(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 213 545**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **86111512.9**

(22) Date of filing: **20.08.86**

(51) Int. Cl.⁴: **D21F 5/18** , D21F 11/00

(30) Priority: **23.08.85 US 768643**
23.08.85 US 768784

(43) Date of publication of application:
11.03.87 Bulletin 87/11

(84) Designated Contracting States:
DE FR SE

(71) Applicant: **International Paper Company**
77 West 45th Street
New York New York 10036(US)

(72) Inventor: **Wagle, Dinkar G.**
Seven Springs Mountain Road
Monroe, New York 10950(US)
Inventor: **Yasnowsky, Vacheslav M.**
61 Lester Drive
Orangeburg, New York 10962(US)
Inventor: **Floyd, Jerome MC Kinley**
758 Savannah Street
Mobile, Alabama 36603(US)

(74) Representative: **Vossius & Partner**
Siebertstrasse 4 P.O. Box 86 07 67
D-8000 München 86(DE)

(54) **Heat treatment of paper products and paper products having starch additives.**

(57) The stiffness, wet strength, opacity and folding endurance of paper products are improved by subjecting the products to steps of high temperature treatment and immediate rewetting. According to one embodiment, the paper product is heated with a starch additive and then subjected to heat treatment.

EP 0 213 545 A1

"HEAT TREATMENT OF PAPER PRODUCTS AND PAPER PRODUCTS HAVING STARCH ADDITIVES".

BACKGROUND OF THE INVENTION

Field of the Invention:

This invention relates to the art of papermaking, particularly to treating of formed paper product with heat and subsequent rewetting to improve its properties, including dry and wet stiffness, wet tensile strength and opacity.

Description of the Prior Art:

In the art of papermaking, it is customary to subject felted fibers to wet pressing and then to drying on heated rolls.

There is currently considerable interest in improving various properties of paper and boards. Quantifiable paper properties include: dry and wet tensile strength, folding endurance, stiffness, compressive strength, and opacity, among others. Which qualities should desirably be enhanced depends upon the intended application of the product. In the case of mild carton board, for example, stiffness is of utmost importance. Linerboard has three qualities of particular interest, namely wet strength, folding endurance, and high humidity compression strength.

All of these properties can be measured by well-known standard tests. As used herein, then, "wet strength" means wet tensile strength as measured by America Society for Testing and Materials (ASTM) Standard D829-48. "Folding endurance" is defined as the number of times a board can be folded in two directions without breaking, under conditions specified in Standard D2176-69. " Stiffness" is defined as flexural rigidity and is determined by the bending moment in g-cm. "Linerboard", as used herein, is a medium-weight paper product used as the facing material in corrugated carton construction. Kraft linerboard is linerboard made according to the kraft process, and is well known in the industry. Folding carton board is a medium to heavy weight paper product made of unbleached and/or bleached pulps of basis weights from 40-350 g/m².

Prior workers in this field have recognized that high-temperature treatment of linerboard can improve its wet strength. See, for example E. Back, "Wet stiffness by heat treatment of the running web", Pulp & Paper Canada, vol. 77, No. 12, pp. 97-106 (Dec. 1976). This increase has been attributed to the development and cross-linking of naturally occurring lignins and other polymers, which phenomenon may be sufficient to preserve product wet strength even where conventional synthetic resins or other binders are entirely omitted.

It is noteworthy that wet strength improvement by heat curing has previously been thought attainable only at the price of increased brittleness (i.e., reduced folding endurance). Embrittled board is not acceptable for many applications involving subsequent deformation, and therefore heat treatment alone, to develop the wet strength of linerboard and carton board, has not gained widespread acceptance. As Dr. Back has pointed out in the article cited above, "the heat treatment conditions must be selected to balance the desirable increase in wet stiffness against the simultaneous embrittlement in dry climates." Also, in U.S. Patent 3,875,680, Dr. Back has disclosed a process for heat treating already manufactured corrugated board to set previously placed resins, wherein the specific purpose is to avoid running embrittled material through a corrugator.

It is plain that improved stiffness and wet strength, on one hand, and improved folding endurance, on the other, were previously thought to be incompatible results.

It is, therefore, an object of the invention to produce linerboard having both improved stiffness, and wet strength, and improved folding endurance.

