

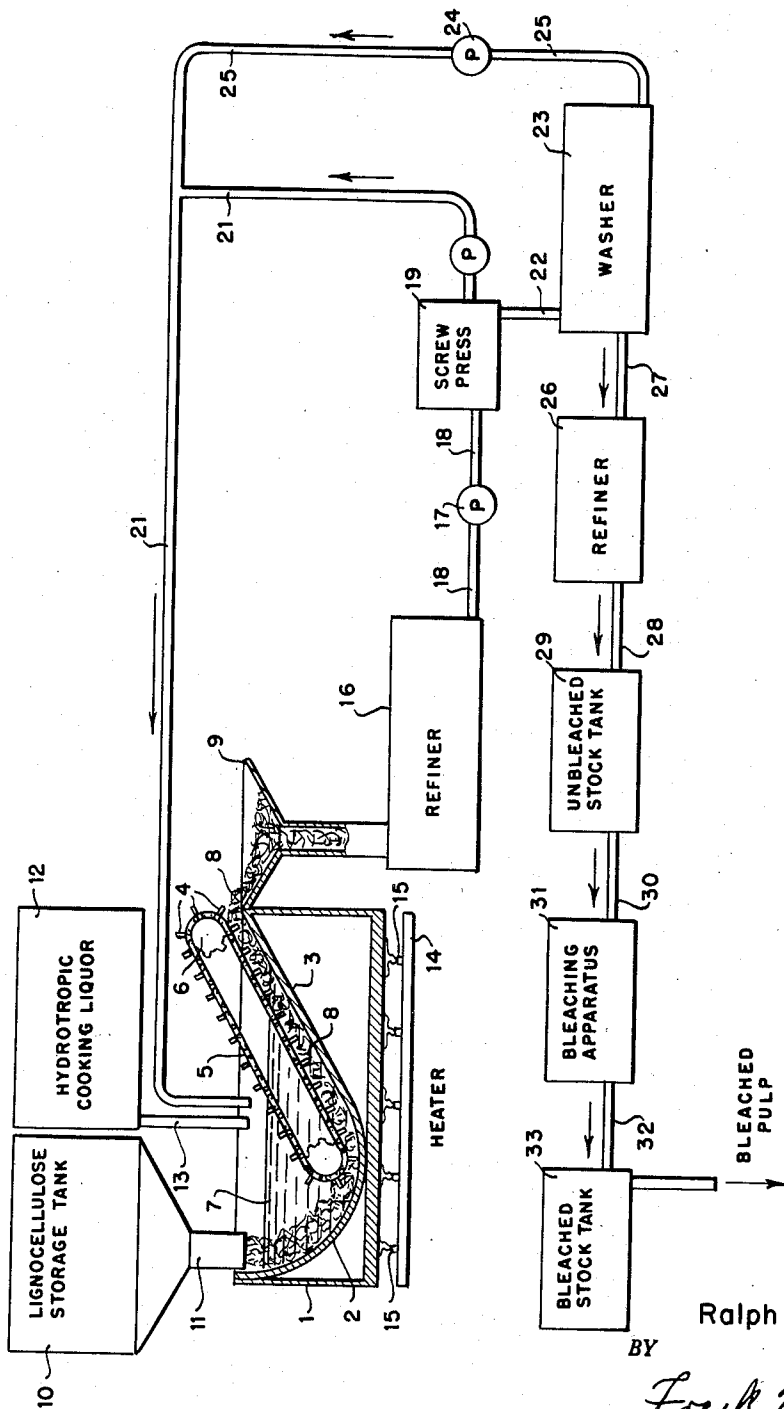
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SEMI-HYDROTROPIC CHEMICAL LIGNOCELLULOSE PULPING PROCESS

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1

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## SEMI-HYDROTROPIC CHEMICAL LIGNOCELLULOSE PULPING PROCESS

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This invention relates to a process for making cellulosic pulps and the product therefrom. More particularly, it relates to a process for cooking lignin containing cellulosic material, without appreciable loss in weight of the lignin content of the material due to solvent action, to render said material suitable for rapid disintegration into its fibrous components.

Most chemical processes for treating ligno-cellulosic material to obtain the cellulose fibers therefrom, require a cooking with a chemical solution at an elevated temperature to induce a solvent action upon the lignin. The dissolving of the lignin frees the cellulose fibers but since lignin constitutes about 20 to 30 percent of the ligno-cellulosic material, it is apparent that a considerable portion of the wood is not available in this type of chemical pulp.

It is an objective of this invention to provide a process for pulping lignocellulose material which will yield a high percent of pulp, for example 90 percent of the original material being pulp.

