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## METHOD OF PRODUCING CELLULOSE PULP

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This invention relates to the production of fibrous materials from wood and other cellulosic substances.

The object of this invention is to provide paper, boxboard or the like composed of uniformly softened cellulose fibers and a relatively large proportion of ligneous material in homogeneous intermixture, giving desired qualities of strength and durability to the product.

A further object of the invention is to provide a cellulose material readily worked into sheet and other forms and combining with the cellulose fibers a treated or reacted form of the noncellulosic ingredients of the original material.

A further object of the invention is to provide a process adapted to soften interfiber material of the wood so as to preserve and at the same time release the fibers for recombination with the softened ingredients in any desired proportions.

The object of the system of this invention is to provide a mass of softened flexible wood fibers or fiber bundles capable of being felted and bonded into sheet or board form, intimately associated with the original incrusting material of the wood. All or nearly all of the noncellulosic material originally present may be retained and in modified form redistributed uniformly and intimately throughout the mass of softened fibers and in combination with these fibers constitute a pulp product in which substantially all of the original constituents of the wood are utilized. The fibrous mass may comprise a preponderance of bundles of a few dozen fibers each, or of completely separated fibers. But regardless of the extent of the defiberization, the pulp is distinguished by the flexibility of the individual members of the fibrous mass and of the mass itself, and the high yield of pulp material capable of being milled in a Hollander or other type of beater or apparatus for the purpose of developing the qualities conducive to good sheet or board strength properties and with less mutilation of the fibers than usually results with the milling of conventional pulps. Such material is particularly suitable for boxboard, wrapping and other non-cultural paper purposes.

Another object of this invention is to produce an intermediate pulp product comprising softened, flexible fibers or small flexible bundles of fibers or both with which remain associated substantially all of the original noncellulosic material of the wood in modified form dispersed uniformly throughout the fibrous mass and capable of being readily delignified to any desired extent by means of any type of reagent under most favorable conditions with respect to minimum reaction upon the cellulose itself. The ease with which delignification of this new pulp product may be accomplished is due to the accessibility of the noncellulosic component to chemical reagents arising from the vastly increased surface area exposed to the treating liquors by reason of the largely or completely defibered condition of the pulp product.

A further object of the invention is to provide a process for the production of said material which will be simple and economical and readily adaptable to a wide variety of products of different properties.

In prior practice the ligneous materials of the wood have been in a large part removed to free the cellulosic fibers, and where any considerable amount of incrusting materials was retained the resulting partially treated material has been of non-uniform composition with respect to the character and distribution of the residual lignin and has therefore required more drastic mechanical action to break down the less treated portion of the woody structure. Such processes are expensive in use and also tend to degrade the cellulose, destroy the strength properties of the fibers, reduce the yield, or lead to objectionable complications resulting from the operations required to separate the fibers and the noncellulosic material or both. The prior attempts to utilize the natural binding material associated with the cellulose fibers in the wood have been deficient because of the inadequacy of the treatment either to effect a uniform softening to a sufficient degree, or uniformly to effect the solution or alteration of a sufficient amount of the incrusting material to permit separation of the fibers without serious detriment to or destruction of the physical properties of the fibers.

In the process of this invention the woody material is subjected to a uniform lime softening treatment, which without appreciable degradation of the cellulose renders all of the material easily defiberable to pulp form with the retention of a nearly full content of ligneous material and without objectionable destruction of the strength characteristics of the fibers themselves.

I have found that wood chips or the like boiled in a lime solution for a sufficient time to remove the air will on raising of the temperature to the reactive point, such as 135° C., be penetrated by the lime solution of maintained strength and after sufficient time, seven hours for instance, with ordinary chips, the reaction will penetrate to the innermost interstices of the wood and uni-

formly soften the noncellulosic material to the point of permitting the wood to be defibered. During initial impregnation for air exclusion lime may be omitted or some other penetrant substituted therefor in the impregnating water, and the impregnation treatment may be continued sufficiently long not only to remove the air by penetration with water, one half hour, but may be continued sufficiently long after the addition of lime, e. g., three hours, to distribute the lime uniformly throughout the chip.

