

UNITED STATES PATENT OFFICE

2,454,532

PROCESS FOR DEFIBERING LIGNOCELLULOSE WHILE SUBJECTED TO STEAM AND A DIGESTIVE CHEMICAL

Henry E. Walter, Cloquet, Minn., assignor to
Wood Conversion Company, Cloquet, Minn., a
corporation of Delaware

No Drawing. Application August 3, 1940,
Serial No. 351,239

9 Claims. (Cl. 92—6)

1

The present invention relates to the production of fiber from lignocellulose materials, and more particularly from wood, generally in a gaseous environment having moisture or water vapor, and particularly in steam, and in the presence of a chemical active upon the substance of the lignocellulose.

Heretofore, it has been proposed to reduce wood, straw, cane, bagasse, grasses and the like to fiber mechanically in the absence of suspending water. This has been effected by rotary means at elevated temperatures of 212° F. and over, in an environment of gas, particularly steam in a pressure chamber, employing the temperature to soften the ligneous content of the raw material to ease the mechanical process. Such procedure is offered as a substitute for wet grinding processes and for chemical cooking processes. One aim of the process has been to operate quickly upon the raw material, in a period of 40 seconds more or less, to minimize or avoid incidental chemical action upon the material or incidental change in the material. Such a process and a machine therefore are described in the U. S. Asplund Patents No. 2,008,892 and No. 2,145,851. Auxiliary to these is a third U. S. Asplund Patent No. 2,047,170, relating to carrying out the process in the presence of fusible sizing agents such as rosin, wax, and the like to size the resulting fibers.

Such prior art procedure and its products have been studied, and it has been determined that the product is of a predetermined character because of chemical action induced by the heat from said conditions of operation, involving the natural constituents of the lignocellulose. In detail, these reactions and the effects thereof are complex, but in general it may be stated that they are effected in an acid medium and produce more acid, all resulting from the natural constituents of the lignocellulose material. Acid with and without heat in general has an embrittling effect upon lignocellulose and cellulose. Accordingly, the said steam defibering process produces a product which is the result in part at least, of an acid condition at high temperature.

The general object of the present invention is to employ one or more chemical agents in such a defibering process, which is effective to alter the conditions whereby a different fiber product results.

An object of the present invention is to add one or more chemical reagents with the lignocellulose or prior to completion of its defibration, which chemical material alters the acid condition present in the substance of, and resulting from, the lignocellulose, and which imposes new controlling conditions. The reagents may act not only to generate more acidity, but to buffer the acidity, or to neutralize it in whole or in part, or to provide an alkaline condition.

2

A further object of the invention is to add an agent in quantity and character according to the results desired, whereby a wide variety of fiber products of varying utilities, may be obtained.

A particular object of the invention is to employ a reagent which provides in the presence of lignocellulose a supply of base to neutralize acidity of, or resulting from, the lignocellulose in the mechanical defibering process, or in the mechanical defibering process in the presence of the agent.

A further object of the invention is to employ alkaline reacting substances in amount from 15 more to less than sufficient to bring the discharged fibers to a neutral condition.

Still another object of the invention is to employ a chemical which modifies the lignocellulose.

Still another object is to employ a chemical 20 having a reducing power, or an oxidizing power.

A further object of the invention is to employ a chemical combining several functions, such as carrying a reserve of alkali, being an agent to modify lignocellulose, and being a reagent with 25 reducing power.

The fiber from such a process as that of Asplund is useful in many directions. It may be dried directly as discharged, and used for thermal or sound insulation, or as a raw material for 30 fractionation for special-purpose fibers. The moist fiber as discharged may be felted to mats directly, with or without adhesives or other added agents. The moist fiber as discharged may be taken up in water or chemical treating solutions 35 for further modifying the properties, or for various uses. In water for example, the fiber may be refined or hydrated for forming board or paper by wet-felting processes.

The character of the mechanically produced 40 fiber for these various uses greatly influences the processing of the fiber and the products thereof. For improvements in the processing and in the products, an alteration of the fiber during its production may be made by the present invention.

It is, therefore, a general object of the invention, by adding chemicals, chemically to alter 45 lignocellulose material while reducing it to fiber in a gaseous environment including moisture or water vapor at from normal to elevated temperature of 212° F. or higher. 50

Various other and ancillary objects and advantages of the invention will become apparent from the following description and explanation of the invention.

55 In carrying out the invention, it is to be understood that the mechanical defibering action reduces the wood or other material quickly to fibrous condition and simultaneously mixes the material and fiber with any other material present. The amount of water present may only 60

be that entering with green wood, or the equivalent in dry wood with added water, or the equivalent of green wood with added water in quantity controlled to avoid suspending the fibers, and preferably to avoid highly soaking the fibers, whereby to discharge fiber from which water may not be squeezed. The water present may be in part derived by adding a solution of a chemical. Solid chemicals or a solution, may be added separately from the lignocellulose, or mixed with the lignocellulose being introduced to the defibering machine.