It is another objective of this invention to provide a process requiring little equipment cost and which may be carried out in open tanks.

It is a further objective of this invention to provide a continuous process for pulping cellulosic raw materials.

It is another objective to provide a chemical pulp having substantially all the original lignin and having a high opacity.

It is another objective to provide a chemical paper pulp having a high absorbency value and which is resistant to becoming brittle due to light and which does not discolor appreciably due to ultra-violet light.

It is another objective of this invention to provide a paper pulp making process wherein the cooking solution may be used a plurality of times and with successively increasing effectiveness.

It is yet another objective of this invention to provide a chemical paper pulp having substantially natural lignin and in an amount substantially that present in the raw lignocellulose material to obtain said pulp.

These and other objectives of this invention will become apparent upon reading the following descriptive disclosure of several illustrative embodiments of this invention taken in conjunction with a flow sheet diagram showing the continuous pulping of lignocellulose material by the inventive process.

According to this invention, a chemical paper pulp is produced which contains substantially all the lignin originally present in the ligno-cellulosic material being treated. The paper pulp obtained by the process of this invention has a composition substantially that of the original ligno-cellulosic material, differing therefrom in that a portion of the hemicelluloses, notably the pentosans, have been dissolved away. Approximately  $\frac{1}{3}$  to  $\frac{1}{2}$  of the pentosans originally present in the lignocellulose material are dissolved by this inventive process. As a result, a high yield of chemical pulp, for example 90 percent of the weight

2

of the original lignocellulose is obtainable by the process of this invention. The commonly used sulfite or sulfate processes gives a pulp yield of only about 50 percent of the original weight of the lignocellulose material.

Substantially any lignocellulose material may be pulped by this process, for example, the various woody plants, such as poplar, maple, etc. the various grasses such as kunai and wheat straw, also bamboo, kenaf and the like type of lignocellulose may be pulped by this process, as well as the bagasse obtained from the sugar cane industry.

The pulp obtained by the process of this invention is a chemical pulp. It contains about  $\frac{1}{2}$  the pentosan content of the original lignocellulose just as is the case for chemical pulps. Yet it possesses many of the desirable qualities of groundwood, which contains substantially 100 percent of the pentosans, without possessing the undesirable groundwood properties such as turning yellow or brown on exposure to ultra-violet light.

The pulp obtained in this invention is a novel product and inventive as such, since it possesses a fibrous texture and strength characteristics similar to that of the commonly available chemical sulfite and sulfate pulps, yet it also possesses the high opacity of groundwood pulps. Chemical pulps for example, bleached sulfate pulp, exhibits an opacity of about 79 percent, whereas applicant's bleached pulp has an opacity of over 90 percent. Thus the novel pulp of this invention process has the high opacity commonly associated with groundwood but it does not possess the tear test and burst test weakness shown in a sheet of paper made from groundwood. On the contrary, a sheet of paper made from chemical pulp produced by this process compares very well to the tear test and burst test properties of paper made from sulfite or sulfate pulp.

In short, the high lignin pulp of this invention is a chemical pulp exhibiting qualities comparable to substantially lignin-free sulfite or sulfate chemical pulp. Thus, while the percentage of chemical constituents of this pulp approximates groundwood pulp, the desirable physical properties of this new pulp approximates that of the commonly available unbleached chemical sulfite or sulfate pulps. The chemical pulp of this invention is distinguished in that it contains the naturally occurring lignin in substantially its natural chemical condition and in substantially the percentage amount occurring in the lignocellulose raw material used.

In U. S. Patent No. 2,308,564 a process employing a concentrated (25 to 40 percent) solution of hydrotropic salts was employed to dissolve out substantially all of the lignin present in the lignocellulose raw material being treated.

The chemical pulp process of this present invention is different in kind since substantially no lignin is dissolved.

In this present process a weak hydrotropic solution is used. Such a weak solution contains only about 1 to about 5 percent of a hydrotropic salt solution, and by the term hydrotropic salts as used herein, the term is intended to include the hydrotropic acids which may be looked upon as salts of the element hydrogen.

In this invention the dilute hydrotropic salt solutions were discovered to possess a selective action for pentosans and to have substantially no effect on the lignin. In short, the pulping or chemical loosening of the fibers in the raw material is effected in this process by the selective removal of a substantial portion of  $\frac{1}{3}$  to  $\frac{1}{2}$  of the pentosan content originally present, whereas the prior art hydrotropic process is based upon the removal of lignin. In other words, in the instant hydrotropic process the cellulose fibers are liberated by removing or weakening the cementing or bonding action due to pentosans whereas in the prior art hydrotropic process the fibers are

liberated by removing the cementing or bonding action due to substantially all the lignin.

