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PROCESS OF IMPREGNATING WOOD CHIPS

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This invention relates to the production of cellulose pulp from woody material and the like by the treatment of such material with softening or digesting liquors.

The object of the invention is to provide a process for the treatment of wood in the form of chips, flakes, slices or other suitable subdivisions which comprises a means for uniformly and intimately associating the treating liquors with the wood prior to attaining reactive temperatures and thereafter controlling the reaction conditions to effect the desired degree of lignin softening or removal with a minimum of cellulose degradation.

Another object of the invention is to provide pulp products distinguished by the homogeneous association of any desired proportion of the original ligneous component of the wood with substantially undegraded cellulose fibers in amount ranging from nearly all of the original ligneous material present in the wood to less than 1%.

Another object of the invention is to provide a process which will bring the required amount of chemicals and those components of the wood which are to be softened or removed into proper relation for reaction under digesting conditions with a minimum of transfer of the chemical from the liquor surrounding the wood during the digestion.

Another object is to minimize or overcome the hindrances which the delignifying liquors normally encounter in their attempt to penetrate the woody material so that the desired reaction may proceed uniformly and rapidly to effect any predetermined degree of lignin removal.

Another object is to overcome the preferential adsorption of reagents from the treating liquors in the outer portions of the chips or other subdivisions of the wood and to effect a nearly uniform distribution of same throughout the wood.

A further object is to largely reduce or entirely overcome the undesirable inequalities in pulping wood which arise from the widespread and varying differences in the amount and rate of absorption of treating liquors by different species of wood and by the heartwood and sapwood portions of the same species.

A great problem in the pulping of wood and the like since the inception of the art has been the penetration and permeation of the wood with treating liquors of effective strength with thoroughness and uniformity. The study of the morphology of wood discloses an extremely complex form and structure presenting many difficulties to its penetration by liquids. The capac-

ity of wood to absorb liquids varies widely between different species and between the heartwood and the sapwood of the same species so that unless these variations are taken into account some portions of the wood under treatment may have an excess of reagent and others an insufficient amount for effecting the desired degree of lignin solution with consequent variability of reaction. Wood has the property of preferentially adsorbing reagents from some of the treating liquors most widely used in the pulping industry such as, for instance, soda and kraft liquors, so that a uniform distribution of such reagents through the wood has not resulted from penetration or saturation of the wood with the treating solution. The gradient in concentration thus formed is of great consequence being for instance of the magnitude of 5:1 or more between the exterior half by volume and the interior half of a treated wood block. These and other hindrances to the proper association of the chemical reagents with the wood have resulted in the development of conventional processing systems which, even to this day, whether recognized or not, depend in the main for associating reagent with the interior portions of the chip on a progressive delignification process itself which first reacts with the ligneous material on the exterior portions of the chips and thus gradually permits the treating liquors to work their way towards the centers with the concomitant overtreatment of the exterior content and undertreatment of the interior portions of the chip. Such progressive delignification following from the non-uniform distribution of the reagent results in excessive losses and degradation of cellulose, the production of shives or chips with hard, undercooked centers, or both. The undissolved lignin in such pulps is not uniformly associated with the cellulose fibers, actual measurements showing that the amount present in the inner half (by volume) of the chips may be twice as much as in the outer half. The fibers thus having undergone a corresponding variability of treatment, are unequally depolymerized and possess variable properties, for instance, viscosities of different portions extending widely above and below the average viscosity of the whole. These inequalities are detrimental, regardless of how the pulp is to be utilized, but for the production of certain cellulose derivatives, for example, acetyl cellulose, they may be so serious as to render the product unfit for the purpose; but irrespective of the utilization, whether in the paper industry or for cellulose compounds, the prevailing characteristics of these

pulps are unsatisfactory yield and lack of uniformity.

In the process of this invention, I attain intimate association of digesting liquors having proper reactive strength and, at the same time, nearly uniform distribution of the delignifying chemicals throughout all portions of the wood or other cellulosic material before providing reactive temperatures so that when the proper temperature is reached the reaction proceeds rapidly and simultaneously throughout all portions of the wood including the difficultly penetrable centers of the wood subdivisions.

I have found that the key to properly relating the reagents and woody material prior to reactive temperatures consists in the removal and exclusion of the normal air content of the wood. My investigations have shown that any air within the interstices of the wood clings to the inner portions with great tenacity so that the effect of the usual penetration methods advocated by those skilled in the art is to imprison and compress this air and retain it within the central portions of the wood. The normal amount of air space in wood is quite considerable, being, for example, in some varieties of spruce 78% of the volume of the wood. The ordinary processes of digestion entrap a considerable portion of this normal air content, and such entrapped air excludes the digesting liquors and resists their penetration into the heart or interior portions of the chips or other subdivisions of the wood so that no matter how thoroughly the outer portions are penetrated, there is a failure of the liquors to reach and properly react with the interior non-cellulosic material until after the outer portions have been substantially digested.