The foregoing limitation in the quantity of water present makes in effect a strong solution of any solid chemical added, and an inappreciable dilution of any chemical solution added. Thus, a small amount of chemical may be efficiently used to act upon the lignocellulose. There is no part of the chemical not in contact with the lignocellulose as is the case where chips are suspended in cooking liquors. There is no time required for cooking liquor to penetrate the wood substance to exert its effect. There are no effective over-action of some material, as at the surface of chips, and under-action as at the center of chips. All the substance of the wood is exposed to the action of the chemical by the mechanical defibering means. These function to exert tremendous pressures on the material, which if softened, as by steam, is quickly mixed with chemical. In the Asplund machine having disks, as the fiber leaves the disks, it is exposed to the high temperature, to the chemical distributed on it, and to the moist gaseous environment, whereby chemical effects on the substance are favored. The time for which this may occur in any particular machine, may be controlled by the rate of operations in feeding and discharging.

The Asplund machine in particular permits chemicals as solids or solutions to be fed into the preheating magazine of the machine with the wood or other lignocellulose, which is highly compressed into a pressure-sealing plug. On entering the magazine the material is immediately exposed to the high temperature therein, and becomes heated as it is advanced by mechanical means toward the defibering disks. The time in the preheater until defibered, is of the order of less than one minute. In cases where strong chemicals, such as solid caustic soda fed in with wood chips, produces an undesirable reaction prior to defibering, this effect may be avoided. In any case, the chemical may be introduced as a separate ingredient, either as a solid or in solution, to the material at least prior to completion of defibration, and permissibly after the beginning of defibration. In the Asplund machine having one rotary plate and one stationary plate, the latter may be used with openings for such introduction. Feeding means for chemical may be carried into the machine to discharge chemical onto the lignocellulose material in the defibering zone. However, as a matter of fact, it has not been found to be an absolute necessity to avoid feeding caustic soda as solid, or as a 50% solution, mixed with wood chips, into the Asplund machine.

DIGESTING CHEMICALS

Practically all favorable cooking processes for wood are alkaline, or neutral with a high content of salt of weak acid and strong base, or are acid with acid-salts of weak acids and strong base. Alkaline processes are represented by the soda process, and the sulfate process including

several modifications. Neutral type processes are represented by the sodium inonosulfite base processes, which are more favorable when slightly alkaline with sodium carbonates. Acid processes are represented by the acid-sulfite salts of sodium, calcium or magnesium, and more rarely ammonium.

All of the above types provide available base for neutralizing the natural acid character of wood and other lignocellulose. This is even true in the case of the normal and acid sulfite salts. In such cases, the sulfite radical becomes available for combination with lignin of the lignocellulose, leaving the basic elements of the salts as available alkali equivalent for neutralizing acidity of the substance, as present or developed. The salts such as carbonates of magnesium, alkali, metals and alkaline-earth meals, likewise provide available alkali equivalent for neutralizing acidity in the lignocellulose material.

One advantage of the present invention is the facility for quickly securing fiber having been treated with small, rather than large, amounts of chemical. In a water suspension of lignocellulose to secure a result from small amounts of chemical, it is necessary to suspend formed fiber, or chips or the like not yet defibered. The relative proportion of water to lignocellulose is so much higher than in the present invention, that the small amount of chemical is in very dilute solution. In the case of chips, the chemical will be expended first and largely on the outer portions of the chips, producing non-uniform results. That is one reason why, heretofore, strong chemical solutions have been required, accompanied by action in pressure digesters. In the case of fibers in suspension in dilute solution, the fibers must have been produced, and soluble material in the lignocellulose will enter the solution. Obviously, it is an advantage of the present invention that the fibers are produced in the presence of the chemical and small amounts of water, with preservation in the fiber of substantially all the solid content of the original cellulosic raw material. The invention therefore provides a process for securing substantially maximum benefits from both small and large amounts of chemical agents without extracting material from the lignocellulose, and with very uniform results from fiber to fiber.

The retention of water extractable material in the fiber is an economic advantage avoiding waste in raw material, where the fiber is used without an extracting aqueous treatment. It is an economic advantage in eliminating equipment, and operations. Also, the retention of water-extractable material in the fiber, including solubles resulting particularly from the chemical treatment, gives a first type of new fiber with extractable solubles, which solubles may be removed as a useful byproduct, leaving a second type of new fiber. These two types of new fiber may be used as raw material for structures, or for additional chemical processing, or for felting from water suspension, without, or with varying degrees of refinement or hydration.

MIXTURES OF CHEMICALS

The present invention is not limited to use of one chemical at a time. Several may be mixed. Thus, sodium monosulfite may be mixed with sodium carbonate, or sodium bicarbonate, or both, or with sodium hydroxide, or with sodium hydroxide and a sodium carbonate. Caustic soda and calcium oxide or hydroxide may be mixed. Borax

may be mixed with boric acid, or sodium monosulfite. Various other combinations may be used. Some combinations may be used wherein the several chemicals may interact, yet produce effective products. Thus, sodium bisulfite may be mixed with a sodium carbonate, every 2 moles of sodium bisulfite lost, producing one mole of sodium monosulfite.