With a view to the foregoing, a heat treatment process has been developed which dramatically and unexpectedly increases not only the stiffness and wet strength of different boards, but also preserves their folding endurance. In its broadest sense, the invention comprises steps of 1) heating a board produced from either unbleached or bleached kraft pulp to an internal temperature of at least 400°F (205°C) for a period of time sufficient to increase the wet strength of the board; and 2) rewetting the board immediately after the heat treatment to at least 1% moisture by weight. These steps are followed by conventional drying and/or conditioning of the treated board. It is to be understood that steps 1 and 2 can be repeated several times.

This method produces a product having folding endurance greatly exceeding that of similar board whose stiffness and wet strength have been increased by heat alone. This is clearly shown by our tests exemplified below.

According to one embodiment of the invention, starch is added prior to heating. Every year, the paper industry comsumes millions of pounds of starch --an inexpensive natural polymer closely related to cellulose in chemical composition. Prepara-

tions of starch are added to papers and board compositions principally to improve their dry strength and their surface properties (J.P. Casey, Pulp and Paper, 3rd edition, pp. 1475-1500; 1688-1969, 1981).

We have found that heat treatment unexpectedly improves the wet strength of papers and boards containing starch. In its broadest sense, the invention comprises steps of 1) adding starch preparation into the pulp slurry or onto surface of formed paper or board; 2) heating the said paper or board to an internal temperature of at least 400°F - (205°C) for a period of time sufficient to increase the wet strength of the product; and 3) rewetting the product immediately after the heat treatment to at least 1% moisture by weight. These steps are followed by conventional drying and/or conditioning of the treated product. It should be understood that steps 1 and 2 or 1,2, and 3 can be repeated several times.

This method produces a product having folding endurance greatly exceeding that of similar product whose stiffness and wet strength have been increased by heat alone, or by starch addition alone. This is clearly shown by our tests exemplified below.

Of course, those skilled in the art will recognize the necessity of the product conditioning to a normal moisture content after this very hot treatment. See, for example, U.S. Patent 3,395,219. A certain amount of rewetting is normally done, and in fact product properties are never even tested prior to conditioning. However, conventional rehumidification is done after the product has substantially cooled.

Our treatment principally differs from conditioning in that we add water, by spraying or otherwise, to a very hot and dry paper or board at the very end of the heat treatment, without intermediate cooling. It is critical to our process that water be applied to the product while it is still hot, certainly above 50°C (122°F), and preferably above 205°C - (400°F). Another heat treatment or drying step may follow rewetting, on or off the machine, during a subsequent operation such as sizing, coating or calendering.

We prefer to raise the internal temperature of the board to at least 450°F (232°C) during the heat treating step, as greater stiffness and wet strength are then achieved. This may be because at higher temperatures, shorter step duration is necessary to develop bonding, and there is consequently less time for fiber degradation to occur. Also, shorter durations enable one to achieve higher production speeds.

While the invention may be practiced over a range of temperatures, pressures and duration, these factors are interrelated. For example, the use of higher temperatures requires a heat treating step of shorter duration, and vice-versa. For example, at 550°F (289°C), a duration of 2 seconds has been found sufficient to obtain the desired improvements, while at 420°F, considerably longer is required.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention can be carried out either on a conventional papermaking machine or off the machine in an oven after a size-press. When starch is added, as a first step in carrying out the invention, a starch solution is added either to the paper pulp, prior to forming, or to a formed product in any of various ways known in the art.

The invention is preferably practiced on a papermaking machine. The water content of the web must first be reduced to at least 40% by weight and preferably to within the 10-15% range. Sufficient heat is then applied to the board to achieve an internal paper temperature of at least 400°F (205°C). The heat can be applied in the form of hot air, superheated steam, heated drying cylinders, infrared heaters, or by other means.

Alternatively, the invention may be practiced by heating paper product in an oven after a size-press. The internal temperature of the board should be brought to at least 400°F for at least 10 sec. Again, the nature of the heat source is not important.

Following the heat treating step, and while the paper is still hot, water is applied to it, preferably by spraying. Even though one effect of the water application is to cool the paper, it is important that the paper not be allowed to cool substantially before the water application.

The heat treated and rewetted paper is then cooled, conditioned, and calendered according to conventional procedure. The invention has been practiced as described in the following examples. The improvement in board quality will be apparent from an examination of the test results listed in the tables below.

