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(54) Method for making tissue product containing carboxylated cellulosic fibers

(57) A tissue product having two or more layers, with at least one layer including carboxylated cellulosic fibers. Methods for making the tissue product.

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Description

[0001] The present invention relates to a tissue product containing carboxylated cellulosic fibers and methods for making the tissue product.

[0002] Tissue paper or sheets, such as facial and toilet tissues and paper toweling, are common commercially available consumer products. Important physical attributes of these products include strength, absorbency, and softness, among others.

[0003] An ideal tissue product has high wet and dry strength. Strength is the ability of the tissue product, as well as tissue product webs, to maintain physical integrity and to resist tearing, bursting, and shredding under use conditions, including when wet. An ideal tissue product, more specifically paper toweling, also has high liquid absorbency. Absorbency is the measure of the ability of the tissue product and tissue webs to absorb quantities to liquids, including aqueous solutions and dispersions. Ideally, a tissue product will have high absorbency with respect to the total quantity of liquid absorbed given a mass of the tissue product as well as a fast rate that the tissue product absorbs liquid.

[0004] Tissue products are paper sheets made by a process that includes the steps of forming an aqueous papermaking furnish, depositing the furnish on a forming wire, and removing the water from the furnish to provide the sheet. The aqueous papermaking furnish is an aqueous slurry of papermaking fibers and chemicals. Although wood pulp is the major constituent of papermaking fibers, other fibers can be included. Wood pulps include chemical pulps, such as kraft and sulfite pulps; and mechanical pulps, such as ground wood, thermomechanical pulps, and chemi-thermomechanical pulps. Although blends of pulp fibers are often used in the furnish for making tissue products, strengthening agents are commonly included to increase tissue product wet and dry strength. In addition to wood pulp, the furnish includes chemicals, for example, strengthening agents and debonding agents, to enhance the strength and softness of the tissue product.

[0005] Although suitable tissue products exist and significant advances in tissue products have occurred, there exists a need for further improvements in tissue products, particularly for tissue products having increased strength and more particularly, increased wet strength.

[0006] In the process of making tissue products, water from the fibrous furnish deposit onto the foraminous support, must be withdrawn and the wet sheet dried to provide the ultimate tissue product. Again, although suitable processes exist and significant advances in process development have occurred, there exists a need for improved processes, particularly with regard to dewatering and drying. The present invention seeks to fulfill these needs.

[0007] In one aspect, the invention provides a tissue product having two or more layers, with at least one layer including carboxylated cellulosic fibers. The carboxylated fiber-containing layer can include from about 0.5 to about 100 percent by weight carboxylated cellulosic fibers. The carboxylated fiber-containing layer can also include a variety of other cellulosic and synthetic fibers. In one embodiment, the carboxylated fiber-containing layer includes about 75 percent by weight carboxylated fibers and about 25 percent by weight bleached spruce chemi-thermomechanical pulp fibers. The carboxylated fiber-containing layer can also include a wet strength agent and other additives, such as carboxymethyl cellulose (CMC). The tissue product including carboxylated cellulosic fibers, other fibers, wet strength agents, and other additions has improved wet strength compared to tissues made with conventional cellulosic fibers.

[0008] In another aspect of the invention, methods for making the tissue product are provided. The product can be made on any type of tissue machine, such as a through-air dried tissue machine or a conventional tissue machine. In one embodiment of the method, the tissue product is made by depositing a first fibrous furnish onto a forming wire to provide a first deposited furnish; depositing a second fibrous furnish onto the first deposited furnish to provide a wet web; withdrawing water from the wet web to provide a sheet; and drying the sheet to provide the tissue product having at least two layers. At least one of the first fibrous furnish or the second fibrous furnish includes carboxylated cellulosic fibers to provide the tissue product in which at least one layer includes carboxylated cellulosic fibers. In other embodiments, more than two fibrous furnishes are deposited to provide a tissue product having more than two layers.

[0009] The foregoing aspects and many of the attendant advantages of this invention will become more readily appreciated as the same become better understood by reference to the following detailed description, when taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a schematic illustration of a through-air dried tissue machine useful in making the tissue product of the invention;

FIGURE 2 is a table summarizing the composition and softwood pulp refining conditions of representative tissue products of the invention (sheets) compared to control sheets;

FIGURE 3 is a table comparing the properties of sheets prepared from control pulps;

FIGURE 4 is a table summarizing the properties of sheets prepared from a carboxylated fiber pulp and a control at 460-480 CSF, 25 lb/ton wet strength agent, and 4 lb/ton carboxymethyl cellulose;

FIGURE 5 is a table illustrating the effect of carboxymethyl cellulose on the properties of sheets prepared from a carboxylated fiber pulp and a control pulp at constant refining energy input and 25 lb/ton wet strength agent;

FIGURE 6 is a table summarizing the composition and properties of representative tissue products of the invention (handsheets) prepared from pulps having three different carboxyl contents (4, 10, and 16 meq/100 g), three different refining conditions (7, 10, and 13 sec^2 PFR), three different wet strength agent addition rates (20, 35, and 50 lb/ton), and three different carboxymethyl cellulose addition rates (0, 2, and 4 lb/ton);

FIGURE 7 is a graph illustrating pulp filtration resistance (PFR) versus pulp PFI mill revolutions (PFI revs) for two representative carboxylated fibers compared to control;

FIGURE 8 is a graph illustrating wet burst versus pulp filtration resistance for representative tissue (handsheets) compared to control;

FIGURE 9 is a graph illustrating tensile strength versus pulp filtration resistance for representative tissue products of the invention (handsheets) compared to control;

FIGURE 10 is a graph comparing wet burst/dry tensile strength ratio versus pulp filtration rate for representative tissue products of the invention (handsheets) compared to control;

FIGURES 11A and 11B are a table summarizing the composition and properties of representative tissue products of the invention (handsheets) compared to control tissue products at three different refining conditions (375, 475, and 575 CSF), three different wet strength addition rates (0, 4, and 8 lb/ton), and three different carboxymethyl cellulose addition rates (0, 4, and 8 lb/ton);

FIGURES 12A and 12B are graphs comparing actual and predicted wet burst versus wet strength agent (KYMENE) amount added for representative tissue products of the invention compared to tissue products that do not include carboxylated cellulosic fibers; the predicted curves are based on a combined regression model; FIGURE 12A illustrates wet burst versus wet strength agent addition for pulp refined to CSF = 475, and FIGURE 12B illustrates wet burst versus wet strength agent addition for pulp refined to CSF = 375; the dashed curve is the predicted curve for tissues containing carboxylated pulp, the (+) points are actual points for tissues containing carboxylated fiber pulp, the solid curve is the predicted curve for control tissues including non-carboxylated fiber pulp, and the (♦) points are actual points for control tissues containing non-carboxylated fibers;

FIGURES 13A and 13B are graphs comparing actual and predicted dry tensile versus wet strength agent (KYMENE) amount added for representative tissue products of the invention compared to tissue products that do not include carboxylated cellulosic fibers; the predicted curves are based on a combined regression model; FIGURE 13A illustrates dry tensile versus wet strength agent addition for pulp refined to CSF = 475, and FIGURE 13B illustrates dry tensile versus wet strength agent addition for pulp refined to CSF = 375; the dashed curve is the predicted curve for tissues containing carboxylated pulp, the (+) points are actual points for tissues containing carboxylated fiber pulp, the solid curve is the predicted curve for control tissues including non-carboxylated fiber pulp, and the (♦) points are actual points for control tissues containing non-carboxylated fibers;

FIGURES 14A and 14B are graphs comparing actual and predicted wet burst/dry tensile ratio versus wet strength agent (KYMENE) amount added for representative tissue products of the invention compared to tissue products that do not include carboxylated cellulosic fibers; the predicted curves are based on a combined regression model; FIGURE 14A illustrates wet burst/dry tensile versus wet strength agent addition for pulp refined to CSF = 475, and FIGURE 14B illustrates wet burst/dry tensile versus wet strength agent addition for pulp refined to CSF = 375; the dashed curve is the predicted curve for tissues containing carboxylated pulp, the (+) points are actual points for tissues containing carboxylated fiber pulp, the solid curve is the predicted curve for control tissues including non-carboxylated fiber pulp, and the (♦) points are actual points for control tissues containing non-carboxylated fibers; and

FIGURES 15A and 15B illustrate representative tissue products of the invention having two and three layers, respectively.

[0010] In one aspect, the present invention provides a tissue product that includes carboxylated cellulosic fibers. In another aspect of the invention, methods for making the tissue product are provided.

[0011] The tissue product of the invention includes carboxylated cellulosic fibers that impart advantageous properties to these tissue products superior to those for other tissue products that do not include carboxylated cellulosic fibers. The tissue product of the invention can be a facial tissue, toilet tissue, disposable wipe, napkin, handkerchief, or paper towel.

[0012] The tissue product of the invention includes two or more layers, and may include one or more plies. Layers can be made on a tissue machine. A layer can include one or more types of fibers. For example, a representative tissue of the invention is a three layered paper towel sheet with two fiber types in each layer. A representative toilet tissue may have three layers with the middle layer having a different fiber type than the outer layers. Plies refer to combining two or more tissues (sheets) during the converting process. A finished product paper towel, toilet tissue, facial tissue, or napkin may include one or more plies. The tissue product of the invention includes at least two layers, with at least one layer including carboxylated cellulosic fibers.

[0013] In one embodiment, the tissue product includes a layer that includes carboxylated cellulosic fibers, other cellulosic fibers, cationic additives such as wet strength agents, and, optionally, other strength additives. The tissue product of the invention is characterized as having comparable or improved wet strength, cationic additive interaction, water retention value, bulk, dry strength, absorbency, fiber refining energy requirement, and on-machine dewatering compared to tissue products that do not include carboxylated cellulosic fibers.

[0014] The tissue product includes at least one layer that includes carboxylated cellulosic fibers. Carboxylated fibers can be prepared by a variety of processes. Suitable carboxylated fibers have a carboxyl content from about 5 to about 60 meq/100 g cellulose and a degree of polymerization of at least about 600. Suitable carboxylated fibers can be prepared by carboxylation processes described in WO 01/29309 and U.S. Patent No. 6,379,494, entitled Method of Making Carboxylated Cellulose Fibers in Products of the Method, each incorporated herein by reference in its entirety. In these processes, the carboxylated fiber is produced by a two-stage process: (1) catalytic cellulose oxidation (e.g., a catalytic oxidizer and a secondary oxidizer, such as chlorine dioxide) and (2) oxidized cellulose stabilization (e.g., reduction or oxidation). The process can be integrated into a pulp mill bleach plant to provide the carboxylated fiber pulp. In one embodiment, suitable carboxylated fibers are prepared by chlorine dioxide oxidation using triacetone amine ethylene glycol ketal catalyst followed by oxidative stabilization with sodium chlorite and hydrogen peroxide.