The history of the pulping art reveals many attempts to associate the digesting chemicals with the non-cellulosic content of the wood to promote and improve delignification, for example, by so-called preimpregnation and saturation but all of these have been unsatisfactory due to the resulting shallowness of the penetration by the digesting reagents, incomplete saturation or lack of uniformity or distribution of the reagents or the delay in attaining proper association of the digesting chemicals with all the non-cellulosic content of the wood, i. e., the inner portions of the chips or the like as well as the exterior portions, until actual digesting conditions have been in effect for such length of time as to preclude all possibility of uniformity of treatment. In none of these practices was the fundamental prerequisite to complete penetration achieved, namely, the removal and exclusion of the air from the wood prior to the introduction of the impregnating fluids, with the consequence that the digesting reagents could never be completely associated with the non-cellulosic components of the wood.

The result has been that in practice, whether appreciated or not, one of the main problems of digestion has been to effect a transfer and redistribution of the unevenly deposited chemicals with relation to the uniformly distributed ligneous material within the chip. Such diffusing, spreading, and permeating of the chemical in the complicated interstices, capillaries and solid ligneous sections of the wood require time and are necessarily attained with degradation and loss of the outer cellulose and with the tendency of the residual ligneous material to be quite unevenly distributed and concentrated toward the center portions of the chip. The re-

sult has been that the purification procedure has to be sufficiently drastic to take care of the portions having the highest lignin content and both the digestion and purification have to work in the face of these relatively high variables with consequent overtreatment of the remaining portions of the mass.

Since the structure of wood is known to involve the presence of not only macroscopic pores and capillaries, but also microscopic and submicroscopic pores, the problem of retention of air in very small cavities becomes one of fundamental importance. The air is held in these cavities with great tenacity and its displacement is exceedingly difficult because of the minute dimensions which prevent the easy flow of liquid through these pores. I have found that the use of strong suction or various low pressure devices does not effectively remove the adsorbed air and in practice I depend on the preferential wetting of the surfaces of wood cavities by water or other treating liquids to displace the adsorbed air film.

Moreover, the air in the capillaries of wood cannot leave the chips as long as the digester is sealed. It is only by providing adequate relief under such conditions as will permit a very large volume of air entrained in the wood to escape that the pores can be filled with liquid. The conditions employed in the commercial practice of relief in the digestion of wood do not provide an opportunity for this complete removal of air during that period of the digestion when it is most important that the cooking liquors shall gain free access to the innermost portions of the wood.

Partial air removal still leaves residual air to be entrapped and unless substantially all of the air is removed prior to obtaining digestion conditions, the impregnating fluids will be prevented by the remaining entrapped air from reaching the innermost portions of the wood, inevitably resulting in nonuniform delignification, the production of shives and other objectionable features. When it is considered that a relatively small volume of residual air in each chip will prevent the necessary intimate contact between the digesting liquor and a substantial portion of the ligneous material within the chip for a considerable portion of the digesting cycle, the importance of attaining substantially complete air removal before digesting temperatures are reached can be appreciated.

With the system of this invention the complete removal and exclusion of air and thorough and homogeneous impregnation permit the chemical reagent to be distributed in direct association with the noncellulosic ingredients throughout the woody material even to the innermost parts of the most intricate inaccessible structures. Widely different species can be treated together and when the more difficultly penetrable type is thoroughly permeated, it follows that the more accessible species is also completely saturated though in such practice the absorptive capacities of the different species must be taken into account. A similar result is obtained with the different characteristics of heartwood and sapwood of the same species.

I effect air removal and subsequent uniform association of the cooking liquors with all portions of the wood by first submerging the chips or other subdivisions of the wood in a liquid which may be treating liquor of the required concentration which is maintained under freely vented boiling conditions for a length of time, usually

thirty minutes or less, depending on the wood subdivisions and heat distribution, sufficient to expel all the air originally present from the innermost portions of the chips. This treatment may be carried out in my convenient pressure vessel such as a tank or digester. In practice, tall digesters are frequently used in which the column of liquid may be 50 feet or more. This hydrostatic head involves several degrees difference in temperature between the top and bottom of the charge of liquor and wood to effect boiling and in such cases air removal is effected by closing the digester and bringing the temperature of the charge to from 105° to 120° C. or higher, whereupon fairly rapid and extensive relief through the vent line will promote rapid ebullition throughout the mass. The vent line of the digester may be opened and closed several times with corresponding fall and rise in temperature in order to effect sufficiently complete expulsion of air. The water vapor or the vapors of the other wood constituents present at the boiling temperature or both act as a conveyor in removing or discharging the air from within the chips; as these vapors or gases form within the interstices of the woody structure, they diffuse and merge with the air and carry the air out into the surrounding pool of liquor from which the air escapes. By continuing the boiling process sufficiently long and always under freely vented conditions, all of the air will be removed from the chips and at the termination of the boiling period the chips will be saturated with water vapors and vapors of volatile woody constituents.