Calcium hydroxide is an especially effective reagent for this purpose, though other substances, such as calcium sulfide or milk of magnesia may be used. Lime on account of its limited dissolving action and low solubility in water (0.08% at 100° C.), may be added to the treating liquor in an amount in excess of that which will go into the solution, which has the resulting important and desirable effect of maintaining the strength of the treating solution constant throughout the cook. Thus the ligneous or incrusting material is subjected to the action of a fixed effective concentration of reagent for any desired treating period, with the result that the entire woody substance is so modified as to become quite softened, while the cellulose fibers themselves are uninjured and are rendered flexible even when occurring in small bundles of, for example, two or more fibers in thickness and four or more fibers in length. Due to the fact that most of the compounds which lime forms with the incrusting substances of wood are largely insoluble in lime solutions, a large part of the modified nonfibrous components of the wood (calcium lignates) remain associated with the mass of flexible fibers, with the result that overall yields of useful pulp material of 95% and even 100% by weight of the original oven dried wood are readily attainable by procedure of the following types:

*Procedure A.*—Wood chips or flakes are submerged in boiling milk of lime solution in a freely vented condition for approximately one half hour to remove the gas content of the wood from the interstices, after which the container is closed and the temperature raised to 135° C. or more. The container is maintained at this temperature for a sufficient time to thoroughly soften the wood throughout the entire mass. At 135° C. the time of the treatment will vary from six to eight hours, according to the material being treated. Sufficient lime is present to supply the treating liquor with the desired amount of dissolved lime to give the required softening. This will involve using an amount of lime which maintains a saturated solution throughout the cook, or the lime may be so regulated that substantially no free lime is present at the end of the digestion. Any desired intermediate condition may be used.

*Procedure B.*—The wood chips or flakes are submerged in lime water and boiled for approximately three hours until there is a complete penetration of the entire woody structure by the lime. After this three hour boiling at 100° C., the container is closed without exposure to re-entry of air and the temperature raised, for instance, to 135° C. or over, for a period of time sufficient to soften the chips to desired degree. This time will vary from four to five hours depending upon the kind of wood being treated. Throughout the entire process the treating solution may be reinforced with lime to maintain it saturated, or this saturated condition may be maintained for only a part of the cooking period depending on the degree of softening desired.

A point of fundamental importance is the thorough impregnation of the wood by the reagent with the concomitant displacement of air. It is also to be emphasized that the action of the lime during this impregnation and in the subsequent digestion is quite unique since its results cannot be paralleled by the use of any concentration of the usual alkalies, for example, caustic soda. If very small amounts of caustic soda are used such as will permit high yields in excess of 85%, experience shows that similar softening of the chip is not attained. The dilute caustic soda solution behaves as if it reacted with the lignin immediately accessible, and as if the caustic which started to penetrate the chip was prevented from further traveling into the chip through the depletion of the reactive chemicals from the entering liquors. It is also quite possible that the well known behavior of caustic soda in promoting swelling of polysaccharides may have effectively blocked up the minute passages to infiltration of the caustic solution.

In contrast with this behavior of caustic soda is the action of lime which either because of its very low concentration even in saturated solutions, or because of its lower tendency to promote swelling, or because of its formation of insoluble calcium compounds, (or whichever one or combination of these principles may be involved) the lime behaves as if it were uniformly penetrating the wood and softening or reacting with the lignin perhaps primarily of the middle lamella, so that subsequent mechanical action is capable of effecting any desired degree of defibering.

Another advantage of lime in the softening of woody material follows from its rather high degree of insolubility which permits the maintenance of a suitable supply of reagent held in suspension in all reservoirs of liquid from which the active reagent can be drawn whenever chemical action or adsorption or other action removes the reagent from solution. From an economic standpoint the very low cost of lime permits its use in such chemical ratios as will perform the desired degree of delignification or softening without requiring that we resort to the use of recovery systems. Even if lime were as expensive as caustic soda it would probably be still the most suitable reagent for use in producing high yield pulps of uniform defiberability because of its property of low solubility, low reactivity at 100° C. and low capacity for swelling wood.

The pulp product of this invention is the cheapest form of defibered pulp attainable since substantially all the lignin is retained and to the lignin there is attached a metallic ion, calcium, in the form of an insoluble calcium lignin complex. This ligneous material remains an essential part of the pulp in the subsequent formation of the paper or board.