[0015] Suitable carboxylated fibers can be made from hardwood and softwood chemical pulps. Suitable carboxylated fibers have a total carboxyl content greater than about 6 meq/100 g cellulose and less than about 60 meq/100 g cellulose. In one embodiment, the C6 carboxyl content is greater than about 2 meq/100 g cellulose. C6 carboxyl content refers to extent of carboxylation at C6 of the anhydroglucose unit of cellulose to provide a glucuronic acid derivative. Suitable carboxylated fibers have a low aldehyde content, less than about 1 meq/100 g cellulose. Suitable carboxylated fibers has a degree of polymerization greater than 700 in pre-acid form and greater than 850 in sodium salt form. In one embodiment, the carboxylated fiber has an ISO brightness in the range from about 75 to about 95 percent. In one embodiment, the softwood carboxylated fiber viscosity is greater than about 18 mPa. The carboxylated fiber can be provided to the tissue machine in either dried or never-dried form.

[0016] The carboxylated fiber can be refined to drainage and strength targets in a dilute aqueous suspension using commercially available pulp refiners.

[0017] In addition to carboxylated fibers, the carboxylated fiber-containing layer of the tissue product of the invention can include one or more other pulp fibers. Suitable other pulp fibers include, for example, recycled fibers, bleached kraft hardwood fibers, bleached kraft softwood fibers (e.g., northern bleached softwood kraft pulp, NBSK), bleached sulfite fibers, and bleached chemi-thermomechanical pulp (BCTMP) fibers. In one embodiment, the tissue product useful as a paper towel includes a layer that includes a combination of carboxylated cellulosic fibers and BCTMP fibers. Unbleached pulp fibers and non-pulp fibers can also be used. The selection criteria of other fibers for inclusion in addition to the carboxylated fiber will depend upon the end use product being produced, and are well know to those familiar with the art.

[0018] The carboxylated fiber content of a particular tissue product will vary according to the end use of the product. For example, a paper towel may include a layer that can contain from about 0.5 to about 100 percent by weight carboxylated fiber based on the total weight of fiber, and a facial or toilet tissue may include a layer that can contain from about 10 to about 100 percent carboxylated fiber based on the total weight of fiber.

[0019] In one embodiment, the carboxylated fiber-containing layer of the tissue product of the invention includes a wet strength agent. Suitable wet strength agents are cationic additives such as, for example, cationic starch, urea-formaldehyde resins, melamine-formaldehyde resins, polyethylenimine resins, polyacrylamide resins, and polyacrylamide-epichlorohydrin resins. In one embodiment, the wet strength agent is a polyacrylamide-epichlorohydrin resin commercially available under the designation KYMENE from Hercules Inc., Wilmington DE. The wet strength agent can be present in the tissue product in an amount from about 5 to about 50 lb/ton fiber. In one embodiment, the wet strength agent is present in about 10 lb/ton fiber; in another embodiment, about 25 lb/ton fiber; and in another embodiment, about 40 lb/ton fiber.

[0020] For paper towel products, the wet strength agent is a permanent wet strength agent, such as a polyacrylamide-epichlorohydrin resin. For toilet and facial tissue products, the wet strength agent is a temporary wet strength agent, such as cationic starch.

[0021] The carboxylated fiber-containing layer of the tissue product can also include other strength additives. Other suitable strength additives include, for example, carboxymethyl cellulose (CMC). The carboxylated fiber-containing layer can include up to about 10 lb/ton CMC based on the total weight of fibers. In one embodiment, the carboxylated fiber-containing layer includes about 4 lb/ton CMC, and in another embodiment, the carboxylated fiber-containing layer includes about 8 lb/ton CMC.

[0022] Other chemicals useful in making tissue products can optionally be used during the tissue making process. Other useful chemicals include retention aids, softeners, surfactants, Yankee coating, and through-air dryer release spray.

[0023] As noted above, the tissue product of the invention is characterized as having greater wet tensile

and burst strength than tissue made from commercial pulps (e.g., bleached northern softwood kraft pulps); greater wet strength/dry strength ratio (wet burst/dry tensile, WB/DT ratio, or wet tensile/dry tensile, WT/DT ratio) than tissues made with commercial pulps; dry tensile strength that is equal to or greater than that of tissue products made from commercial pulps; and a greater Tensile Energy Absorption (TEA) Index than tissue products made with commercial pulps.

[0024] In one embodiment, the tissue product of the invention including carboxylated fibers has a wet burst/dry tensile ratio from about 0.20 to about 0.40.

[0025] The other layers of the tissue product of the invention can include one or more of the materials described above including, for example, carboxylated cellulosic fibers.

[0026] In another aspect of the invention, a method for making a tissue product that includes carboxylated cellulosic fibers is provided. In one embodiment, the tissue product is made on a tissue machine. In the method, the carboxylated fiber, which may be refined, is combined with one or more other pulps, and strength additives, as desired, and fed into the tissue machine headbox. The carboxylated fiber can be a separate furnish or one of several pulps mixed together to create one layer in the multi-layered tissue sheet. The carboxylated fibers can make up from about 0.5 percent to 100 percent of the tissue furnish. The carboxylated fiber can be present in one or more layers of a multi-layered tissue sheet. The wet web or sheet produced by depositing the headbox contents onto a foraminous support is processed through the various unit operations of the tissue machine to produce a dry tissue jumbo roll. The tissue jumbo roll can be further processed through various converting equipment into the finished consumer product, for example, toilet tissue, facial tissue, paper toweling. The tissue product of the invention can be produced on a variety of tissue machines including, for example, conventional machines, creped through-air dried machines, or un-creped through-air dried machines.

[0027] A schematic illustration of a through-air dried tissue machine useful in making the representative tissue product of the invention (i.e., a three-layered product) is shown in FIGURE 1. Referring to FIGURE 1, tissue machine 100 includes layered head box 10 having top chamber 12, center chamber 16, and bottom chamber 14, Fourdrinier wire 20 looped over and about breast roll 101, vacuum suction boxes 30, and couch roll 102. In a representative operation for making a three-layered tissue product, a first papermaking furnish is pumped through top chamber 12, a second papermaking furnish is pumped through center chamber 16, and a third furnish is pumped through bottom chamber 14 onto wire 20 to form embryonic web 40 having layers 40a, 40b, and 40c. Dewatering occurs through wire 20 and vacuum boxes 30. As the wire makes its return in the direction shown by the arrow, showers 50 clean the wire prior to its beginning another pass over breast roll 101. At web transfer zone 60, embryonic web 40 is transferred to foraminous carrier fabric 62 by the action of vacuum transfer box 64. Carrier fabric 62 carries the web from transfer zone 60 past vacuum dewatering box 66 through predryers, or through-air dryers, 68 after which the web is transferred to a Yankee dryer 70 by the action of pressure roll 103. The carrier fabric 62 is then cleaned and dewatered as it completes its loop by passing showers 52 and vacuum dewatering box 54. The predried paper web is adhesively secured to the cylindrical surface of Yankee dryer 70 by adhesive supplied by spray applicator 80. Drying is completed on steam-heated Yankee dryer 70 and by hot air heated and circulated through drying hood 90. The web is then dry creped from Yankee drier 70 by doctor blade 82 after which sheet 42 including a Yankee-side layer 42a, a center layer 42b, and an off-Yankee-side layer 42c. Sheet 42 then passes between calendar rolls 104 and 105 and is reeled onto core 106 disposed on shaft 107 to provide roll 44.

[0028] In the method described above, a manufacture of a three-layered tissue product is described. It will be appreciated that two-layered tissue products and tissue products having more than three layers can be prepared by the method and are within the scope of this invention. With regard to the described method, the carboxylated fiber-containing layer may be any one or more of the layers. For example, the carboxylated fiber-containing layer of the tissue product may be the middle layer of the tissue product, or one or both of the outer layers of the tissue product.

[0029] In a representative trial, the NBSK (carboxylated fiber or control) inclusion rate was 75 percent; the basis weight split between layers (air/core/Yankee) was 33 percent/34 percent/33 percent; the reel basis weight was 20.5 gsm; the Yankee speed was 1100 mpm; and the twin-wire former/through-air drier wire speed ratio was 1.15 which created a fabric crepe of 15 percent. The machine was operated to control several machine variables: (1) refining energy input to achieve target NBSK freeness or NBSK refining energy input; and (2) through-air drier energy input was adjusted to keep sheet solids exiting the through-air drier greater than 85 percent. This trial was conducted on Metso Paper Karlstad AB's pilot through-air dried paper machine located in Karlstad, Sweden.

[0030] Representative tissue products in roll form were prepared on the tissue machine described above. The tissue product produced by the paper machine was typical of a premium consumer paper towel. The tissue product included either commercial pulp (NBSK) or carboxylated NBSK pulp fibers, bleached chemi-thermomechanical pulp (BCTMP), a wet strength agent, and, optionally, carboxymethyl cellulose. Experimental variables included NBSK or carboxylated fiber refining energy input and strengthening agents' addition rates.

[0031] The trial conditions are tabulated in FIGURE 2. In the table, PA control refers to a northern bleached softwood kraft pulp (Prince Albert, Saskatchewan);

TR962 refers to carboxylated pulp fibers; TR963 refers to a fully bleached, Prince Albert northern bleached softwood kraft pulp dried in the same manner as TR962; inclusion rate refers to the percentage of the PA Control or TR962 or TR963 pulp included in the sheet, the remainder of the pulp included in the sheet was a bleached chemi-thermomechanical pulp (BCTMP) having a brightness of 80 and a Canadian Standard Freeness (CSF) of 525, commercially available from Södra Cell AB; the wet strength agent was a polyamide-epichlorohydrin resin, KYMENE SLX from Hercules; and the strength additive was carboxymethyl cellulose, CMC 7-MT from Metsa Chemical.

[0032] The tissue products and their characteristics are summarized in FIGURES 3-5. FIGURE 3 is a table comparing the properties of sheets prepared from control pulps. FIGURE 4 is a table summarizing the properties of sheets prepared from a carboxylated fiber pulp and a control at 460-480 CSF, 25 lb/ton wet strength agent, and 4 lb/ton carboxymethyl cellulose. FIGURE 5 is a table illustrating the effect of carboxymethyl cellulose on the properties of sheets prepared from a carboxylated fiber pulp and a control pulp at 53 kWh/mt refining energy input and 25 lb/ton wet strength agent.