INERT ADDITION AGENTS

The use of chemical agents active on the lignocellulose does not bar the use of non-active agents. The chemical agents have been used simultaneously with added substance such as: suspensions of rubber, rubber latex, asphalt, wax, protein, sodium pentachlorophenol, fireproofing agents, sodium silicofluoride, rosin, and many others. These substantially inert agents may be employed to add certain preservative or resistant properties to the fiber, or to size them. Such additions are more particularly useful in the cases where the discharged fiber is used directly without a water extraction. However, where such addition agents are not water soluble, the fiber may be subjected to a water treatment. For example, asphalt-treated fibers may be hydrated and formed into board as disclosed in Heritage Serial No. 334,761, filed May 13, 1940, now Patent No. 2,402,160. The use of rubber dispersions and latex is described in Heritage Serial No. 336,577, filed May 22, 1940, now Patent No. 2,375,414. The use of proofing agents for mold and decay, such as pentachlorophenol, is described in Heritage Serial No. 345,610, filed July 15, 1940, now abandoned. The use of fireproofing agents is described in Heritage-Walter Serial No. 332,682, filed May 1, 1940, now abandoned, and Serial No. 332,683, filed May 1, 1940, now abandoned.

In some circumstances the inert agent and the chemical agent may be combined for some convenience or advantage, the combination being subject to effective action as a chemical, by the presence of the material being defibrated. For example, protein may be dispersed in alkali, or rosin may be used as a soap. The fiber or lignocellulose, being or developing acid, acts like added alum in the case of paper pulp sizing, to effect a so-called precipitation of the size. Thus, the alkali present with protein, however it is associated, or the alkali in a rosin or other soap, provides base for neutralizing acid in the lignocellulose.

INDICATIONS OF FIBER CHANGE

A mass of fiber has mass properties which depend upon the individual fibers, the sizes of the individual fibers, and the state of aggregation of the fibers. Consequently, a determination of a mass property means little without knowledge of many other properties and of inter-relationships of properties. Individual fibers vary in size and character, in part according to the original location in the wood. Therefore, measurements of properties of individual fibers, may vary from fiber to fiber. Practically, all measurements are made on masses of fiber for mass properties, or on many fibers, to strike an average. For example, the acidity of a mass must be the average measurement resulting from the acidity of the fibers exposed to influence the test. It has been found that in spite of all these handicaps, the trends of changes by treatment or other cause, are evidenced by consideration of not only a single property, but also numerous properties as a group. The following discussions and definitions

are intended to be an aid in understanding the meaning of the properties reported hereinafter.

The term "pH of the fiber" is in effect the pH of a water extract of the fiber determined as follows:

A sample of 10 grams of oven-dry fiber, or 10.7 grams of air-dry fiber, is extracted for $\frac{3}{4}$ hours at 50° to 60° C. in 100 cc. of distilled water which has been boiled. The water is separated, stoppered and cooled to room temperature, and its pH is measured.

The measurement of insulating value, also known as "k-value" is made on a fiber mat of 1-inch thickness at a density of 3.8 lbs. per cu. ft. (which is 3.15 board-feet per pound. It is defined in terms of heat transmitted in B. t. u. per sq. ft., per 1-inch of thickness, per 1° F. temperature differential, per hour, when the test sample is in facial contact with a hot and a cold plate, in a well known type of testing equipment used in the insulating art.

"Compressive properties" are those of dry bulk unfelted fiber as set forth in the copending application of Anway U. S. Serial No. 313,920, filed January 15, 1940, now U. S. Patent No. 2,325,026, issued July 27, 1943. Briefly, two columns of weighed fibers in cylinders of different diameters are compressed by a moving piston at a slow and standardized rate. The pressures exerted by the columns as a result of the compression are correlated to the density of the columns. From the data the properties are calculated.

"Sliding friction" indicates the surface character of a mass of fibers to exhibit friction, as it does on the cylinder in compressing.

"Free-footage" is an extrapolated density value, expressed as a reciprocal density in "board-feet per pound of fiber" when the fiber is unfelted by pressure other than its own weight. It is akin to "fluffiness."

"Specific elasticity" (K_E) is an indication of the elastic properties when the fiber being compressed is at an arbitrary reciprocal density of 3.15 board feet per pound.

"Absolute elasticity" is an index, or an indicative slope of a line produced in the mathematical solution, on which line the value K_E is read.

"Specific felting" (K_F) is an indication of the force which felts the fiber as it is being compressed and at 3.15 board feet per pound.

"Absolute felting" (M_F) is an index, or an indicative slope of a line produced in the mathematical solution, on which line the value K_F is read.

"Friability" is a measure of the ease of the fiber to break as set forth in Anway U. S. Serial No. 290,999, filed August 19, 1939, now U. S. Patent No. 2,324,126, issued July 13, 1943. It involves a standardized pounding of the fiber, giving the rate of dust formation with pounding.

"Permanence to heat" is an indication of how heat changes the friability of fiber. It is the ratio of friability of a specimen not heated to the friability of a specimen heated at a given temperature for a given time. This is set forth also in said Anway Patent No. 2,324,126.

"Impact resistance" is related to compressive properties. It is determined as described in Anway U. S. Serial No. 313,919, filed January 15, 1940, now U. S. Patent No. 2,375,182, issued May 8, 1945. Briefly explained, a vertically axial container, carrying a column of fiber to be tested is dropped repeatedly to give an impact of 1 foot-pound on the column. The fiber thus acquires

a constant density or volume. The final density expressed as its reciprocal in board feet per pound of fiber at 1 foot-pound impact is the impact resistance adopted for comparisons of fiber.