During and after the boiling period the chips must be maintained continuously submerged, for instance, in the treating liquor and while thus submerged, the vapors and gases within the interstices of the chips are condensed by lowering the temperature of the surrounding liquor one or two degrees or more below the boiling point. The resulting condensation of the vapors and gases creates a relatively reduced pressure condition within the chips which draws in the treating liquor and only the treating liquor so that a complete and immediate dispersion of same throughout the wood is effected with the exclusion of air. During this condensation the wood absorbs a considerable amount of the immersing liquid.

In order to reduce the time cycle where this may be of importance the step of lowering the temperature may be omitted and condensation of the steam within the cavities effected by increasing the temperature and therefore the pressure of the surrounding medium. The differential pressure thus established permits the penetration of the outer liquor into the air-free cavities. With aspen heartwood, I have found, for instance, that the increase in weight of the wood from the inflow of the surrounding liquid boiling medium during the condensation of the vapors and/or gases is even greater than the previous gain during boiling. In some cases, for instance, with calcium bisulfite liquors it may be desirable to take advantage of this fact by first boiling the wood in H₂O or other substantially non-delignifying solutions until all the air in the system has been removed, thereupon the excess solution in the digester is drained or blown by means of steam added at the top of the vessel after which the treating liquor is added and the actual cooking schedule is started. It is therefore of vital importance not only to carry on the boiling sufficiently long to diffuse out the air completely but also to protect the wood against any re-entry

of air during the condensation period and to confine the impregnation to the desired treating liquor. The chips may now be brought to reactive temperatures in as short time as the available apparatus will permit and the desired solution of lignin may be effected but in shorter time than is possible by current practices or any processes of the prior art employing the same reagent.

The reaction between the ligneous material of wood and many of the chemicals ordinarily employed in the pulping art, for instance, caustic soda, is quite rapid so that when the proper conditions are provided the desired action on the ligneous material is capable of being accomplished in very short time, for example, five minutes or less. With the treating liquors properly associated with the wood, as just described, the attainment of delignification in such short time is limited only by the existing facilities for uniformly effecting the necessary heat transfer to all portions of the chips; in the digesters in common use in the alkaline pulping industry, each charge of liquor and wood may amount to 100 tons or even more, consequently, the problem of raising the temperature of the mass from the ebullition temperature to the reactive temperatures of 160°-170° C. requires time and while these very short times for delignification can never be realized in the standard type of existing digester, the usual "cover to cover" time cycle is reduced by the system of my invention by one third or one half or more of that ordinarily employed.

The digestion may be effected by preimpregnating the chips with an alkaline treating solution, for example, a kraft liquor of higher concentration than ordinarily employed, for example, such that the ratio of absorbed chemical to wood will be .15 to .18, and draining all surplus liquor from the wood after impregnation so that the ratio of liquor to wood in the case of heartwood moist drained chips will be about 2 to 1. With facilities available for effecting rapid and uniform transfer of heat to the drained chips as, for example, in a tumbling digester heated by means of a steam jacket or by surrounding the moist chips with an unreactive suitable heat transfer medium, delignification may be accomplished by raising the temperature of the chips in twenty minutes from room temperature to 170° C. and terminating the cook immediately upon reaching this temperature. Under the reduced time of reaction of this procedure the material is subjected to the digestion temperature only a short period with corresponding minimizing of any objectionable effect on the cellulose content.

The short time required to effect the necessary reaction with the ligneous material may be taken advantage of more completely by means of a continuous digestion apparatus. Wood chips which have been pretreated by the system of my invention so that just the proper amount of reagent to satisfy the lignin demand is uniformly associated with the lignin throughout all portions of the chips, can be pulped in any type of continuous digesting apparatus which will permit the rapid and uniform application of heat to the moist drained wood so that the desired reactive temperatures may be attained in minimum time and the chips continuously removed from the reactive temperature zone in a predetermined short time. Satisfactory results may also be obtained with the advantages of short-time cooking where for the purpose of accomplishing uniform heat transfer, it is desirable without actual draining

to employ relatively low liquor to wood ratios, for example, 2.0-2.5 to 1; in these cases the concentration of the impregnating liquor is so adjusted as to meet the lignin demand, taking into account the larger total amount of liquor present than in the case of preimpregnated drained moist chips.

