, except that sheet #3 218 has its top side facing upward, and sleds 5a, 5b, 6a, and 6b are used.

Test pulls 13-16 are performed in the same manner as 1-4, except that sheet #4 218 has its bottom side facing upward, and sleds 7a, 7b, 8a, and 8b are used.

Test pulls 17-20 are performed in the same manner as 1-4, except that sheet #5 218 has its top side facing upward, and sleds 9a, 9b, 10a, and 10b are used.

Test pulls 21-24 are performed in the same manner as 1-4, except that sheet #6 218 has its bottom side facing upward, and sleds 11a, 11b, 12a, and 12b are used.

Test pulls 25-28 are performed in the same manner as 1-4, except that sheet #7 218 has its top side facing upward, and sleds 13a, 13b, 14a, and 14b are used.

Test pulls 29-32 are performed in the same manner as 1-4, except that sheet #8 218 has its bottom side facing upward, and sleds 15a, 15b, 16a, and 16b are used.

Calculations and Results

The collected force data (grams) is used to calculate Slip Stick COF for each of the 32 test pulls, and subsequently the overall average Slip Stick COF for the sample being tested. In order to calculate Slip Stick COF for each test pull, the following calculations are made. First, the standard deviation is calculated for the force data centered on 131st data point (which is 2.5 seconds after the start of the test) +/- 26 data points (i.e., the 53 data points that cover the range from 2.0 to 3.0 seconds). This standard deviation calculation is repeated for each subsequent data point, and stopped after the 493rd point (about 9.5 sec). The numerical average of these 363 standard deviation values is then divided by the sled weight (31.7 g) and multiplied by 10,000 to generate the Slip Stick COF *10,000 for each test pull. This calculation is repeated for all 32 test pulls. The numerical average of these 32 Slip Stick COF * 10,000 values is the reported value of the Slip Stick COF * 10,000 for the sample. For simplicity, it is referred to as just Slip Stick COF, or more simply as Slip Stick, without units (dimensionless), and is reported to the nearest 1.0.

Outliers and Noise

It is not uncommon, with this described method, to observe about one out of the 32 test pulls to exhibit force data with a harmonic wave of vibrations superimposed upon it. For whatever reason, the pulled sled periodically gets into a relatively high frequency, oscillating 'shaking' mode, which can be seen in graphed force vs. time. The sine wave-like noise was found to have a frequency of about 10 sec-1 and amplitude in the 3-5 grams force range. This adds a bias to the true Slip Stick result for that test; thus, it is appropriate for this test pull be treated as an outlier, the data removed, and replaced with a new test of that same scenario (e.g., CD top face) and sled number (e.g. 3a).

To get an estimate of the overall measurement noise, 'blanks' were run on the test instrument without any touching the load cell (i.e., no sled). The average force from these tests is

zero grams, but the calculated Slip Stick COF was 66. Thus, it is speculated that, for this instrument measurement system, this value represents that absolute lower limit for Slip Stick COF.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

CLAIMS

What is claimed is:

1. A sanitary tissue product comprising a plurality of pulp fibers, wherein the sanitary tissue product exhibits one or more of the following properties:

a. an average TS7 value (dB $V^2$ rms) as measured according to the Emtec Test Method and a Slip Stick Coefficient of Friction (COF*10000) as measured according to the Slip Stick Coefficient of Friction Test Method such that the sanitary tissue product falls below a line having the following equation: $y = 0.0096x + 1.9291$ graphed on a plot of average TS7 value (dB $V^2$ rms) to Slip Stick Coefficient of Friction (COF*10000) where the x-axis is Slip Stick Coefficient of Friction value (COF*10000) and the y-axis is Average TS7 value (dB $V^2$ rms); and

b. an average TS7 value of less than 7.5 dB $V^2$ rms as measured according to the Emtec Test Method and a Compressibility value of greater than 38.0 [mils/(log(g/in$^2$))] as measured according to the Stack Compressibility and Resilient Bulk Test Method.

2. The sanitary tissue product according to Claim 1 wherein the sanitary tissue product exhibits an average TS7 value of less than 9 dB $V^2$ rms as measured according to the Emtec Test Method.

3. The sanitary tissue product according to Claim 1 wherein the Slip Stick Coefficient of Friction is greater than 230 (COF*10000) as measured according to the Slip Stick Coefficient of Friction Test Method.

4. The sanitary tissue product according to Claim 1 wherein the pulp fibers comprise wood pulp fibers.

5. The sanitary tissue product according to Claim 1 wherein the pulp fibers comprise non-wood pulp fibers.

6. The sanitary tissue product according to Claim 1 wherein the sanitary tissue product comprises an embossed fibrous structure ply.

7. The sanitary tissue product according to Claim 1 wherein the sanitary tissue product comprises a 3D patterned fibrous structure ply, preferably wherein the 3D patterned fibrous structure ply comprises a through-air-dried fibrous structure ply, more preferably wherein the through-air-dried fibrous structure ply comprises a creped through-air-dried fibrous structure ply,

even more preferably wherein the creped through-air-dried fibrous structure ply is an uncreped through-air-dried fibrous structure ply.

8. The sanitary tissue product according to Claim 7 wherein the 3D patterned fibrous structure ply comprises a fabric creped fibrous structure ply.

9. The sanitary tissue product according to Claim 7 wherein the 3D patterned fibrous structure ply comprises a belt creped fibrous structure ply.

10. The sanitary tissue product according to Claim 1 wherein the sanitary tissue product comprises a conventional wet-pressed fibrous structure ply.

11. The sanitary tissue product according to Claim 1 wherein the sanitary tissue product is a single-ply sanitary tissue product.

12. The sanitary tissue product according to Claim 1 wherein the sanitary tissue product is a multi-ply sanitary tissue product.

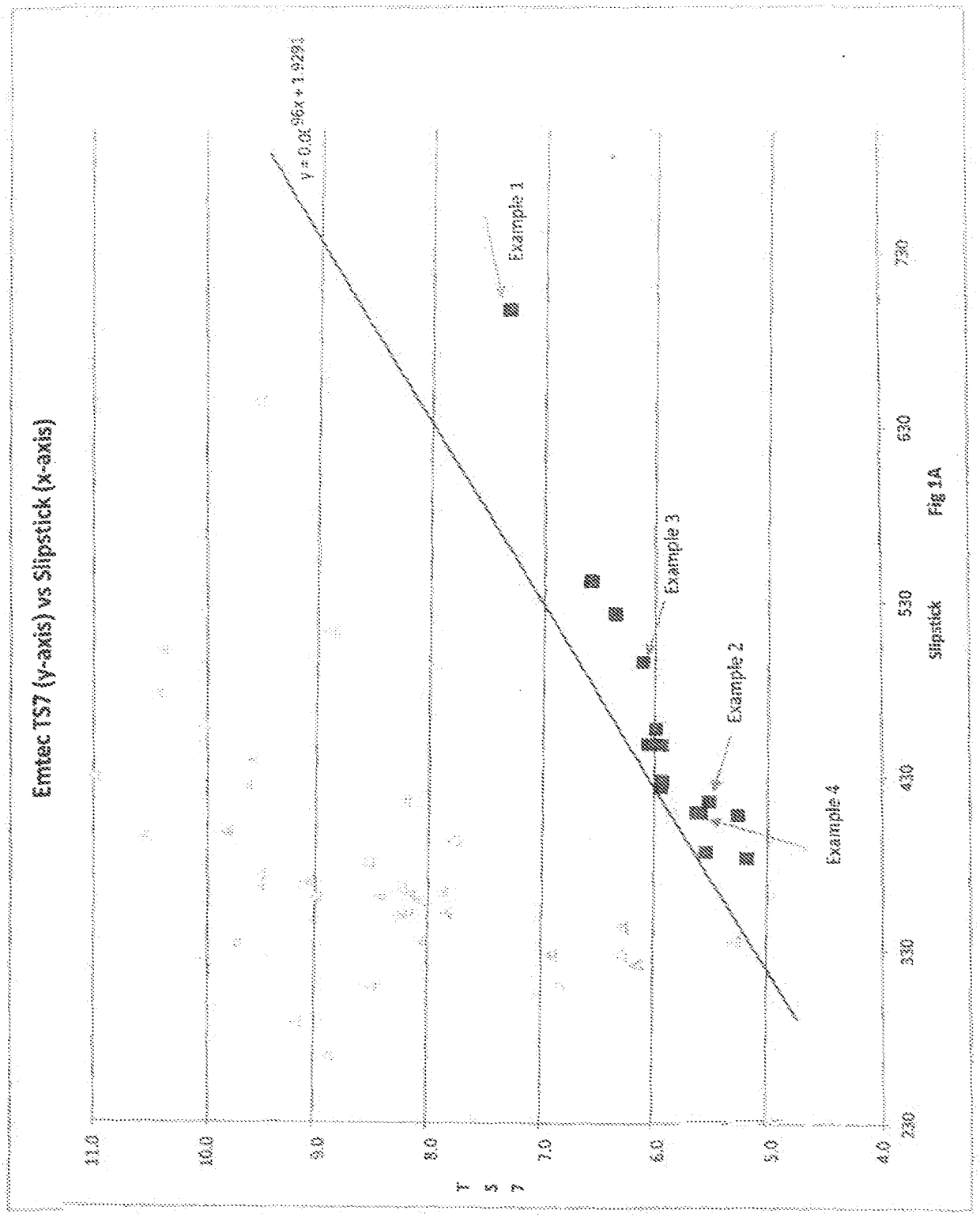

Emtec TS7 (y-axis) vs Slipstick (x-axis)
y = 0.0196x + 1.9293
Example 1
Example 3
Example 2
Example 4
TS7
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
230
330
430
530
630
730
Slipstick
Fig 1A