"Coarseness modulus" or C. M. is an arbitrary but standardized measure of particle size distribution. The method and apparatus is set forth in Heritage U. S. Serial No. 336,495, filed May 22, 1940, now U. S. Patent No. 2,325,055, issued July 27, 1943. Briefly, a specimen is divided by screening, into fractions according to screen size, and the percents as fractions are weighted in totaling, to give a significant figure, larger as the general coarseness of the fiber increases. Numerous systems different in detail are used to classify fiber, but different systems give correlatable values for conversion from one to another.

EXAMPLES

The following examples illustrate the present invention. In these examples it is to be understood that where the conditions of defibration are not specifically stated, the Asplund machine has been used for jack pine at about 150 lbs. steam pressure corresponding to about 365° F., and at about 135 lbs. steam pressure for aspen, and further, that the lignocellulose material passes through the machine in a time period of roughly one minute. The term "usage" in the examples refers to the percentum (%) of material used on the basis of dry wood content.

EXAMPLE 1.—SODIUM CARBONATE

Wood chips were defibered as shown below, the fiber dried directly in a hot oven, and tested.

Sample S-218

	1	2	3	4
Usage of Na ₂ CO ₃ , percent.....	0	1	5	10
Fiber acidity as pH.....	4.32	4.89	7.61	9.57
Friability.....	0.0160	0.0233	0.0389	0.0091
Permanence to heat.....	0.439	0.633	1.010	0.362

¹ Excess over 1.00 due to experimental error.

A usage over about 4% soda ash is necessary to neutralize the acidity of the wood used. The over-neutral fiber at pH 7.61 has a high permanence to heat, due to the fact that no acid is or becomes available to embrittle the fiber.

EXAMPLE 2.—CAUSTIC SODA

Fibers made in the same way with and without 1% usage of caustic soda gave results as follows:

Sample S-190

	28	27
Usage of NaOH, per cent.....	0	1
Coefficient of sliding friction.....	0.52	0.37
Free-foilage.....	8.42	8.12
Specific elasticity (K _E).....	235	235
Absolute Elasticity (M _E).....	0.608	0.892
Specific felting (K _F).....	46.1	47.1
Absolute felting (M _F).....	0.315	0.333

EXAMPLE 3.—CAUSTIC SODA OR SODIUM SULFITE

Peeled aspen wood as a control, with 5% usage of NaOH in one case, and 5.75% usage of sodium sulfite plus 0.15% usage of Na₂CO₃ (as mixed carbonates) in the second case, have been compared as follows: The fiber is first extracted with water by boiling for two hours, then it is hydrated for the purpose of making board and paper. On the basis of 100 parts of dry fiber, and upon aspen

wood containing 20.7 parts of lignin and 51 parts of alpha cellulose, the following results are noted:

Sample S-226

	Parts by weight		
	Control 65	NaOH 466	Na ₂ SO ₃ + 467
Fiber produced.....	90.2	76.0	81.5
Lignin in fiber.....	16.9	14.4	15.1
Solubles.....	9.8	24.0	18.5
Carbohydrates in solubles.....	6.0	17.7	12.9
Lignin in solubles.....	3.8	6.3	5.6
Composition:			
Per cent Alpha cellulose.....	56.6	67.0	62.5
Per cent Lignin.....	18.7	19.0	18.5
Per cent Carbohydrates not cellulose.....	24.7	14.0	19.0

Fibers produced as above in the Asplund machine, but washed with cold water (60° F.) in place of being extracted as above stated, are then refined in a ball mill in a standardized procedure and at 7.5% consistency in water without added agent. Refining continues until a slowness of 19 seconds (Williams slowness and porosity tester) is attained, and the time recorded. Before and after ball-milling the particle size as coarseness modulus is determined. The results of forming the fiber and refining are shown as follows:

Sample S-226

	Control 65	NaOH 466	Na ₂ SO ₃ + 467
Acidity as pH:			
Before washing.....	5.3	7.18	6.15
After washing.....		6.84	6.85
After ball-milling.....	5.5	6.72	5.90
Minutes to attain slowness of 19 seconds.....	100	75	115
Coarseness modulus:			
Before ball-milling.....	145	125	124
After ball-milling.....	81	84	73
Per cent reduction by milling.....	44	33	41

MAKING OF BOARD

The above fibers after hydration, without other treatment, are formed into boards of the character referred to as insulation board. This comprises merely felting a slurry of the fibers on a wire in a suitable manner to provide roughly a board of ½-inch thickness. The wet mat thus formed is pressed to ⅜-inch thickness. It is then dried in several ways. One extreme is to dry the mat without restraint, whereby it may swell or spring back, or shrink in drying, if it will. Another way is to dry with restraint on the wet mat. This may be by means to maintain constant thickness, or means to maintain constant pressure. The latter is preferred for comparisons, and is used at 100 lbs. per sq. ft., to obtain the "restraint" values given below.