[0033] The data shows that the tissue products including the carboxylated cellulosic fibers have improved sheet properties at equal inclusion rate, equal NBSK refining energy input, equal wet strength agent addition rate, and equal CMC addition rate compared to the tissue product made from commercial pulps. Improvements were observed in dry tensile, wet tensile, and wet burst strength.

[0034] The tissue machine data shows that through-air drier requires comparable total through-air drying power to dry the tissues containing the carboxylated cellulosic fibers compared to tissues made from commercial pulps at equal inclusion rate, equal NBSK refining energy input, equal wet strength agent addition rate, and equal carboxymethyl cellulose addition rate.

[0035] The data also shows that the carboxylated cellulosic fiber pulp has a lower unrefined freeness than the control pulp and refines to a lower freeness than the control pulp at equivalent refining energy input or refines to an equal freeness with lower refining energy.

[0036] Carboxylated fibers were used as single fiber furnishes to produce tissue handsheets. In one series of experiments, tissue handsheets were prepared from carboxylated cellulosic fibers prepared from northern bleached softwood kraft pulp at three carboxyl levels (3, 7, and 12 meq/100 g cellulose). These pulps were refined to three different levels of refinement as measured by pulp filtration resistance (PFR), 7, 10, and 13 sec^2. Pulp filtration resistance (PFR), like Canadian Standard Freeness (CSF), is a measure of drainage of water from the pulp. In these handsheets, the wet strength agent (KYMENE) was added at three different levels (20, 35, and 50 lb/ton fiber). The tissue products also included carboxymethyl cellulose (CMC) as a strength additive at three different levels, 0, 2, and 4 lb/ton fiber. The results are tabulated in FIGURE 6.

[0037] The results show improvements in the tissue handsheet properties of handsheets that include carboxylated fibers compared to commercial NBSK pulp. Typical commercially available NBSK pulps have a carboxyl level of about 3 to about 4 meq/100 g cellulose. The data shows that handsheets including the carboxylated pulps have higher wet burst strength and wet burst strength/dry tensile strength ratio than handsheets made from commercial pulps.

[0038] Handsheets were also made including carboxylated pulp fibers and compared to handsheets made using a northern bleached softwood kraft pulp control (Prince Albert NBSK). The effect of refining, as well as the amounts of strengthening agents, was determined. The handsheets including the carboxylated pulps have a higher wet burst strength and wet burst strength/dry tensile strength ratio compared to the control handsheets made from commercial pulps. The handsheets including carboxylated fibers had a dry tensile strength that was slightly higher than control at lower refinement, and slightly lower than the control at higher refinement. The results are shown in FIGURES 7-10.

[0039] FIGURE 7 is a graph illustrating pulp filtration resistance (PFR) versus pulp PFI mill revolutions (PFI revs) for two representative carboxylated fibers compared to control. Pulp filtration resistance increases with pulp filtration instrument revolutions for all handsheets.

[0040] FIGURE 8 is a graph illustrating wet burst versus pulp filtration resistance for representative tissue (handsheets) compared to control with an equal wet strength agent addition rate for all samples. Wet burst strength was measured on a Thwing Albert Model 1300-177 Wet Burst Tester manufactured by Thwing Albert Instrument Co., Philadelphia, Pennsylvania. Wet burst increases with increasing pulp filtration resistance. Handsheets including carboxylated fibers showed significantly greater wet burst as a function of pulp filtration resistance compared to the control handsheet.

[0041] FIGURE 9 is a graph illustrating dry tensile strength versus pulp filtration resistance for representative tissue products of the invention (handsheets) compared to control. Dry tensile increases with increasing pulp filtration resistance for all handsheets. The greatest increase in dry tensile is seen from 5 to about 10 sec^2.

[0042] FIGURE 10 is a graph comparing wet burst/dry tensile strength ratio versus pulp filtration rate for representative tissue products of the invention (handsheets) compared to control with an equal wet strength agent addition rate for all samples. The wet burst/dry tensile ratio increased slightly with increasing pulp filtration resistance. The wet burst/dry tensile ratio for the handsheets containing carboxylated fibers was significantly greater than for the control handsheet.

[0043] The composition and properties of representative tissue products of the invention (handsheets) and handsheets made from commercial pulps (controls) are

summarized in FIGURES 11A and 11B. In the table, PA-pilot dried refers to a fully bleached, never-dried northern bleached softwood kraft pulp that was dried at the Paper and Pulp Research Institute of Canada (Point-Claire, Quebec); Prince Albert refers to a northern bleached softwood pulp produced commercially at Weyerhaeuser's Prince Albert, Saskatchewan pulp mill; carboxylated refers to a carboxylated cellulosic fiber pulp dried at the Paper and Pulp Research Institute of Canada (Point-Claire, Quebec); CSF refers to Canadian Standard Freeness (an alternative measure of drainage to PFR); BSWT refers to basis weight (gsm); WB/DT refers to the wet burst/dry tensile ratio; and WRV refers to water retention value.

[0044] The control handsheets included either a NBSK control pulp (Prince Albert) or a second NBSK control pulp (PA-pilot dried) that was dried in the same manner as the carboxylated fiber used in the handsheets of the invention. For these handsheets, CSF was either 375, 475, or 575 ml, KYMENE was included at either 10, 25, or 40 lb/ton, CMC was included at either 0, 4, Or 8 lb/ton. The handsheets including the carboxylated fibers had improved wet burst strength, tensile strength, and wet burst/dry tensile ratio compared to those handsheets made from either commercial NBSK pulps at any given drainage (CSF).

[0045] Low density, low basis weight tissue handsheets were also prepared from these pulps refined using an Esher-Wyss refiner and including varying amounts of wet strength agent (KYMENE) and carboxymethyl cellulose (CMC). FIGURES 12-14 compare the actual and predicted performance of these handsheets based on regression analysis of the handsheets data, and compare wet burst strength, dry tensile strength, and wet burst/dry tensile strength versus wet strength agent amount at various freeness.

[0046] Products of the invention more effectively utilize wet strength agents (e.g., KYMENE) to create higher wet strength in tissues. FIGURES 12A and 12B are graphs comparing the actual and predicted wet burst strength of handsheets made with carboxylated fibers with those of handsheets made with a control pulp at various KYMENE addition rates. NBSK refining varies for each graph, and CMC addition rate is 0 lbs./ton in both examples. The wet burst strength of the handsheets containing carboxylated fibers is higher than the control's at all KYMENE addition rates. FIGURE 12A illustrates wet burst versus wet strength agent addition for pulp refined to CSF = 475, and FIGURE 12B illustrates wet burst versus wet strength agent addition for pulp refined to CSF = 375. The dashed curve is the predicted curve for tissues containing carboxylated pulp, the (+) points are actual points for tissues containing carboxylated fiber pulp, the solid curve is the predicted curve for control tissues including non-carboxylated fiber pulp, and the (♦) points are actual points for control tissues containing non-carboxylated fibers. Handsheets prepared from the carboxylated fiber pulp have greater wet burst strength than the control pulp in the commercially useful wet strength addition ranges.

[0047] A preferred objective of this invention would be to produce tissues with higher wet strength without increasing the tissues' dry strength. FIGURES 13A and 13B are graphs comparing actual and predicted dry tensile strength of handsheets made with carboxylated fibers with those of handsheets made with control pulp at various KYMENE addition rates. NBSK refining varies for each graph, and CMC addition rate is 0 lbs./ton in both examples. The dry tensile strength of the two handsheets are comparable up to approximately 25 lbs. KYMENE/ton. Therefore, one familiar with the art will recognize that that the dry strength of the two handsheets are comparable in the normally commercially viable range for KYMENE inclusion. FIGURE 13A illustrates dry tensile versus wet strength agent addition for pulp refined to CSF = 475, and FIGURE 13B illustrates dry tensile versus wet strength agent addition for pulp refined to CSF = 375. The dashed curve is the predicted curve for tissues containing carboxylated pulp, the (+) points are actual points for tissues containing carboxylated fiber pulp, the solid curve is the predicted curve for control tissues including non-carboxylated fiber pulp, and the (♦) points are actual points for control tissues containing non-carboxylated fibers. Handsheets prepared from the carboxylated fiber pulp have comparable dry tensile strength to the control pulp in the commercially useful wet strength addition ranges.

[0048] FIGURES 14A and 14B are graphs comparing actual and predicted wet burst/dry tensile strength ratio of handsheets made with carboxylated fibers with those of handsheets made with control pulp versus KYMENE addition rate. NBSK refining varies for each graph, and CMC addition rate is 0 lbs./ton in both examples. This wet burst strength/dry tensile strength ratio combines the data from FIGURES 12A - 13B. Products of the invention show substantial improvement in this ratio at all KYMENE addition rates. FIGURE 14A illustrates wet burst/dry tensile versus wet strength agent addition for pulp refined to CSF = 475, and FIGURE 14B illustrates wet burst/dry tensile versus wet strength agent addition for pulp refined to CSF = 375. The dashed curve is the predicted curve for tissues containing carboxylated pulp, the (+) points are actual points for tissues containing carboxylated fiber pulp, the solid curve is the predicted curve for control tissues including non-carboxylated fiber pulp, and the (♦) points are actual points for control tissues containing non-carboxylated fibers. Handsheets prepared from the carboxylated fiber pulp have greater wet burst/dry tensile ratio than the control pulp in the commercially useful wet strength addition ranges.

[0049] Representative tissue products of the invention are illustrated in FIGURES 15A and 15B. FIGURE 15A illustrates a representative two-layer tissue product (200) having first layer 202 and second layer 204. FIGURE 15B illustrates a representative three-layer tissue

product (210) having first layer 212, second layer 214, and third layer 216.

[0050] The methods used for determining the parameters noted herein are described below.

BASIS WEIGHT DETERMINATION METHOD

[0051] The area of several sheets of paper is determined from lineal measurements and the mass is determined by weighing. The ratio of the mass to the area is the basis weight (i.e., g/m^2). The values of many physical properties of paper such as burst, tear, tensile, bulk, and caliper are interpreted and specified with regard to the particular basis weight involved. Ten sheets of sample paper are selected and cut to obtain a total sample target area of 5,000 cm^2. From each sample, randomly select two sheets. Measure each side of the selected sheet. If the lengths of any two opposite edges differ by more than 1 mm, the sample must be recut, as the sides are not sufficiently parallel. Average the measurements of the opposing sides and record to the nearest 0.25 mm. Weigh each specimen on the balance and record the weight. The basis weight (or grammage), g/m^2, for each specimen is calculated as follows:

$$BW(g/m^2) = 10^6 \times M/(L \times W)$$

where M = mass of the specimen (g); L = mean length of sample specimens (mm); and W = mean width of sample specimens (mm).

