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(54) **Method for making a multi-ply paperboard**

(57) Methods for improving the internal bond strength of paperboard with greater than 25 percent crosslinked fiber in at least one ply are described.. In the methods, additives are added to the slurry in various com-

binations and order while maintaining the ionic demand of the slurry at less than zero. Paperboard with high ZDT, Scott Bond and Taber Stiffness is obtained.

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**Description**

**[0001]** The present application relates to increasing the bond strength in a multi-ply paperboard that has high crosslinked cellulose fiber present in at least one of the plies.

**[0002]** This invention provides a method for forming a paperboard comprising the steps of forming a slurry of cellulose fibers comprising crosslinked fibers, adding a cationic fixative and mixing with said slurry, adding an anionic starch subsequent to adding said cationic fixative, adding a cationic starch subsequent to adding said anionic starch, wherein, after each addition step, the slurry ionic demand is less than zero, forming a fibrous web layer by withdrawing liquid from said slurry, drying said web to form a paperboard.

**[0003]** Said crosslinked fibers may be present at a level from 25 to 80 percent of the total fiber weight in at least one ply of the paperboard, and preferably are present at a level from 40 to 75 percent of the total dry weight of the fiber weight in at least one ply of the paperboard.

**[0004]** The total starch level may be 50 to 120 lb/ t, preferably 60 to 100 lb/ t and more preferably 80 to 90 lb/ t.

**[0005]** In any of the above methods the cationic starch may be added to the furnish before the anionic starch and the cationic fixative is added after the anionic starch.

**[0006]** A method for forming a paperboard comprising the steps of forming a slurry of cellulose fibers comprising crosslinked fibers, adding a cationic fixative and mixing with said slurry, adding an anionic starch subsequent to adding said cationic fixative, wherein, after each addition step, the slurry ionic demand is less than zero, forming a fibrous web layer by withdrawing liquid from said slurry, drying said web to form a paperboard.

**[0007]** The anionic starch may be added to the slurry before the cationic fixative.

**[0008]** Preferably said crosslinked fibers are present at a level from 25 to 80 percent of the total fiber weight in at least one ply of the paperboard and more specifically are present at a level from 40 to 60 percent of the total dry weight of the fiber weight in at least one ply of the paperboard.

**[0009]** In any of the above methods the total starch level may be 50 to 120 lb/t, more specifically 60 to 100 lb/t, and preferably 80 to 90 lb/t.

**[0010]** The invention still further provides a method for forming a paperboard comprising the steps of forming a slurry of cellulose fibers comprising crosslinked fibers, adding a cationic starch and mixing with said slurry, adding an anionic starch subsequent to adding said cationic fixative, wherein, after each addition step the slurry ionic demand is less than zero, forming a fibrous web layer by withdrawing liquid from said slurry, drying said web to form a paperboard.

**[0011]** Thus the application is directed to improving the internal bond strength of paperboard with greater than 25 percent crosslinked fiber in at least one ply. In the method, additives are added to the slurry in various combinations and order while maintaining the ionic demand of the slurry at less than zero. Paperboard with high ZDT, Scott Bond and Taber Stiffness is obtained.

**[0012]** The following is a description of some specific embodiments of the invention reference being made to the accompanying drawings, in which:

FIGURE 1 shows the effect of various chemical additions on ionic demand of a 3-3.2 percent slurry;

FIGURE 2 shows the effect of chemical addition on ionic demand of mid-ply simulation using polyacrylic acid crosslinked cellulosic fibers;

FIGURE 3 shows the effect of chemical addition on ionic demand of mid-ply simulation using citric acid crosslinked cellulosic fibers.

FIGURE 4 is a schematic representation of the machine chest and additive entry points suitable for carrying out the process in the present application;

FIGURE 5 represents a multi-ply paperboard machine suitable for a multi-ply product;

**[0013]** In single or multi-ply paperboard where the inner plies contain greater than approximately 25 percent crosslinked cellulose fiber the density of the stratum will drop below 0.4 g/cc. As a result, the internal bond strength can drop so low as to not only be well below levels required for converting the paperboard into packaging products but also below the level where conventional methods of increasing the internal strength cannot provide enough increase to meet minimum levels needed for converting. The present application provides a method for increasing the internal bond of low density paperboard back into the range which is useable for converting.

**[0014]** In this application, use of high concentrations of wet end additives have been demonstrated while producing low density paperboard.

**[0015]** A distinguishing characteristic of the present application is that at least one ply of the paperboard, whether a single-ply or a multiple-ply structure, contains crosslinked cellulose fibers and strength enhancing additives such as anionic and cationic starches to offset the board strength lost by adding the crosslinked cellulosic fibers. The crosslinked cellulosic fibers increase the bulk density of the insulating paperboard characteristics of the board. The paperboard also contains chemical pulp fibers. As defined herein chemical pulp fibers useable in the present application are derived

primarily from wood pulp. Suitable wood pulp fibers for use with the application can be obtained from well-known chemical processes such as the kraft and sulfite processes, with or without subsequent bleaching. Softwoods and hardwoods can be used. Details of the selection of wood pulp fibers are well known to those skilled in the art. For example, suitable cellulosic fibers produced from southern pine that are useable in the present application are available from a number of companies including Weyerhaeuser Company under the designations C-Pine, Chinook, CF416, FR416, and NB416. A bleached Kraft Douglas Fir pulp, KKT, Prince Albert Softwood and Grande Prairie Softwood, all manufactured by Weyerhaeuser are examples of northern softwoods that can be used. Mercerized fibers such as HPZ and mercerized flash dried fibers such as HPZ III, both manufactured by Buckeye Technologies, Memphis TN, and Porosinier- J-HP available from Rayonier Performance Fibers Division, Jessup, GA are also suitable for use in the present application when used with crosslinked cellulose fibers. Other non crosslinked cellulose fibers include chemithermomechanical pulp fibers (CTMP), bleached chemithermomechanical pulp fibers (BCTMP), thermomechanical pulp fibers (TMP), refiner ground-wood pulp fibers, groundwood pulp fibers, TMP (thermomechanical pulp) made by Weyerhaeuser, Federal Way, WA, and CTMP (chemi-thermomechanical pulp) obtained from NORPAC, Longview, WA, sold as a CTMP NORPAC Newsprint Grade, jet dried cellulosic fibers and treated jet dried cellulosic fibers manufactured by the Weyerhaeuser Company by the method described in U.S. Application No. 10/923,447 filed August 20, 2004. These fibers are twisted kinked and curled. Additional fibers include flash dried and treated flash dried fibers as described in U.S. 6,837,970,

