

UNITED STATES PATENT OFFICE

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PULPED MATERIAL AND PROCESS OF PREPARING THE SAME

No Drawing.

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This invention relates to the production of fiber suitable for manufacture of paper and pertains particularly to the treatment of wood and other vegetable fibrous material by the steps of the particular process of the present invention.

The process provides for the softening of woody material and the converting of it into a ligno-cellulosic intermediate product of uniform composition which may be pounded and rubbed into pulp without breaking the fibers and without the reduction to fragments of more than an insignificant proportion of the fibers and cells.

Especially does this invention relate to fiber producing processes and to the resulting fibrous material suitable for paper manufacture and for other purposes, obtained from wood as for example by boiling the same under pressure in the process of aqueous solutions of caustic soda and sodium sulphide, caustic soda and sulphur, sodium sulphite and sodium bicarbonate, or sodium sulphite and sodium carbonate of suitable concentration to soften the woody material and to form the ligno-cellulosic intermediate product above mentioned.

At the present state of the pulp makers' art the processes used may be divided into two groups, the mechanical and the chemical. The mechanical process consists essentially of pressing blocks of wood against a revolving grindstone in the presence of water and the wood is reduced to pulp by grinding and the frictional heat developed. In this process the action is so severe that comparatively few of the fibers survive in their entity and a large portion of the pulp consists of fragments of single fibers or of bundles of fibers.

In the chemical processes the wood is cut to chips and digested under pressure in aqueous solutions of the bisulphites of the alkaline earths and sulphurous acid or caustic soda or caustic soda and sodium sulphide or sodium sulphite. The digestion is carried to such a point that over fifty per cent of the wood substance is dissolved and a product testing over 90% cellulose is left. In these processes the ultimate fibers are intact, but the bond between them has been removed so

that they separate with the slightest mechanical agitation. By ultimate fiber is meant the elongated cells which are attached longitudinally and cemented together radially by incrusting matter consisting largely of lignin and hemicelluloses. Their entity is readily discernible under the microscope and their length is approximately 100 times or more than diameter in the coniferous woods and approximately 50 times diameter in the deciduous woods.

In the present improvement the wood is also cut to chips and the chips subjected to aqueous solutions of suitable chemicals at elevated temperatures after first being subjected to an impregnation treatment under pressure. The digestion however is only carried to the point that the middle lamella or cementing material between the fibers is softened, but not completely dissolved. The middle lamella is essentially lignin. The softened chips are then capable of reduction to their ultimate fibers and cells by suitable pounding or rubbing or a combination of both. A pulp is obtained that has the general appearance of pulp obtained by the chemical processes mentioned, but instead of a yield of from 40 to 50 per cent being obtained, a yield of from 60 to 85 per cent is realized, depending on the species of wood and the severity of the treatment. While these pulps are similar in appearance to what are generally known as chemical pulps they have distinct chemical characteristics, as will be shown in the following table of analysis. In this table the terms used may be explained as follows:

Solubility in 1% sodium hydroxide

This test is the amount of material dissolved on treatment of the pulp one hour in a 1% solution of sodium hydroxide at 100° C.

Cellulose

The cellulose is determined by subjecting the material to alternate treatments with chlorine gas in the presence of water and washing with sodium sulphite solutions under the conditions suggested by Cross and Bevan and described by A. W. Schorger