[0052] Related methods for determining basis weight include ISO 536: 1995 (E), Paper and Board, Determination of Grammage; and TAPPI T 410 om-98, Grammage of Paper and Paperboard (Weight per Unit Area).

TENSILE STRENGTH DETERMINATION METHOD

[0053] This method is used to determine three breaking properties of paper: the force required to cause tensile failure in a specimen of specified width (breaking load or tensile strength); the elongation of the specimen at failure (the difference between the strained length and the original length expressed as a ratio); and the energy absorbed per unit area by the specimen for failure (tensile energy absorption or TEA). The tests are performed on an Instron 4422 Universal Testing System. The crosshead moves at a uniform predetermined rate of speed. The modulus of elasticity (Young's modulus) can also be determined with this method. For measuring tensile index and/or breaking length, basis weight of the sample is required.

[0054] The tensile properties of paper in paper products generally indicate resistance to potential breaking during printing and other converting operations where a variety of in-plane stresses act upon the sheet. The elongation is indicative of the ability of the paper to conform to a desired contour, and this occurs repeatedly in printing presses and other processes. The tensile energy absorption (TEA) is an indicator of how the paper will stand up to repetitive stresses, and is, therefore, a measure of durability. Tensile properties are dependent upon characteristics of the original pulp (wood species, pulping type and conditions, degree of bleaching) and subsequent treatment during papermaking (degree of refining, type and amount of additives, amount of recycled material). Tensile strength is important in pulp manufacture because its strength properties influence those of the paper from which it is made.

[0055] All samples should be conditioned and tested at 23+/- 1°C and 50 +/- 2% relative humidity. Cut specimens 25 mm (about 1 inch) wide and about 250 mm long, with the test direction (machine direction or cross machine direction) parallel with the long dimension. Handsheet specimens should be cut 15 mm wide by 125 - 145 mm long. The specimen length must be sufficient for the test span plus clamping regions of about 25 mm for each clamp. Select the load cell appropriate for the materials being tested. For most tests, a 50 kg type load cell having a test range from 1 - 50 kg is used. For testing very strong grades (linerboard and containerboard), use a "CT" type load cell having the capacity to test from 5 - 250 lb (100 kg). For handsheets, a 25 kg load cell having a test range from 0.5 - 25 kg is appropriate. Prepare the Instron instrument by identifying the test method needed, which is instrument frame specific and load cell specific. Alternatively, the method can be created or modified using the technician's guidebook and Instron manuals. Set the grip span at 180 mm with the jog remote and a steel ruler in the bottom clamp. Rezero the span by activating GL reset on the control panel. Label the specimen and test direction (i.e., MD or CD). For determination of modulus of the elasticity, measure each test strip for thickness at three positions along the strip length. Record the average strip thickness in mm.

[0056] For calibration, connect the appropriate load cell and its connector cable to the correct Instron frame. The electronic calibration method then calibrates the Instron device.

[0057] To obtain sample measurements, select the appropriate test method and follow the program prompts for specific instructions and inputs. The standard speed used is 25.4 mm per minute (about 1 inch per minute) and clamping pressure should remain constant at 65 psi. Insert specimens, up to 10 at a time for thin papers, into the upper jaw to ensure vertical alignment with the lower jaw when both jaws are clamped. The clamps must be perpendicular to the length of the specimen (and to the direction of pull) for accurate testing. Once the specimen is clamped into the lower jaw, follow the method prompts and allow the computer to start testing. To verify the software calculations, print out the REP file and a graph of the first sample. Use the elongation and maximum load values from the graph to calculate tensile, elongation, and breaking length. Modulus of elasticity can be calculated by drawing a line tangent to the

elastic region of the curve and calculating the slope. Ten specimens per sample are tested.

[0058] To calculate breaking load (B) in units of kN/m, the following formula is used:

$$B\ (kN/m) = 9.80665f/w$$

where f = load at failure (kg) and w = specimen width (mm).

[0059] To calculate tensile index (T) in units of Nm/g, the following formula is used:

$$T\ (Nm/g) = 9810f/wg$$

where g = condition to basis weight (g/m^2).

[0060] To calculate breaking length (L) in units of km, the following formula is used:

$$L = 1000f/wg.$$

[0061] To calculate elongation (ε) in units of %, the following formula is used:

$$\varepsilon(\%) = 100(sf - s)/s$$

where s = initial (unstrained) span (mm); and sf = span at failure (mm).

[0062] Tensile energy absorption (TEA), J/m^2, is the work done in stressing the specimen to failure and is measured by the integral of the tensile stress over the range of the tensile strain, from zero to maximum strain. The TEA is expressed as energy per unit area (test span X width) of the test specimen. The TEA computation is performed by the acquisition software. The TEA index, J/g, is obtained by dividing the TEA by the specimen basis weight (g/m^2). The modulus of elasticity (E), GPa, is calculated from the slope of the elastic region of the stress/strain curve using the following formula:

$$E\ (GPa) = 0.00981\ [(L2-L1(s)]/[(w)(t)(E2-E1)]$$

where L1 = the lower of two loads located in the elastic region of the curve (kg); L2 = the higher of the two loads (kg); E1 = the specimen elongation at L1 (mm); E2 = the specimen elongation at L2 (mm); and T = average specimen thickness (mm).

[0063] Related methods for determining tensile properties include ISO 1924-2: 1994-(E) Paper and Board, Determination of Tensile Properties, Part 2: Constant Rate of Elongation Method; and TAPPI T 494 om-96, Tensile Breaking Properties of Paper and Paperboard (Using Constant Rate of Elongation Apparatus).

THICKNESS DETERMINATION METHOD

[0064] This method is used to determine the single sheet thickness of paper and paperboard by use of a motor driven micrometer using a specified load applied for a specified time. The method is suitable for using the IPC Soft Platen technique for measuring apparent thickness. This technique employs a micrometer with pressure faces covered with soft neoprene rubber. This has the effect of reducing thickness readings due to the ability of the latex to conform to surface irregularities. This is useful when measuring materials with rough or irregular surfaces, such as linerboard and corrugated medium.

[0065] Thickness is an important property for paper as it influences properties such as structure (bulk), stiffness, opacity, and fold. Variations in thickness are also very useful in order to monitor important machine variables.

[0066] Samples are conditioned and tested at 23 +/- 1°C and at 50 +/- 2% relative humidity.

[0067] The samples should be sufficient to obtain a minimal of 20 and up to 50 readings. Clean the surfaces of the platens with lint-free paper and adjust the micrometer reading to zero. Insert a single specimen into the caliper opening, allowing the pressure faces to close and the reading to stabilize. Perform 50 tests per sample (e.g., 5 readings per sheet on each of 10 sheets). After each sample, check that the instrument zero has not drifted. If it has, clean the platens and readjust as necessary.

[0068] Single sheet thickness is reported in mm (to the nearest 0.001 mm) or in mils (thousandths of inch).

[0069] To calculate air-dry bulk (cm^3/g), the following formula is used:

$$Bulk\ (cm^3/g) = 1000\ A/B$$

where A = thickness (mm), and B = air-dry basis weight (g/m^2).

[0070] To calculate air-dry ("apparent") density (kg/m^3), the following formula is used:

$$Density\ (kg/m^3) = B/A$$

where A = thickness (mm), and B = air-dry basis weight (g/m^2).

[0071] Related methods for determining thickness include TAPPI T 411 om-97, Thickness (Caliper) of Paper, Paperboard, and Combined Board; TAPPI T 551 pm-92, Thickness of Paper and Paperboard (Soft Platen Method); and ISO 534: 1988(E) Paper and Board, Determination of Thickness and Apparent Bulk Density or Apparent Sheet Density.

CANADIAN STANDARD FREENESS DETERMINATION METHOD

[0072] The Canadian Standard Freeness (CSF) test method is used to evaluate the changes in the drainage characteristics of pulp during refining. In addition, the method is used to monitor head box stock as a precursor of how the dilute pulp suspension will behave on the wet end of the paper machine in releasing water. The freeness is highly dependent on degree of refining and therefore is a fairly good indicator of pulp bulk and strength properties. The method is suitable for all types of pulps that can be used by itself or in connection with other test methods (laboratory refining using the PFI, Escher-Wyss, Valley Beater). The method is based on a modification of ISO 5267-2. In the method, the volume of water drained from 3 oven-dried (OD) g of pulp at 0.3% consistency in a standard tester is captured and measured. The amount drained depends mainly on the quantity of debris (i.e., fines) present and to a lesser extent on the degree of fibrillation, flexibility, and compressibility of the fibers.

[0073] Pulps with a dry matter content equal to or greater than 20% are soaked in deionized water for at least four hours and for no longer than 48 hours. The pulp is then disintegrated as described in method WM I-5263 Disintegration of Pulp. For pulps not being refined, disintegrate the equivalent of 24-30 OD g in 2450 - 2900 mL deionized water for 5 minutes (15,000 revolutions) in the standard disintegrator. All samples are tested immediately after preparation (e.g., disintegration, refining). The CSF of refined pulps can change with time. The oven-dry consistency of the sample being tested should be 0.3% +/- 0.02%. Using the testing device, which includes a chamber and a funnel having a traditional bottom orifice and a second side orifice, place a graduated cylinder under the side orifice of the funnel to collect discharge. Place a 1000 mL beaker under the bottom orifice to collect all discharge. Thoroughly mix the diluted sample and withdraw the equivalent of 3.00 OD g in a 1000-mL graduated cylinder. This amount is calculated from a consistency measurement of the sample:

[0074] Amount of sample withdrawn (g) = 3.00 g (100) /% consistency. Adjust the sample to 0.30% consistency by diluting the graduated cylinder contents to the 1000 mL mark. Pour the contents into the upper chamber of freeness tester. Close and clamp the top lid of the chamber and close the air-cock on the top lid of the chamber. Open the bottom lid and open the air-cock on the top. When the discharge has completely stopped from the side orifice, collect the volume in the appropriate graduated cylinder. Read the volume of this discharge to the nearest 1 mL for values below 100 mL, to the nearest 2 mL for values between 100 mL and 250 mL, and to the nearest 500 mL for values exceeding 250 mL. Freeness (CSF) is reported to the nearest whole mL.