**[0016]** Suitable crosslinking agents for making crosslinked fibers include carboxylic acid crosslinking agents such as polycarboxylic acids. Polycarboxylic acid crosslinking agents (e.g., citric acid, propane tricarboxylic acid, and butane tetracarboxylic acid) and catalysts are described in U.S. Patent Nos. 3,526,048; 4,820,307; 4,936,865; 4,975,209; and 5,221,285. The use of C<sub>2</sub>-C<sub>9</sub> polycarboxylic acids that contain at least three carboxyl groups (e.g., citric acid and oxydisuccinic acid) as crosslinking agents is described in U.S. Patent Nos. 5,137,537; 5,183,707; 5,190,563; 5,562,740; and 5,873,979.

**[0017]** Polymeric polycarboxylic acids are also suitable crosslinking agents for making crosslinked fibers. These include polymeric polycarboxylic acid crosslinking agents are described in U.S. Patent Nos. 4,391,878; 4,420,368; 4,431,481; 5,049,235; 5,160,789; 5,442,899; 5,698,074; 5,496,476; 5,496,477; 5,728,771; 5,705,475; and 5,981,739. Polyacrylic acid and related copolymers as crosslinking agents are described U.S. Patent Nos. 5,549,791 and 5,998,511. Polymaleic acid crosslinking agents are described in U.S. Patent No. 5,998,511 and U.S. Application Serial No. 09/886,821. CHB405, a citric acid crosslinked cellulose fiber and CHB505, a polyacrylic acid crosslinked cellulose, both commercially available from Weyerhaeuser Company, Federal Way, WA were used in this work.

**[0018]** In single or multi-ply paperboard construction a mixture of wood pulp fibers and crosslinked cellulose fibers are used. In one embodiment the crosslinked cellulosic fibers are present in at least one layer at a level of 25 to 80 percent by total fiber weight of the ply. In another embodiment the crosslinked fibers are present at a level of 40 to 75 percent by total fiber weight of the ply and in yet another embodiment they are present at a level of 50 to 70 percent by total fiber weight of the ply.

**[0019]** Single-ply handsheets designed to simulate the mid-ply of low density multi-ply paperboard were made. A 0.015 percent to 0.035 percent consistency slurry was used in these studies. The handsheet making equipment was a standard 8" x 8" sheet mold modified with an extended headbox so that twice the normal volume of stock was used. This modification was necessary to improve handsheet formation when using materials designed to generate high bulk such as crosslinked cellulosic fibers. Fiber weights are expressed as a weight percent of the total fiber dry weight; additives are based on weight of dry fiber.

**[0020]** A series of handsheets were made using different levels of wet-end additives and different addition order to demonstrate the level of internal bond strength that could be generated by starch loading the web. The additives were added to the slurry in the order across each sample row and the slurry stirred after each addition. Avebe® AP25, an anionic starch, was obtained from Carolina Starches, North Charleston, SC, Stay-Lok®300 and Stay-Lok®330, both cationic starches, were obtained from A.E. Staley, a subsidiary of Tate and Lyle, Decatur, IL Kymene® was obtained from Hercules, Wilmington DE and RediBOND® 3050 from National Starch, Indianapolis IN. Each handsheet was then coated with Polyvinyl Alcohol (PVA) coating, Celvol V24203 supplied by Celanese Ltd., Houston, TX. The total coat weight was about 50 g/m<sup>2</sup> and was divided equally to each side of the sheet. The coating was added to the surface to facilitate testing Z-direction tensile (ZDT) and Internal Scott Bond, because low density structures without the coating tended to separate at the tape instead of the within the sheet. Each sheet was evaluated for several physical properties including Basis weight, ZDT, Internal Scott Bond and Taber Stiffness (15°). Table I below shows the results for these key characteristics.

55 50 45 40 35 30 25 20 15 10 5

Table I Handsheet formulation and addition order

Sample No.	Target BW, g/m <sup>2</sup>	CHB405, wt. %	D.Fir, wt. %	Avebe® AP25*, #/t	Sta-Loc® 300, #/t	Kymene®, #/t	Sta-Loc®® 300, #/t	Aquapel®, #/t	Basis Wt., g/m <sup>2</sup>	Density, g/cm <sup>3</sup>	ZDT, kPa	Scott Bond, J/m <sup>2</sup>	Taber Stiffness, g cm
1	250	60	40	0	0	5	25	4	301	0.264	40	67	364
2	250	60	40	40	20	5	20	4	306	0.262	85	113	433
3	250	60	40	80	20	10	10	4	305	0.273	204	119	403
D. Fir, Douglas Fir													

**[0021]** ZDT (Z-direction tensile) strength was determined by TAPPI method T 541 om-05, Scott Bond strength was determined by TAPPI 569 om-00 and Taber Stiffness by TAPPI T 489 om-04.

**[0022]** Sample 1 is a fiber formulation designed to deliver low density paper and uses conventional wet chemistry. The result is a very low ZDT and Scott bond. Samples 2 shows that by adding 4% total starch to the furnish, the ZDT and Scott Bond essentially double. Samples 3 shows that when the amount of anionic starch is doubled, the cationic starch remains constant and Kymeme® 557H, a higher ionic demand cationic polymer (+ 2.2 meq /g) than the cationic starch, (+0.3 meq/g, Table III), is used to balance the additional anionic charge, the result is a further increase in internal bond, increasing ZDT by 500% over the control; Scott Bond is nearly doubled.