While effective air removal and exclusion and uniform intimate association of treating liquors with the wood prior to reactive temperatures is attained by the system of my invention just described, I have found that the distribution of the reacting chemical itself is affected by the tendency of the wood to preferentially adsorb from the liquor some of the commonly used reagents, for example, sodium hydroxide. The effect of this preferential adsorption as the liquor passes into the woody structure is to associate an excess amount of reagent with the exterior and a less amount with the interior portions of the chips so that, upon the attainment of the reactive temperature, the lignin demand in the outer portions of the chips is satisfied and the excess reagent is in prolonged contact with the liberated cellulose fibers while any deficiency of reagent in the interior portions of the chips is being met by the process of diffusion or the gradual penetration of additional reagent from the surrounding pool of liquor or both. Where residual quantities of entrapped air remain in the chip, the foregoing unfavorable conditions have superimposed upon them the further necessity for the solution of the entrapped air by the treating liquors before either the liquor or the reagent can penetrate those interior portions occupied by the entrapped air.

The outermost fibers of a block of wood adsorb considerable quantities of chemical from the cooking liquor. Consequently, the liquor which penetrates to the interior portions of the block is depleted with respect to the concentration of the delignifying chemicals. In fact, this unequal distribution of the chemical constituents of alkaline cooking liquors in the chips or blocks occurs regardless of the concentrations between 0.5% and 25% with which the chips are treated, and constitutes an insurmountable obstacle to uniformity of suitable treatment under conditions ordinarily employed in the alkaline pulping industry. It has been calculated by Stamm (Ind. & Eng. Chem. Anal. Ed. volume 1, 94; 1929) that the surfaces of the skeletal structure of a gram of wood amount to about 310,000 square centimeters and, as adsorption is a surface phenomenon, the depletion of the delignifying liquors by adsorption of chemical in its progress towards the innermost portions of the wood must necessarily become a significant factor in the treatment. I have found, for example, that when blocks of wood 1" long measured with the grain, 1" wide and $\frac{3}{8}$ " thick are treated in a sodium hydroxide solution of suitable concentration and boiled at atmospheric pressure for one hour and then allowed to soak for thirty minutes while submerged in the treating liquor, the exterior 50% (by volume) of the blocks contains approximately ten times more alkali than the interior 50% section. A similar preferential adsorption occurs where blocks or chips of wood are immersed in kraft liquors. In this connection, it is perhaps helpful in an understanding of the mechanism of alkaline delignification to consider that the reaction between, for instance, caustic soda and lignin, is an exceedingly rapid one, apparently following fairly closely a doubling of the rate of reaction with each increase of 10° C. in temperature. Hence, at the rather high temperatures

used in delignification, the reaction will only proceed at its appropriate rate provided the reagents, in sufficient quantity necessary for this reaction, are present in the exact location where the reaction is to take place. If, therefore, only part of the lignin demand of reagent is present in a certain portion of the wood, diffusion which requires appreciable time through very fine capillaries will have to be relied upon to bring an additional supply of chemical from the liquor surrounding the chips to this spot. It is conjectured that a considerable portion of the time of digestion is spent on this effort to secure the additional amount of chemical required to satisfy the demand by diffusion, which, under conditions imposed by the complex structure of the wood, is relatively slow. This additional time spent in delignification at high temperatures is destructive to the cellulosic material which it is the object of this invention to retain, besides being uneconomical from an operating standpoint.

I have discovered that these difficulties with specially adsorbed reagents can be overcome by pretreating the wood chips in a substantially nondelignifying electrolyte solution under conditions which remove and exclude the air followed by the appropriate penetration of delignifying liquors and control of the pulping conditions. The adsorption of the delignifying reagents on the surfaces of the wood may be largely avoided and the rate of diffusion of the treating liquors through the capillaries and membranes promoted by pretreating the wood with such suitable electrolyte solution under proper conditions of time, temperature and concentration. I have discovered that it is possible to obtain uniform impregnation, for instance, of caustic soda throughout the mass of wood chips or blocks, flakes and the like by subjecting them to a pretreatment with a dilute solution of a substantially non-delignifying electrolyte under proper conditions of time, temperature and concentration prior to the impregnation with caustic. The concentration of the electrolyte solutions employed is of critical importance, the optimum being approximately 10^{-2} molar in the case of sodium chloride and 10^{-5} molar in the case of aluminum sulfate, these being typical examples of suitable non-delignifying electrolytes. I boil the wood in a solution of non-delignifying electrolytes of proper concentration for one hour at atmospheric pressure, after which the solution is allowed to cool to a few degrees below the boiling point, i. e., 97°-98° C., and the chips are allowed to stand in the liquor at the reduced temperature for one hour; they are then drained and the delignifying solution, for instance caustic soda, is introduced at or near 100° C., preferably between 95° C. and 98° C. in sufficient amount to completely cover the entire charge of chips. My practice for effecting complete penetration, described above, is then carried out and now results in a uniform distribution of reagent as well as liquid throughout the chips, including the innermost, difficultly-reached centers.