[0075] Related methods for determining pulp freeness are described in TAPPI T 227 om-94, Freeness of Pulp; and ISO 5267-2: 1980 Pulps, Determination of Drainability, Part 2: "Canadian Standard" Freeness Method.

WATER RETENTION VALUE DETERMINATION METHOD

[0076] Water retention value (WRV) can be a useful tool in evaluating the performance of pulps relative to dewatering behavior on the paper machine. The usefulness of the method on a particular application may vary depending upon the type of stock, additives, machine configuration, and other factors. The method provides standard values of centrifugal force, time of centrifuging, and simple preparation so that results can be compared at standard values. WRV, as measured by this method, is the amount of water retained by a pulp sample after being subjected to a centrifugal force equal to 900 times the force of gravity for 30 minutes (2 minutes to reach maximum speed). The basis weight of the pulp is 1400 g/m^2 (OD). The method is a modification of TAPPI UM-256. To perform the tests, a laboratory centrifuge with free-swinging head (IEC model HN-SII or equivalent) with digital rpm meter is required.

[0077] The consistency of the pulp, if in dilute form, must be accurately known to the nearest 0.1%. Dried pulps should be soaked. Weigh the equivalent of 0.709 OD g of pulp, if dry soak in small container with deionized water for a minimum of four hours. Tear the soaked pulp into "pea"-sized pieces (3-7 mm) if previously dried and place into a container and fill with deionized water. Blend the pulp and water mixture for about 30 seconds, carefully pour the slurry into a centrifuge tube making sure a uniform pad is formed and remove supernatant water. Centrifuge at 2600 +/- 20 rpm for 30 minutes. After centrifuging, remove the pads from the tubes and weigh the pads to the nearest 0.001 g. Dry the pads by placing in an oven and drying at 105 +/- 3°C for at least 12 hours, but not more than 72 hours. Weigh the dry pads to the nearest 0.001 g.

[0078] The water retention value (WRV), in units of g water/g fiber, is calculated using the following formula:

$$WRV\ (g/g) = (W - D)/D$$

where W = mass of pad after centrifuging (g), and D = dry mass of pad (g).

PULP FILTRATION RESISTANCE DETERMINATION METHOD

[0079] Pulp filtration resistance (PFR) is a measure of a pulp's resistance to drainage. PFR is an important tool for judging a pulp's ability to dewater at various levels of refining. This has a direct impact on paper machine predrier temperatures and machine speed. The test

consists of three timed filtrations of 100 mL of the slurry through a screen in the PFR nozzle. This screen is made of the same monofilament material used as handsheet wires. The method for carrying out the PFR measurement is described in U.S. Patent No. 5,228,954.

[0080] The PFR is, like the Canadian Standard Freeness (CSF), a method for measuring the drainage rate of pulp slurries. It is believed that the PFR is a superior method for characterizing fibers with respect to their drainage characteristics. For purposes of estimation, the CSF may be related to the PFR by the following formula:

$$PFR = 11270/CSF\text{-}10.77,$$

where the PFR is in units of seconds and the CSF is in units of milliliters. Because this relationship is subject to error it should be used for estimation purposes only. A more accurate method of measuring the PFR is as follows.

[0081] The PFR is measured by discharging three successive aliquots of a 0.1% consistency slurry from a proportioner and filtering through a screen connected to the proportioner discharge. The time required to collect each aliquot is recorded and the screen is not removed or cleaned between filtrations.

[0082] The proportioner (obtained from Special Machinery Corporation, 546 Este Avenue, Cincinnati, OH 45232, Drawing #C-PP-318) is equipped with a PFR attachment (also obtained from Special Machinery Corporation, Drawing #4A-PP-103, part #8). The PFR attachment is loaded with a clean screen (a 1-1/8" die cut circle of the same type of screen used for handsheeting, Appleton Wire 84 × 76M, is used and it is loaded with the sheet side "up" in the tester).

[0083] A 0.10% consistency slurry of disintegrated pulp is prepared in the proportioner at a volume of 19 liters, with the PFR attachment in position. A 100 ml volumetric flask is positioned under the outlet of the PFR attachment. The proportioner outlet valve is opened and a timer started, the valve is closed and timer stopped the instant 100 ml is collected in the volumetric flask (additional liquid will probably drain into the flask after the valve is closed). The time is recorded to the nearest 0.10 seconds, noted as "A".

[0084] The filtrate is discarded, the flask repositioned, and another 100 ml aliquot is collected by the same procedure without removing or cleaning the screen between filtrations. This time interval is recorded as "B".

[0085] Again, the filtrate is discarded, the flask repositioned, and another 100 ml aliquot is collected by the same procedure without removing or cleaning the screen between filtrations. This time interval is recorded as "C".

[0086] PFR is then calculated using the following equation:

$$PFR = \sqrt{\frac{(E) \times (B + C - (2 \times A))}{1.5}}$$

where A, B, and C are the recorded time intervals, and E is a function of temperature used to correct the PFR to the value that would be observed at 75 °F:

$$E = 1+(0.013 \times (T\text{-}75)),$$

where T is the slurry temperature measured to the nearest °F in the proportioner after taking the last aliquot.

HANDSHEET PREPARATION AND WET BURST TEST METHOD

[0087] Handsheet Preparation. About 30-31 g of pulp was refined in a PFI Refiner to 570±5 mL Canadian Standard Freeness. Nineteen grams (dry basis) of the refined pulp in a total of 2000 mL of water was placed in a British disintegrator, 2.28 g of 12.5% KYMENE 557H solution was added, and the slurry was disintegrated for 10 minutes. The resulting disintegrated pulp slurry was diluted to 19 L to form a 0.1% consistency slurry. The drainage rate of this slurry was measured by the amount of time taken to pass 300 mL of filtrate water, using a liquid slurry head height of 36 inches, through a 1.0 inch diameter circular handsheet forming wire containing 84×76 wires per inch. The forming wire was obtained from Albany International, 435 Sixth St., Menasha, Wis., 54952.

[0088] Wet Burst Test Method. A 12 inch×12 inch deckle box was used to form handsheets of approximately 26 g/m^2 basis weight and approximately 240 kg/r^3 density on the forming wire described above. Five sheets were formed for each pulp. The sheets were not wet pressed. Dewatering of the handsheets was accomplished by passing the sheets still on the forming wire over a vacuum slit. The sheets were dried on a steam-heated drum dryer and cured in an oven for one hour at 105°C. Wet burst strength of the sheets was measured on a Thwing Albert Model 1300-177 Wet Burst Tester manufactured by Thwing Albert Instrument Co., Philadelphia, Pa., 19154. Eight measurements were made for each pulp and the average calculated and taken as the wet burst strength.

[0089] While the preferred embodiment of the invention has been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention.

Claims

1. A method for making a tissue product, comprising:

(a) depositing a first fibrous furnish onto a forming wire to provide a first deposited furnish;
(b) depositing a second fibrous furnish onto the first deposited furnish to provide a wet web, wherein at least one of the first fibrous furnish or the second fibrous furnish comprises carboxylated cellulosic fibers;
(c) withdrawing water from the wet web to provide a sheet; and
(d) drying the sheet to provide the tissue product having at least two layers, wherein at least one layer comprises carboxylated cellulosic fibers.

2. A method as claimed in claim 1, wherein the carboxylated cellulosic fibers have a carboxyl content of from 6 to 60 meq/100 g cellulose.

3. A method as claimed in claim 1 or claim 2, wherein the carboxylated cellulosic fibers have an aldehyde content of less than 1 meq/100 g cellulose.

4. A method as claimed in any one of the preceding claims, wherein the first fibrous furnish or second fibrous furnish comprises non-carboxylated fibers.

5. A method as claimed in claim 4, wherein the non-carboxylated fibers are at least one of recycled fibers, bleached kraft hardwood pulp fibers, bleached kraft softwood pulp fibers, bleached sulfite pulp fibers, or bleached chemi-thermomechanical pulp fibers.

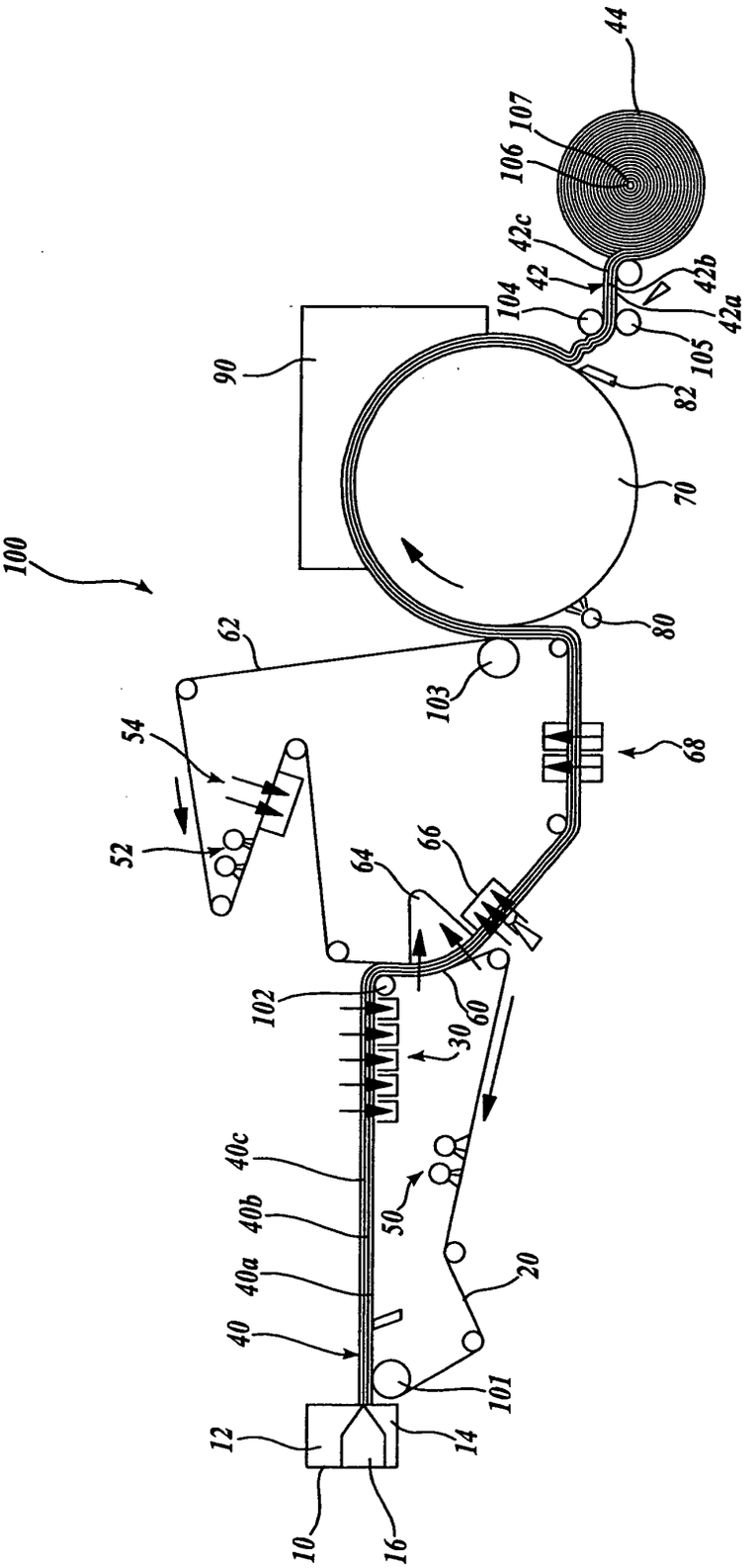
6. A method as claimed in any one of the preceding claims, wherein the first fibrous furnish or second fibrous furnish comprises a wet strength agent.