Fig. 1A

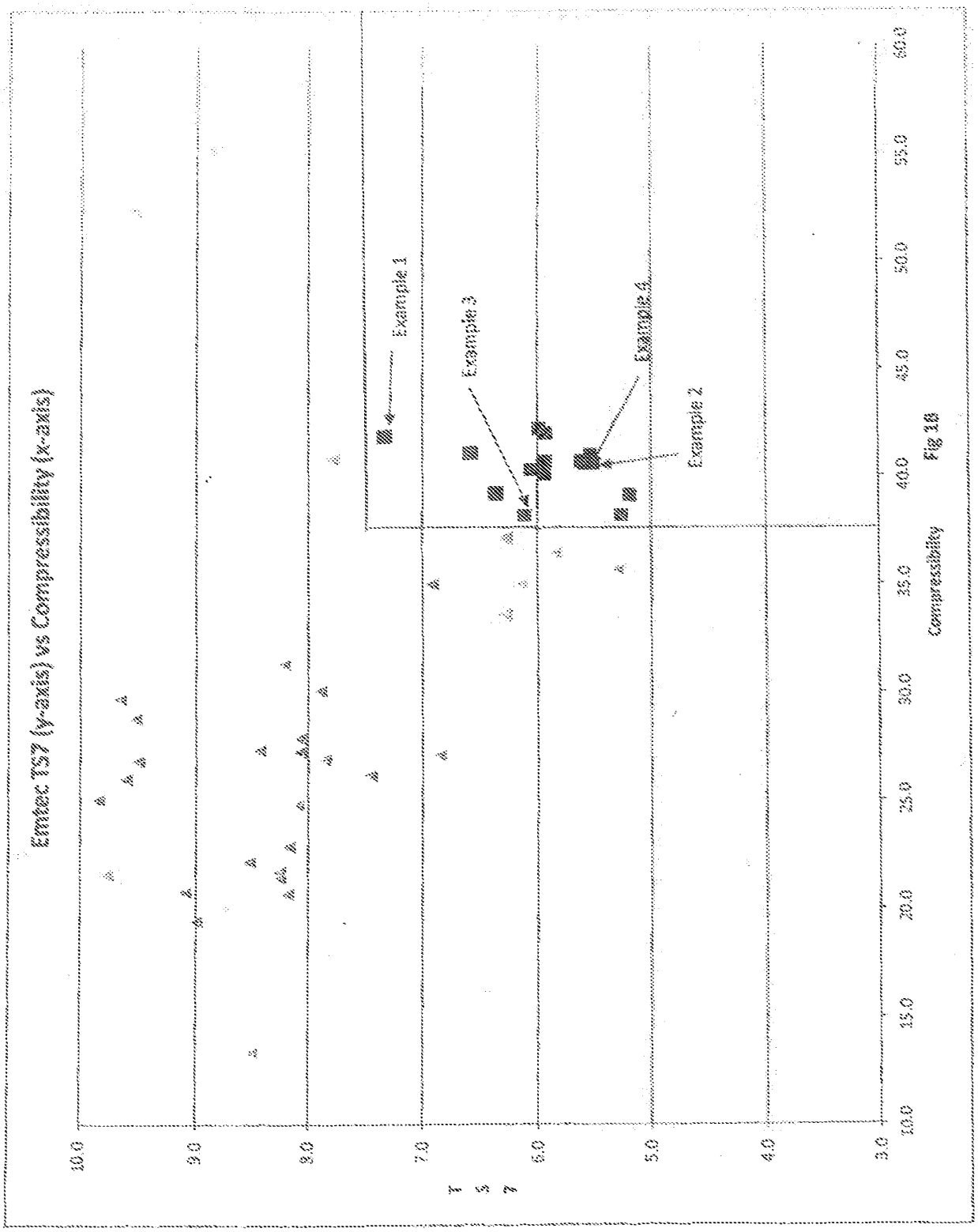

Emtec TS7 (y-axis) vs Compressibility (x-axis)
Example 1
Example 3
Example 4
Example 2
Compressibility
Fig 1B

Fig. 1B

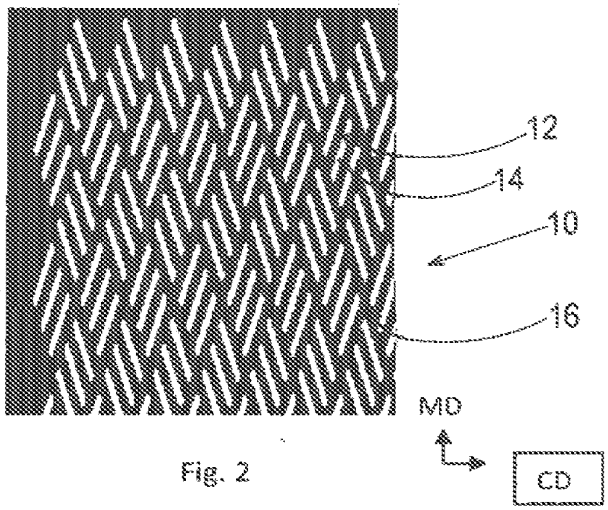



Fig. 2

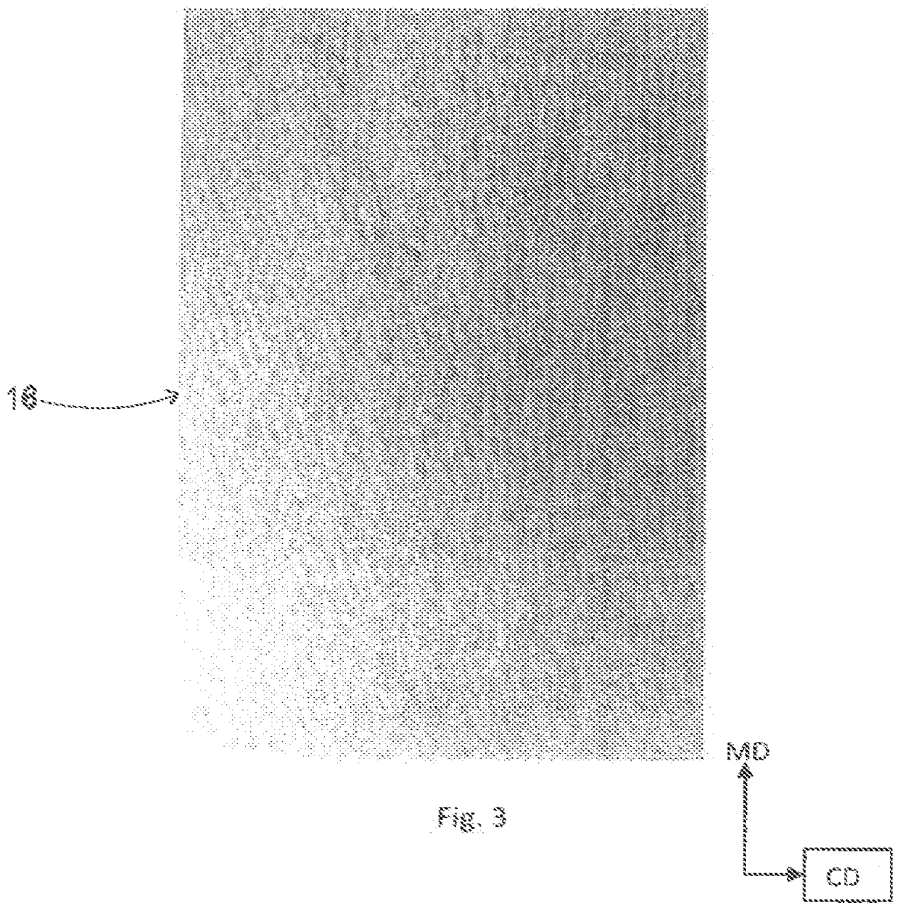



Fig. 3

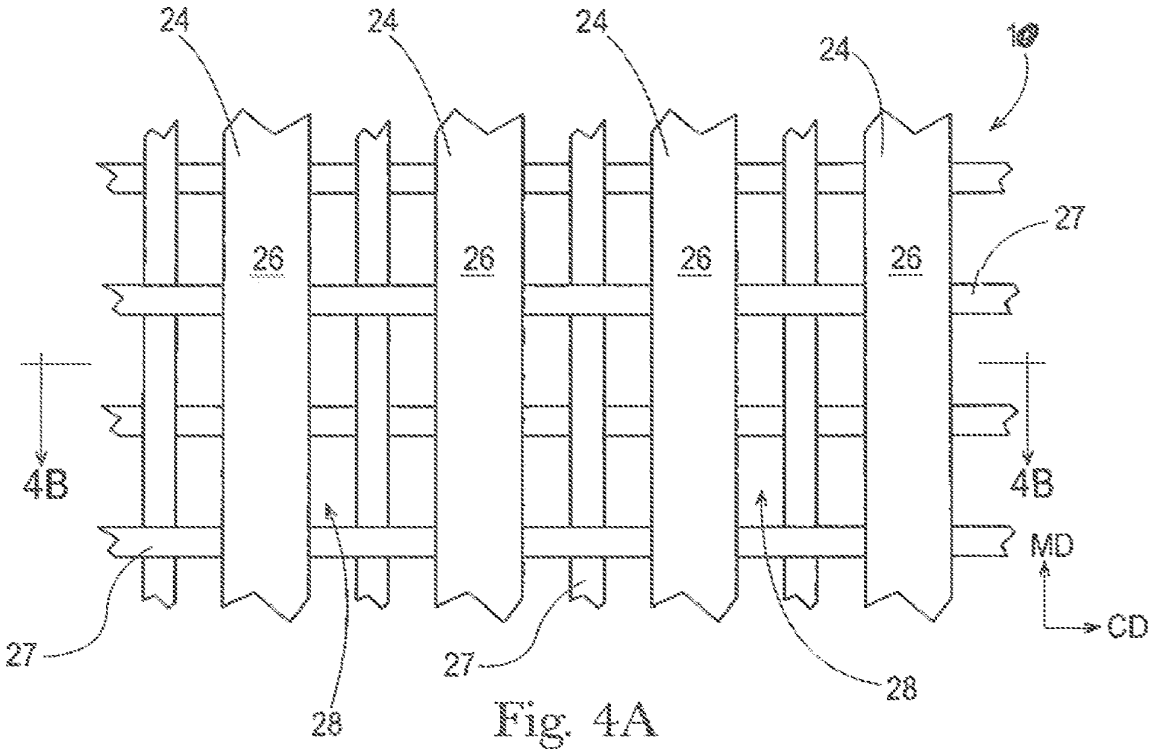

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4B
4B
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CD
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Fig. 4A

