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

(57) The stiffness, wet strength, opacity and folding endurance of paper products containing various wet strength additives are improved by subjecting the products to steps of high temperature treatment and immediate rewetting.

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New York, USA

:AT TREATMENT OF PAPER PRODUCTS HAVING MILK AND OTHER ADDITIVES

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Field of the Invention:

This invention relates to the art of papermaking, particularly to treating paper products having additives such as protein, carboxy methyl cellulose, polyvinyl alcohol, latex, milk, or starch with heat and then immediately rewetting the product 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, to consolidate the web, 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 milk 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 American 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/m^2.

Prior workers in this field have recognized that high-temperature treatment of paperboard 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 paperboard 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 paperboard having both improved stiffness and wet strength, and improved folding endurance.

With a view to the foregoing, a process has been developed which dramatically and unexpectedly increases not only the stiffness and wet strength of various paperboards, but also preserves their folding endurance. In its broadest sense, the invention comprises steps of 1) applying one or more additives selected from the group including protein, carboxy methyl cellulose, polyvinyl alcohol, latex, milk or starch to paperboard; 2) heating the paperboard so treated 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 optionally 3) 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 2 and 3 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.

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 rewetting treatment differs from conventional 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 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; for high speed production, a papermaking machine is preferred.

In either event, the paper product is first treated by adding to it one or more of the following additives: protein, polyvinyl, alcohol, carboxy methyl cellulose, starch, latex or milk. The additive may be mixed with the pulp prior to sheet forming, or it may be added to a formed sheet by spraying or other means. Following wet pressing, the paper product is heat treated.

In the heat treatment step, the initial water content of the web must be in the range of 1-40% 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.

It is preferred that the paper be immediately rewetted following the heat treating step, and while the paper is still hot. Water may be applied by spraying or other means. 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 commercial bleached kraft board was sized with different starch protein (casein) mixtures. Both starch and casein solutions had the same concentration of 8% polymer by weight. The size press was adjusted to have a polymer add-on of 2.4% by weight. A part of the samples was conventionally dried (C) on Emerson speed drier, model 10 at 230°F (110°C). Another portion of the samples was heat treated (HT) at 400°F (205°C) for 30 seconds and rewetted immediately after heat treated. After conditioning for 48 hours under standard conditions (70°F, 65% relative humidity), the samples were tested for stiffness (Table I).

TABLE I

PROPERTIES	CONTROL DRIED (HT)	POTATO STARCH (PS) DRIED (HT)	PS:CASEIN 70:30 DRIED (HT)	PS:CASEIN 50:50 DRIED (HT)
Basis weight ($lb/3000\ ft^2$)	160.1 (150.3)	165.0 (162.8)	164.8 (163.2)	164.9 (164.0)
Caliper (mils)	18.9 (19.0)	18.8 (18.2)	18.9 (18.2)	18.8 (18.4)
Corrected Stiffness, g-cm (MD/CD)	158/75 (164/68)	153/90 (166/90)	167/84 (174/95)	168/86 (181/94)
% Stiffness Improvement (MD/CD)	-- (+3.8/-9)	-3/16 (+4.4/+16)	+5.7/+12 (+12.6/ +26.6)	+6.3/+13.3 (+14.5/ +25.3)

EXAMPLE 2

Board as in Example I was sized with different starch - whole milk mixtures. Starch and milk concentrations were 8% and 4% by weight respectively. The size press pressure was adjusted to achieve an add-on value of 2.4% by weight. A part of the sized samples was conventionally dried on an Emerson speed drier, model 10 at 230°F (110°C). Another portion of the samples was heat treated at 400°F (205°C) for 30 seconds. All the samples were conditioned for 48 hours under standard conditions. The resultant properties are listed in Table II.