7. A method as claimed in claim 6, wherein the wet strength agent comprises a polyacrylamide-epichlorohydrin resin.

8. A method as claimed in claim 6, wherein the wet strength agent comprises cationic starch.

9. A method as claimed in any one of the preceding claims, wherein the first fibrous furnish or second fibrous furnish comprises carboxymethyl cellulose.

10. A method as claimed in any one of the preceding claims, further comprising depositing a third fibrous furnish onto the second deposited fibrous furnish, wherein at least one of the first fibrous furnish, the second fibrous furnish, or the third fibrous furnish comprises carboxylated cellulosic fibers, to provide the tissue product having at least three layers, wherein at least one layer comprises carboxylated cellulosic fibers.


100
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40b
40c
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42a
42b
42c
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80
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103
104
105
106
107

Fig.1.

Sample Number	NBSK	Inclusion Rate, %	Actual Refining Energy, kWh/mt	Kymene Addition, lbs./ton	CMC Addition, lbs./ton
199:100	PA Control	75%	40	25	4
199:101	PA Control	75%	53	25	4
199:102	PA Control	75%	27	25	4
199:105	PA Control	75%	27	40	0
199:115	PA Control	75%	27	10	8
199:120	PA Control	75%	53	40	4
199:125	PA Control	75%	27	10	0
199:130	PA Control	78%	108*	40	0
199:131	PA Control	78%	108	10	0
199:135	PA Control	66%	108	40	8
199:140	PA Control	66%	108	25	4
199:145	PA Control	75%	53	25	0
199:150	PA Control	75%	53	10	4
199:155	PA Control	75%	53	25	4
199:160	TR 962	75%	53	25	4
199:165	TR 962	75%	53	25	0
199:170	TR 963	75%	53	25	4

FIGURE 2

Sample Number	199:101	199:155	199:170
Pulp	Prince Albert	Prince Albert	TR963
Refining Energy Input, kWh/mt	53	53	53
CSF, ml	550	550	540
Calculated PFR, sec^2	12.1	12.1	12.4
Basis Weight, g/m^2	22.0	21.3	20.9
Bulk, $m^3/1000$ kg	16.0	17.0	17.0
Machine Direction (MD) Dry Tensile Index, Nm/g	13.03	11.78	13.38
Cross Machine Direction (CD) Dry Tensile Index, Nm/g	10.48	9.89	12.67
Square Root of MD*CD Tensile Index, Nm/g	11.69	10.79	13.02
MD Dry Tensile, N/m	287	251	280
CD Dry Tensile, N/m	231	211	265
Total Dry Tensile, N/m	518	462	545
MD/CD Tensile Strength Ratio	1.24	1.19	1.06
MD Stretch, %	17.8	18.4	18.3
MD TEA Index, J/kg	1189	1117	1263
CD Wet Tensile Index, Nm/g	3.05	2.90	3.21
CD Wet Tensile, N/m	67	62	67
CD Wet Tensile/CD Dry Tensile, %	29.0	29.4	25.3
Wet Burst Strength, g	211.0	205.4	247.2
Wet Burst Strength/Square Root MD*CD Tensile, in	0.32	0.34	0.37
Water Absorbency, g water/g sheet	7.4	7.4	7.1

FIGURE 3

Sample Number	199135	199160
Pulp	Prince Albert	TR962
NBSK Inclusion Rate, %	66	75
Refining Energy Input, kWh/mt	108	53
CSF, ml	480	460
Calculated PFR, sec^2	14.7	15.5
Basis Weight, g/m^2	21.4	22.6
Bulk, $m^3/1000$ kg	17.9	16.1
Machine Direction (MD) Dry Tensile Index, Nm/g	12.77	12.21
Cross Machine Direction (CD) Dry Tensile Index, Nm/g	11.67	11.5
Square Root of MD*CD Tensile Index, Nm/g	12.21	14.61
MD Dry Tensile, N/m	273	276
CD Dry Tensile, N/m	250	260
Total Dry Tensile, N/m	523	536
MD/CD Tensile Strength Ratio	1.09	1.06
MD Stretch, %	18.0	19.2
MD TEA Index, J/kg	1243	1163
CD Wet Tensile Index, Nm/g	3.67	3.31
CD Wet Tensile, N/m	78	75
CD Wet Tensile/CD Dry Tensile, %	31.2	28.8
Wet Burst Strength, g	272.4	263.4
Wet Burst Strength/Square Root MD*CD Tensile, in	0.40	0.32
Water Absorbency, g water/g sheet	7.5	7.2

FIGURE 4

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Sample Number	199-101	199-155	199-145	199-160	199-165
Pulp	Prince Albert	Prince Albert	Prince Albert	TR962	TR962
CMC Addition Rate, lbs./ton	4	4	0	4	0
CSF, ml	550	550	550	460	520
Calculated PFR, sec^2	12.1	12.1	12.1	15.5	13.1
Basis Weight, g/m^2	22.0	21.3	20.7	21.8	22.6
Bulk, $m^3/1000$ kg	16.0	17.0	16.6	17.3	16.1
Machine Direction (MD) Dry Tensile Index, Nm/g	13.03	11.78	9.71	15.09	12.21
Cross Machine Direction (CD) Dry Tensile Index, Nm/g	10.48	9.89	8.25	14.15	11.5
Square Root of MD*CD Tensile Index, Nm/g	11.69	10.79	8.95	14.61	11.85
MD Dry Tensile, N/m	287	251	201	329	276
CD Dry Tensile, N/m	231	211	171	308	260
Total Dry Tensile, N/m	518	462	372	637	536
MD/CD Tensile Strength Ratio	1.24	1.19	1.18	1.07	1.06
MD Stretch, %	17.8	18.4	19.4	19.4	19.2
MD TEA Index, J/kg	1189	1117	934	1422	1163
CD Wet Tensile Index, Nm/g	3.05	2.90	2.06	3.72	3.31
CD Wet Tensile, N/m	67	62	43	103	75
CD Wet Tensile/CD Dry Tensile, %	29.0	29.4	25.1	33.4	28.8
Wet Burst Strength, g	211.0	205.4	139.3	263.4	206.3
Wet Burst Strength/Square Root MD*CD Tensile, in	0.32	0.34	0.29	0.32	0.30
Water Absorbency, g water/g sheet	7.4	7.4	7.6	7.6	7.2

FIGURE 5

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Box-Behnken Design

Standard Order	Run Order	Block	Carboxyl Level meq/100g	Refined PFR sec2	Kymene lb/t	CMC lb/t	Type of Point
1	22	Block 1	4	7	35	2	Edge center
2	2	Block 1	16	7	35	2	Edge center
3	26	Block 1	4	13	35	2	Edge center
4	8	Block 1	16	13	35	2	Edge center
5	20	Block 1	10	10	20	0	Edge center
6	7	Block 1	10	10	50	0	Edge center
7	18	Block 1	10	10	20	4	Edge center
8	5	Block 1	10	10	50	4	Edge center
9	3	Block 1	4	10	35	0	Edge center
10	28	Block 1	16	10	35	0	Edge center
11	11	Block 1	4	10	35	4	Edge center
12	4	Block 1	16	10	35	4	Edge center
13	25	Block 1	10	7	20	2	Edge center
14	13	Block 1	10	13	20	2	Edge center
15	16	Block 1	10	7	50	2	Edge center
16	17	Block 1	10	13	50	2	Edge center
17	14	Block 1	4	10	20	2	Edge center
18	12	Block 1	16	10	20	2	Edge center
19	10	Block 1	4	10	50	2	Edge center
20	9	Block 1	16	10	50	2	Edge center
21	24	Block 1	10	7	35	0	Edge center
22	21	Block 1	10	13	35	0	Edge center
23	23	Block 1	10	7	35	4	Edge center
24	15	Block 1	10	13	35	4	Edge center
25	6	Block 1	10	10	35	2	Center
26	19	Block 1	10	10	35	2	Center
27	27	Block 1	10	10	35	2	Center
28	1	Block 1	10	10	35	2	Center
extra	29			7	35	0	
extra	30			7	35	0	

Data

Actual Carboxyl meq/100g	Dry Tensile g/in	Wet Burst g	Wet Burst /Dry Tensile	Bulk cc/g	Actual PFR sec2	WRV g/g
3	4774	1268	0.2656	3.87	7.7	1.99
12	4922	1456	0.2958	3.90	7.0	1.77
3	6482	1989	0.3068	3.12	18.1	2.27
12	6027	1902	0.3156	3.18	11.6	2.15
7	5734	1600	0.2790	3.39	10.6	2.08
7	5067	1680	0.3316	3.60	10.0	2.19
7	5915	1798	0.3040	3.36	8.6	2.14
7	5792	1856	0.3204	3.46	10.8	2.06
3	5563	1563	0.2810	3.47	12.8	2.16
12	6472	1929	0.2981	3.09	14.4	2.17
3	5760	1791	0.3109	3.33	12.3	2.07
12	5863	1880	0.3207	3.45	8.7	1.99
7	4201	1179	0.2806	4.14	6.0	1.79
7	5723	1795	0.3136	3.23	11.3	2.13
7	4625	1358	0.2936	4.04	6.8	1.95
7	6289	2216	0.3524	3.18	14.8	2.21
3	5786	1642	0.2838	3.54	10.8	2.08
12	5617	1593	0.2836	3.48	8.4	2.03
3	5444	1600	0.2939	3.45	12.7	2.17
12	6034	1923	0.3187	3.32	11.0	2.05
7	4500	1261	0.2802	4.01	7.0	1.90
7	6101	2032	0.3331	3.19	14.0	2.19
7	5125	1630	0.3180	3.85	6.6	1.84
7	6212	2019	0.3250	3.35	11.5	2.13
7	5718	1812	0.3169	3.45	10.5	2.01
7	6250	1970	0.3152	3.31	10.7	2.15
7	5890	1853	0.3146	3.37	10.5	2.09
7	5916	1765	0.2983	3.53	10.6	1.96
3	5076	1127	0.2220	3.74	8.3	1.91
12	5071	1453	0.2865	3.80	7.2	1.80