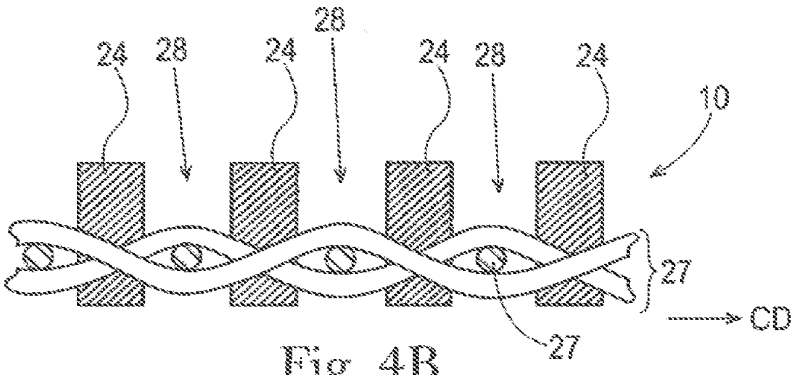

28
24
28
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24
10
27
CD
27

Fig. 4B

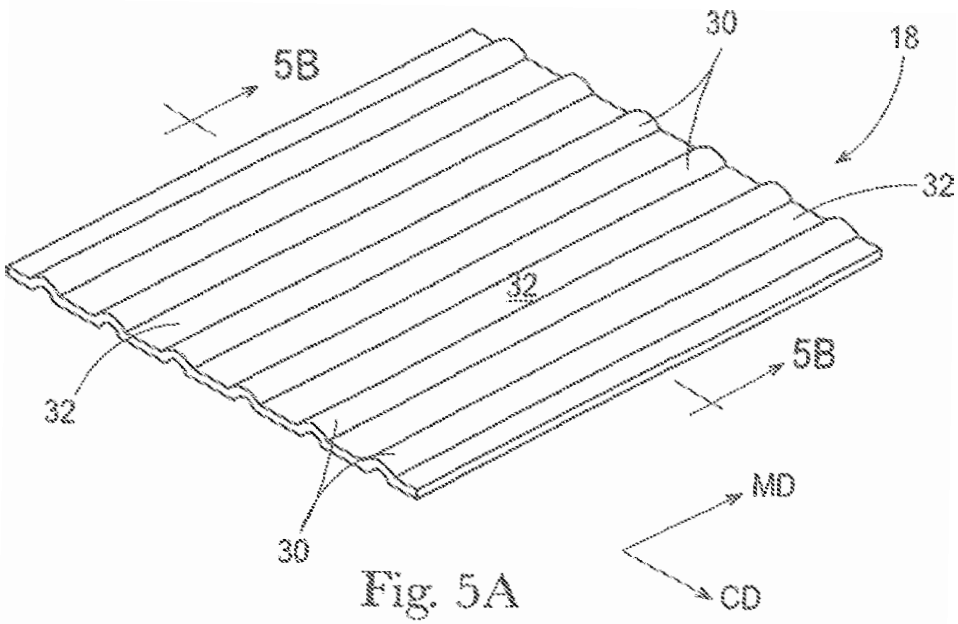



Fig. 5A

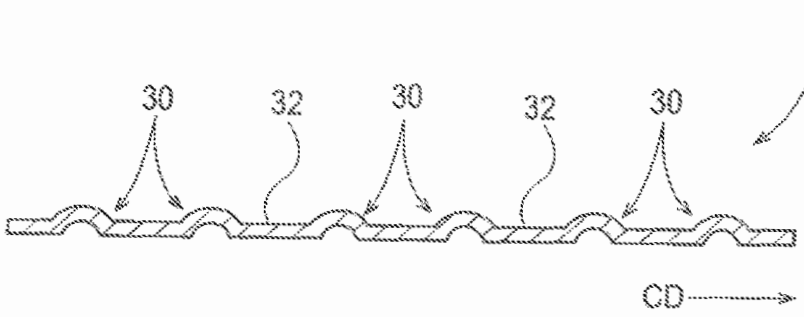



Fig. 5B

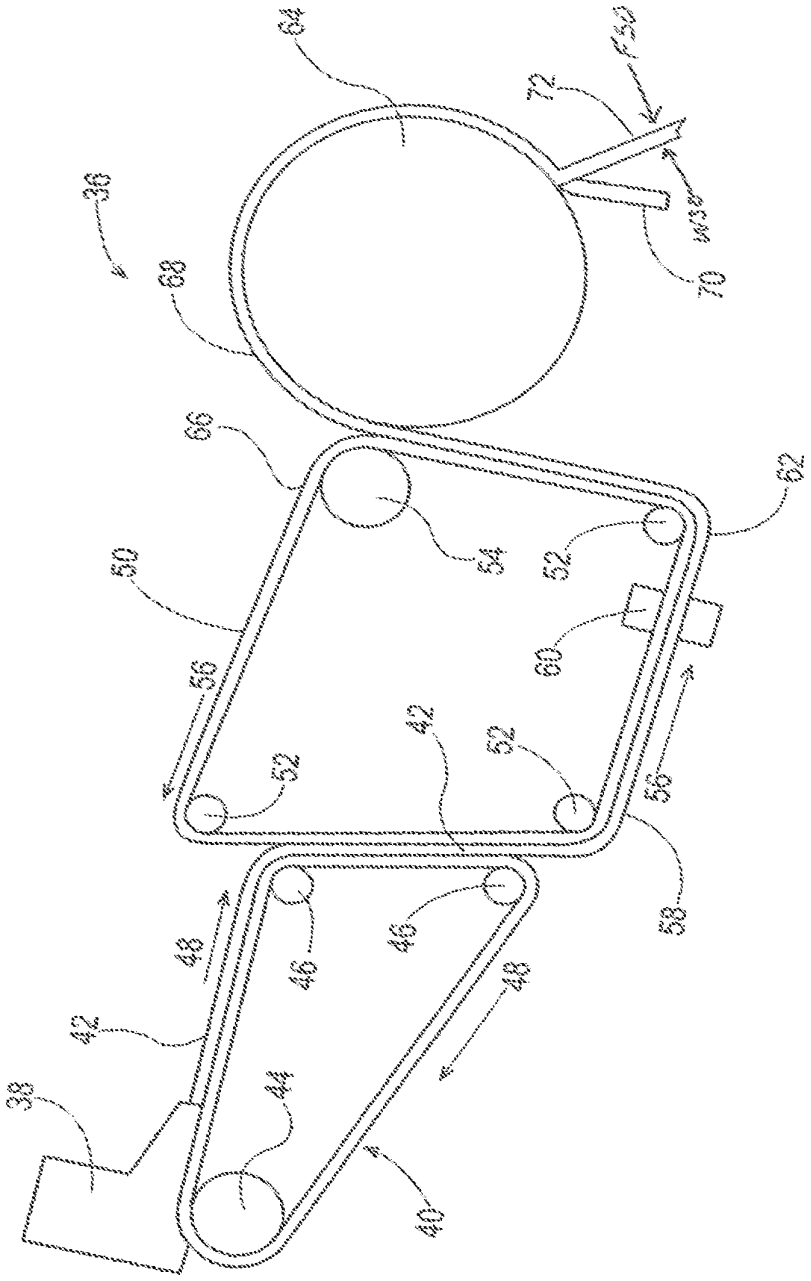

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Fig. 6

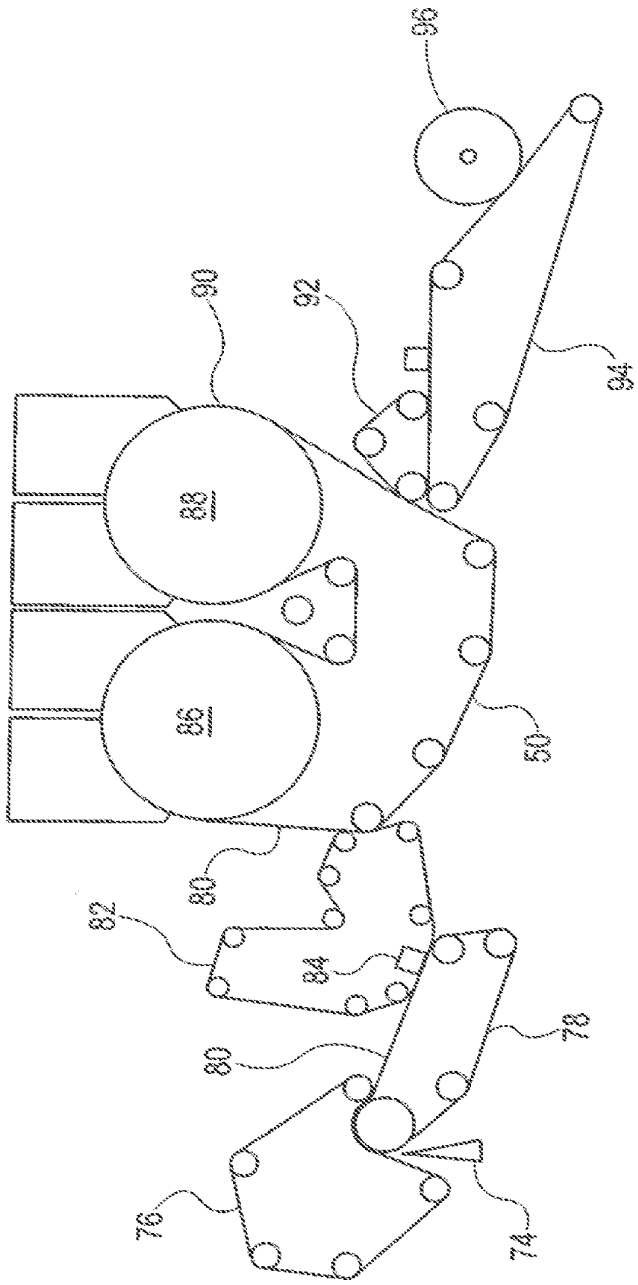



Fig. 7

Kimberly Clark EX1002, p. 1933
PGR2026-00078

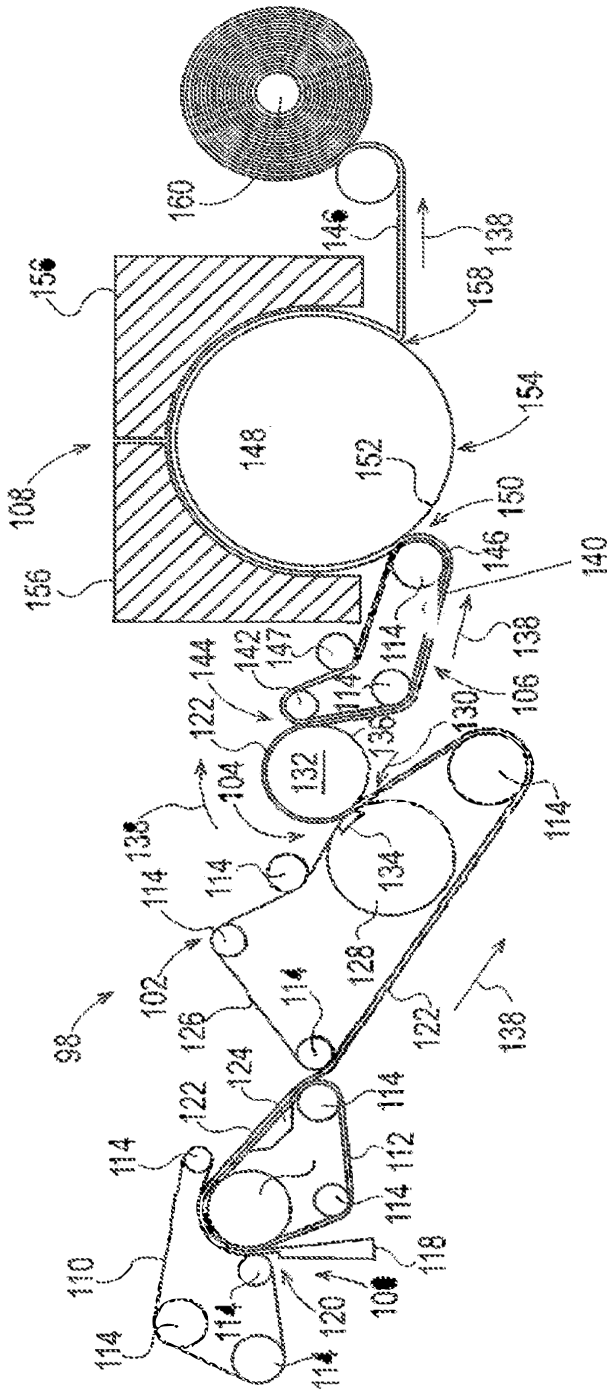



Fig. 8

Kimberly Clark EX1002, p. 1934
PGR2026-00078

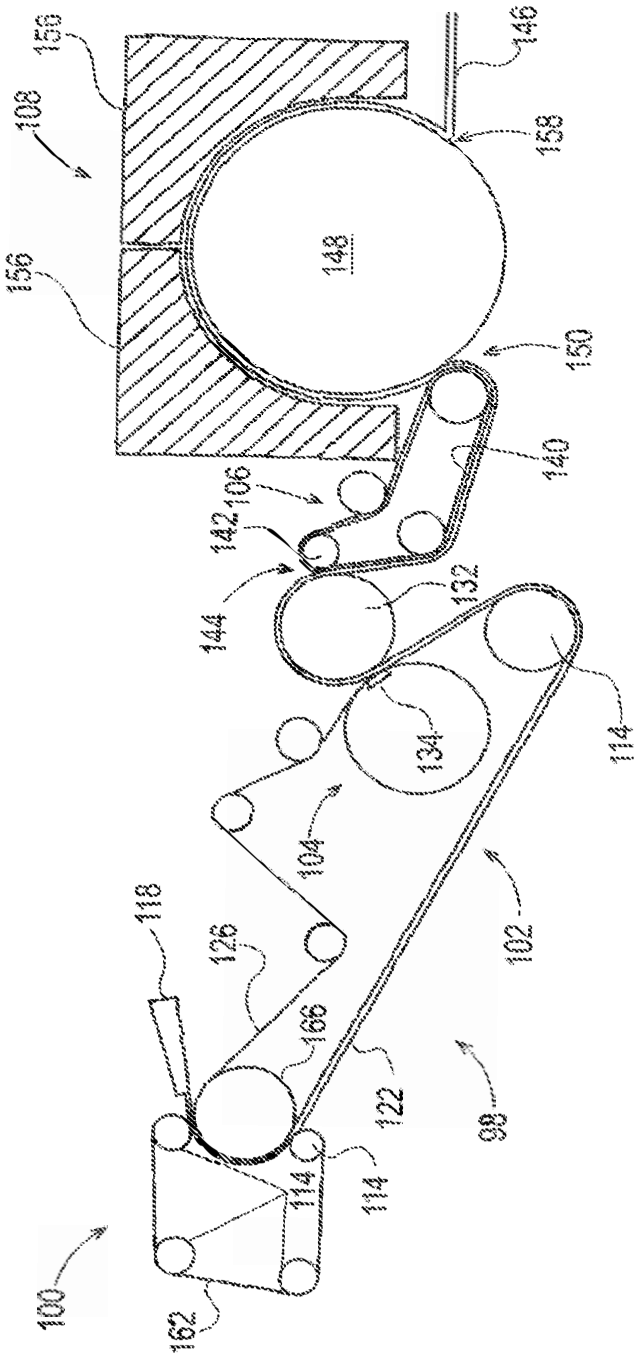



Fig. 9

Kimberly Clark EX1002, p. 1935
PGR2026-00078

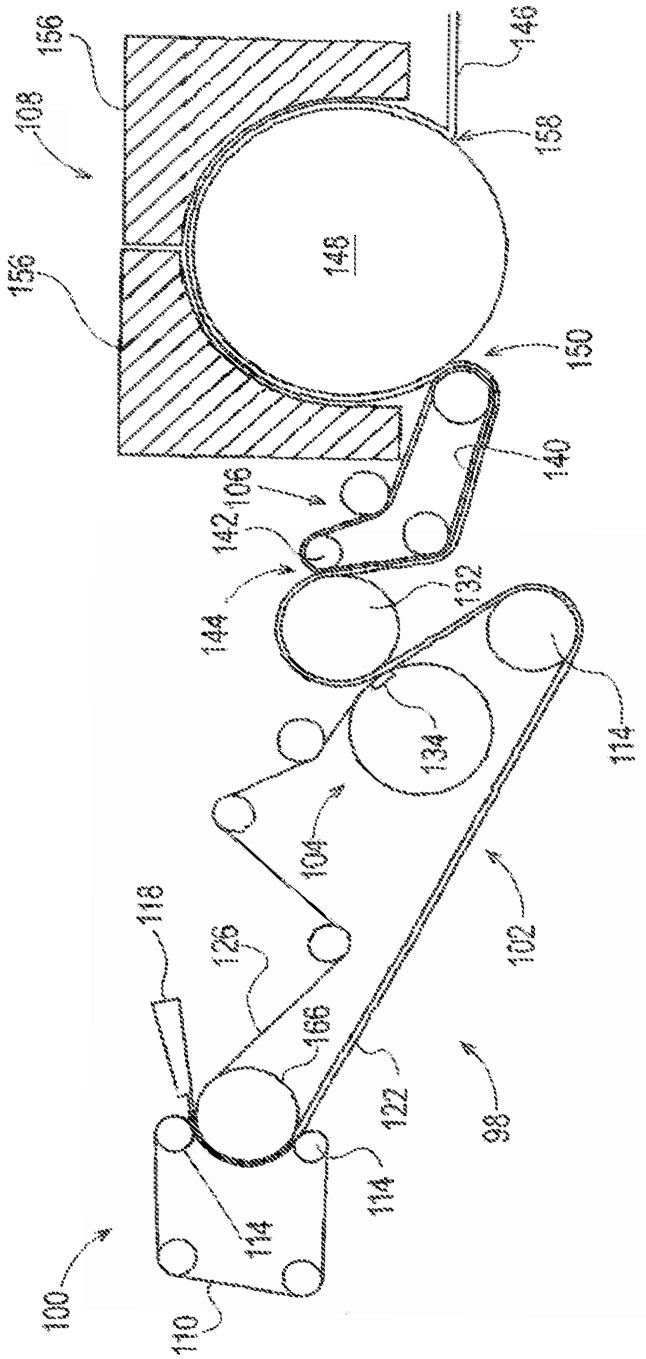



Fig. 10

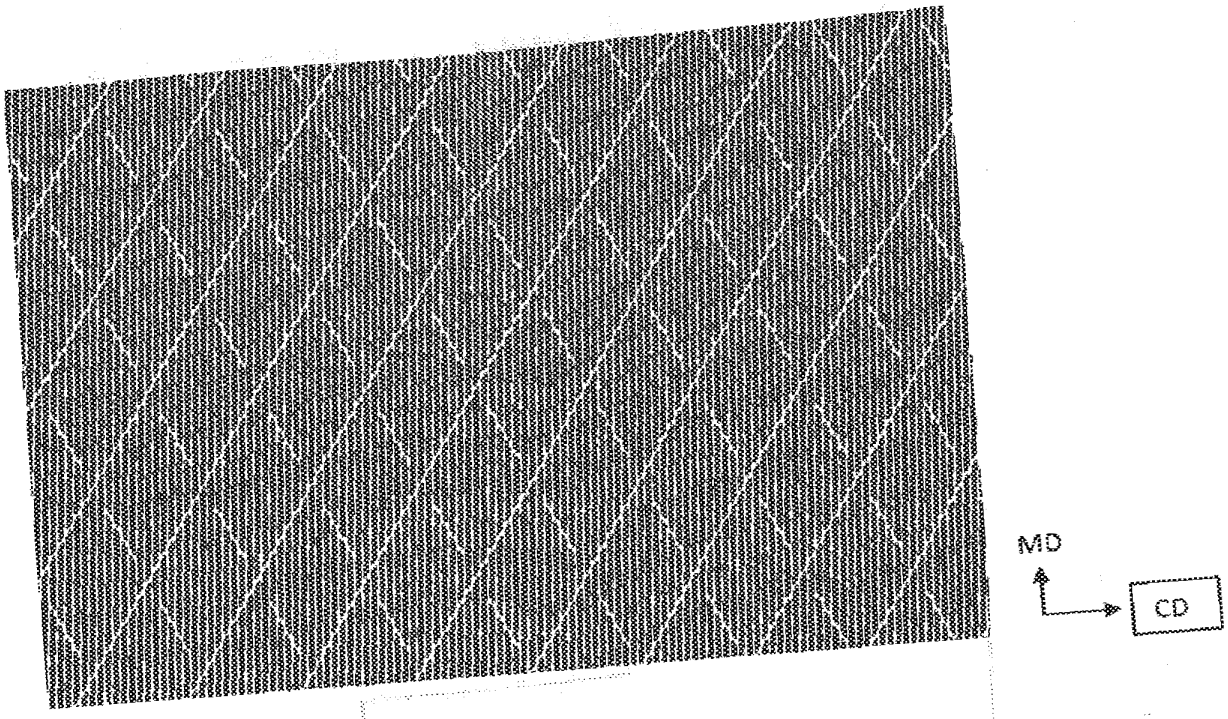



Fig. 11

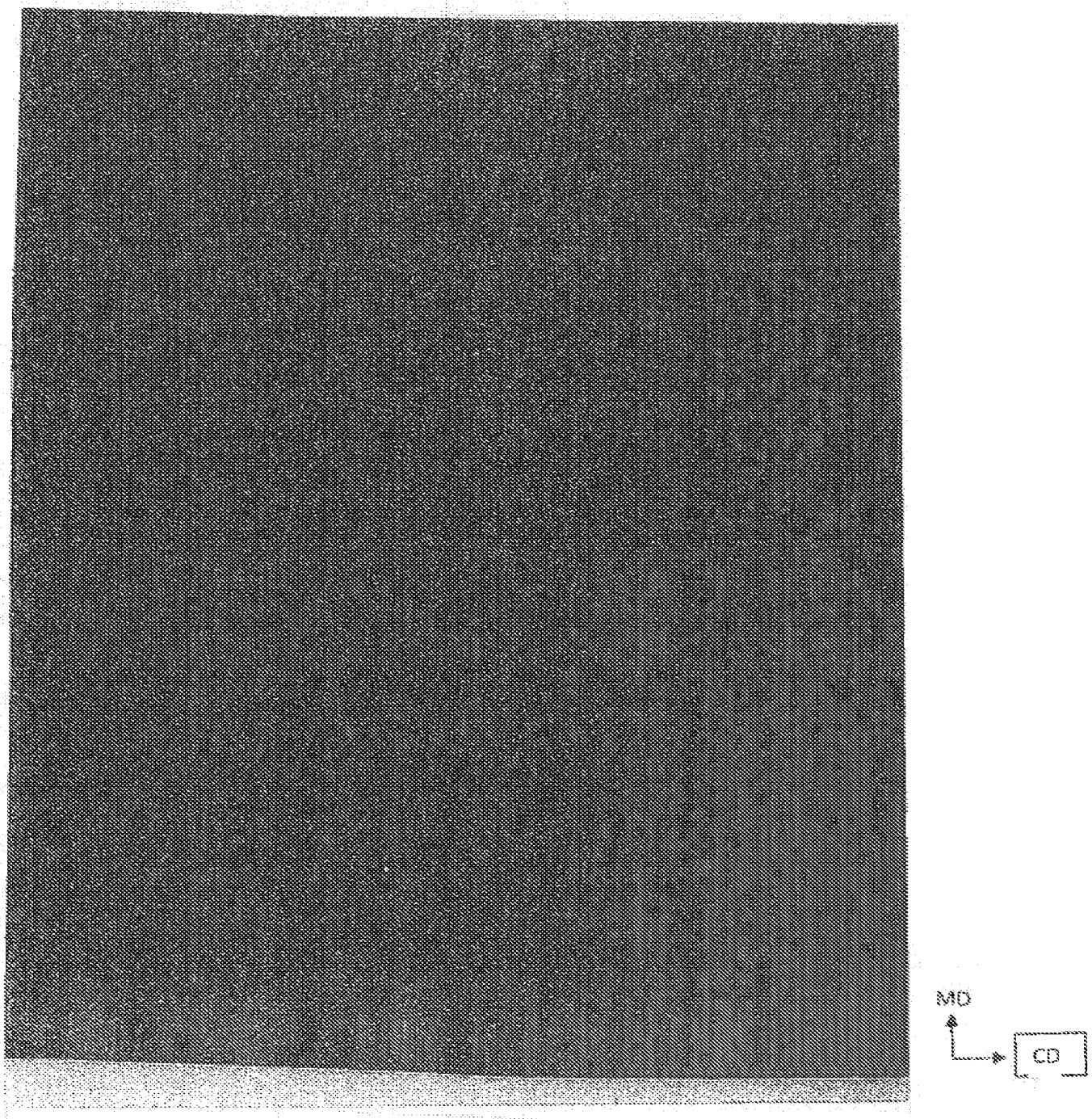



Fig. 12

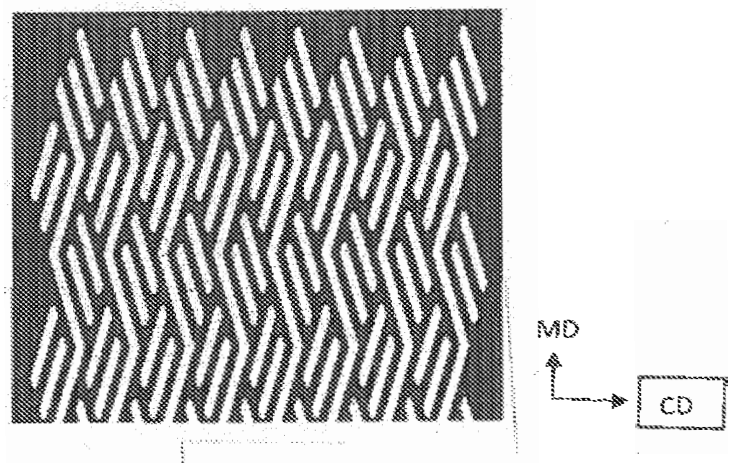



Fig. 13

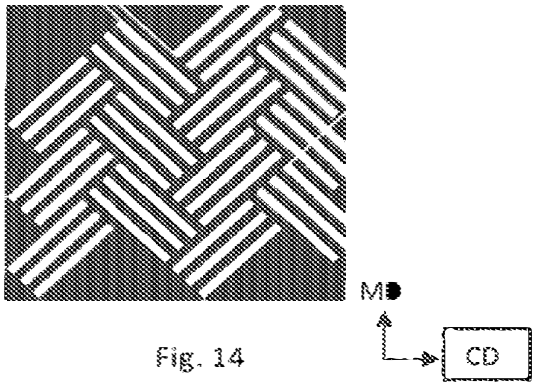



Fig. 14

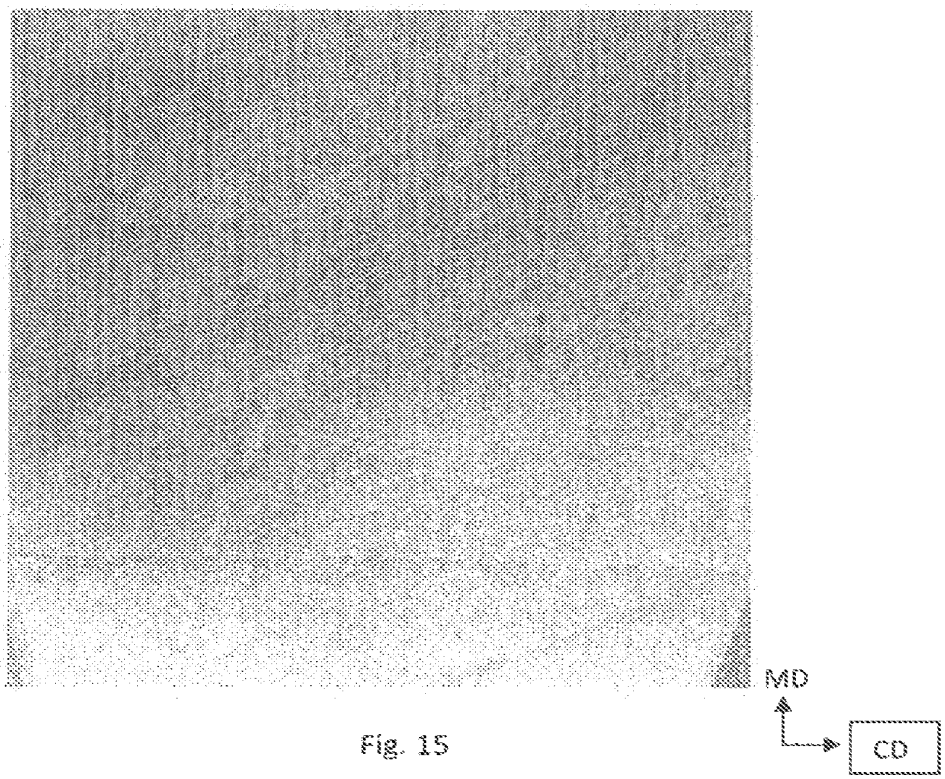



Fig. 15

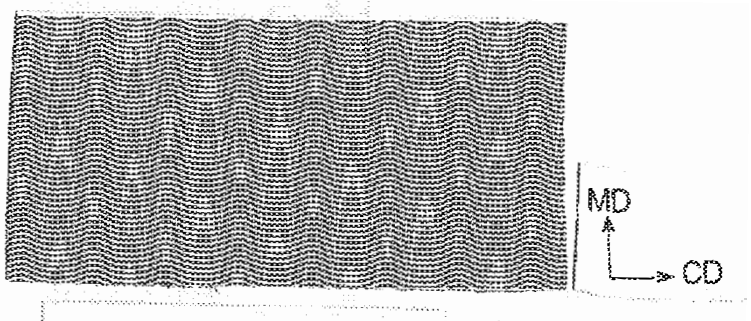



Fig. 16
PRIOR ART

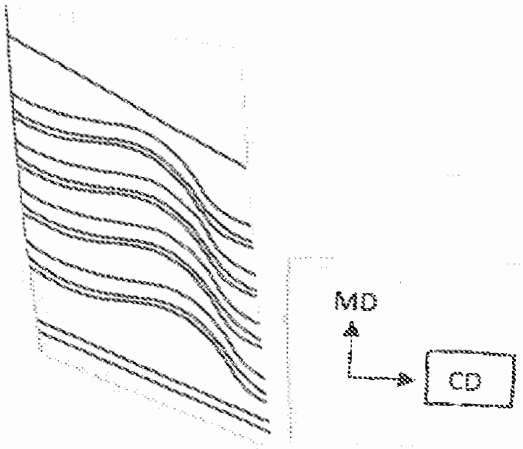



Fig. 17
PRIOR ART

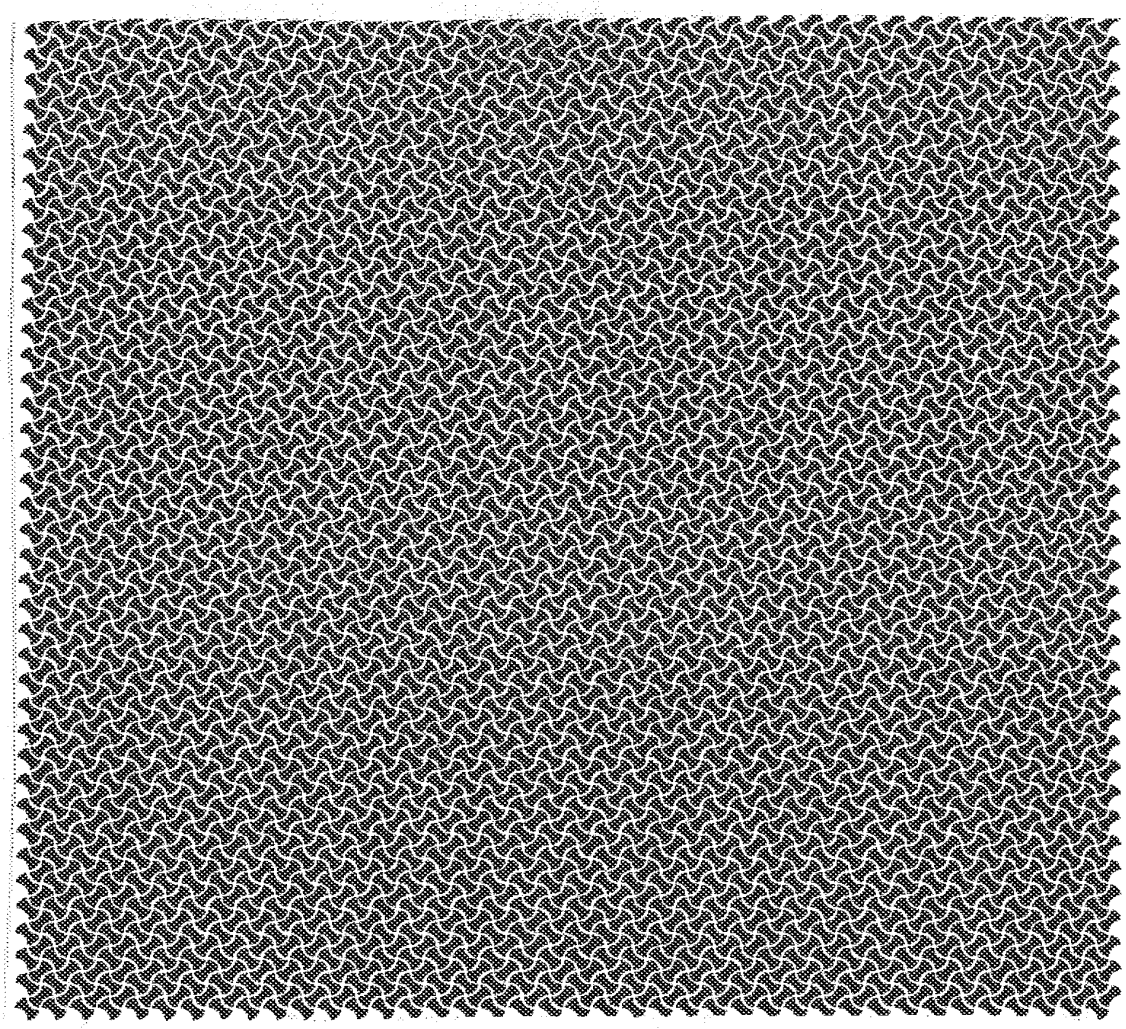


Fig. 18
PRIOR ART

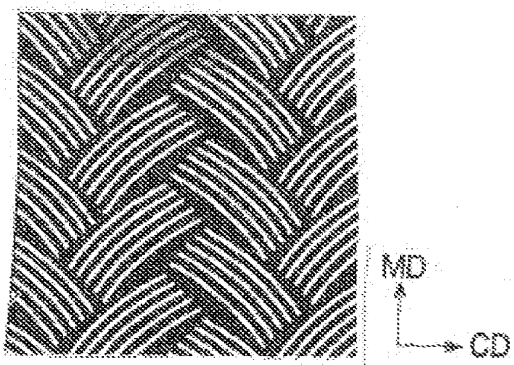



Fig. 19
PRIOR ART

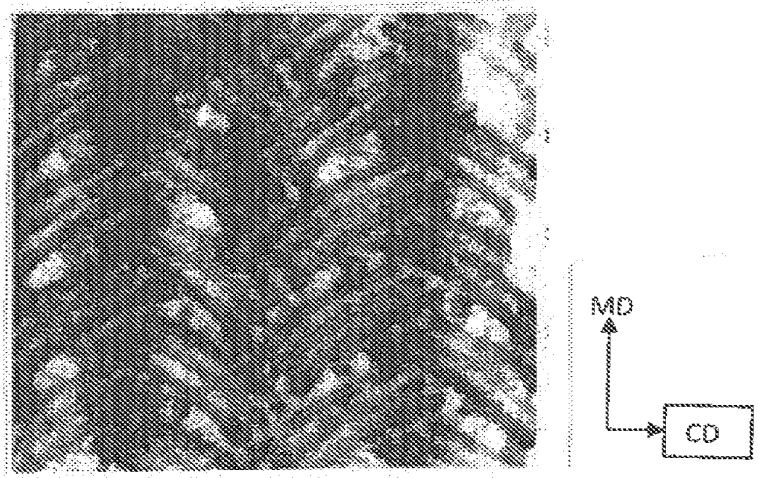



Fig. 20
PRIOR ART

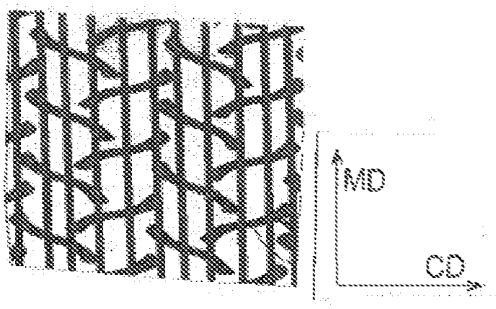



Fig. 21
PRIOR ART

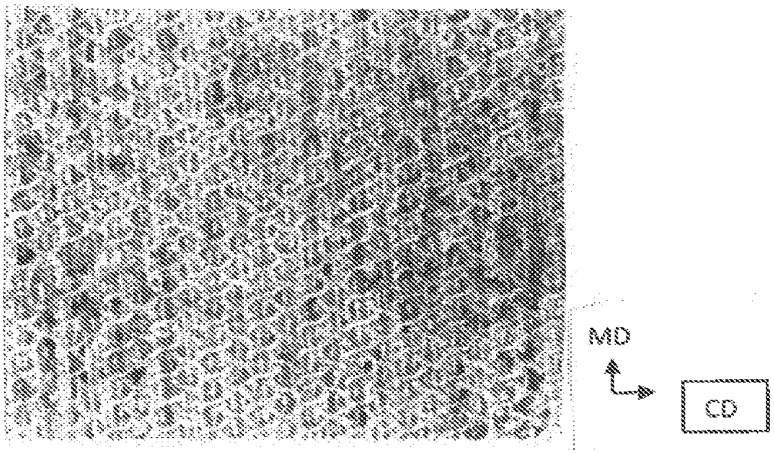



Fig. 22
PRIOR ART

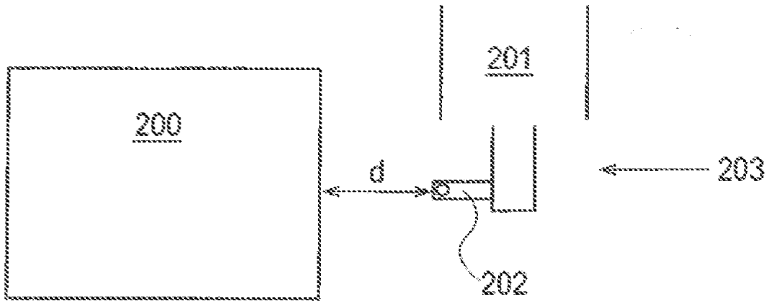



Fig. 23

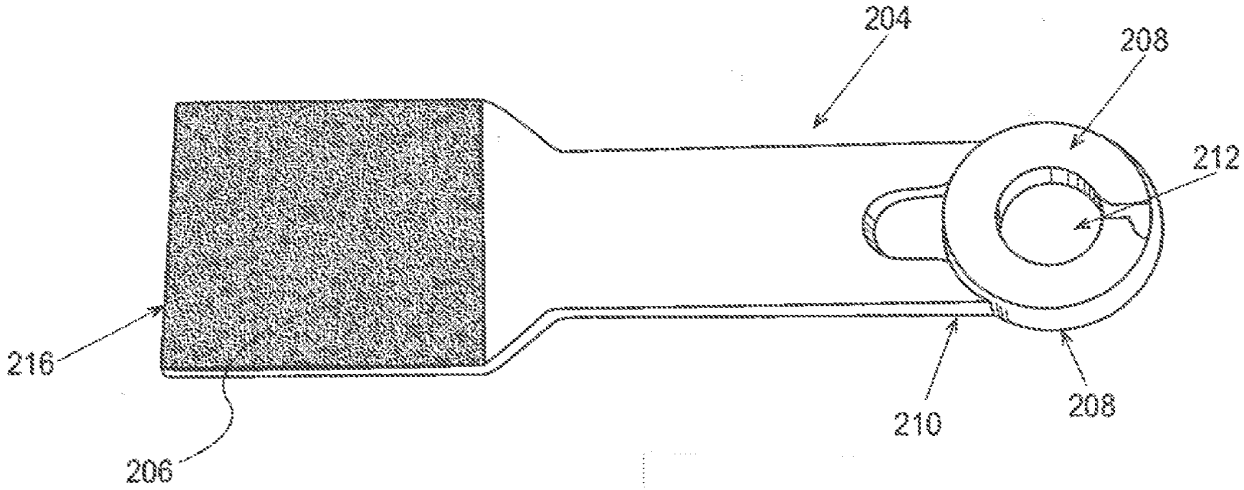



Fig. 24

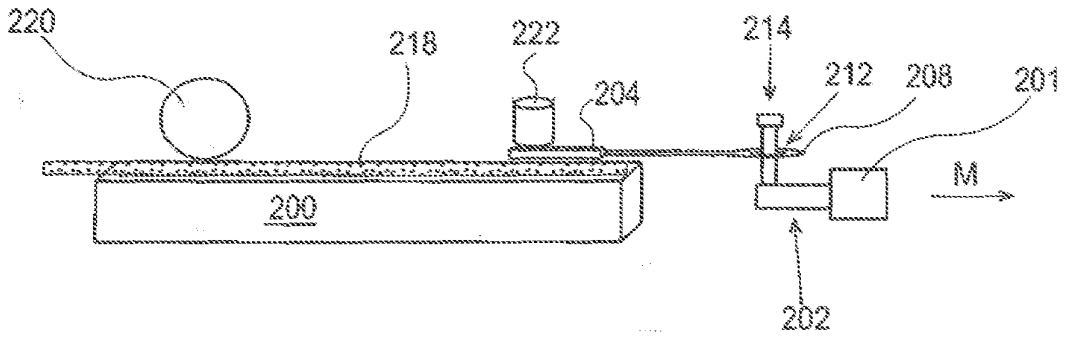



Fig. 25

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/043238

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H27/00 D21H27/30 D21H27/02
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. |
|---|---|---|
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| X | US 2014/096924 A1 (REKOSKE MICHAEL JOHN [US] ET AL) 10 April 2014 (2014-04-10) claims 1, 3, 13 paragraphs [0046] - [0050] | 1-7, 10-12 |
| X | US 2015/176218 A1 (MALADEN RYAN DOMINIC [US] ET AL) 25 June 2015 (2015-06-25) paragraphs [0001] - [0006], [0054], [0055], [0116] paragraphs [0013], [0125], [0036] - [0040] paragraphs [0006] - [0019]; claims 1-20 | 1-12 |

-/--

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

[X] See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 12 October 2016 | 20/10/2016 |

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

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



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PGR2026-00078