EXAMPLE 1

A bleached kraft board with ambient moisture content of 5.0% (no HT) was tested for various properties of interest in both the machine direction (MD) and the cross-machine direction (CD). A portion of the board was then heat treated at 410°F -

(210°C) for 15 seconds (HT). A portion of the heat-treated board was immediately rewetted to 10.6% moisture content and then dried conventionally (HT & RW). Both samples were conditioned for 48 hours at 70°F (21°C), 65% relative humidity and were then tested. Properties of these samples are given in Table I.

TABLE I

Property	Control Sample (no HT)	Heat Treated (HT)	Rewetted Sample (HT&RW)
Basis weight (lb/3000 ft^2)	153.4	154.0	154.3
Caliper (mils)	15.7	15.8	15.0
Corrected Taber stiffness MD/CD (g-cm)	121/60	131/72	127/71
% stiffness improvement MD/CD	--	8.3/20.0	5.0/18.3
MIT Fold counts MD/CD	98/75	85/70	131/55

It can be seen that heat treating alone produces a substantial increase in stiffness, but some reduction in folding endurance. The latter property is restored, and more, by rewetting, which causes only a slight decrease in stiffness. The net result is a significant improvement in both properties.

EXAMPLE 2

A commercial bleached kraft board (C) was wetted to contain 10.5% moisture by weight and heat treated at 410°F (210°C) for 26.5 seconds - (HT). The board was conditioned for 48 hours under standard (70°F, 65% relative moisture) conditions. Resultant board properties are listed in Table II

TABLE II

Properties	Control Board (C)	Heat Treated Example 1 (HT)
Basis weight (lb/3000 ft^2)	139.5	136.3
Caliper (mils)	15.1	15.6
Corrected stiffness (gm-cm)	90/38	86/36
Stiffness improvement %	--	-4/-5
Dry Tensile lb/in (MD/CD)	45/26.1	43.5/30.7
Wet Tensile, lb/in (MD/CD)	1.6/1.1	4.5/3.2
Wet Strength Retention, % (MD/CD)	3.6/4.2	10.3/10.4
Cracking resistance % not cracked	98/100	99/99
MIT Fold, count	55/38	39/43

EXAMPLE 3

A bleached kraft board identical to that used for Example 1 was wetted to 10.2% moisture content and heat treated at 406°F (208°C) for 9 seconds (HT). A portion of the heat-treated board was immediately rewetted to 1.5% moisture content and then heat treated under same conditions again for 9 seconds (HT & RW). Both samples were conditioned for 24 hrs. under standard conditions and were the tested. Properties of these samples are given in Table III.

TABLE III

Property	Control Sample (no HT)	Heat Treated (HT)	Rewetted Sample (HT&RW)
Basis weight (lb/3000 ft^2)	153.4	154.5	155.3
Caliper (mils)	15.7	16.6	16.1
Corrected Taber stiffness MD/CD (g-cm)	121/60	132/60	133/67
% stiffness improvement MD/CD	--	9.1/0	9.9/11.7
Dry Tensile Strength MD/CD (lb/in)	66.1/37.4	72.9/38.1	64.2/48.5
Wet Tensile Strength MD/CD (lb/in)	2.5/1.6	5.7/3.6	5.0/3.7
% Wet/Dry Tensile MD/CD	6.6/4.4	14.9/9.4	10.3/7.5
Cracking resistance % not cracked MD/CD	100/100	85/7	94/58

The steps of heat treating followed immediately by rewetting doubled wet strength and improved stiffness of the paperboard, with only a slight degradation of other properties. Rewetting was necessary to prevent the severe embrittling caused by heat treatment alone.

EXAMPLE 4

A sample of a linerboard with ambient moisture at 5.5% (no HT) was tested for various properties of interest. A portion of the board was then heat treated at 464°F (240°C) for 30 seconds and tested after conditioning for 24 hours under standard conditions (HT). Properties of the sample in the machine direction only are given in Table IV

TABLE IV

Property	Control Sample (no HT)	Heat Treated (HT)
Basis weight (lb/3000 ft^2)	42.5	41.4
Caliper (mils)	12.5	12.3
L & N Stiffness (g-cm)	51	50
STFI Compression Strength (lb/in)	40.9	48.7
Wet Tensile Strength (lb/in)	5.9	28.4
Folding Endurance cycles to failure	834	463

EXAMPLE 5

Another sample of same linerboard as in was wetted to 8.5% moisture content and then tested for various properties of interest (no HT). A portion of the board was then heat treated at 464°F - (240°C) for 10 seconds (HT). A portion of the heat-treated board was immediately rewetted to 7.6% moisture content (HT & RW) and then dried conventionally. Both samples were conditioned for 24 hours under standard conditions and tested. Properties of these samples in the machine direction only are given in Table V.