**[0023]** The data show that anionic starch in combination with a cationic fixative allows for effective retention of starch in the wet end. As defined herein, a fixative is a charged polymer that ionically bonds to a molecule of the opposite charge by an ionic bond. Examples of fixatives include, but are not limited to cationic starch, polyamines, polyaluminum chloride® (PAC), poly DADMAC (polydiallyldimethylammonium chloride), EPEDMA, Kymene®, PAAE (polyamidoamine-epichlorohydrin), PASS (polyaluminiumsilicasulate), PEI (polyethyleneimine), and cationic polyacrylamide.

**[0024]** In one embodiment a cationic fixative is added to the slurry followed by addition of an anionic starch and then followed by addition of a cationic starch. In each case, after addition of the additive, the ionic demand of the slurry is less than zero. In another embodiment the cationic starch is added to the slurry before the anionic starch and the cationic fixative is added after the anionic starch. In yet another embodiment a cationic fixative is added to the slurry and the anionic starch is added to the slurry subsequent to addition of the cationic fixative. In each case, after addition of the additive, the ionic demand of the slurry is less than zero. In a further embodiment the anionic starch is added to the slurry before addition of the cationic fixative, in each case, after addition of the starch or fixative, the ionic demand of the slurry is less than zero. A combination of anionic and cationic starches can also be used. In one embodiment a cationic starch is added to the slurry followed by addition of an anionic starch, in each case, after addition of the starch, the ionic demand of the slurry is less than zero. In yet another embodiment the anionic starch is added to the slurry followed by addition of the cationic starch. After addition of the starch the ionic demand of the slurry is less than zero..

**[0025]** In one embodiment Kymene® is added at a level of from 2.5 lb /t to 20 lb/t. In another embodiment it is added at a level of 5 lb/t to 15 lb/t and in yet another embodiment it is added at a level of 8 lb/t to 10 lb/t.

**[0026]** In general the impact of the starch loading on taber stiffness at 15° bend is small. For single ply handsheets this is reasonable because caliper is the dominate variable effecting bending stiffness. The impact of the starch loading on density is small enough that the increase in elastic modulus of the sheets due to the starch loading compensates for the small changes in caliper. In a multi-ply web the same response is expected.

#### Comparison of different anionic and cationic starches

**[0027]** Table II shows the basic formulations and conditions used in making handsheets in this study.

Table II. Handsheet Formulation, Addition Order and Sheet Properties

Sample No.	Basis Wt., g/m <sup>2</sup>	CHB505 wt. %	Douglas Fir, wt. %	Aniofax®, AP25, #/t	Redibond ® 3050 #/t	Sta-Lok® 300, #/t	Sta-Lok® 330 #/t	Basis Wt., g/m <sup>2</sup>	Density, g/m <sup>2</sup>	ZDT, kPa	Scott Bond, J/m <sup>2</sup>	Taber Stiffness, g cm
4	250	60	40	0	0	20	0	302	0.258	36	96	334
5	250	60	40	40	0	20	0	303	0.263	60	89	325
6	250	60	40	0	40	20	0	307	0.254	53	100	351
7	250	60	40	80	0	40	0	307	0.263	84	93	378
8	250	60	40	0	80	40	0	310	0.264	72	110	350
9	250	60	40	40	0	0	20	308	0.257	57	102	368
10	250	60	40	0	40	0	20	311	0.247	51	111	378

All samples had 5 lb/t Kymene® added before the anionic starch addition and 4.5 lb/t Aquapel® added after the cationic starch, Sta-Loc®330, addition.

**[0028]** In these studies both the addition level of anionic and cationic starches was changed as well as the ionic demand of the starch. Ionic demand refers to the number of charges (both positive or negative) needed to bring the net charge of a given volume of furnish to zero. Cationic demand refers to the quantity of cationic charges needed to bring the sample to a net zero charge. A sample with a cationic demand is net anionic. Anionic demand refers to the quantity of anionic charges needed to bring the sample to net zero charge. A sample with an anionic demand is net cationic.

**[0029]** Aniofax® AP25 (-0.25 meq/ g ionic demand) was exchanged with Hercules RediBOND® 3050 which has a lower ionic demand of ~ -0.19 meq/g . Further the Sta-Loc® 300, with an ionic demand of +0.30 meq/g was exchanged for Sta-Lok® 330 having an ionic demand of about +0.41 meq/g. The results shown in Table II indicate that an equal mass of the RediBOND® 3050 as Aniofax® AP25 results in about 10% lower ZDT. This decrease is believed to be due to the lower charge contribution of the RediBOND® 3050 resulting in a lower retention of the subsequent addition of the starch. However, the Scott Bond and Taber Stiffness development are approximately equivalent (Sample no. 5 vs. 6, 7 vs. 8 and 9 vs. 10).

Ionic Demand Balance

**[0030]** The technology relies on the ability to balance the ionic demand in the wet end of the paper machine such that 1) anionic polymeric materials can be retained on the fibers and fines without excess remaining in the water system, 2) the fibers and system do not pass through the zero charge point which destabilizes retention and drainage 3) since pulp fibers are anionic, some cationic material can be added, however, adding too much cationic material without balancing the excess anionic demand will either cause the fibers to flocculate reducing formation and/or cause the drainage to drop, impacting the runnability.

**[0031]** Each of the components used in the paperboard containing crosslinked fiber in this disclosure has a specific charge density typically measured by ionic demand titration. A Mutek PCD - Titrator was used for the particle charge titration coupled with the PCD 02 Particle Charge Detector for measuring the ionic demand of the component or fiber furnish. The method was performed according to a procedure from A.E. Staley Manufacturing, a subsidiary of Tate and Lyle, Decatur, IL The method is as follows.

1. Turn the Mutek on using the power switch on the back of the instrument.
2. Place 10 mL of a well mixed sample in the sample vessel. Insert the plunger and washer into the vessel. The sample consistency should be no more than 0.83. Thick stock samples should be diluted.
3. With the instrument turned on, the plunger should move up and down and a mV potential should be displayed. The sign of the potential (+ or -) indicates whether the sample is cationic (+) or anionic.(-).
4. Titrate the sample with the appropriate titrant until the mV potential reads 0 mV (PolyDADMAC is the cationic polymer and is used to titrate anionic samples; PVSK or PESNa are the anionic polymers used to titrate the cationic samples). A buret or syringe can be used to deliver the titrant to the sample. Titration should not be conducted with no more than 4 mL of titrant since higher volumes will give inaccurate measurements. If the sample requires more than 4 mL of titrant, the sample should be diluted or more concentrated titrant should be used.
5. Record the amount of titrant used to titrate the sample. To calculate the demand of the system, use the following equation:

$$\text{“Ionic Demand” (ueq/L)} = (\text{mL titrant}) \times (\% \text{ titrant dilution}) \times (\text{sample dilution})$$

**[0032]** Specific components whose ionic demand were measured by the Mutek method are noted in Table III, other component values are from suppliers.