The amount of Cross & Bevan cellulose and alpha cellulose in wood varies according to species, ranging from 50% to 62% of the weight of the wood and 38% to 46% respectively, depending on the species, the percentages for spruce being approximately 58% and 44%. Cross & Bevan cellulose is the commonly accepted designation for that component of the wood pulp which remains after successive chlorinations carried out under a precise known standard method

and includes the three classes of cellulose, namely alpha, beta and gamma. Alpha cellulose is that component of the pulp which survives the treatment in cold caustic soda solution of 17.5% concentration, also carried out under a precise known standard method. Thus the Cross & Bevan cellulose contains the alpha cellulose component plus the amount of beta and gamma that occurs in the pulp. In the pulping art, one of the objectives is to retain all of the Cross & Bevan cellulose where the pulps are intended for use in paper manufactured and all of the alpha cellulose where the pulps are intended for use mainly in the production of cellulose derivatives, but these objectives are never attained, the losses in many cases being 20% or even more. By the system of my invention, the losses of Cross & Bevan and alpha cellulose are largely or completely overcome so that by my practice substantially all either of the Cross & Bevan or alpha cellulose alone originally present in the wood is retained, and in either case, in undegraded form and uniformly distributed.

Following is an example of the practical application of my discoveries to the pulping of yellow birch chips with the use of caustic soda solutions for the production of magazine and book paper pulp.

Example A

The digester is filled with yellow birch chips of the standard size, usually $\frac{3}{8}$ " x $\frac{1}{8}$ " long, the chips are boiled at atmospheric pressure in solution of aluminum sulfate of about 10^{-5} molar, after which the liquid is allowed to cool to a few degrees below the boiling point, for instance, 97° C. to 98° C. The time of treatment is preferably about one hour to allow for the removal of air and the deposit of the electrolyte and after this is completed the batch is allowed to stand for one hour, the chips during this period remaining submerged. The solution is then drained from the wood and a caustic soda solution added without delay until the ratio of liquor to wood is 3.25 pounds to 1. The concentration of the caustic solution is so adjusted that after taking into consideration the amount of liquid present in the pretreated chips, the ratio of chemical to wood in the system will be .20 to 1.

The caustic soda solution is added to the digester at 70° C. or higher and after the chips are submerged by this liquor, heating and circulation is started by means of a circulation pump which draws off the liquor at the bottom of the digester and discharges it at the top through a circular perforated pipeline located at the top of the cylindrical section of the digester while high pressure steam is simultaneously introduced into the bottom of the digester at a temperature of approximately 200° C. The relief valve on the digester is "cracked" during the initial steaming to permit the air above the liquor level to escape and avoid any false pressure. The temperature rise of the mass is halted at about 96°-98° C. and maintained at this point for one hour. This pause permits the caustic to penetrate the chips without reaction and at a temperature below boiling tending to preserve the electrolyte deposit and at the same time sufficiently high to expedite the entry of the caustic into the interstices of the wood. The relief valve is then closed and the temperature raised to 170° C. as rapidly as the facilities will permit, the usual requirement being from one and a half to two hours. The temperature is held between the limits of 170° C. minimum and 173° C. maximum for two

hours. The liquor circulation pump is stopped fifteen to twenty minutes before the termination of the cook so that incoming steam may break up any packing of the pulp, that sometimes occurs and tends to prevent the blowing of the digester cleanly. At the end of the cooking time, steam is shut off and the pressure in the digester, which is usually about 100 pounds, is utilized to discharge the pulp through the blow valve located in the bottom of the digester, the stream of pulp usually being directed at a steel target in the blowpit, which impact serves to largely break down the chips into a pulpy mass. As soon as the blow valve is opened, waste black liquor from a previous digestion is pumped into the digester for about fifteen minutes to assist in attaining a clean blow or discharge of the pulp. Only in rare instances, for example, in not more than one cook in two hundred and fifty, is there a necessity for re-blowing the digester when the cooking is carried out under this practice.

The pulp from this operation will have a bleachability of 20% or less and the yield of oven-dried pulp, based on the original oven-dry weight of the wood, will be from 50% to 52%, the product being distinguished by its uniformity, softness, opacity and other properties desirable for pulp to be used in the manufacture of book and magazine paper. This yield compares with 40%-46% of pulps of similar bleachability obtained by ordinary current mill practice.