UNRESTRAINED DRYING

Sample S-226

	Control 475	NaOH 476	Na ₂ SO ₃ + 477
Dried specimen weight in grams.....	30.4	31.3	29.7
Dried specimen thickness, inches.....	0.600	0.533	0.544
Density lbs./cu. ft.....	15.4	17.8	16.5
Per cent increase over pressed wet thickness on:			
(a) Releasing pressure.....	72.0	50.0	54.4
(b) After drying.....	60.0	42.1	45.1

RESTRAINED DRYING

Sample S-226

	Control 472	NaOH 473	Na ₂ SO ₃ + 474
Density of dried board, lbs./cu. ft.	17.23	22.79	16.95
Per increase over pressed wet thickness on drying with 100 lbs./sq. ft. pressure	34.7	9.9	17.3
Board Thickness in inches	0.492	0.383	0.417
Physical Property Values in Bending:			
Load in lbs. at elastic limit	14.7	21.0	12.0
Load in lbs. at point of rupture	20	31.6	18.0
Modulus of elasticity	33,200	77,200	43,900
Modulus of transverse strength	182	429	207
Modulus of rupture	248	647	311

The foregoing shows that the chemical treatment in forming of fiber, considerably strengthens and rigidifies the boards made from the fibers.

MAKING OF PAPER

Paper has also been made from the same fibers as described above for board. The fiber as discharged from the machine was screened moist, to remove coarser particles, by use of a 12-mesh screen. The fines were washed in cold water, and at 7.5% consistency, the fibers were ball-milled, formed into sheets on a wire-screen, and dried directly from formation, without pressing and without restraint.

The following data concerns the three types referred to:

Sample S-226

	Untreated 463	NaOH Treated 464	Na ₂ SO ₃ + Treated 465
pH:			
Before washing	5.25	7.10	6.05
After washing		6.50	6.60
After ball-milling	5.86	5.90	6.35
Minutes to attain slowness of 300 seconds	255	170	210
Coarseness Modulus:			
Before ball-milling	135	108	125
After ball-milling	29	55	57
Per Cent Reduction in C. M. by ball-milling	78	49	55
Paper:			
Thickness in inches	.017	.014	.016
Weight in lbs./M sq. ft.	12.13	12.58	11.56
Weight in lbs./ream (Ream size 480 sheets 24 x 36 inches)	34.92	36.22	33.31
Apparent density, lbs. ream-weight per point (0.001 inch)	2.06	2.59	2.08
Tear (16 sheets), grams on Elmendorf tester	12	36	24
Mullen burst, lbs./sq. in.	Less than 2	3.0	Less than 2
Mullen factor		.08	

used in the art. The sheets were made without the usual wet-pressing.

EXAMPLE 4.—SODIUM SULFITE, SODIUM CARBONATE

To wood chips to be defibered is added a solution containing sodium monosulfite and a small amount of mixed carbonates of sodium, in the amount per cu. ft. of about 18.4 lbs of Na₂SO₃, and 0.5 lb. of mixed carbonates calculated as Na₂CO₃. The usages are 1.15% Na₂SO₃ and .031% Na₂CO₃ equivalent. The water thus introduced is not sufficient to suspend the wood or the fiber, nor to destroy the steam environment.

The effect of the chemical is to increase the qualities of resilience and compressibilities, to raise the pH, and to lighten the color. It also improved the uniformity of defibering, for example, lessening "sticks." It makes the fiber feel softer to the hand.

Wax added.—In addition 2% usage of paraffin wax has been added to the above usage of the said sulfite solution, to add water-resistant properties to the fiber.

EXAMPLE 5.—CALCIUM HYDROXIDE

Calcium hydroxide has been used in amounts bringing the fiber to a pH above and below neutral. The samples S-202-48 and 51, given below, were made in accordance with the usage of 1/3% (based on dry wood) of sodium pentachlorophenol proofing agent for mold and decay in a 20% aqueous solution, as set forth in Heritage Serial No. 345,610, filed July 15, 1940.

Sample S-202

	40	48	51
Usage of Ca(OH) ₂	2.73	2.38	2.38
Acidity of fiber as pH	7.18	7.08	6.9
Free-footage	9.6	10.1	9.8
Specific elasticity (K _s)	140	119	115
Absolute elasticity (M _e)	0.330	0.301	0.313
Specific felting (K _f)	43.9	41.8	35
Absolute felting (M _f)	0.254	0.233	0.232
Dust content in per cent	6.6	6.4	6.7
Thermal conductivity (k)		0.227	
Friability	0.0028	0.0070	0.0206
Permanence to heat	0.04	0.05	0.16

EXAMPLE 6.—BORAX

Borax has been used with and without other chemicals as shown by the following series:

Sample S-230

	141	142	143	144	146
Chemical used	None	Borax	Borax	Borax	Borax
Usage		10%	6%	10%	10%
Chemical used			Boric acid	NaHSO ₃	H ₂ O ₂ (100%)
Usage				4%	3.34%
pH, predried fiber	5.11	7.34	7.51	7.65	5.62
pH, dried fiber	3.9	6.9	7.15	7.02	7.19
Friability	0.0102	0.0205	0.0359	0.0078	0.0410
Fire Resistance (grams loss per min. burning rate)	2.79	1.96	2.22	1.83	2.16
Color (total reflectance), per cent	34	26	29.8	40.2	27.1