Table III Ionic Demand Of Specific Components

Component	Ionic Demand, meq/g
Fully Bleached Softwood Pulp (a)	-0.015, total (a)
Fully Bleached Softwood Pulp*	-0.0015, available (a)
CHB505	-0.63, total (a)
CHB505	-0.017, available (a)
CHB 405	-0.43 total (a)

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(continued)

Component	Ionic Demand, meq/g
CHB405	-0.015, available (a)
Kymene ®577H	+2.2
Hercobond® 2000	-1.8
Sta-Loc 300	+0.3
RediBOND®3050 (HRB®3050)	-0.19
Aniofax AP25	-0.25
Sta-Lok ®®330	+0.41
PSM -Particol®BX	-
Aquapel®650	0
(a) determined by Mutek method; other values were obtained from suppliers.	

**[0033]** With reference to the table, the difference between the total and available ionic demand represents the amount of charge that is internal to the fiber that is not accessible to polymers of molecular weight above 300,000 g/mole. For papermaking, the available ionic demand is more representative of the results obtained in practice than the total ionic demand.

**[0034]** The situation is further complicated in a paper machine wet-end where dilution water from outside sources and/or wash water from pulp mill bleaching stages contain ionic materials, ( both dissolved and dispersed), is used to control consistency of the pulp slurry. In integrated mills where excess ionic materials are present, materials added to the pulp slurry to increase internal bond strength can be consumed by the excess ionic materials. Also, the available ionic sites on pulp will also depend on how much refining has been done and on the basic fiber morphology, i.e. the smaller the fiber or partial fiber the higher available surface area, and therefore the higher available ionic demand.

**[0035]** In general it may be stated that the fiber slurry is anionic to start with and should remain anionic through the paper making process i.e. the ionic demand of the slurry should less than zero.

Calculated Balance

**[0036]** For the purpose of this work the ionic demand for formulations listed in Tables I and II were calculated using the ionic demand values in Table III and the ionic material in the slurry, other than the materials listed, was ignored.

**[0037]** The addition order of ionic additives and the amount should dictate the ionic demand of the stock furnish at any time during the forming process. For these experiments the estimated ionic demand is shown in Tables IV and V.

Table IV. Calculated Cumulative Ionic Demand Of The Slurry At Each Addition Step In Table I

Sample No	CHB405 (ueq/kg)	D. Fir (ueq/kg)	Pulp Stock (ueq/kg)	Anionic Starch Avebe Aniofax® AP25 (ueq/kg)	Cationic Starch Sta-Lok® 300 (ueq/kg)	Anionic Starch Avebe Aniofax® AP25 (ueq/kg)	Kymene® 557H (ueq/kg)	Cationic Starch Sta-Lok® 300 (ueq/kg)	Aquapel® 650 (ueq/kg)	At forming (ueq/kg)
1	-9000	-600	-9600				-4100 5500	-350 3750	-4350	-350
2	-9000	-600	-9600	-15600 -5000	-11600 3000		-6100 5500	-3100 3000	-3100	-3100
3	-9000	-600	-9600	-19600 -10000	-16600 3000		-5600 11000	-3600 1500	-3600	-3600
<p><b>Note:</b> All additions are on an oven dry basis. The second entry in a cell is the ionic demand contribution by the component</p>										

Table V. Calculated Cumulative Ionic Demand Of The Slurry At Each Addition Step In Table II

Sample No	CHB50 5 ueq/kg	D. Fir ueq/kg	Pulp Stock ueq/kg	Kymene® ueq/kg	Avebe Aniofax® AP25 ueq/kg	Hercules RediBOND® ueq/kg	Starch Sta- Lok® 300 ueq/kg	Starch Sta- Lok® 330 ueq/kg	Aquapel® 650 ueq/kg	At forming ueq/kg
4	-10200	-600	-10800	-5300 5500			-2300 3000		-2300	-2300
5	-10200	-600	-10800	-5300 5500	-10300 -5000		-7300 3000		-7300	-7300
6	-10200	-600	-10800	-5300 5500		-9100 -3800	-6100 3000		-6100	-6100
7	-10200	-600	-10800	-5300 5500	-15300 -10000		-9300 6000		-9300	-9300
8	-10200	-600	-10800	-5300 5500		-12900 -7600	-6900 6000		-6900	-6900
9	-10200	-600	-10800	-5300 5500	-10300 -5000			-6200 4100	-6200	-6200
10	-10200	-600	-10800	-5300 5500		-9100 -3800		-5000 4100	-5000	-5000
Note: 1 kg of oven dry furnish was used as the basis. The second entry in a cell is the ionic contribution by the component										

Table VI. Measured Ionic Demand Of Mid-Ply Stock After Various Chemical Additions