FIGURE 6

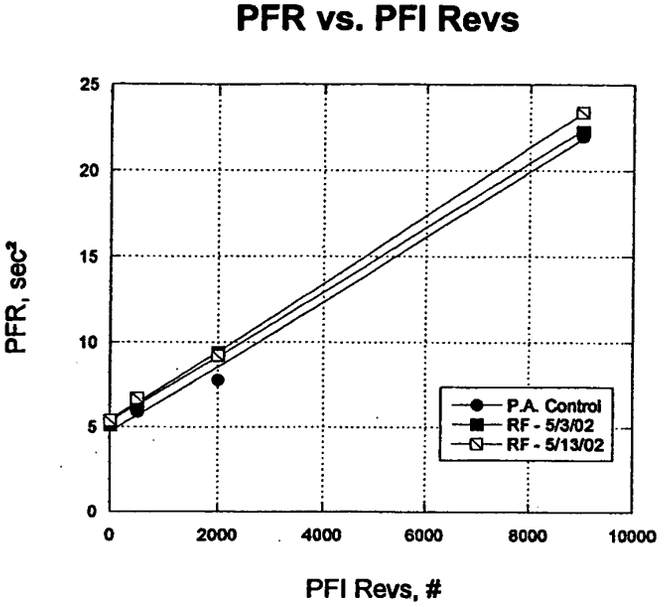
PFR vs. PFI Revs
PFR, sec²
25
20
15
10
5
0
0
2000
4000
6000
8000
10000
PFI Revs, #
P.A. Control
RF - 5/3/02
RF - 5/13/02

FIGURE 7

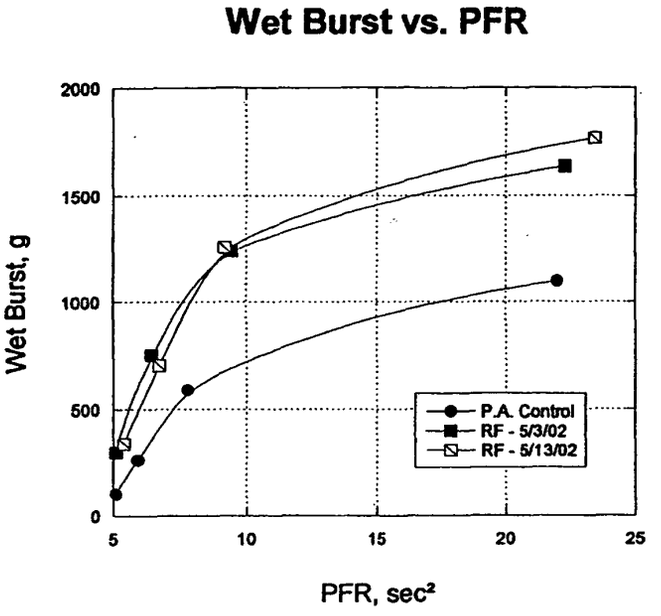
Wet Burst vs. PFR
Wet Burst, g
2000
1500
1000
500
0
5
10
15
20
25
PFR, sec²
P.A. Control
RF - 5/3/02
RF - 5/13/02

FIGURE 8

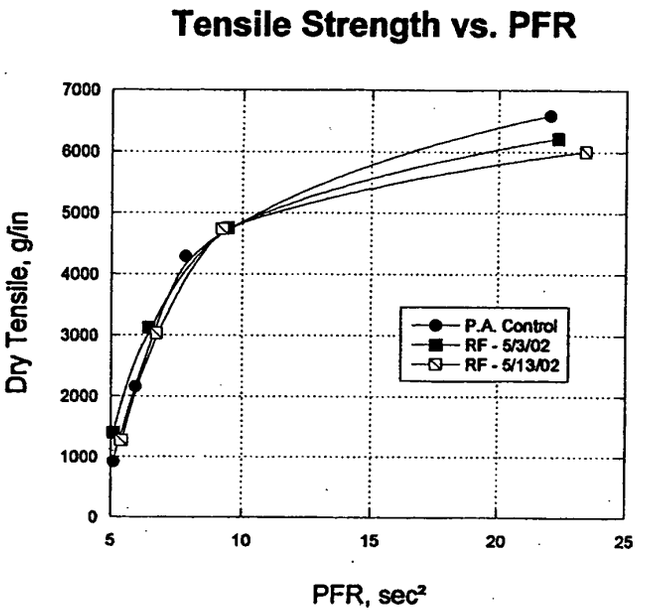
Tensile Strength vs. PFR
Dry Tensile, g/in
7000
6000
5000
4000
3000
2000
1000
0
5
10
15
20
25
PFR, sec²
P.A. Control
RF - 5/3/02
RF - 5/13/02

FIGURE 9

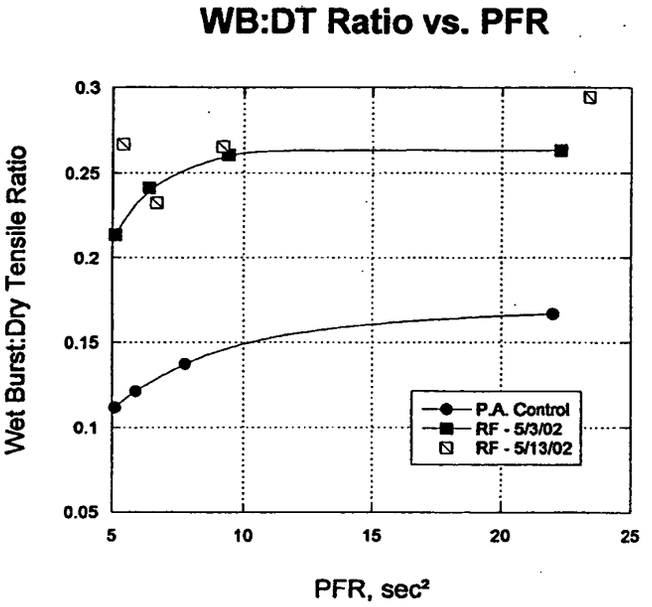
WB:DT Ratio vs. PFR
Wet Burst:Dry Tensile Ratio
0.3
0.25
0.2
0.15
0.1
0.05
5
10
15
20
25
PFR, sec²
P.A. Control
RF - 5/3/02
RF - 5/13/02

FIGURE 10

Run	Pulp	CSF	Kymene lbs./ton	CMC lbs./ton	BSWT g/m^2	Bulk cm^3/g	Wet Burst g	Tensile g/in.	WB/DT in.	WRV g/g
1	PA-Pilot Dried	475	25	4	26.9	3.647	1388	5091	0.273	1.774
2	Prince Albert	475	10	0	26.8	3.802	891	4415	0.202	
3	PA-Pilot Dried	575	25	8	26.7	3.651	1341	4750	0.282	
4	Carboxylated	375	40	4	27.0	3.354	1615	5619	0.287	
5	Prince Albert	475	40	8	26.3	3.725	1486	4929	0.301	1.802
6	Prince Albert	475	25	4	26.8	3.717	1334	4976	0.268	
7	Carboxylated	375	25	0	27.0	3.261	1332	5305	0.251	
8	Prince Albert	375	25	0	27.3	3.568	1047	4803	0.218	
9	PA-Pilot Dried	575	25	0	26.9	3.748	882	4086	0.216	
10	Carboxylated	475	25	4	27.0	3.427	1306	5113	0.255	1.711
11	Carboxylated	575	40	4	26.9	3.559	1258	4612	0.273	
12	PA-Pilot Dried	375	25	0	26.9	3.384	1324	5228	0.253	
13	Carboxylated	575	25	0	26.9	3.554	1071	4455	0.240	
14	PA-Pilot Dried	375	40	4	27.2	3.291	1578	5480	0.288	
15	Prince Albert	575	40	4	26.6	3.962	949	3965	0.239	
16	Carboxylated	475	10	8	26.7	3.253	1112	5217	0.213	
17	Prince Albert	475	10	8	27.3	3.609	1115	4714	0.237	
18	Prince Albert	375	25	8	26.7	3.577	1365	5418	0.252	
19	Carboxylated	475	40	0	27.2	3.465	1214	5167	0.235	
20	Carboxylated	475	40	8	26.7	3.384	1436	5333	0.269	
21	PA-Pilot Dried	475	25	4	24.9	3.669	1455	5349	0.272	1.758
22	PA-Pilot Dried	475	40	0	27.1	3.537	1081	4711	0.230	
23	Prince Albert	375	10	4	26.4	3.509	1143	5119	0.223	

FIGURE 11A

Run	Pulp	CSF	Kymene lbs./ton	CMC lbs./ton	BSWT g/m^2	Bulk cm^3/g	Wet Burst g	Tensile g/in.	WB/DT in.	WRV g/g
24	Carboxylated	575	10	4	27.0	3.455	945	4419	0.214	
25	PA-Pilot Dried	575	40	4	26.6	3.755	1139	4621	0.246	
26	PA-Pilot Dried	475	40	8	26.5	3.553	1488	5498	0.271	
27	Carboxylated	475	25	4	27.2	3.451	1298	5087	0.255	1.519
28	PA-Pilot Dried	475	10	8	27.0	3.425	1157	5259	0.220	
29	Prince Albert	475	25	4	27.2	3.726	1360	5013	0.271	1.839
30	Prince Albert	375	40	4	27.3	3.484	1411	5147	0.274	
31	PA-Pilot Dried	475	10	0	26.9	3.559	1089	4605	0.236	
32	Carboxylated	375	25	8	26.4	3.086	1517	5638	0.269	
33	Carboxylated	375	10	4	26.8	3.536	1069	5354	0.200	
34	PA-Pilot Dried	375	10	4	26.8	3.663	1207	5368	0.225	
35	Prince Albert	575	25	0	27.0	4.305	654	3303	0.198	
36	PA-Pilot Dried	375	25	8	26.9	3.626	1578	5546	0.285	
37	Carboxylated	575	25	8	26.7	3.722	1215	4560	0.266	
38	PA-Pilot Dried	475	25	4	26.7	3.855	1346	4949	0.272	1.734
39	Prince Albert	475	40	0	27.2	3.988	991	4274	0.232	
40	Carboxylated	475	25	4	27.1	3.652	1304	5084	0.257	1.741
41	PA-Pilot Dried	575	10	4	26.6	3.985	967	4458	0.217	
42	Prince Albert	575	25	8	26.8	4.245	1062	3956	0.268	
43	Prince Albert	475	25	4	27.2	3.973	1221	4734	0.258	1.752
44	Carboxylated	475	10	0	26.7	3.697	1005	4686	0.215	
45	Prince Albert	575	10	4	26.8	4.269	846	3766	0.225	