The type of digestion just described does not, however, reflect the maximum economies capable of being realized by the system of this invention for papermaking pulp but has been selected to afford a direct yield comparison of pulp of approximately the same bleach requirements to which soda pulp is normally cooked in general practice. Where the time and temperature and chemical to wood ratios of digestion are so related that a raw pulp is produced which will give the maximum yield of bleached pulp when bleached to the required standard of whiteness by a multiple stage system, or by any efficient two-stage high-density system, further economies result. Cooking conditions may be readily selected which will result in pulps of maximum yield of any desired bleachability; where the output of the digester is the controlling factor, the optimum chemical ratio for a given bleachability in the shortest cooking time is readily found.

When kraft cooking liquors are employed in which the ratio of caustic soda to sodium sulphide is 3:1, 3%-4% higher yields of pulp of any given bleachability or of bleached pulp may be obtained from wood chips.

There is a similar relation between the yield-time chemical to wood ratio and bleachability for each species of wood; examples given are for the typical hardwood, yellow birch. The iso-bleachability curves for maple occupy a slightly higher position in the range of yields while the iso-bleachability curves for aspen, another commonly used hardwood, occupy a position 2%-3% higher in yield than yellow birch.

Where the pulp or cellulose is to be used for purposes in which fiber strength is not a controlling factor, such as, for example, in the production of cellulose derivatives, the following procedure may be taken as typical of the practice of this invention:

Example B

Black gum wood, preferably selected to insure freedom from knots and decay, is treated under

conditions which provide uniformity of distribution of treating liquors with all portions of the woody structure before the attainment of reacting temperatures. Advantages may frequently be obtained by selecting only such wood as is essentially all sapwood, since the rates of delignification of sapwood and heartwood differ sufficiently to permit a greater uniformity of product being obtained if only sapwood is used. Furthermore, in the case of sapwood, the cellulosic material has not had an opportunity to change and fibrous material capable of greater uniformity of treatment can be obtained.

The natural sap content of the wood is maintained as nearly as possible by using freshly cut wood and maintaining the protecting bark on the logs until ready for flaking or chipping. The bark is then removed and the logs are thoroughly washed free of particles of bark and dirt and cut into flakes of approximately .020" to .030" in thickness or chips $\frac{1}{4}$ " long. Water may be used in the flaking or chipping operation in order to protect the wood from the drying action of the air. The wood will thus retain the greater part of its natural moisture which, in most cases, will be in excess of 30% and the flakes or chips are stored in air-tight containers until ready for charging into the digester so as to retain their moisture content.

The wood is then charged into the digester, which is preferably of the rotary type, and constructed of chrome-nickel steel of 20-10 alloy or its equivalent, equipped with means of injecting both steam and acid directly into the interior while either stationary or during rotation. The treating liquors consist of ammonium bisulfite of a composition comprising a total SO_2 content of 4.45% and a combined SO_2 content 1.1%. The ratio of treating liquor to wood employed is 6.0 to 1. The flakes or chips may be preimpregnated by submerging in water in the digester and vigorously boiled for 15 minutes after which the temperature of the mass is allowed to cool to 97 or 98° C., and the wood allowed to soak, care being taken to maintain it submerged for 30 minutes. The water in excess to that which has been adsorbed by the wood is then drained or forced from the digester and the treating liquor which has been previously heated to 90° to 110° C. in a separate acid accumulator tank is pumped into the digester. Allowance must be made for the water adsorbed by the wood in calculating the composition of the treating liquor and its ratio to the wood. In many cases it may be desirable to eject the water in which the chips are boiled by the introduction of steam in order to get the amount of absorbed water to a minimum. This is particularly of advantage where very strong bisulfite liquors are not available. If desired the preimpregnation of the wood with water may be omitted and the chips boiled in sodium sulphite or ammonium bisulfite containing practically no free SO_2 in which case the drainage of the excess liquor is unnecessary. Where the wood is thus directly impregnated with ammonium bisulfite liquor containing practically no free SO_2 the requisite amount of SO_2 is added after the impregnation has been accomplished.

If desired the preimpregnation of the wood with water may be omitted in which case the liquor of the composition described above is preheated in the acid accumulator tank to 90° C. to 110° C. and is pumped directly into the digester charge of wood. After the introduction of the proper amount of treating liquor the rotation of

the digester is started, steam is introduced with the vent line leading from the digester to the accumulator tank closed and the heating continued until the temperature of the wood and liquor reaches 103°-105° C. The digester with for instance a pressure of fifty-five pounds and a temperature of 104° C. may be connected with an accumulator tank, which is at forty pounds pressure and a temperature of 90° C. The relief line of the digester is then partly opened for a period of 1 to 3 minutes and this operation repeated from one to five times at intervals of five minutes between each operation, the number of vent periods depending on the kind of wood subdivisions used.