Sample	Crosslink Fiber, (%)	D. Fir (%)	Kymene® (#/t)	HRB® 3050, (lb/t)	Starch Sta- Lok® 300 (lb/t)	Aquapel® 650, (%)	HRB® 3050, (lb/t)	Pulp Stock ueq/mL	Kymene® ueq/mL	HRB® 3050, ueq/m , L	Starch Stalok® 300 ueq/mL	Aquapel® 650 ueq/mL	HRB ® 3050 ueq/m L	PMA Particol BX ueq/mL	At Forming ueq/mL
11	60	40	4.5		15	4.5		-305	-121		-68	-68			-68
12	60	40	9		60	4.5	40	-124	-40		385	385	195		195
13	60	40	9	40	60	4.5		-154	0	-359	-29	-29			-29
14	60	40	9		27	4.5	40	-120	-43		167	167	-33		-33
15	60	40	9	40	27	4.5		-150	-17	-325	-27	-27			-27
16	60	40	9	40	27	4.5		-191	-40	-298	-211	-211		-191	-191
11	60	40	4.5		15	4.5		-180	-118		0	0			0
11	60	40	4.5		15	4.5		-157	-83		-28	-28			-28
15	60	40	9	40	27	4.5		-208	-22	-453	-412	-412			-412
15	60	40	9	40	27	4.5		-168	-19	-444	-222	-222			-222
16	60	40	9	40	27	4.5		-139	-49	-417	-249	-249		-222	-249
16	60	40	9	40	27	4.5		-160	-34	-563	-133	-133			-356
17	60	40	4.5		15	4.5		-224	-153		-72	-72			-72
17	60	40	4.5		15	4.5		-269	-165		-70				-70
18	60	40	9	40	27	4.5		-351	-28	-542	-268	-268			-268
18	60	40	9	40	27	4.5		-286	-45	-504	-241	-241			-241
19	60	40	9	40	27	4.5		-297	-24	-468	-209	-209		-249	-249
19	60	40	9	40	27	4.5		-257	-34	-496	-223	-223		-271	-271

**[0038]** Table VI represents the measured amount of ionic demand of similar combinations of additives at a 0.5 percent slurry consistency using mill white water for dilution.

**[0039]** In the cases where the cationic material was all added prior to the additional anionic starch the ionic demand of the system crossed zero charge point, Table VI, 12 and 14 and Figure 1. This is known to destabilize fines retention and impacts flocculation and drainage in the wet end of the machine, potentially resulting in a loss in ZDT. In Figure 1, the addition points are as follows: A is pulp stock furnish, B is Kymene® addition, C is Hercules RediBOND® 3050 addition for 13, 1 and 16 and Sta-Loc®300 for 12 and 14 and D is Hercules RediBOND® addition. Samples 11-16 were made with CHB405 and samples 17-19 were made with CHB505. Sample 16 and 19 each had 0.5 lb/t PSM Particol®BX added after the addition of HRB®3050. Comparing samples made with CHB405, (citric acid crosslinked fibers) with CHB505 (polyacrylic acid crosslinked fibers), Table V1, 15 and 16 vs 18 and 19, Figures 2 and 3 indicates there is a small difference in ionic demand between the two crosslinked cellulose fibers grades. The net result is no specific impact on the number of available sites for retaining binding materials. This is supported by the fact that adding the same amount of Kymene® produces the same ionic demand.

**[0040]** A single or multi-ply board can be made using a 3-3.2 percent slurry consistency of a 50/50 dry weight ratio of a crosslinked fiber such as polyacrylic acid crosslinked fiber, (CHB505), and Douglas Fir fiber. Slurry consistencies from 0.05 percent to 4 percent can also be used in preparing the paperboard. The term "consistency" means the percent solids content of a solid and liquid mixture, for example, a two percent consistency means there are two grams of cellulose fibers in one hundred grams of fiber and liquid. Dry weight as defined herein means representative fibers are dried at 105°C±2°C and weighed at one hour increments until a constant weight is obtained. In practice, the moisture content of the commercial grade fibers is approximately 9 percent. The Douglas Fir can be refined to 500 CSF or lower prior to addition to the machine chest. A standard 4 mm barrier screen can be used before the headbox. Addition points of the various additives such as Kymene®, anionic and cationic starch are shown in Figure 4. The paperboard formed can have a basis weight of 200 to 500 g/m<sup>2</sup> with surface plies of 15- 25 percent by dry weight each of the total fiber and the center ply at 50-70 percent of the total fiber dry weight. In one embodiment a single ply paperboard is made. In another embodiment a paperboard with at least two plies is made. Crosslinked cellulose fiber can be in both plies or in only one. In yet another embodiment a paperboard can be made with three plies. The plies may all be the same, all different or there can be combination of the various plies.

**[0041]** Starch and other additives can be added at the locations shown in Figure 4.

**[0042]** Surface plies can be formed separately from the mid-ply using conventional Fourdrinier technology with stock consistency ~0.6 percent, as shown in Figure 5.

**[0043]** The mid-ply can be formed using Beloit top former directly on the bottom-ply on the Fourdrinier table. Dewatering can be accomplished by a top wire drainage unit.

**[0044]** The top ply can be combined with the bottom and middle plies via a pick-up roll. The combined web can subsequently be processed by typical paper machine unit operations, wet pressing with conventional felted wet presses, steam can drying, size press where ~2 to 2.5 percent starch based on dry weight fiber can be applied to the web, followed by steam can drying to 6.5 percent moisture, wet calendering, dry calendering and winding.

## Claims

1. A method for forming a paperboard comprising the steps of:

forming a slurry of cellulose fibers comprising crosslinked fibers;  
 adding a cationic fixative and mixing with said slurry;  
 adding an anionic starch subsequent to adding said cationic fixative;  
 adding a cationic starch subsequent to adding said anionic starch;

wherein, after each addition step, the slurry ionic demand is less than zero;  
 forming a fibrous web layer by withdrawing liquid from said slurry;  
 drying said web to form a paperboard.

2. A method as claimed in Claim 1, wherein said crosslinked fibers are present at a level from 25 to 80 percent of the total fiber weight in at least one ply of the paperboard.