FIGURE 11B

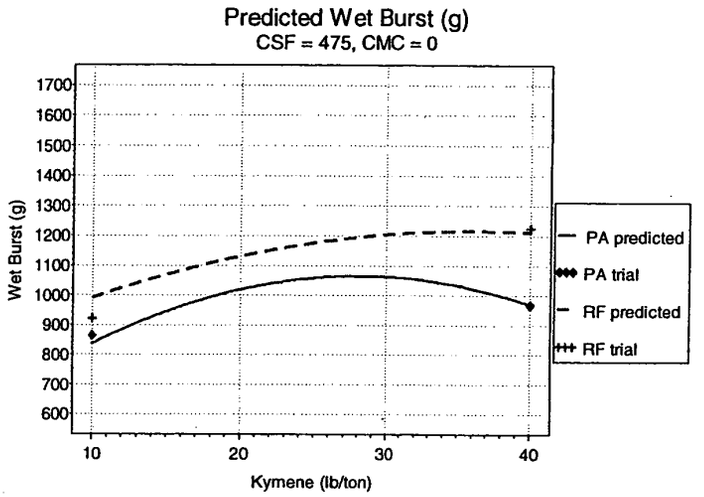

FIGURE 12A

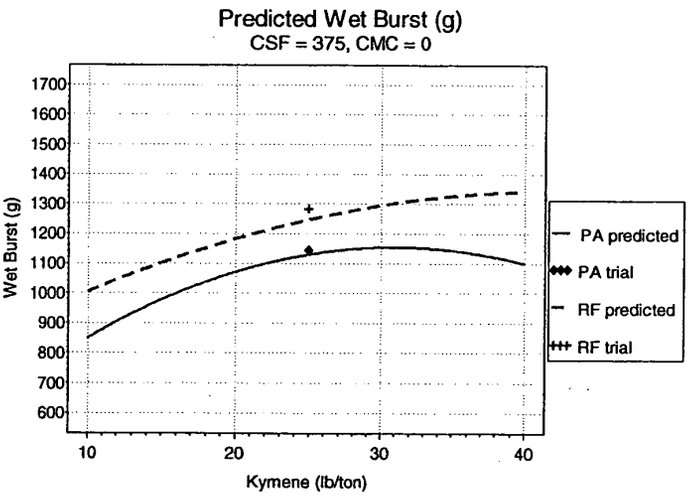

FIGURE 12B

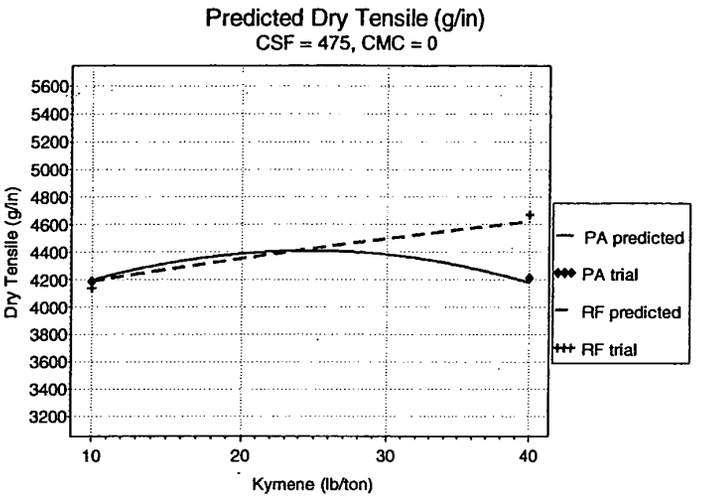

FIGURE 13A

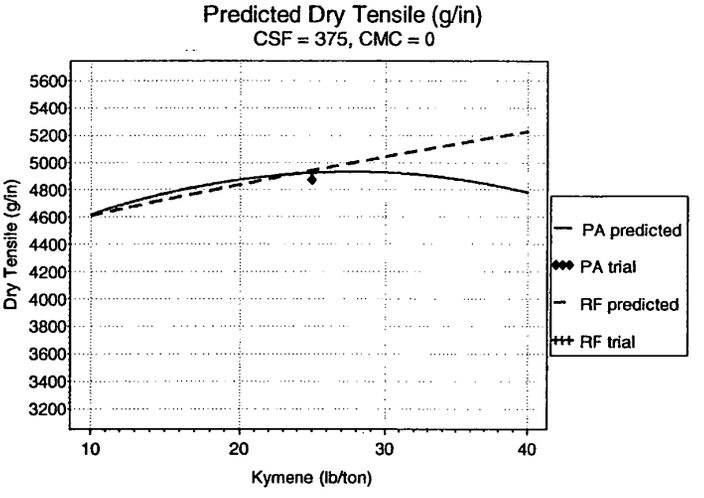

FIGURE 13B

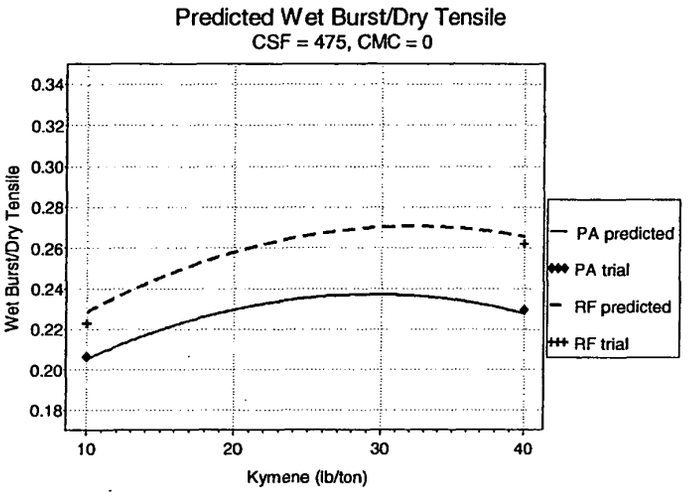

FIGURE 14A

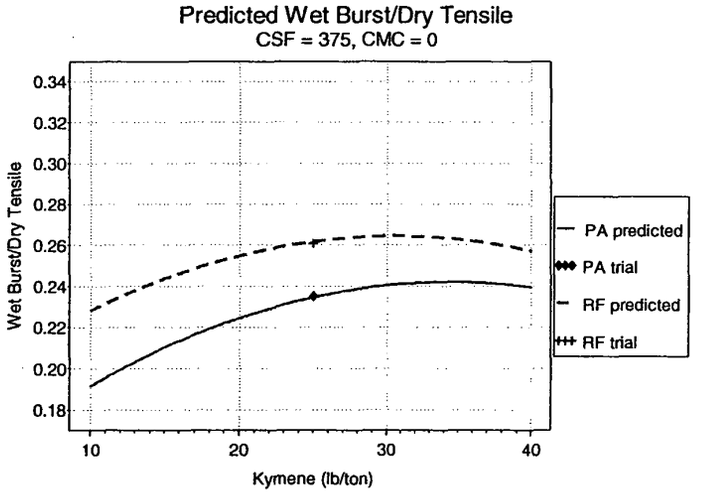

FIGURE 14B

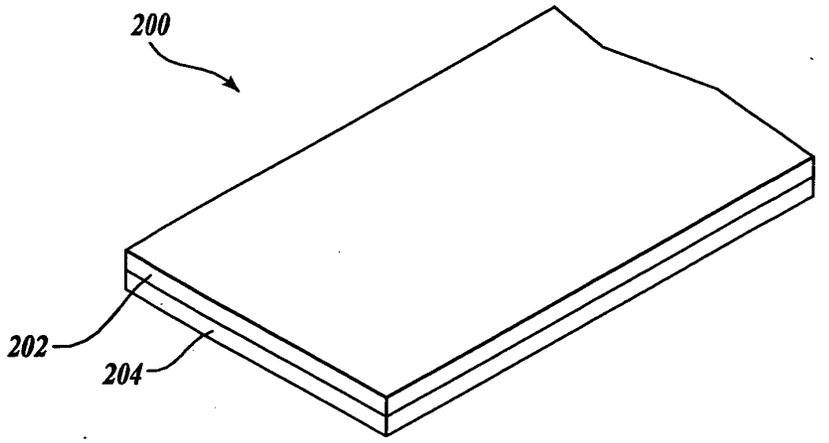

Fig.15A.

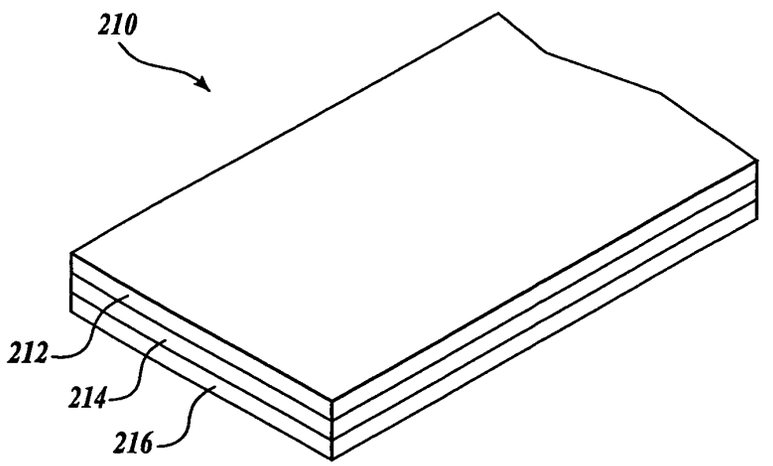

Fig.15B.