TABLE II

PROPERTIES	CONTROL DRIED (HT)	PS:MILK 50:50 DRIED (HT)	WHOLE MILK 70:30 DRIED (HT)
Basis weight ($lb/3000\ ft^2$)	160.1 (150.3)	168.5 (165.9)	165.4 (164.0)
Caliper (mils)	18.9 (19.0)	19.2 (18.6)	19.2 (18.6)
Corrected Stiffness, g-cm (MD/CD)	158/75 (164/68)	161/81 (182/91)	145/69 (166/81)
% Stiffness Improvement (MD/CD)	-- (+3.8/-9)	+1.9/+8 (+15.2/+21)	-8.2/-8 (+45.1/+8)

EXAMPLE 3

Board as in Example 1 was treated with a 50:50 mixture of starch and acrylic latex (Rohm-Maas Rhoplex HA-16). The starch and latex concentrations were 8% and 50% respectively. The size press pressure was adjusted to achieve a polymer add-on of 10.5%. A portion of the samples was conventionally dried on Emerson Speed drier, model 10 at 230°F (110°C). Another portion of the samples was heat treated at 400°F (250°C) for 30 seconds. All the samples were conditioned for 48 hours under standard conditions. The resultant sample properties are listed in Table III.

TABLE III

PROPERTIES	CONTROL DRIED (HT)	PS:LATEX 50:50 DRIED (HT)
Basis weight ($lb/3000\ ft^2$)	160.1 (150.3)	179 (177)
Caliper (mils)	18.9 (19.0)	19.2 (18.6)
Corrected Stiffness, g-cm (MD/CD)	158/75 (164/60)	166/92 (188/89)
% Stiffness Improvement (MD/CD)	-- (+3.8/-9)	+5.1/+22.6 (+19.5/+32)

EXAMPLE 4

A commercial kraft linerboard having a kappa number of 105 and Canadian Standard Freeness of 720 mls was sized and treated as in Example 1. After conditioning for 48 hours under standard conditions, all the samples were tested for their properties (Tables IVa and IVb).

TABLE IVa -Conventionally Dried

Properties	CONTROL	POTATO STARCH (PS)	PS:CASEIN 70:30	PS:CASEIN 50:50	100% CASEIN
Basis weight lb/3000 ft^2	135.2	135.2	133.7	131.2	132.9
Caliper (mils)	12.9	12.9	11.9	12.1	11.7
Dry Tensile lb/in MD/CD	64.6/ 21.6	71.8/ 24.0	71.5/ 26.0	69.2/ 22.5	71.1/ 23.9
Wet Tensile lb/in MD/CD	8.1/ 3.1	6.8/ 3.4	8.3/ 2.7	7.9/ 2.8	7.2/ 2.7
Stiffness g-cm	14.8/ 5.0	16.5/ 6.0	13.8/ 6.0	13.5/ 4.75	13.0/ 4.8
STFI comp. MD/CD	46.7/ 24.5	51.1/ 25.9	47.3/ 26.6	45.3/ 26.1	48.4/ 25.6
Mullen	147.3	173.0	178.6	183.3	165.3

TABLE IVb - HEAT TREATED

Properties	CONTROL	POTATO STARCH (PS)	PS:CASEIN 70:30	PS:CASEIN 50:50	100% CASEIN
Basis weight lb/3000 ft^2	128.0	136.5	133.9	133.6	130.6
Caliper (mils)	12.4	12.4	12.3	12.3	11.2
Dry Tensile lb/in MD/CD	62.4/ 20.6	75.3/ 29.2	75.1/ 27.7	75.5/ 24.8	71.5/ 26.6
Wet Tensile lb/in MD/CD	9.6/ 3.3	15.5/ 6.2	14.8/ 5.5	14.0/ 5.6	16.1/ 5.6
Stiffness g-cm	14.0/ 5.0	16.8 5.0	14.75/ 5.5	15.5/ 5.5	15.5/ 5.3
STFI comp. MD/CD	21.7/ 44.6	52.2/ 29.3	51.5/ 28.9	52.2/ 27.3	51.6/ 29.8
MIT Fold MD/CD	703/ 424	1085/ 413	1171/ 672	1149/ 810	1075/ 878
Mullen	121.3	181.3	159.3	166.0	170.7

EXAMPLE 5

The same board as in Example 4 was sized and treated as in Example 2. All the samples were conditioned for 48 hours under standard conditions. The resultant board properties are listed in Table V.