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | US 2013/143001 A1 (MANIFOLD JOHN ALLEN [US] ET AL) 6 June 2013 (2013-06-06) paragraphs [0094] - [0108], [0158] paragraph [0160]; claims 1-18 | 1-12 |

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Kimberly Clark EX1002, p. 1947
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2016/043238

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(19) Europäisches Patentamt
European Patent Office
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(11) EP 1 319 749 A1

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(30) Priority: **18.09.2000 JP 2000324756**

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# (54) PROCESSED BOARD-TYPE PRODUCTS MADE OF NON-WOODEN FIBERS

(57) [ Objects ] To provide a typically plate-shaped or sheet-shaped inexpensive web product that is prepared on a large scale and using cheaper raw materials that have not been used, with the web being tenacious and non-toxic when used as construction parts of houses, and capable of being discarded under the ground so as to be readily decomposed by bacteria and enzymes, and further capable of being burnt at lower temperatures preventing generation of toxic substances.

[ Means for Achieving the Objects ] The web is made from a non-woody fibre pulp that is any one of fibres originating from gramineous, palmaceous and polygonaceous plants, or any mmixture of them. The gramineous plants are of a self-reproducing nature and the polygonaceous plants are any buckwheat. The web of this composition is rendered sheet-shaped before hot-pressed or dried to give concrete formwork articles, wallpapers or the coverings for Japanese sliding doors.

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## Description

[ Detailed Description of Invention ]

FIELD OF THE INVENTION

**[0001]** The present invention relates to building materials and papery covering sheets that are produced by papering a composite material whose principal ingredients are nonwoody fibres.

PRIOR ART

**[0002]** Papers have been the most typical examples of plate-shaped or sheet-shaped products made from woody fibres. Among them, Japan papers have been made by collecting the bast fibres of shrubs such as *Broussonetia kajinoki* (viz., "kohzo" in Japanese) and *Edgeworthia papyriferas* (viz., "mitsumata" in Japanese) and adding them a proper amount of binder (viz. a sizing agent). Other papers for use in offices or as the packaging materials are provided inexpensively by mass-production. In this general case, needle-leaf trees and/or