Jour. Ind. and Eng. Chem. 9, (1917) 556. In accordance with this, the following procedure is used. Two grams of air dry pulp in an alundum crucible are extracted three to four hours with a mixture of 67 per cent of benzol and 33 per cent alcohol. After evaporation of the solvent the shavings are thoroughly washed with hot water using the suction pump. The moist pulp is then transferred with a pointed glass rod to a 250 cc. beaker, evenly distributed over the bottom, and subjected to a stream (about forty bubbles per minute for each sample) of water washed chlorine gas for half an hour. The end of the tube delivering the chlorine gas should be about one-half inch above the pulp. At intervals of six to seven minutes the contents of the beaker are stirred to insure uniformity of chlorination. After the chlorine treatment the pulp is treated with a solution of SO_2 until the chlorine odor disappears, transferred to the alundum crucible, and washed with hot water. The pulp is again returned with the glass rod to the beaker, and 100 cc. of a two per cent sodium sulphite solution are added and the beaker, covered with a watch glass, placed in a boiling water bath for 30 minutes. The fibers are then transferred to the crucible and washed with water. The above procedure is seldom sufficient to remove all the lignin, so that the treatment with chlorine and subsequent treatment as outlined above is repeated until the fibers are practically a uniform white. The second and following treatments with chlorine should not be longer than 15 to 30 minutes. After all the lignin has been removed the fibers are given a final bleaching by adding 20 cc. of a 0.1 per cent solution of potassium permanganate, allowed to stand 10 minutes and rendered colorless with SO_2 solution. The fibers are then thoroughly washed with hot water, dilute acetic acid, then with hot water, then with alcohol and finally with ether, and dried for two hours at 105°C . in the air oven. After cooling by a dessicator over H_2SO_4 , the crucible is weighed in a weighing bottle.

Lignin

This result consists of the residue left after treatment with sulphuric acid under conditions prescribed by Ost and Wilkening and reported by Cross and Bevan in "Researches on Cellulose", III, 39, (1906-10). In adapting that method to the present problems the following steps are followed. Two to four grams of air dry pulp are weighed in an alundum thimble, extracted with ether in a soxhlet apparatus for 3 to 4 hours, and dried at 105°C . The pulp is then removed from the alundum extraction thimbles, placed in 250 cc. beakers, divided into fine particles and treated with 40 cc. of 72.0 per cent sulphuric acid. The hydrolysis is al-

lowed to proceed for 16 hours at room temperature, with frequent stirring at the beginning of the operation. The resulting solution is transferred to a two liter Erlenmeyer flask diluted to 1570 cc. with distilled water, which makes the concentration of H_2SO_4 exactly 3 per cent, and boiled under a reflux condenser for two hours. This causes a coagulation of the suspended particles of lignin, which is then filtered on an alundum crucible, washed thoroughly with hot water, dried and weighed as lignin.

Material analyzed	Soluble in 1% sodium hydroxide	Cellulose	Lignin	
	Per cent	Per cent	Per cent	
Wood:				
Aspen.....	20	62	23	
Spruce.....	15	58	28	
Loblolly pine.....	13	60	30	
Jack pine.....	16	60	33	85
Mechanical pulp—spruce.....	10	60	30	
Very raw sulphite pulp—spruce.....	13	77	17	
Standard sulphite pulp—spruce.....	12	93	4	
Soda pulp:				
Spruce.....	5	94	4	
Jack pine.....	4	94	6	
Loblolly pine.....	3	92	5	90
Aspen.....	2	97	2	
Sulphate pulp:				
Spruce.....	6	95	3	
Jack pine.....	3	94	4	
Loblolly pine.....	2	94	6	
Longleaf pine.....	3	94	5	95
Ligno-cellulosic material, strongly alkaline reagents:				
Aspen (soda liquor).....	2-9	91-70	8-23	
Loblolly pine (soda liquor).....	4-7	80-64	20-31	
Jack pine (soda liquor).....	3-6	80-63	23-32	
Jack pine (sulphate liquor).....	4-7	80-66	20-30	
Ligno-cellulosic material, neutral or slightly alkaline reagents:				100
Aspen.....	6	76	19	
Tupelo gum.....	5	70	14	
Chestnut.....	8	77	18	
Jack pine.....	5	75	22	
Loblolly pine.....	4	68	28	
Tamarack.....	5	71	23	

The ligno-cellulosic material may be differentiated from mechanical pulps in that it contains less than 10% of substances soluble in 1% caustic soda solution and 80% or more of the fibers retain 50% or more of their ultimate fiber length. It may be differentiated from the sulphite pulps of commerce in that when obtained from deciduous wood, it is not more than 9% soluble in 1% caustic soda solution, containing from 70% to 91% cellulose, and from 8% to 23% of lignin. It may be differentiated from the soda or sulphate pulps of commerce in that it contains less than 91% cellulose and more than 8% of lignin. When derived from coniferous species it contains from 63% to 80% of cellulose and from 20% to 32% of lignin and is not more than 7% soluble in sodium hydroxide.