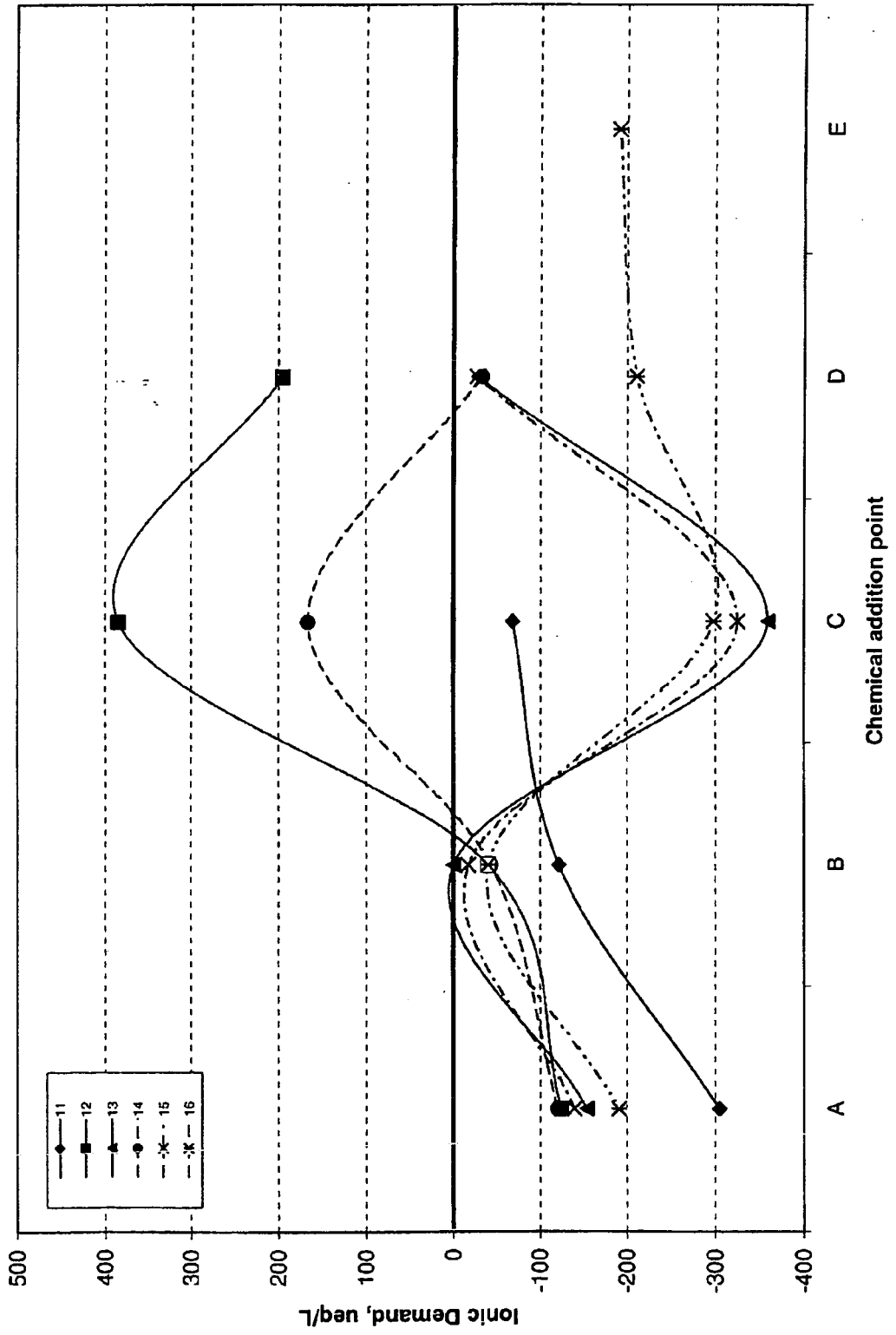
3. A method as claimed in Claim 2, wherein the crosslinked fibers are present at a level from 40 to 75 percent of the total dry weight of the fiber weight in at least one ply of the paperboard.

4. A method as claimed in any of Claims 1 to 3, wherein the total starch level is 50 to 120 lb/t.

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5. A method as claimed in Claim 4, wherein the total starch level is 60 to 100 lb/t.
6. A method as claimed in Claim 5, wherein the total starch level is 80 to 90 lb/ t.
- 5 7. A method as claimed in any of Claims 1 to 6, wherein the cationic starch is added to the furnish before the anionic starch and the cationic fixative is added after the anionic starch.
8. A method for forming a paperboard comprising the steps of:
- 10 forming a slurry of cellulose fibers comprising crosslinked fibers;  
adding a cationic fixative and mixing with said slurry;  
adding an anionic starch subsequent to adding said cationic fixative;
- 15 wherein, after each addition step, the slurry ionic demand is less than zero;  
forming a fibrous web layer by withdrawing liquid from said slurry;  
drying said web to form a paperboard.
9. A method as claimed in Claim 8, wherein the anionic starch is added to the slurry before the cationic fixative.
- 20 10. A method as claimed in Claim 8 or Claim 9, wherein said crosslinked fibers are present at a level from 25 to 80 percent of the total fiber weight in at least one ply of the paperboard.
11. A method as claimed in any of Claims 8 to 10, wherein the crosslinked fibers are present at a level from 40 to 60 percent of the total dry weight of the fiber weight in at least one ply of the paperboard.
- 25 12. A method as claimed in any of Claims 8 to 11, wherein the total starch level is 50 to 120 lb/t.
13. A method as claimed in Claim 12, wherein the total starch level is 60 to 100 lb/t.
- 30 14. A method as claimed in Claim 13, wherein the total starch level is 80 to 90 lb/t.
15. A method for forming a paperboard comprising the steps of:
- 35 forming a slurry of cellulose fibers comprising crosslinked fibers;  
adding a cationic starch and mixing with said slurry;  
adding an anionic starch subsequent to adding said cationic fixative;
- 40 wherein, after each addition step the slurry ionic demand is less than zero;  
forming a fibrous web layer by withdrawing liquid from said slurry;  
drying said web to form a paperboard.
16. A method as claimed in Claim 15, wherein the anionic starch is added to the slurry before the cationic fixative.
17. A method as claimed in Claim 15 or Claim 16, wherein said crosslinked fibers are present at a level from 25 to 80 percent of the total fiber weight in at least one ply of the paperboard.
- 45 18. A method as claimed in any of Claims 15 to 17, wherein the crosslinked fibers are present at a level from 40 to 60 percent of the total dry weight of the fiber weight in at least one ply of the paperboard.
- 50 19. A method as claimed in any of Claims 15 to 18, wherein the total starch level is 50 to 120 lb/ t.
20. A method as claimed in Claim 19, wherein the total starch level is 60 to 100 16/ t.
21. A method as claimed in Claim 20, wherein the total starch level is 80 to 90 lb/ t.
- 55

Figure 1. Effect of Wet-End Chemical addition on Ionic Demand of Thick Stock (3 to 3.2% slurry)