At the conclusion of the boiling period, the vent line is closed, the rotation of the digester is started and steaming is continued as rapidly as possible until the temperature within the digester reaches 120° C., which will require three quarters of an hour. The temperature is held at 120° C. for four hours after which it is raised to 135° C. in one and one half hours and held at this point within $\pm 1^\circ$ for an additional two and one half hours. Then the cooking is terminated and the used liquor in the digester drawn off and hot water, preferably at above 100° C., is injected until the digester is approximately two thirds filled, after which it is rotated for five minutes as a means of washing the pulp and then the water is drawn off into the sewer and the washing operation repeated twice. During the draining and washing, steam is maintained in the digester so that air is excluded from it and the washing is done substantially in the absence of air.

The pulp is then discharged from the digester into a dump tank equipped with agitation, where it is subjected to further washing until neutral to litmus and to violent agitation to break down any bundles of fibers which it may contain.

The pulp is now ready for purification.

I am the first, so far as I am aware, to provide a practical solution of this inherent problem which has confronted the pulping industry—whether realized or not—since its inception. Thus according to this invention the degree of cellulose degradation or solution under pulping conditions depends upon the time and temperature of treatment, concentration of the delignifying solutions, and the ratio of chemical to wood. By the system of my invention the time of exposure of the cellulose to the treating liquors at reactive temperatures may be reduced, or the temperature of the treatment may be lowered, or the concentration of the treating solutions may be reduced and the ratio of chemical to wood adjusted, or all of these factors may operate together to minimize or altogether avoid any unfavorable action on the cellulose itself.

An advantage of the method of this invention is that it maintains the capillaries of the wood open and accessible for the entry of the reagent. In alkaline processes of the prior art, the swelling action of the cooking liquor on the wood constitutes an additional factor which operates against the attainment of favorable yields and uniformity of pulps when, as in the processes now in commercial use, proper means for the uniform impregnation of the digesting chemicals are not provided. This follows because the transfer of chemical to the interior of the chip depends entirely on diffusion, the rate of which is greatly diminished by the swelling which fibers undergo on contact with solutions of caustic soda and the like since the swelling of the fiber walls causes a

decrease in the diameters of the capillary passages through the wood both within and between the fibers. Furthermore, the favorable effect which the diffusion of chemical might be expected to produce by partial delignification of the outermost parts of the chips at temperatures of 100° C. or higher is nullified by the increased swelling of the fibers which occurs under such circumstances.

When wood is treated with solutions of delignifying electrolytes, for instance, caustic soda, ions are adsorbed on the surface of the capillary walls, forming electrical double layers. These electrical double layers may affect the penetration of the cooking liquors into the interior sections of wood in several ways; the presence of such double layers, even though their thickness may not exceed several molecular diameters, may nevertheless be sufficient to decrease the effective cross-sectional area of the minute capillaries of the wood since the rate of flow through small capillaries is proportional to the fourth power of the radius. Furthermore, the movement of liquid in the capillaries past the electrical double layers on the capillary walls produces a streaming potential which may in itself also have the effect of retarding the flow of the liquid through the capillaries. Similarly the flow of the treating liquors through the membranes of the wood structure produces a membrane streaming potential having a similar retarding effect on the flow as in the movement of liquids in the capillaries.

Penetration may also be influenced by osmotic effects as there is a possibility that some of the membranes in the wood may be impermeable or only semi-permeable to the delignifying chemicals contained in the cooking liquors so that these ions in solution or at least some of them cannot penetrate beyond the impermeable or semi-permeable membranes.

The delignifying action itself of the treating liquors may obstruct penetration by producing colloidal substances capable of mechanically blocking or plugging the membranes and capillaries of the wood through which the liquors must penetrate. Alkaline liquors may form a sort of gelatinous membrane in the outer layers of the wood which is permeable to water but which may not be permeable to alkali, thus producing the effect of a filter, restraining the passage of the alkaline reagents.

These inequalities of distribution of reagent, due to imperfect penetration, preferential surface adsorption of reagent from the treating liquors, electrical double layers, osmotic effects, mechanical blocking of pores by colloidal particles resulting from the progressive delignifying action itself, formation of restraining membranes in the outer layers of the wood, and other hindrances, may be and in many cases are cumulative in their objectionable effects. Especially are difficulties encountered when the concentrations of solution are made very low because with dilute caustic soda solutions, for example, the reagent is used up by the most reactive lignin with which the chemical comes in contact as soon as the liquid starts to penetrate the wood. Consequently, the chemicals are all consumed before they reach the center and the cooked chips contain undefiberable centers which gives rise to splintery, non-flexible fiber bundles.