From the foregoing, it will be seen that both treatments improve fiber which is generally unsatisfactory to make a testable sheet of paper, so that a testable and improved sheet results. Of course, the treatment is far from satisfactory at the usages given to produce so directly a paper-making pulp comparable to those commonly

The foregoing results show changes in pH in both directions upon drying. In the blank sample, the acidity drops considerably. In the borax-silicate sample the pH rises, due perhaps to silica forming from silicate, releasing the base thereof. One of the objectives of this series was improvement in color while introducing borax. It

11

shows that the presence of sodium sulfite with borax, gives the whitest color of the series, substantially improved over no chemical usage, and the burning rate is materially reduced.

EXAMPLE 7.—CAUSTIC SODA AND PROTEIN SIZE

With a usage of 5% soya bean protein, 0.15% NaOH and .03% formalin, all based on dry weight of Jack pine wood, the chemical effect on easily measurable properties is masked by the effect of the protein.

EXAMPLE 8.—CHEMICAL SALTS

Chemical salts of various types have measurable effects upon the fiber as illustrated below.

Usage and Chemical	Control	1% Na ₂ SiO ₃	3% Aluminum Stearate
Sample.....	S-224-6	S-224-11	S-224-13
Free-footage (FF)	6.97	6.62	6.40
Specific elasticity (K _E)	84	42	43
Absolute elasticity (M _E)	0.502	0.544	0.511
Specific felting (K _F)	30	20	19
Absolute felting (M _F)	0.386	0.372	0.394
k-value	0.246	0.259	0.254
Friability	0.1105	2.200	0.1930
Impact Resistance	3.9	3.2	4.4
Coarseness modulus (C. M.)	96	142	88
Hygroscopicity, per cent at equilibrium:			
Humidity 93%—55° F.....	19.8	17.9	18.9
Humidity 55%—55° F.....	10.1	6.8	7.9

EXAMPLE 9.—NEUTRALIZING CHEMICALS

A comparative series of several chemical agents was made at the same time against a control, showing the pH raised toward or past the neutral point, with other properties as follows:

Sample S-218

	19	11	12	13	14	20
Chemical Added	None	Na ₂ CO ₃	Na ₂ AlO ₃	Ca(OH) ₂	Na ₂ SiO ₃	NaHCO ₃
Usage in per cent		4.0	3.7	2.8	2.7	3.2
Acidity of Fiber as pH	3.8	7.7	6.2	7.5	5.1	7.5
Coarseness modulus	197	229	203	173	208	210
Free-Footage	9.7	8.9	10.3	9.8	10.2	9.1
Specific elasticity (K _E)	155	196	230	235	140	105
Absolute elasticity (M _E)	0.33	0.40	0.33	0.35	0.30	0.34
Specific felting (K _F)	43	49	96	62	53	30
Absolute felting (M _F)	0.25	0.29	0.27	0.27	0.24	0.24
Friability	0.0077	0.0130	0.0027	0.0063	0.0025	0.0050
Permanence to heat	0.097	0.420	0.218	0.197	0.040	0.234
Dust content in per cent	4.5	5.7	5.2	6.2	4.5	5.5
Impact resistance	3.9	4.0	3.8	4.0	3.7	3.6

The foregoing table indicates that the properties of the fiber are not dependent only upon the neutralization, or the pH, but also and in part upon the type of chemical added. The effects produced by sodium aluminate are highly specific. The permanence to heat is greatly increased by partial and over-neutralization.

EXAMPLE 10.—CALCIUM CARBONATE AND WAX

Wood chips are defibered with a usage of 10% paraffin wax and a usage of 5% calcium carbonate, forming a sized fiber.

DISCUSSION

Practically all of the chemicals used as above given, provide alkali for neutralizing acid. The sulfites in addition provide sulfur dioxide equivalent for modifying the lignin, it being commonly understood that lignin-sulfonate is formed. In addition, it is a reducing chemical, and this is believed to be in part the reason that a lighter-colored fiber is produced.

The chemicals exert changes on the fiber, indicated by changes in physical properties, or

12

chemical properties, or composition, all as exemplified above. Not only is the fiber changed to adapt it to specific physical uses, but also to adapt it to making a better board and paper, and to make it differently susceptible to other chemical change.

Lignocellulose is not a stable substance. It is impossible at boiling temperatures with water, to extract the "water-soluble" content, in over 300 hours' treatment, because the extracting action changes the composition to form more extract. Changing the water to fresh water even hastens the change in composition. Steam treatment at elevated temperatures makes such a change, evidenced by increasing the water-soluble content determined by a standardized extraction. Added chemicals in water, or in the presence of steam also hasten such a change, especially those providing available alkali. Therefore, one measure of the effectiveness of a chemical is to measure the water-extractable contents, by standardized procedures, of fibers produced in the same way, one without the chemical and one with the chemical. This simple analysis of the fiber for extracts of substance from the original lignocellulose, is an evidence of the chemical action, which conditions the fiber as to physical and chemical properties. The present invention contemplates the use in defibering of chemicals which increase the water-soluble extractives. This has been illustrated and explained in Example 3.