**Figure 2. Effect of Chemical Addition on Ionic Demand**  
**Mid-ply simulation Using CHB405**

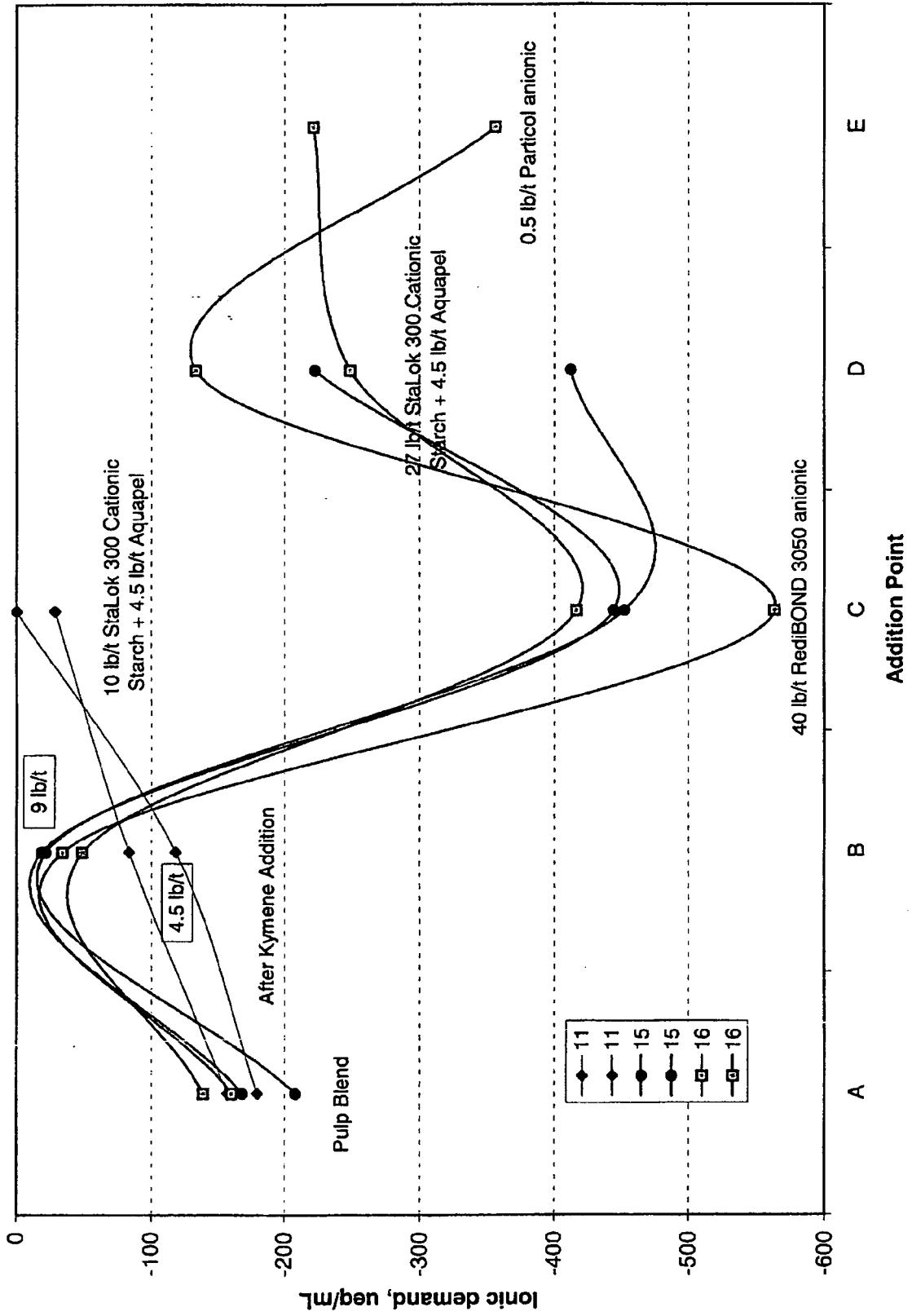


Figure 3. Effect of Chemical Addition on Ionic Demand  
Mid-ply Simulation Using CHB505