The hydrotropic salts, which term as used herein includes hydrotropic acids, of this invention are derived from a single benzene ring. Examples of suitable operable salts are the alkali metal salts of benzoic, salicylic, xylenesulfonic, cymenesulfonic, phenolsulfonic and toluenesulfonic acids. Of course, the acids themselves are also operable in this process. Hydrotropic salts are also spoken of and known as "solubilizing agents" by the British.

The hydrotropic salts useable in this invention are, for example therefore sulfonates or the sulfonic acids of aliphatic substituted benzene. The hydrotropic substituted benzene sulfonates or sulfonic acids useful in this process have at least one group, preferably an aliphatic or alkyl group, substituted for a hydrogen atom in the benzene nucleus.

The phenomenon exhibited by hydrotropic salts is that of a "salting in" effect. In other words, the salt solution acts as a solvent.

While the salt solutions alone serve in the practice of this invention, yet in general the action is more rapid if the solution used is made acid preferably to a pH of about 4 before use. While acidification decreases the speed of penetration of the solution into the lignocellulose particle or wood chip, it effects a more rapid removal of the hemi-celluloses such as the pentosans, etc. The acidification is best accomplished by the use of the acid of the hydrotropic alkali metal salt. Thus to produce an acid aqueous cooking solution of sodium xylenesulfonate, use is made of xylenesulfonic acid, which is added to the solution until a pH of about 4 is obtained.

Furthermore, while dilute solutions of 1 to 5 percent of alkali metal hydrotropic salts are preferred, it is possible to use 1 to 5 percent solutions of the alkaline earth metal hydrotropic salts in place thereof. Even 1 to 5 percent solutions of hydrotropic acids are operable to selectively remove pentosans from lignocellulose.

However, where the alkaline earth metal salts or the acids are used alone the removal of the pentosans is not as rapid as when an alkali metal salt solution adjusted to a pH of 4 is employed.

The strength of the hydrotropic solutions preferred are of 1 to 5 percent and the amount of solution employed varies considerably due to a plurality of factors, but 6 to 12 parts by weight of solution to 1 part by weight of the lignocellulose starting material is preferred.

The solution used in cooking lignocellulose may be repeatedly reused by bringing it up to the desired strength and pH by the addition of hydrotropic salt or hydrotropic acid.

While open reaction vessels are preferred, the process of this invention can also be conducted in closed containers or in digesters or under reflux conditions. Where digesters are employed the cooking solution can be used at a temperature above its normal boiling point. The cooking of lignocellulose material at digester temperatures using the dilute hydrotropic salt solutions of this invention is especially useful where resinous woods such as the various conifers and the dense woods are used as the raw lignocellulose starting material. Where digesters or other closed containers are used as the reaction vessel the cooking may be effected at 120° C. in which event the cooking time is shortened to about one hour. Bamboo being a dense material may be easily pulped in digesters with the use of dilute hydrotropic salt solution.

Groundwood pulp cannot be used to make newspaper but must be mixed with about 20 percent sulfite to obtain a newspaper of sufficient strength. However, the chemical pulp of this invention can be used for newspaper without addition of sulfite pulp and yields a superior paper in that it does not yellow nor become brittle with age as does groundwood.

The temperature for cooking is preferably close to the

boiling point of the aqueous solution, for example, 95° C., but lower temperatures are operable although requiring a correspondingly longer time of reaction. The cooking time for lignocellulose using the same strength solution varies with the density of the specie of lignocellulose material being cooked. Thus bagasse may be pulped in one hour whereas bamboo would require 3 to 5 hours under the same conditions of cooking temperature and strength of cooking solution. Generally, where a 2 percent solution in a digester held at 120° C. is employed to cook or pulp a given wood in one hour, the same wood requires 5 hours at 90° C. in an open vessel and a solution strength of 2 to 5 percent hydrotropic salt.

The accompanying illustrative schematic drawing shows one of several possible ways of continuously pulping comminuted or broken up particles of lignocellulose starting material, such as bagasse or bamboo available in the tropical regions.