TABLE V

Properties	CONTROL DRIED	CONTROL HT	PS:MILK 50:50 DRIED	PS:MILK 50:50 HT	WHOLE MILK DRIED	WHOLE MILK HT
Basis weight lb/3000 ft^2	135.2	128.0	137.1	138.6	136.6	138.2
Caliper (mils)	12.9	12.4	12.9	12.6	13.0	12.4
Dry Tensile lb/in MD/CD	64.6/ 21.6	62.4/ 20.6	66.1/ 22.4	72.0/ 26.2	65.9/ 21.1	74.7/ 22.3
Wet Tensile lb/in MD/CD	8.1/ 3.1	9.6/ 3.3	6.9/ 2.5	15.3/ 4.9	6.2/ 2.3	16.4/ 5.5
Stiffness g-cm	14.8/ 5.0	14.0/ 5.0	16.5/ 5.3	16.0/ 6.3	16.3/ 4.8	15.8/ 4.8
STFI comp. MD/CD	46.7/ 24.5	21.7/ 44.6	46.7/ 26.6	51.0/ 27.7	44.2/ 22.6	48.6/ 21.5
MIT Fold MD/CD	-- --	703/ 424	-- --	1027/ 618	-- --	1101/ 724
Mullen	147.3	121.3	164.0	156.7	15.7	148.7

Example 6

The same board as in Example 4 was sized and treated as in Example 3. All the samples were conditioned for 48 hours under standard conditions. The resultant product properties are listed in Table VI.

TABLE VI

Properties	CONTROL DRIED	CONTROL HT	PS:LATEX 50:50 DRIED	PS:LATEX 50:50 HT
Basis weight lb/3000 ft^2	135.2	128.0	143.7	145.0
Caliper (mils)	12.9	12.4	13.1	12.3
Dry Tensile lb/in MD/CD	64.6/ 21.6	62.4/ 20.6	83.5/ 31.2	82.2/ 30.1
Wet Tensile lb/in MD/CD	8.1/ 3.1	9.6/ 3.3	13.7/ 4.7	24.8/ 9.6
Stiffness g-cm	14.8/ 5.0	14.0/ 5.0	15.3/ 6.8	16.5/ 6.0
STFI comp. MD/CD	46.7/ 24.5	21.7/ 44.6	53.6/ 29.6	57.0/ 31.0
MIT Fold MD/CD	-- --	703/ 424	-- --	939/ 559
Mullen	147.3	121.3	191.0	178.0

Example 7

Another sample of commercial kraft linerboard having a kappa number of 110 and Canadian Standard Freeness of 750 mls was sized with 8% solutions of carboxy methyl cellulose (Finn Fix). The size press pressure was adjusted to achieve 0.3 to 1.0% add-on by weight. After heat treatment at 400°F (250°C) for 30 seconds, samples were conditioned for 48 hours under standard conditions. The resultant properties are listed in Table VII.

TABLE VII

Properties	Control NO HT (HT)	FINN FIX (% ON PULP) NO HT (HT) 0.3%	0.6%	1.0%
Basis Weight lb/1000 ft^2	42.7 (42.8)	42.7 (40.4)	43.4 (40.7)	43.8 (41.1)
Caliper (mils)	13.1 (13.4)	14.4 (13.0)	14.9 (12.9)	15.2 (12.9)
Wet Tensile lbs/inch	7.9 (13.8)	7.3 (18.8)	8.2 (15.4)	6.5 (15.4)
Dry Tensile lbs/inch	105.3 (87.7)	84.5 (95.0)	82.9 (89.4)	83.1 (94.9)
Wet Strength % of Dry	7.5 (15.3)	8.6 (19.7)	9.9 (17.2)	7.8 (16.2)
Stiffness g-cm	92.5 (100.5)	110 (90.5)	107.0 (88.0)	113.5 (111.0)
Mullen psi	-- (--)	87.7 (82.0)	106.1 (93.2)	105.8 (90.4)
Compression STFI, lb/inch	-- (--)	31.1 (34.5)	32.0 (36.3)	32.3 (36.8)
MIT Fold	1702 (2064)	1929 (1554)	1711 (1028)	1639 (984)
Tear, gm	-- (--)	510 (422)	427 (451)	416 (390)