The softening and partially completed pulping provided for by the chemical treatment of this invention is adapted to be followed by any mechanical disintegration which will not break the softened fibers and thus needlessly shorten them. Peculiarly

adapted for such mechanical treatment is the rod mill process and apparatus described and claimed in the copending application of Sidney D. Wells, one of the applicants herein, Serial No. 49,461, filed August 10, 1925. That apparatus provides a rotatable drum structure within which the pulp is tumbled, pounded and beaten by intermingling contact with a plurality of rods which extend in parallel relation lengthwise of the axis of the drum and are free to roll and tumble therein under the influence of the rotary movement of the drum. With this improved pulping apparatus the length of the fiber is maintained and the fibers are not disintegrated into the sawdust-like particles commonly produced and observed in processes in which the grinding apparatus includes a rotary abrading element or cutting element.

The following procedure may be used in treating fresh wood fibrous material to produce the ligno-cellulosic material described. The wood is first converted to chips in the manner used in chemical pulp mills and charged into a digester. They are then impregnated by steaming and then forcing the softening solution into them by filling the digester therewith and thereby completely immersing the chips and producing hydrostatic pressure by means of a pump, steam, air, or any other method known to the art. After impregnation for half an hour or more at 100 pounds pressure the softening solution will be found to have practically penetrated the chips and the excess over that required for softening is removed. Using 10 parts of sodium sulphite and 4 parts of sodium bicarbonate per 100 parts dry weight of gum chips gives excellent results. The substitution of sodium carbonate for bicarbonate is also satisfactory. The substitution of 2 parts caustic soda for the bicarbonate gives satisfactory results with loblolly pine. For pulps from the pines where greater strength is desired 8 parts of caustic soda and one part of sulphur is satisfactory. 8% calcium bisulphite and 2% sulphurous acid gave good results with tamarack. It can thus be seen that a wide range of chemicals may be used. This impregnation feature is important because it makes possible the softening of the wood uniformly through its thickness. By the term "uniform" is meant the even softening to substantially the same degree from the exterior to the center of each piece of wood. Thus the chips after treatment are practically as soft at their centers as they are on the outside. Without previous impregnation and with the use of the direct cook only, the woody material is likely to become damaged by over cooking on the exterior portions before the interior is adequately softened. Thus, with ordinary cooking methods, the undigested chips will be almost completely cooked on the outside, and in extreme cases, the center

will be bright wood, not even discolored by the cooking liquor. Accordingly, in view of the fact that the particular subsequent mechanical separation of this invention requires uniform softening, it becomes extremely important that the softening step be conducted in accordance with the procedure herein prescribed.

After the excess of liquor has been withdrawn the contents of the digester are heated until a temperature of over 120° C. has been attained and the contents held thereat until the desired softening has taken place. In the first three instances two hours at 160° C. was sufficient. Four hours at 160° C. was sufficient in the fourth, and six hours coming up to a temperature of 120° C. was sufficient in the last. The contents are then removed from the digester and reduced to ultimate fibers by passing through a rod mill or by other mechanical treatment.

Should a mixture of coniferous and deciduous material be treated in accordance with the process of this invention, the resultant ligno-cellulosic pulped material would have varying proportions of lignin and cellulose in its content, ranging from 8 per cent to 32 per cent of lignin and from 63 per cent to 91 per cent of cellulose, depending on the proportion of coniferous and deciduous material present.

The process of the present invention may be followed in treating vegetable fibrous material other than wood and as provided for the treatment of straw and grasses as described and claimed in our copending application Serial No. 133,516, filed September 3, 1926.

This application is a continuation in part of our application, Serial No. 100,685, filed April 8, 1926, entitled Treatment of wood for the production of pulp.