It is of course to be understood that the hydration in water, and the felting from water, are merely convenient test procedures, and do not limit the invention. Hydration may be effected with moist fiber in the absence of suspending

water, and felting may be done from suspension in other liquids, or gases, to form boards and papers, or other felted structures.

The invention is of course not limited to use of chemicals as solid, or in solution. The use of a sulfite salt is known to produce sulfur dioxide in the defibering Asplund machine, making the sulfur dioxide a gaseous reagent. The reagent may be any other gaseous one introduced into the machine, or generated therein. Thus, sulfur dioxide may be introduced as a gas. Ammonia gas may be used. It may be introduced as a gas, or as a solution in water, whereby it may become a gas in the machine.

The mechanical defibering may be accomplished in various machines which operate also to distribute chemicals or solutions. Machines or processes, like that of Asplund, but not operating at above 212° F. in a steam atmosphere are shown in British Patent No. 15,105 of 1911, and Schouten U. S. No. 1,367,895. The Banbury apparatus (see Robinson U. S. No. 2,142,334 referring to Serial No. 101,014, filed September 16, 1936), also described in U. S. No. 1,523,387, and

the Respats apparatus and process of Respass U. S. No. 1,976,297 are all useful. In the latter, wood as chips is steamed and thus softened, and the softer chips are defiberated by pressure from heavy rolls. Chemicals present at this stage are effective according to the present invention. The rolling process takes longer than the Asplund process, and this is a compensation for its lower temperature.

Reference is made to my copending applications Serial No. 351,240, filed August 3, 1940, wherein the use of caustic alkali is specifically claimed, and Serial No. 351,238, filed August 3, 1940, wherein the use of sulfites is specifically claimed. In the latter case an example is given where a usage of 10% of a sulfite salt has been employed.

I claim:

1. The method of treating lignocellulose which comprises heating lignocellulose in the absence of suspending liquid and in an atmosphere of steam at an elevated temperature above 212° F. at which the lignocellulose is rendered plastic, and simultaneously defibering the plastic lignocellulose and incorporating substantially uniformly throughout the lignocellulose chemical reagent reactive therewith, whereby to produce chemically treated fibers without substantial loss of constituents of the original lignocellulose.

2. The method of producing fiber which comprises supplying undefibered lignocellulose to a mechanical defibering device, supplying to said device a chemical which is reactive with lignocellulose and a fiber-producing digestant therefor other than water, mechanically defibering said lignocellulose in the absence of suspending water and in the presence of moisture in a gaseous environment by operation of said device while rubbing and pressing said lignocellulose, while distributing said chemical digestant substantially uniformly throughout the lignocellulose as the latter is being defibered and while reacting said chemical digestant with said lignocellulose thereby to effect modification of the lignocellulose by reaction with said chemical, whereby to produce a fiber of chemically modified lignocellulose, said fiber containing substantially all the solid content of the original lignocellulose.

3. The method of producing fiber which comprises supplying undefibered lignocellulose to a mechanical defibering device, supplying to said device a chemical which is reactive with lignocellulose and a fiber-producing digestant therefor other than water, mechanically defibering said lignocellulose in the absence of suspending water in an atmosphere of steam at an elevated temperature above 212° F. and at which the lignocellulose softens to a plastic state, said defibering being effected by operation of said device while rubbing and pressing said plastic lignocellulose and while distributing said chemical digestant substantially uniformly throughout the lignocellulose as the latter is being defibered and while reacting said chemical digestant with said lignocellulose thereby to effect modification of the lignocellulose by reaction with said chemical, whereby to produce a fiber of chemically modified lignocellulose, said fiber containing substantially all the solid content of the original lignocellulose.

4. The method of producing fiber which comprises supplying undefibered lignocellulose to a mechanical defibering device, supplying to said device a chemical material, which material is a fiber-producing digestant therefor and which material includes available base for neutralizing

acidity of said lignocellulose, mechanically defibering said lignocellulose in the absence of suspending water and in the presence of moisture in a gaseous environment by operation of said device while rubbing and pressing said lignocellulose, while distributing said chemical digestant substantially uniformly throughout the lignocellulose as the latter is being defibered and while reacting said chemical digestant with said lignocellulose, thereby to effect modification of the lignocellulose including neutralization of at least a part of the acidity available therein, whereby to produce a fiber of chemically modified lignocellulose, said fiber containing substantially all the solid content of the original lignocellulose.

5. The method of producing fiber which comprises supplying undefibered lignocellulose to a mechanical defibering device, supplying to said device chemical material which material is a fiber-producing digestant therefor and which material includes available base for neutralizing acidity of said lignocellulose, mechanically defibering said lignocellulose in the absence of suspending water and in the presence of moisture in a gaseous environment by operation of said device while rubbing and pressing said lignocellulose, while distributing said chemical digestant substantially uniformly throughout the lignocellulose as the latter is being defibered and while reacting said chemical digestant with said lignocellulose, said material being supplied in quantity to provide fibers having a pH of at least 7, thereby to effect modification of the lignocellulose and the provision of non-acid fibers containing substantially all the solid content of the original lignocellulose.