Referring to the drawing an open rectangular reaction tank 1 is provided with a curved bottom wall 2 having a flat inclined section 3 up which the treated lignocellulose particles are pushed by means of pusher bars 4 disposed on an endless belt 5. The endless belt 5 is disposed over a driven sprocket wheel 6 disposed above the solution 7 of the reaction tank 1 in a suitable spaced apart relationship to the lowest point of the tank so that the pusher bars 4 engage the treated particles 8 and push them to the top of tank 2 where they fall into a funnel 9. The aqueous solution 7 may be of sodium xylenesulfonate of two percent concentration and is adjusted to a pH of 4.0 obtained by acidification with xylenesulfonic acid. The comminuted particles 8 of bagasse are treated for a period of 4 hours at about 95° C. to yield a tan colored pulpy product having 1/3 to 1/2 of its pentosan content removed as it enters funnel 9.

The raw material bagasse in cut-up or comminuted form is stored in a hopper 10 having a depending outlet conduit 11 disposed over tank 1 and the fresh solution of cooking liquor is stored in a vessel 12 which is provided with a conduit 13 for introducing the cooking liquor into said tank 1.

The cooking liquor 7 is used at a temperature close to that of the boiling point of water or 95° C., and is held at this temperature by heating means preferably by steam coils or by injection of steam into the cooking liquor, but for purposes of schematic simplification the heating means is shown in the drawing as a fuel gas conduit 14 having a plurality of gas burners 15 thereon.

The cooked pulpy or softened lignocellulose particles are conducted through funnel 9 into a refiner 16 where the cooked particles are disintegrated into the coarse fibrous constituents thereof.

As shown in the drawing the pulped fibers from the refiner 16 are pumped as a slush by pump 17 through a conduit 18 into a screw press 19 where the pulp is separated from the solvent solution. The used cooking liquor solution from screw press 19 is pumped by pump 20 through conduit 21 back to the reaction tank 1 where it is reused. The pulp from screw press 18 is conducted through a conduit 22 into a washer 23 where it is washed with water to remove the residual solvent therefrom. The wash waters from washer 23 are pumped by pump 24 through conduit 25 into conduit 21 whence it is conducted into the reaction tank 1.

To prepare a fine chemical pulp, the pulp from washer 23 is conducted to a refiner 26 through conduit 27. The fine unbleached pulp from refiner 26 is then conducted through conduit 28 into a stock tank 29 and from tank 29 the unbleached pulp is conducted through conduit 30 to a conventional bleaching apparatus 31.

The bleached stock from the bleaching apparatus 31 is conducted through conduit 32 to a stock tank 33 for the bleached pulp. The bleached stock from tank 33 is now ready for manufacture into paper either alone or mixed with longer fibered paper.

Various changes may be made in the continuous process

## 5

shown in the drawing, as for example, two refiners in series may be used in place of the single refiner 26. Also where bamboo, kenaf, bagasse and some woods are pulped the product from the refiner 26, being cream colored, it is useable as such without bleaching.

This invention will be better understood by reference to the following illustrative examples, which show the broad latitude of the scope of this invention.

## Example I

One part by weight of bagasse was heated with twelve parts by weight of a 1 percent aqueous solution of sodium xylenesulfonate for two hours at 95° C. The pulp was removed from the cooking solution, then washed with water, refined and bleached using three treatments of dilute hypochlorite solution with intermediate washings with water. The resulting product was refined and made into paper. This paper compared with paper made from 100 percent commercially produced spruce ground-wood pulp, a high opacity pulp. The paper made from 100 percent spruce groundwood pulp showed an opacity of only 92 percent whereas the paper made from 100 percent bagasse pulp made by the hydrotropic process of this invention showed an opacity figure 4 percent higher or 96 percent. Standard newsprint of 80 percent ground-wood and 20 percent spruce sulphite shows an opacity of about 90 percent and whole bagasse bleached kraft chemical pulp shows an opacity of about 79 percent.

Analysis of the bagasse pulp showed a lignin content of 17 percent and a pentosan content of 21 percent. The original bagasse composition was 19 percent lignin and 27 percent pentosans. Therefore, there was 2 percent removal of lignin and 6 percent removal of pentosans. The used solvent had a pH of about 4 and was the color of very weak tea.

## Example II

Bamboo chips (*Phyllostachy bambusoides*) were heated with ten times its weight of a 2 percent aqueous solution of sodium xylenesulfonate which had been previously used for the same purpose and which had a pH of about 4. The heating was in an open kettle for three hours at 95° to 100° C. The residual chips were washed with water and refined but not bleached, since the resulting bamboo pulp was light in color and sufficiently opaque to be used in newsprint in place of groundwood. The residual light colored cooking liquor had a pH of 4 and with a slight strengthening back to 2 percent with additional hydrotropic salt it was ready for reuse. Analysis of the pulp showed that the bamboo pulp had substantially the same lignin content as the bamboo chips but only about ⅓ of the original pentosan content. The yield of pulp was 87 percent of the bamboo chips taken.