We claim:—

1. In the production of fibers from vegetable material for use in making paper, the method of softening and separating the fibers which comprises first, and prior to cooking, impregnating the vegetable material throughout with a softening agent, subjecting the vegetable material while all of it is covered with a softening agent in a closed vessel to heat and pressure to effect a substantially uniform softening of the material throughout the particles, thereafter subjecting the impregnated pulp in the presence of a chemical consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid to a cooking treatment and stopping the cooking treatment when the particles are uniformly softened and the middle lamella thereof is softened and before it is completely dissolved, and thereafter mechanically separating the vegetable material thus previously chemically treated.

2. In the production of fibers from vegeta-

ble fibrous material, the method of softening and separating the fibers, which method comprises first and prior to cooking, impregnating chips of woody vegetable material throughout with a softening agent by subjecting the woody material in a closed vessel to heat and pressure to effect a substantially uniform softening of the material throughout the particles, thereafter subjecting the impregnated woody material to a cooking treatment in the presence of a chemical softening agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid and stopping the cooking treatment when the particles are uniformly softened and the middle lamella thereof is softened and before it is completely dissolved, and thereafter mechanically separating the fibrous material thus previously chemically treated.

3. In the production of fibers from vegetable fibrous material, the method of softening and separating the fibers which comprises first and prior to cooking, impregnating chips of the vegetable material throughout with a softening chemical agent by completely immersing all of the chips in a chemical agent and subjecting both in a closed vessel to heat and pressure until the chips are impregnated substantially uniformly throughout with the softening agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid, removing part of the chemical, subjecting the impregnated chips thus freed from an excess of chemical, to a cooking treatment and stopping the cooking treatment when the particles are uniformly softened and the middle lamella thereof is softened and before it is completely dissolved, and thereafter separating the vegetable fibers thus chemically treated.

4. A ligno-cellulosic pulped material containing the softened woody material from deciduous woods and containing from 8 per cent to 23 per cent lignin and from 70 per cent to 91 per cent of cellulose and with substantial maintenance of fiber length, said material being resultant of a treatment of vegetable fibrous material comprising first, and prior to cooking, impregnating the vegetable material throughout with a softening agent subjecting the vegetable material while all of it is covered with a softening agent in a closed vessel to heat and pressure to effect a substantially uniform softening of the material throughout the particles, thereafter subjecting the impregnated pulp to a cooking treatment in the presence of a chemical agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid and stopping the cooking treatment when the particles are uniformly softened and the middle lamella thereof is softened and before it is completely dissolved, and thereafter mechanically separating the vegetable

material thus previously chemically treated.

5. A ligno-cellulosic pulped material containing the softened woody material from deciduous woods, containing from 8 per cent to 23 per cent of lignin and not more than 91 per cent of cellulose, and characterized by the fact that not more than 9 per cent of the material is soluble in a 1 per cent sodium hydroxide solution, and with substantial maintenance of fiber length, said material being resultant of a treatment of vegetable fibrous material comprising first, and prior to cooking, impregnating the vegetable material throughout with a softening agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid, subjecting the vegetable material while all of it is covered with a softening agent in a closed vessel to heat and pressure to effect a substantially uniform softening of the material throughout the particles, thereafter subjecting the impregnated pulp in the presence of a chemical to a cooking treatment and stopping the cooking treatment when the particles are uniformly softened and the middle lamella thereof is softened and before it is completely dissolved, and thereafter mechanically separating the vegetable material thus previously chemically treated.

6. A ligno-cellulosic pulped material containing the softened woody material from deciduous woods, containing over 8 per cent of lignin and not more than 91 per cent of cellulose, characterized by the fact that not more than 9 per cent of the material is soluble in a 1 per cent sodium hydroxide solution, and that over 80 per cent of the fibers retain substantially their ultimate fiber length, and with substantial maintenance of fiber length, said material being resultant of a treatment of vegetable fibrous material comprising first, and prior to cooking, impregnating the vegetable material throughout with a softening agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid subjecting the vegetable material while all of it is covered with a softening agent in a closed vessel to heat and pressure to effect a substantially uniform softening of the material throughout the particles, thereafter subjecting the impregnated pulp in the presence of a chemical to a cooking treatment and stopping the cooking treatment when the particles are uniformly softened and the middle lamella thereof is softened and before it is completely dissolved, and thereafter mechanically separating the vegetable material thus previously chemically treated.