broadleaf trees are ground at first into chips and then alkaline-digested to give a pulp. The pulp will be disintegrated in water into constituent fibres, before they are blended with amounts of the sizing agent (i.e., binder) and some additives during the papermaking process. Thinner papers thus produced will be used as wallpapers or as other interior finish materials like *fusuma* (viz., Japanese sliding doors), with thicker and more rigid papers being sometimes pressed together with auxiliary materials or otherwise processed to give certain types of fibre boards or the like.

PROBLEMS TO BE RESOLVED

**[0003]** Japan papers made from the raw materials noted above may be advantageous when used to make buildings, because longer fibres afford them a higher tenacity. However, it is considerably difficult to obtain a large lot of raw fibrous materials for such Japan papers, thus disabling inexpensive mass-production of them and delimiting their utility. In contrast, other modern papers made of wood pulps are adapted to mass production, although an enormous number of woods have to be felled and great quantities of chemical reagents are required. These conditions are undesirable to the earth from environmental and ecological points of view. Further, such modern papers are weaker in mechanical strength as compared with Japan papers, thereby rendering impossible their usage as constructive parts of the concrete depositing formworks.

**[0004]** The present invention was made to resolve the described problems, and its primary object is to provide a nonwoody fibre web that somewhat resembles ordinary papers and is capable of mass-production using such inexpensive botanical materials that have scarcely been used heretofore or have not been used at all. The web provided herein has to be stronger, more tenacious and cheaper so that it may qualify not only as concrete formworks and the like but also as safe and non-hazardous interior finish materials in buildings. When the web is discarded and buried under the ground, it should be decomposed readily in a short time by bacteria and/or enzymes, and even if the web is burnt, it should not generate any toxic substances.

MEANS FOR ACHIVING THE OBJECTS