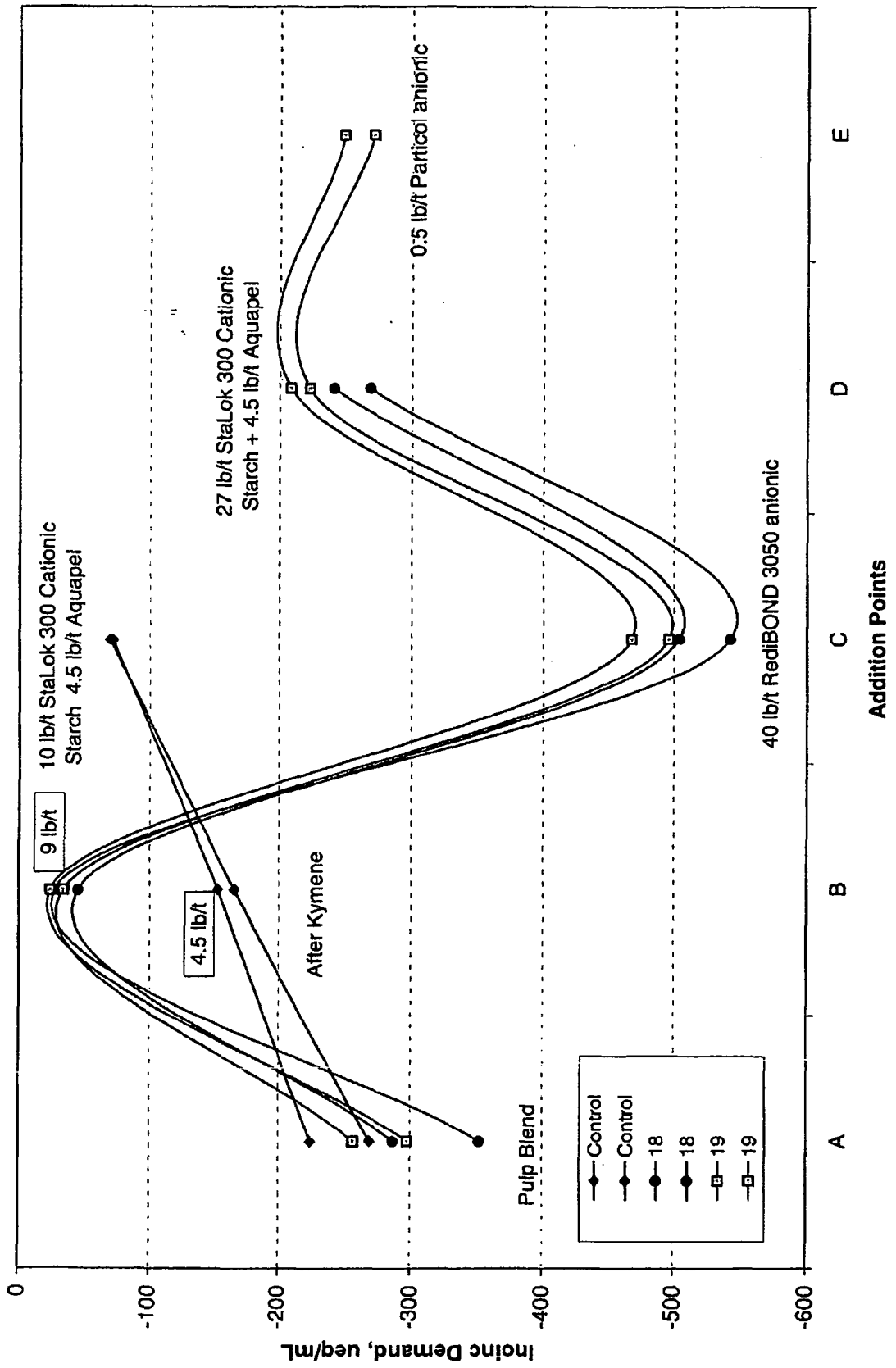
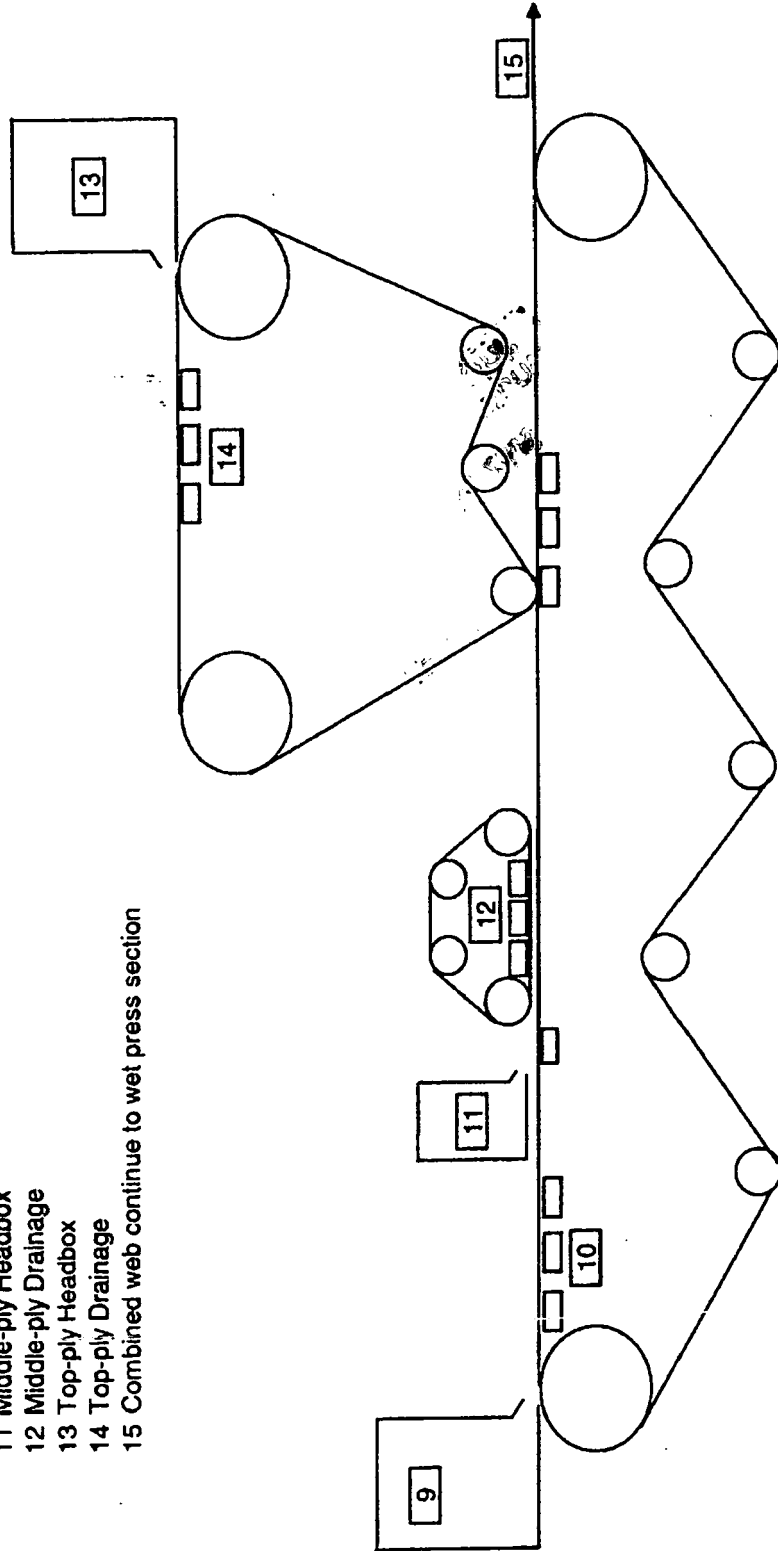




FIGURE 5. Multi-ply Paperboard Machine

- 9 Bottom-ply Headbox
- 10 Bottom-ply Drainage
- 11 Middle-ply Headbox
- 12 Middle-ply Drainage
- 13 Top-ply Headbox
- 14 Top-ply Drainage
- 15 Combined web continue to wet press section



**REFERENCES CITED IN THE DESCRIPTION**

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