7. A ligno-cellulosic pulped material containing the softened deciduous woody material from pulped wood and containing lignin in proportions ranging from 8 per cent to 32 per cent of the material and containing cel-

lulose in proportions ranging from 63 per cent to 91 per cent of the total material, and with substantial maintenance of fiber length, said material being resultant of a treatment of vegetable fibrous material comprising first, and prior to cooking, impregnating the vegetable material throughout with a softening agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid, subjecting the vegetable material while all of it is covered with a softening agent in a closed vessel to heat and pressure to effect a substantially uniform softening of the material throughout the particles, thereafter subjecting the impregnated pulp in the presence of a chemical to a cooking treatment and stopping the cooking treatment when the particles are uniformly softened and the middle lamella thereof is softened and before it is completely dissolved, and thereafter mechanically separating the vegetable material thus previously chemically treated.

8. A ligno-cellulosic pulped material containing the softened woody material from deciduous woods and containing from 8 per cent to 23 per cent lignin and from 70 per cent to 91 per cent of cellulose and with substantial maintenance of fiber length resultant of a treatment comprising first subjecting the vegetable material in the form of chips to a chemical treatment by cooking the same with a chemical agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid to effect a substantially uniform softening of the material throughout the particles, continuing the cooking until the middle lamella is softened and stopping the cooking action before the middle lamella is completely dissolved, and thereafter mechanically separating into its resultant fibers the said softened and loosened fibrous material previously chemically treated.

9. A ligno-cellulosic pulped material containing the softened woody material from deciduous woods, containing from 8 per cent to 23 per cent of lignin and not more than 91 per cent of cellulose, and characterized by the fact that not more than 9 per cent of the material is soluble in a 1 per cent sodium hydroxide solution and with substantial maintenance of fiber length resultant of a treatment comprising first subjecting the vegetable material in the form of chips to a chemical treatment by cooking the same with a chemical agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid to effect a substantially uniform softening of the material throughout the particles, continuing the cooking until the middle lamella is softened and stopping the cooking action before the middle lamella is completely dissolved, and thereafter mechanically separating into its resultant fibers the

said softened and loosened fibrous material previously chemically treated.

10. A ligno-cellulosic pulped material containing the softened woody material from deciduous woods, containing over 8 per cent of lignin and not more than 91 per cent of cellulose, characterized by the fact that not more than 9 per cent of the material is soluble in a 1 per cent sodium hydroxide solution, and that over 80 per cent of the fibers retain substantially their ultimate fiber length and with substantial maintenance of fiber length resultant of a treatment comprising first subjecting the vegetable material in the form of chips to a chemical treatment by cooking the same with a chemical agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid to effect a substantially uniform softening of the material throughout the particles, continuing the cooking until the middle lamella is softened and stopping the cooking action before the middle lamella is completely dissolved, and thereafter mechanically separating into its resultant fibers the said softened and loosened fibrous material previously chemically treated.

11. A ligno-cellulosic pulped material containing the softened woody material from pulped deciduous wood and containing lignin in proportions ranging from 8 per cent to 32 per cent of the material and containing cellulose in proportions ranging from 63 per cent to 91 per cent of the total material and with substantial maintenance of fiber length resultant of a treatment comprising first subjecting the vegetable material in the form of chips to a chemical treatment by cooking the same with a chemical agent consisting of sodium sulphite and the sodium salt of a weakly ionized polybasic acid to effect a substantially uniform softening of the material throughout the particles, continuing the cooking until the middle lamella is softened and stopping the cooking action before the middle lamella is completely dissolved, and thereafter mechanically separating into its resultant fibers the said softened and loosened fibrous material previously chemically treated.

In testimony whereof we affix our signatures.

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