**[0005]** In order to achieve the object, a nonwoody fibre web may be made by the papermaking process and using a pure pulp of fibres originating from any one of gramineous plants, palmaceous plants and polygonaceous plants, or using a mixed pulp of the fibres originating from any two or more of these plants. The gramineous plants may be of a self-reproducing nature, and the polygonaceous plants may be any buckwheat.

**[0006]** From a second aspect of the invention, the pulp of nonwoody fibres originating from gramineous, palmaceous and/or polygonaceous plants may contain at least 70 % by weight of bamboo fibres.

**[0007]** From a third aspect, the nonwoody fibre web made from such a pulp may be a formwork piece for use in the concrete depositing.

**[0008]** From a fourth aspect, the nonwoody fibre web made from such a pulp may be a wallpaper or the like papery covering sheet.

THE PREFERRED EMBODIMENTS

**[0009]** As summarized above, the nonwoody but botanical fibre web will be composed of any one of or of any mixture of gramineous plant fibres, palmaceous plant fibres and polygonaceous plant fibres. The gramineous plants of a self-regenerating nature include bamboos, ditch reed, Indian corn, wheats, Chinese millet, kaoliang and the like. The palmaceous and polygonaceous plants include palm trees and buckwheats, respectively. Their nonwoody fibres may be isolated from their trunks, stems, barks, skins, leaves, stalks, cores and/or the like. At first, these fibrous materials will be ground into chips or into powdery particles so as to prepare a powdery pulp and/or a sheet pulp, by the papermaking or web-making method. Thus, three kinds of powdery and/or sheet pulps are prepared corresponding to the three raw materials so that any one of them is solely used or any mixture of them of a desired mixing ratio is used. These pulps will then be thrown into a dissolving water tank, without or with any natural sizing agent such as a paste, a starch or a seaweed size being added to the pulps. Ratio of the added sizing agent is selected within a range of from 0 % to about 5 % by weight, taking into account the final usage of product, and these ingredients will thus be stirred within the tank to give a pulp slurry. In some cases wherein the inter-



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mediate pulp products need not be stored, they may be directly fed into the slurry tank, immediately after extracted from the botanical raw materials. If the powdery pulp is composed of fine fibrous particles of a size passing a 150 to 200 mesh-sieve, about 20 % by weight of additional pulp from lumbers delivered for a forest by the thinning thereof may be added to the slurry. However, final products in this case will inevitably be inferior to other types of products, with respect to mechanical strength.