The softened material resulting from any of these treatments has substantially the entire content of the ligneous material so modified that the material is readily defibered in machines such as hammer mills of the "Dixie" type, pulp beaters, or hydraulic shearing apparatus of the colloid mill type, by proper adjustment of the reducing action without undue mutilation or impairment of the fibers.

A prominent characteristic of the softened material is its extreme flexibility throughout the entire body of each chip, flake, bundle or other unit, and the material in bending flexes each

fiber in its surrounding softened matrix. The softening also places the material in ideal condition for subsequent treatment of the components to separate the fibers, fibrillate and hydrate them and redistribute the cellulose and ligneous material in desired relation for the particular product being manufactured. The cellulose fibers themselves are undegraded and substantially unaffected from their natural condition in the wood except as they are softened by the alkaline treatment and as some of them are cut and frayed in the chipping or other unit-forming operation prior to the softening treatment and in the following defibering operation.

The softened chips or other units may, if desired, be defibered only to the extent required to obtain a mixture of small bundles of fibers and completely separated fibers. The bundles may be three or more fibers in thickness, but are preferably not more than three; they may be three or more fibers in width and four or more fibers in length. These small bundles, as well as the completely separated fibers, are soft and flexible and are especially well suited to form the structural elements of a network for a new type of coarse sheet in which the single fibers may in part form the filler. By my invention the fibers or other units are so conditioned and the mechanical treatment controlled so that the small bundles as well as the completely defibered component of the pulp will be properly fibrillated, hydrated and otherwise favorably conditioned for felting and bonding and at the same time ligneous compounds will be swollen and so softened that when the pulp is felted and an appropriate pressure applied, the gelatinous materials associated with the mass of bundles and individual fibers and the ligneous compounds which itself may be in a gelatinous state, are spread on and into the network of fiber bundles and fibers, a strong sheet results which is useful for a wide variety of purposes, especially of a non-cultural character such as boxboard, wrapping papers and other kraft-like sheets not specifically intended for writing or magazine stock.

The pulp which results from the system of this invention is a new product possessing properties hitherto unattainable, and capable of forming a strong sheet of coarser texture which is in itself a new product. As distinguished from my invention it is necessary in the current practice of paper making to completely separate the hard incompletely cooked bundles of fibers or shives from the individual fibers in the pulp by screening before beating or other milling operations, since in all attempts heretofore to utilize such material, unsatisfactory sheets have resulted due to the fact that such fiber bundles or shives consist largely of hard, brittle splinters which are incapable of flexing and being fibrillated, hydrated and otherwise conditioned for felting and bonding with the consequence that the sheets are lacking in strength, homogeneity, softness, pliability or other necessary properties.

Attempts in the past to produce strength qualities from the larger building units such as those employed by my invention have been unsuccessful due to the inability to produce the larger elements for the network of the sheets with the requisite flexibility and capability of being fibrillated, hydrated and otherwise conditioned for felting and bonding. The treated wood when discharged from the digester upon completion of the lime treatment retains in large part the original form it had before treatment, i. e., the form of flakes or chips, but these are quite soft, flexible and may be readily separated into small bundles or slivers, or into individual fibers with relatively little effort. To illustrate the readiness with which the defibering may be effected, the largest or thickest treated chips may be easily torn into small bundles or slivers between the fingers. Combined with these softened fibers the pulp contains a large proportion of softened lignin embodying calcium lignates insoluble both in milk of lime and water. The cellulose fibers in addition to being undergraded are largely uncut, unbroken and otherwise unmutilated; consequently their strength is unimpaired.

The new sheet producible by my invention combines much of the desirable strength qualities of kraft pulp with a lower cost of production. Whereas commercial kraft pulps are produced from coniferous woods such as southern pine, hemlock and the like, the system of my invention is also particularly applicable to deciduous woods which in many sections of the country are relatively cheaper than the coniferous species, examples being cotton wood, soft maple, willow, poplar, birch, and gum. The natural color of the treated wood pulp is a brownish tan, sometimes it may be of a more or less reddish hue. The strength of sheets and board made from the pulp of this invention is many times that which can be made from the pulps used in large quantities of boxboard (wastepaper stock). As an example of such increased strength, sheets of pulp made from lime treated wood of this invention have shown a Mullen test considerably higher than that for comparable sheets made from waste paper.