TABLE V

Property	Control Sample (no HT)	Heat Treated (HT)	HT & Rewetted (HT&RW)
Basis weight (lb/3000 ft^2)	43.1	43.0	42.8
Caliper (mils)	12.7	13.1	12.8
L & N Stiffness (g-cm)	53	62	58
STFI Compression Strength (lb/in)	41.0	48.3	47.8
Wet Tensile Strength (lb/in)	5.7	19.9	24.3
Folding Endurance cycles to failure	854	449	751

Heat treating and rewetting notably improved strength and stiffness properties with only a minor reduction in folding endurance. In all the above examples, folding endurance following our treatment was at least 85% that of the original board.

EXAMPLE 6

The bleached kraft board in Example 2 was sized with corn starch (pick-up was 2.8 lb/3000 ft²). One portion of the sized board was conventionally dried (110°C for 9 seconds [C]). A second portion was heat treated at 410°F (210°C) for 28.8 seconds, without intermediate drying (HT). A third portion of the sized board was heat treated for 14.3 seconds under identical conditions, rewetted to contain 15% moisture by weight and heat treated again for 14.3 seconds (HT & RW). The board was conditioned for 48 hours under standard conditions. Resultant board properties are listed in Table VI. Notably conventional drying did not improve the wet tensile of the sized board vs. the unsized one; however, both the wet tensile and stiffness of the heat-treated sized board is higher than that of the unsized board.

TABLE VI

Properties	Control Board (C)	Heat Treated (HT)	Rewetted Example 2b (HT&RW)
Basis weight (lb/3000 ft^2)	140.5	144.6	141.8
Caliper (mils)	15.8	15.9	16.0
Corrected stiffness (gm-cm)	122/71	136/71	134/66
Stiffness improvement %	--	+11/0	+10/-7
Dry Tensile lb/in (MD/CD)	68.0/43.7	70.4/41.6	70.3/43.2
Wet Tensile, lb/in (MD/CD)	1.8/1.3	5.6/3.9	3.7/2.3
Wet Strength Retention, % (MD/CD)	2.7/3.0	8.0/9.4	5.3/5.3
Cracking resistance % not cracked	99/100	21/86	96/99
MIT Fold, count	64/84	10/13	21/72

EXAMPLE 7

A mill sized bleached kraft board sample (C) was wetted to 10.9% moisture content and then treated at 410°F (210°C) for 15 seconds (HT). A portion of heat-treated board was rewetted and dried conventionally (HT & RW). All the samples were conditioned for 48 hours under standard conditions. Properties of these samples are given in Table VII.

TABLE VII

Properties	Control Board (C)	Heat Treated (HT)	Rewetted (HT&RW)
Basis weight (lb/3000 ft^2)	153.4	154.5	155.3
Caliper (mils)	15.7	16.6	16.1
Corrected stiffness	121/60	132/60	133/67
Stiffness improvement %	--	9.1/0	9.9/11.7
Dry Tensile (MD/CD)	66.1/37.4	72.9/38.1	64.2/48.5
Wet Tensile, (MD/CD)	2.5/1.6	5.7/3.6	5.0/3.7
Wet Strength Retention, % (MD/CD)	6.6/4.4	14.9/9.4	10.3/7.5
Cracking resistance % not cracked	100/100	85/7	94/58

EXAMPLE 8

Three unbleached kraft linerboard samples (C) were sized with different amounts of starch and then heat treated at 406°F (208°C) for 30 seconds (HT). All the samples were conditioned for 48 hours under standard conditions. Resultant linerboard properties are given in Table VIII.

TABLE VIII.