**[0010]** A still wet layer of such a powdery or sheet pulp from the nonwoody fibre slurry will then be pressed to form a plate-like product. The wet layer or web to be pressed may preferably contain about 70 % by weight or more of a supplementary pulp of longer fibres, if the concrete formwork pieces of a sufficient strength have to be produced. A bamboo pulp may be most recommendable as such a supplementary pulp, and the pressure of about 1 to 40 $kg/cm^2$ will be applied to such a web may be.

**[0011]** In a case wherein a wallpaper or any other interior finish sheet such as the paper forming a Japanese sliding door *"fusuma"*, a sheet-like article of a predetermined size and shape will be produced. A wet intermediate sheet may be subjected merely to the rolling treatment thereof, if this article is to be finally about 0.2 to 1.0 *mm* thick. A dense slurry of non-woody pulp may be applied to a core plate and dried thereon to produce the interior finish product in an alternative manner.

**[0012]** Generally, each species included in the bamboo subfamily of gramineous plants is composed much longer fibres than other species belonging to the other subfamilies. Bamboos thus useful to enhance strength of the paper products are less likely to become moldy and are of a highly antibacterial nature. More than 30% (more preferably more than 70 %) by weight of bamboo fibres contained in the interior finish sheets will be effective to keep rooms remarkably hygienic.

**[0013]** If a moderately lower pressure is applied to the sheet-like web that is being manufactured in accordance with the method proposed herein, it will serve to automatically control the relative humidity of a room. In the event that the room air would tend to become excessively wet, the web will absorb a noticeable amount of moisture out of the ambient air to prevent the relative humidity from undesirably rising within the room. In the contrary event, the web will desorb an amount of moisture and return it into the room to inhibit it from getting excessively dried. The web used as the interior finish sheets is composed only of natural materials free from any amount of formaldehyde or any other toxic substances, so that respiratory organs of the residents in such a room will be protected from suffering from the so-called sick-house syndrome. The web's ability of automatically controlling the room humidity in a case of its internal texture similar to that of the raw pulp will be about twice as high as that in another case of being finished as a rigid paper.