The material from the defibering operation may be further beaten to expand and hydrate the individual cellulose fibers developing fibrillation, which greatly increases the surface area of the cellulose for redistribution of the lignin, and by proper control in this beater action full strength of the material will be developed for felting of the mass in sheet form in the subsequent milling.

Where desired the softened material either before or after defibering may be subjected to a treatment, for instance, with usual digesting liquors in desired strength to reduce the lignin content to any proportion required in the final product or to eliminate the lignin altogether. The softened material in defibered form is in condition for treatment with chlorine or other chemicals for delignification and color control.

The process of this invention is simple in operation and makes use of existing apparatus. The softening treatment only requires preliminary boiling and subsequent heating treatment at pressures well within the range of the usual digesting apparatus available in strawboard or paper mills. The draining of the softened material and the washing of such material also corresponds to usual operations in paper mill practice so that the system of this invention may be readily installed by slight changes in procedure and by substitution of the new chemical treatments involved. The softening action is economical in its use of chemicals. For instance, it requires only a mild lime treatment using small quantities of the material, which itself is very cheap so that there will be little, if any, advantage in recovery of the lime from the waste liquors. The costs involved in the operation of this process are substantially less than those of any known process of pulp production, even in-

cluding ground wood methods, in use at the present time.

In actual operation it has been observed that with the ordinary testing methods in paper mill practice, the final pulp of the system of this invention may give calculated yields of over 100% indicating that the lime or lime compounds remaining in the material exceeds the woody compounds removed during the softening process, which often retains over 95% of the materials originally present in the wood. For many purposes the presence of this lime in the pulp is not objectionable, and due to its low cost there is no occasion to remove it for recovery.

The process of this invention is not only inexpensive in operation but also very effective in the use of the raw materials to which it is applied. Instead of going to the expense of removing the ligneous components of the wood, it retains these components with corresponding increase in yield, and at the same time avoiding the cost of the removal and the objectionable effect of such removal on the remaining cellulose. Even where the ultimate product requires the removal of lignin, the system of this invention conditions the material most advantageously for such removal effectively and without undesirable degradation of the cellulose and at a minimum of expense.

I claim:

1. The process of treating woody material to form pulp comprising supplying the wood in subdivisions of chip size or smaller, replacing the air in the wood with a solution of a compound of the group calcium hydroxide, calcium sulphide and magnesium hydroxide, raising the temperature and maintaining said raised temperature for a sufficient time uniformly to modify the noncellulosic content of the wood throughout its entire mass while maintaining the strength of the treating solution by continuously replacing the reagent removed from solution by the wood, and defibering the treated wood while maintaining the fibers substantially unaffected from their natural condition in the wood to give a wood pulp product composed of such fibers having uniformly dispersed through the fibrous mass most of the original noncelluloses uniformly softened and modified.

2. The process of treating woody material to form pulp comprising supplying the wood in subdivisions of chip size or smaller, submerging said subdivisions in a boiling solution of calcium hydroxide and continuing the boiling to replace the air in the wood, then raising the temperature to 135° C. or over and maintaining said raised temperature for a sufficient time uniformly to modify the noncellulosic content of the wood of each wood subdivision throughout its entire mass while at the same time maintaining the alkalinity of the treating solution with an excess of calcium hydroxide, and subsequently defibering the treated wood while maintaining the fibers substantially unaffected from their natural condition in the wood to give a wood pulp product composed of such fibers having uniformly dispersed through the fibrous mass most of the original noncelluloses uniformly softened and modified as a flexible complex of ligneous material and calcium hydroxide.

3. The process of treating woody material to form a pulp having a large proportion of the original noncelluloses uniformly softened, modified and dispersed throughout the fibrous mass, comprising supplying the wood in subdivisions of chip size or smaller, replacing the air in the wood with a solution of a reagent of the group calcium hydroxide, calcium sulphide and magnesium hydroxide, raising the temperature to the point of active reaction and maintaining the concentration of the reagent in said solution constant by supplying an amount of reagent in excess of its solubility while maintaining said raised temperature for a sufficient time to modify uniformly the noncellulosic content of the wood throughout its entire mass, and defibering the treated wood while maintaining the fibers substantially unaffected from their natural condition in the wood.

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