Example 8

Board as in Example 7 was sized with 8% solutions of polyvinyl alcohol. The size press pressure was adjusted to achieve the polymer add-on of 0.3 to 1.0% weight. After heat treatment at 400°F (205°C) for 30 seconds, samples were conditioned for 48 hours under standard conditions. The resultant properties are listed in Table VIII.

TABLE VIII

Properties	Control NO HT (HT)	POLYVINYL ALCOHOL (% ON PULP) NO HT (HT) 0.3%	0.6%	1.0%
Basis Weight lb/1000 ft^2	42.7 (42.8)	43.4 (43.5)	43.5 (43.0)	43.5 (42.7)
Caliper (mils)	13.1 (13.4)	14.5 (14.0)	15.0 (13.9)	15.0 (13.4)
Wet Tensile lbs/inch	7.9 (13.8)	7.0 (10.8)	8.7 (19.2)	9.4 (19.6)
Dry Tensile lbs/inch	105.3 (87.7)	84.3 (83.3)	85.0 (89.2)	82.7 (91.8)
Wet Strength % of Dry	7.5 (15.3)	8.3 (13.0)	4.4 (21.5)	11.4 (21.3)
Stiffness g-cm	92.5 (100.5)	113.7 (106.0)	112.0 (96.5)	101.0 (99.0)
Mullen psi	-- (--)	100.9 (89.2)	100.5 (84.8)	100.4 (90.8)
Compression	--	26.8	29.9	27.3
STFI, lb/inch	(--)	(32.3)	(36.5)	(38.9)
MIT Fold	1702 (2064)	1168 (1311)	1737 (1118)	2046 (1142)
Tear, gm	-- (--)	467 (483)	490 (448)	488 (403)

The tables above show clearly that great increases in wet strength, without substantial degradation of other

qualities, are produced by heat treatment of products having certain additives as described above. A rewetting procedure may also be used, particularly when folding endurance is important.

Inasmuch as the invention is subject to many variations and changes in detail the foregoing description and examples should be regarded as illustrative of the invention defined by the following claims.

1. A method of producing a paper product with improved stiffness, wet strength and opacity and with acceptable flexibility thereof comprising the steps of

applying one or more additives selected from the group consisting of milk, latex, polyvinyl alcohol, carboxy methyl cellulose, starch, and protein to said product, and then

heat treating said product at high temperature for a period of time sufficient to increase the wet strength thereof.

2. The method of claim 1, wherein the product has an initial moisture content in the range of 1.0 to 40% by weight before said heat treating step.

3. The method of claim 1 or 2, further comprising a step of rewetting the product immediately after said heat treating step before the product cools substantially.

4. The method of claim 3, wherein the moisture content of said product after rewetting is between 1.0 and 20% by weight.

5. The method of claims 1 to 4, wherein said heat treating step comprises heating said product to within the range of 284 to 482°F (140 to 250°C), for a length of time in the range of 0.5 to 120 seconds.

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

7. The method of claim 6, wherein said carton board has basis weight of about 160 lb/3000 ft^2 (260 g/m^2).

8. A folding carton board of high stiffness and high folding endurance producible with a method according to any of claims 1 to 7.

9. The method of claims 1 to 5, wherein said paper product is a linerboard.

10. The method of claim 9, wherein said linerboard has a basis weight of about 42 lb/1000 ft^2 (205 g/m^2).

11. A linerboard of high wet strength and high folding endurance, producible with a method according to any of claims 1 to 7, 9 or 10.

12. A linerboard as in claim 11, 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.