6. The method of producing fiber which comprises supplying undefibered lignocellulose to a mechanical defibering device, supplying to said device chemical material which material is a fiber-producing digestant therefor and which material includes salt of a strong base and a weak acid, mechanically defibering said lignocellulose in the absence of suspending water and in the presence of moisture in a gaseous environment by operation of said device while rubbing and pressing said lignocellulose, while distributing said chemical digestant substantially uniformly throughout the lignocellulose as the latter is being defibered and while reacting said chemical digestant with said lignocellulose thereby to effect modification of the lignocellulose including neutralization by said base of at least a part of the acidity available in the lignocellulose, whereby to produce a fiber of chemically modified lignocellulose, said fiber containing substantially all the solid content of the original lignocellulose.

7. The method of producing fiber which comprises supplying undefibered lignocellulose to a mechanical defibering device, supplying to said device chemical material, which material is a fiber-producing digestant therefor and which material includes available base for neutralizing acidity of said lignocellulose, mechanically defibering said lignocellulose in the absence of suspending water in an atmosphere of steam at an elevated temperature above 212° F., and at which the lignocellulose softens to a plastic state, said defibering being effected by operation of said device while rubbing and pressing said plastic lignocellulose and while distributing said chemical digestant substantially uniformly throughout the lignocellulose as the latter is being defibered and while reacting said chemical digestant with said lignocellulose thereby to effect modification of the

lignocellulose including neutralization of at least a part of the acidity available therein, whereby to produce a fiber of chemically modified lignocellulose, said fiber containing substantially all the solid content of the original lignocellulose.

8. The method of producing fiber which comprises supplying undefibered lignocellulose to a mechanical defibering device, supplying to said device chemical material, which material is a fiber-producing digestant therefor and which material includes available base for neutralizing acidity of said lignocellulose, mechanically defibering said lignocellulose in the absence of suspending water in an atmosphere of steam at an elevated temperature above 212° F. and at which the lignocellulose softens to a plastic state, said defibering being effected by operation of said device while rubbing and pressing said plastic lignocellulose and while distributing said chemical digestant substantially uniformly throughout the lignocellulose as the latter is being defibered and while reacting said chemical digestant with said lignocellulose, said material being supplied in quantity to provide fibers having a pH of at least 7, thereby to effect modification of the lignocellulose and the provision of non-acid fibers containing substantially all the solid content of the original lignocellulose.

9. The method of producing fiber which comprises supplying undefibered lignocellulose to a mechanical defibering device, supplying to said device chemical material which material is a fiber-producing digestant therefor and which material includes salt of a strong base and a weak acid, mechanically defibering said lignocellulose in the absence of suspending water in an atmosphere of steam at an elevated temperature above 212° F. and at which the lignocellulose softens to a plastic state, said defibering being effected by operation of said device while rubbing and pressing said plastic lignocellulose and while distributing said chemical digestant substantially uniformly throughout the lignocellulose as the latter is being defibered and while reacting said chemical digestant with said lignocellulose, thereby to effect modification of the lignocellulose including neutralization by said base of at least a part of the acidity available in the lignocellulose, whereby to produce a fiber of chemically modified lignocellulose, said fiber containing substantially all the solid content of the original lignocellulose.

HENRY E. WALTER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
Re. 6,646	Herron	Sept. 14, 1875
106,710	Meloch	Aug. 23, 1870
296,780	Pond	Apr. 15, 1885
417,282	Reed	Dec. 17, 1889
1,016,178	Sammet	Mar. 30, 1912
1,153,883	Arledter	Sept. 21, 1915
1,539,633	Schooger	May 26, 1925
1,654,624	Wells	Jan. 3, 1928
1,785,544	Ellis	Dec. 16, 1930
1,794,174	Hatch	Feb. 24, 1931
1,872,996	Mason	Aug. 23, 1932
1,913,607	McMillan	June 13, 1933
1,982,130	Wollenberg	Nov. 27, 1934
2,008,892	Asplund	July 23, 1935
2,047,170	Asplund	July 14, 1936
2,072,686	Robinson	Mar. 2, 1937
2,080,078	Mason	May 11, 1937
2,145,851	Asplund	Feb. 7, 1939
2,164,040	Offermanns	June 27, 1939
2,228,349	Feldman	Jan. 14, 1941
2,234,188	Morgan	Mar. 11, 1941
2,265,622	Basler	Dec. 9, 1941
2,315,372	Kressman	Mar. 30, 1943

FOREIGN PATENTS

Number	Country	Date
12,149	Australia	Apr. 10, 1933
103,709	Australia	Apr. 28, 1938
35,854	Germany	June 10, 1886
393,159	Great Britain	June 1, 1933

OTHER REFERENCES

- Der Papier-Fabrikant, g. 36, 1938, Tiel I, pages 519-531.
- Paper Trade Journal, Oct. 15, 1925, pages 57-59.
- Verein der Zellstoff und Papier-Chemiker und Ingenieure, g. 17, 1936, pages 313-319.
- A Dictionary of Paper and Paper Making Terms, by Labarre (1937), published by N. V. Swets and Zeitlinger, Amsterdam, Holland, page 169.