**[0014]** The gramineous, palmaceous and polygonaceous nonwooden fibres forming the concrete formwork pieces or the wall pulp or "*fusuma*" pulp as in the Examples given below are all much longer than the conventional wooden fibres. Therefore, the web of the invention has a tensile strength that is about twice to thrice as high as that of the ordinary papers. Thanks to this feature, the web can be used to form a variety of commercial products that have been made of certain inorganic materials or certain petroleum materials other than papers.

**[0015]** Further, each web of the invention consists only of natural materials, so that any waste of the web used and worn can be burnt at lower temperatures, without any fear of damaging a waste-burning oven and free from the problem of emitting dioxines. If buried under the ground, it will be biologically decomposed by underground bacteria and/or enzymes so as to serve thereafter as a kind of organic fertilizer or soil conditioner, thus contributing to environmental hygiene.

EXAMPLES

**[0016]** Now some examples will be described making reference to the embodiments as summarized above.

# First Example

**[0017]** A concrete formwork piece was prepared by at first shredding bamboo's trunks, stems, barks, cores and the like to prepare a powder or sheet-shaped pulp. 5 kiloliters of water was added to 3 kilograms of this pulp within a dissolving tank to form a mixture, which was then stirred to provide a fibre slurry. 5 % (with respect to weight of the pulp) of a seaweed size was added to and intermixed well with the slurry, before sieving it through a screening net to provide a wet web. Subsequently, this web was pressed at a pressure of 5 $kg/cm^2$ to give the formwork piece as the first example, with the piece showing a density of 0.1 $kg/m^2$.

# Second Example

**[0018]** A wallpaper or a covering paper for the Japanese sliding door (viz., *fusuma*) was produced as a sheet-shaped product according to the second example. Waste of bamboo stems was processed to give 2.1 *Kg* of a first pulp, and coconut skins were processed to give 0.9 *Kg* of a second pulp. A slurry was prepared by mixing the pulps, with 5 kiloliters of water being added thereto within a dissolving tank. Subsequently, 1 % by weight (with respect to the pulp) of a gelatin as the sizing agent was added to the resultant slurry, before making a wet web as in the usual papermaking process. A hot roller was then used to press and dry the wet web to give a finished sheet having a thickness of 0.5 *mm* and density of 0.1 $kg/m^2$. This sheet-shaped product proved satisfactory in all properties inclusive of strength, protection from getting moldy, antibacterial nature, self-



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control of moisture, no emission of toxic gases, and so on. Sheet's density (reflecting its thickness) and the rolling pressure may be adjusted to optimize its feeling of touch and its appearance, so as to match its usage as any articles other than the wallpaper or *fusuma* paper, for example its usage as curtains or the like coverings for house rooms or for automobile cabins.

**[0019]** In the second example, bamboo fibre as one of the typical gramineous fibres was used together with the coconut skin fibres. However, ditch reed fibre as a further gramineous plant may solely or in addition to buckwheat fibre as one of polygonaceous plants be added to them. Any other natural size originating from seaweed may be used in place of gelatin, possibly changing its feeling of touch and its quality such as self-control of moisture, but without adversely affecting its high strength, wherein the rolling pressure is modified to optimize its overall property.

# Third Example

**[0020]** This example does also relate to a wallpaper pulp or a covering paper for pulp the Japanese sliding door (viz., *fusuma*). However, they were not finished to be any solid sheet but was provided as dense paste-like slurries such that they could be spread over each rigid planer core before dried and solidified to directly form a hard covering thereon. Density of such a paste-like pulp may be adjusted depending upon the covering's desired thickness of for instance about 0.5 *mm* and taking into account the application thickness of said paste. Advantages similar to those which the second example provides are also afforded, but with the capability of self-controlling humidity being much more improved by virtue of such a non-pressed state of the paste type pulp. Blend ratio of the constituent fibres may be designed similarly to that described in the second example.

**[0021]** Some representative embodiments and examples are described above, although they may be modified in varied manners insofar as any similar elements or components are employed to achieve the object of invention and to afford the same effects and advantages as summarized below.

ADVANTAGES AFFORDED HEREIN

**[0022]** The nonwoody fibre web typically sheet- or plate shaped and made of a pulp that is composed of any one of fibres, or any mixture thereof, originating from gramineous, palmaceous and polygonaceous plants. The gramineous plants are of a self-reproducing nature and the polygonaceous plants are any buckwheat, and all kinds of these plants are so cheap that they have not been utilized but discarded wastefully. Major of the fibres of such a plant are so long that the product provided herein is of a higher tensile strength and a higher tenacity.

**[0023]** The papers made from such nonwoody fibres are capable of varying their moisture content depending upon relative humidity of ambient air, in such a manner that said humidity will automatically be kept in a moderate range. The natural fibres are not likely to generate any toxic gases, and the fibres of bamboos belonging to the gramineous family are of antibacterial and mold-killing properties so that respiratory organs are protected well from the "*sick-house*" syndrome.

**[0024]** When the web products are discarded after use, they can not only be burnt at such low temperatures as protecting the oven or furnace from damage, be damaged, but also be buried under the ground to be effectively decomposed by bacteria and/or enzymes so as to serve as a kind of fertilizer and/or soil conditioner. Therefore, many of conventional inorganic raw materials and many petroleum materials can now be replaced advantageously with the web product of the invention to manufacture a variety of articles.

**Claims**

1. A nonwoody fibre web made of a pulp that is composed of any one of fibres, or.any mixture thereof, originating from gramineous plants, palmaceous plants and polygonaceous plants, wherein the gramineous plants are of a self-reproducing nature and the polygonaceous plants are any buckwheat.

2. A nonwoody fibre web as defined in claim 1, wherein the gramineous plants are any bamboo whose fibre is contained at 70 % or more by weight of the pulp.

3. A nonwoody fibre web as defined in claim 1, wherein the web is a formwork piece for use in the concrete depositing.

4. A nonwoody fibre web as defined in claim 1, wherein the web is a wallpaper or the like papery covering sheet.



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# INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/08113

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

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] D21J1/16, D21H11/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001
Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001

Electronic data base consulted during the international search (name of data base and, where practicable, 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. |
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| X<br>Y | JP 8-60571 A (Kanae KUZE),<br>05 March, 1996 (05.03.96),<br>Claims (Family: none) | 1<br>3,4 |
| X<br>Y | JP 10-102392 A (Oji Paper Co., Ltd.),<br>21 April, 1998 (21.04.98),<br>Claims (Family: none) | 1,2<br>3,4 |
| X<br>Y | JP 11-140799 A (Akio ONDA),<br>25 May, 1999 (25.05.99),<br>Claims<br>& WO 99/24666 A1 | 1<br>3,4 |
| X<br>Y | JP 2000-51043 A (Tokan Kogyo Co., Ltd.),<br>22 February, 2000 (22.02.00),<br>Claims (Family: none) | 1,2<br>3,4 |

☒ 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 document but published on or after the international filing date
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"&" document member of the same patent family

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02 November, 2001 (02.11.01)

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**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP01/08113

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | JP 2-48903 A (Kabushiki Kaisha Kinugawa Tekkosho), 19 February, 1990 (19.02.90), Claims (Family: none) | 3 |
| P | JP 2001-55685 A (Shin Seiwa K.K.), 27 February, 2001 (27.02.01), Full text | 1 |
| P | JP 2000-290889 A (Art Nap K.K.), 17 October, 2000 (17.10.00), Full text | 1,2 |
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)



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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | | |
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| Docket No. | : | 16255M3 |
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| Customer No. | : | 27752 |
| Title | : | Soft Sanitary Tissue Products Comprising Non-wood Fibers |

# INFORMATION DISCLOSURE STATEMENT

Pursuant to 37 C.F.R. §§ 1.56, 1.97 and 1.98, it is respectfully requested that the document(s) cited in this submission be carefully considered by the Examiner and made of record in this case. As provided in §1.97(g), no representation is made or intended that a thorough art search was made. As provided in 37 C.F.R. §1.97(h), this Information Disclosure Statement does not constitute an admission of any kind, and specifically is not an admission that the document(s) cited in this submission is (are), or is (are) considered to be, material to the patentability of the above-identified patent application, as defined in 37 C.F.R. §1.56(b).

This Information Disclosure Statement is being submitted under 37 C.F.R. §1.97(b)(3). An Office Action on the merits in the present application has not yet been received. Therefore, no fee is believed to be due. However, in the event that this paper is crossing in the mail with a first Office Action on the merits, authorization is hereby given to charge the required fee pursuant to 37 C.F.R. §1.97(c) and 37 C.F.R. §1.17(p) to Deposit Account No. 16-2480 in the name of The Procter & Gamble Company.

Additional Items to be Noted by the Examiner

In accordance with 37 C.F.R. §1.98(a)(2), one or more foreign patent documents and/or non-patent literature is provided.

The International Search Report and Written Opinion from the PCT/EPO is listed herein and a copy is provided.

Respectfully submitted,

THE PROCTER & GAMBLE COMPANY

/RLA/
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【出願日】

(57)【要約】

【目的】 森林浴、消臭、空気浄化等の効果を発揮することができ、また沪過紙や防音、電磁波軽減用壁紙等の多方面に使用することができる。

【構成】 乾燥した笹及び／又は竹をカッター等により５～１●ｍｍに切断し、切断片を形成する。適当量の切断片を水を入れた耐熱性容器に入れ、これに切断片の投入重量に対して２●重量％の苛性ソーダを入れて約３～６時間煮沸する。笹・竹中のリグニンが溶出されてセルロースが分解し易くなったら、このパルプを水で洗浄してアルカリ分を除去した後、解繊し乾燥することにより笹・竹乾燥繊維を生成する。水１●●に対して笹・竹乾燥繊維２●、糊空木の粘液１、粒度が１●●～３●●メッシュの笹・竹粉末１～５及び珪藻土粉末１～５を重量比の割合で混合し、十分に撹拌して繊維懸濁液を生成する。この繊維懸濁液を漉き網で漉き、脱水、乾燥して笹・竹紙を製造する。

Kimberly Clark EX1002, p. 1957
PGR2026-00078