Properties	CONTROL no HT	CONTROL HT	CORN STARCH, % ADD-ON 0.3	0.6	1.0
Basis weight (lb/1000 ft^2)	42.7	42.8	42.6	43.5	43.4
Caliper (mils)	13.1	13.4	13.7	13.8	13.6
Taber Stiffness (g-cm)	92.5	100.5	91.7	94.5	94.5
Dry Tensile, lb/in.	105.3	87.7	89.9	93.9	97.7
Wet Tensile, lb/in.	7.9	13.8	14.6	16.8	18.2
Wet Strength Retention, %	7.5	15.7	15.5	17.9	18.6
MIT Fold	1702	2064	1389	1435	1740

EXAMPLE 9

A sample never dried kraft linerboard grade pulp having a kappa number at 110 and Canadian Standard Freeness of 750 was slurried in water and starch preparation was added to the slurry in the amount of 1% of the oven dried pulp weight. The starches were "cooked" in water according to conventional practice to contain 8% of starch by weight. A dispersion of the pulp fibers was converted to handsheets using 12x12 inch square sheet mold. The quantity of the fibers in the dispersion was adjusted to give a sheet weight of 19 grams in the oven dry state, said weight being close to that of an air dried; 42 lb/1000 ft² commercial linerboard sheet. The sheets were pressed at 60 psi prior to further treatments. A control sample (C) of handsheets was dried in a conventional dryer (Emerson speed dryer, model 10) at 230°F - (110°C). The rest of the samples was heat treated at 428°F (220°C) for 15 seconds (HT). All the samples were conditioned for 48 hours under standard conditions. Resultant properties are listed in Table IX. One can see that wet tensile of samples containing starch is higher that that of both control and heat treated samples not containing starch.

TABLE IX

		HEAT-TREATED WITH:				
Properties	CONTROL	NO ADDITIVES	CATIONIC STARCH	CORN STARCH	POTATO STARCH	50:50 POTATO STARCH: CAT. STARCH
Basis weight (lb/1000 ft²)	41.0	40.8	42.5	43.9	42.5	43.6
Caliper (mils)	13.4	12.8	13.3	13.8	13.1	13.9
Taber Stiffness (gm-cm)	103.3	93.0	127.5	121.0	89.0	113.0
Dry Tensile, lb/in.	6.5	13.2	20.4	15.8	20.9	15.2
Wet Tensile, lb/in.	0.5	2.1	4.0	2.2	4.6	2.1
Wet Strength Retention, %	8.0	15.6	19.7	13.7	22.2	13.8
MIT Fold	2108	1385	1172	803	479	1225

Claims

1. A method of producing a paper product with improved stiffness, wet strength and opacity and with acceptable flexibility thereof characterized by heat treating incompletely dried or moisturized paper products at high temperature, and then rewetting said product immediately following said heat treating step, before said product cools substantially.

2. The method according to claim 1 characterized by incorporating a starch preparation into the paper product.

3. The method of claims 1 or 2, characterized by the fact that the product has an initial moisture content in the range of 1.0 to 40% by weight before said heat treating step.

4. The method of claims 1 to 3, characterized by the fact that during the rewetting step, the product is rewetted to a moisture content in the range of 1.0 to 20% by weight.

5. The method of claims 2 to 4 wherein the amount of starch preparation added is in the range of 0.2 to 10% of the weight of the paper product.

6. The method of claims 1 to 5, wherein said paper product is milk carton board.

7. The method of claims 1 to 6, characterized by the fact that said heat treatment temperature is in the range of 284 to 482°F (140 to 250°C), and is maintained for a period of time in the range of 0.5 to 120 seconds.

8. The method of claims 1 to 7,wherein pressure on said paper product during said heat treatment step is equal to or less than normal papermaking pressure.

9. The method of claims 1 to 8,wherein said paper is folding carton board.

10. The method of claims 1 to 8,wherein said paper is a linerboard.

11. The method of claim 10 wherein said linerboard has a basis weight of about 42 lb/1000 ft² - (205 g/m²).

12. The method of claim 9, wherein said folding carton board has basis weight of about 160 lb/3000 ft² (260 g/m²).

13. A folding carton board of high stiffness and high folding endurance producible with a method according to any of claims 1 to 12.

14. A linerboard of high wet strength and high folding endurance producible with a method according to any of claims 1 to 12.

15. A linerboard as in claim 14, having a wet strength of at least 15 lb./in (2.63 kN/m) and a folding endurance of at least 85% of the folding endurance of the board prior to application of the heat treating and rewetting steps.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 86111512.9

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE - C - 650 865 (KIENZLE) * Page 1, lines 46-52 * --	1	D 21 F 5/18 D 21 F 11/00
D,A	US - A - 3 875 680 (BACK) * Totality * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

D 21 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	21-11-1986	HOFMANN

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503 03 82