By first treating the wood in a freely-vented boiling solution containing a substantially non-delignifying electrolyte, the air within the wood is removed and all the surfaces of the wood

capillaries are protected by an adsorbed layer of ions which prevents the attack of the lignin or cellulosic material by caustic soda or other reagents subsequently added before fully reactive conditions are reached. As a consequence, any desired concentration—even very dilute solutions—of caustic soda can proceed uniformly to the interior of the chip without diminution from any cause. A constant quantity of chemical is now in intimate association with the lignin or non-cellulosic material in all portions of the wood, so that when the temperature is raised to 160° C. or 170° C. as, for example, where kraft or caustic soda solutions are employed, the desired reaction takes place rapidly and simultaneously throughout all portions of the wood. The very small amount of protective adsorbed ions from the pre-treating electrolyte solution has no influence at these elevated reactive temperatures. Thus, by proper impregnation of the wood with the delignifying reagents or preimpregnation with solutions of non-delignifying electrolytes prior to the association of the delignifying liquors with the wood, or both, I am able to effect uniform distribution of chemical reagents having proper reactive strength throughout all portions of the wood or other cellulosic materials before those temperatures are attained which effect any substantial reaction between the chemicals and the wood so that upon attainment of the proper treating temperatures the desired reaction proceeds to effect delignification rapidly, simultaneously and uniformly to any predetermined degree. These optimum conditions for pulping wood provide the most favorable conditions for avoiding degradation or any other undesirable effect on the cellulose itself with the consequence that for pulps of any given types or properties, higher yields or superior qualities, or both, are attained than is possible through the operation of any of the conventional processes or modifications thereof; they also make possible the attainment of pulps of new, desirable and hitherto unattainable properties especially suitable and valuable for esterification purposes.

I claim:

1. The process of treating wood to form pulp comprising subdividing wood into pieces of chip size or smaller and of relatively flat shape; submerging a mass of said wood pieces in an aqueous liquid; heating the entire mass of wood pieces and liquid to the boiling point of said liquid at not less than atmospheric pressure; continuing the boiling of said submerged wood pieces in said liquid under conditions of active ebullition and vapor removal until the discharge of air ceases; thereafter adjusting the temperature and pressure conditions to those at which steam is condensed in the wood pieces, while they are submerged in an impregnating liquid; continuing such conditions and submergence until impregnation with the impregnating liquid is complete, while maintaining the pieces in an air-excluding medium continuously from the boiling treatment to the completion of impregnation, a delignifying reagent being introduced into the wood pieces by the impregnating liquid at a temperature below that of active reaction; heating the mass of wood pieces in a submerging fluid medium to the range of temperatures of active reaction by said reagent; and digesting the wood pieces with said reagent to form pulp.

2. The process of treating wood as set forth in claim 1 wherein the liquid in which the wood pieces are boiled is a digesting solution of the

delignifying reagent, and the wood pieces are maintained submerged in such solution from the boiling treatment continuously until impregnation with the solution is complete.

- 5 3. The process of treating wood as set forth in claim 1 wherein the liquid in which the wood pieces are boiled is replaced by steam and the steam is replaced by a digesting solution of the delignifying reagent in which the wood pieces are submerged and with which they are im-
10 pregnated.
4. The process of treating wood as set forth in claim 1 wherein the wood pieces are im-
15 pregnated with a solution of a delignifying reagent of sufficiently high concentration to distribute uniformly the full lignin demand of reagent in the wood pieces.
5. The process of treating wood as set forth in claim 1 wherein the wood is maintained at a
20 moisture content of at least 30% from cutting to the end of digestion.
6. The process of treating wood as set forth

in claim 1 wherein the mass of wood pieces and liquid is heated in a closed vertical digester to the boiling temperature of the bottom of the mass under the hydrostatic head in the digester, and active ebullition is obtained by appropriate venting of the digester.

7. The process of treating wood as set forth in claim 1 wherein the steam-condensing conditions in the wood pieces are produced by liquid surrounding the wood pieces at a steam-condensing temperature.

8. The process of treating wood as set forth in claim 1 wherein the steam-condensing conditions in the wood pieces are produced by increasing the pressure.

9. The process of treating wood as set forth in claim 1 wherein the delignifying reagent is a caustic reagent, the mass of wood pieces after impregnation is heated to a temperature of the order of 170° C. to 173° C., and is digested at a temperature substantially within said range.

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