## Example III

One part by weight of the woody residue left from the stalks of kenaf after removal of the fibrous bark was heated at 95° C. for three hours with ten parts by weight of a 1 percent aqueous sodium xylenesulfonate solution to which sufficient xylenesulfonic acid had been added to bring the solution to a pH of 3. The resulting pulp, after washing and refining but with no bleaching, was almost white and possessed a high opacity.

## Example IV

One part of weight of chips of aspen poplar (*Populus tremuloides*) were heated for 4 hours at 100° C. with 7 parts by weight of a 2 percent sodium cymenesulfonate solution made acid to a pH of 4 by addition of a small amount of cymenesulfonic acid. After washing and refining, the pulp was a light tan color which could easily be bleached to a light cream color by use of a hypochlorite or a peroxide solution. The resulting pulp was of excellent quality. It was obtained in high yield and it had a lignin content of 22 percent and only 14 percent pentosans.

## 6

## Example V

One part by weight of commercial pulpable chips of yellow birch (*Betula lutea*) were poured into a tank containing ten parts by weight of a 2 percent solution of sodium xylenesulfonate of pH 6 held at 98° C. A stainless steel weight was then placed upon the chips to keep them submerged in the tank. In twenty minutes the pH of the solvent had changed to 4.5 and in an hour to 4.0.

Heating was continued for a total period of three hours at 97° to 100° C. The liquid was then removed, the chips roughly washed with cold water, and then refined by passage at successively closer settings, three times through a small Sutherland disk refiner. The resulting pulp was screened on a 12 cut screen and the fines re-screened on an 8 cut commercial type screen. Only a small proportion of screenings were obtained. The pulp through the 8 cut screen was bleached at a pH of 9 with about 8 percent of chlorine in the form of hypochlorite solution. The resulting birch pulp on analysis showed a lignin content within 1 percent of the percentage of lignin present in the untreated chips but the percentage of pentosans in the pulp had been reduced by some 8 percent compared to the amount in the original birch chips. The yield pulp was 88 percent and the color of the pulp was a cream white. The pulp possessed high opacity. In general it was not as strong or as permanent a type of pulp as that made by the sulphite process but it was of better color and quality than would have been obtained from yellow birch by the groundwood process.

Having read the disclosure hereinabove it is apparent that a generic invention has been made in that the lignocellulose pulp process of this invention pulps lignocellulose by the selective removal of pentosans without any substantial removal of lignin, whereas the lignocellulose pulping processes prior to this invention effected the pulping process by substantially the complete removal of lignin.

It is also apparent that those skilled in the art, having now been introduced to this invention, will readily perceive various possible changes, but all these changes being within the skill of the art are deemed to be within the scope of this invention and covered by the claims herein.

It is further apparent that this process produces a novel pulp, in large part suggestive of the chemical pulps as to pentosan content, color and strength characteristics, but also the novel pulp is suggestive of groundwood in that it is highly opaque and has good absorbency.

In the following claims by a "dilute solution" is meant one having a concentration of about one to about five percent of the hydrotropic salt in water and by "cooking" is meant a process similar to that of preparing food by boiling food in water in an open vessel or a pressure cooker.

I claim:

1. The process for producing a lignocellulose pulp from pentosan containing lignocellulose material said pulp having substantially the lignin content of the lignocellulose material comprising cooking said starting material with a dilute 1 to 5 percent aqueous solution of a hydrotropic compound selected from the group consisting of benzoic acid, salicylic acid, xylenesulfonic acid, cymenesulfonic acid, phenolsulfonic acid, toluenesulfonic acid and their alkali metal salts until a substantial amount of the pentosans is removed.

2. The process of claim 1 wherein the temperature of cooking is about 100° C. and wherein from ⅓ to ½ of the pentosans are removed.

3. The process of claim 1 wherein the temperature of cooking is substantially the boiling point of the aqueous hydrotropic solution.

4. The process of claim 1 wherein the cooking is done in an open vessel at atmospheric pressure.

5. The process of claim 1 wherein the cooking is done

in a closed vessel at a temperature and pressure above that of normal atmospheric conditions.

6. The process of claim 5 wherein the time of cooking is about one hour.

7. The process of claim 1 wherein the cooking is done under reflux condenser conditions whereby the cooking vapors are condensed.

8. The process for producing a lignocellulose pulp from pentosan containing lignocellulose material said pulp having substantially the lignin content of the lignocellulose material comprising cooking said starting material with a dilute 1 to 5 percent aqueous solution of a hydrotropic compound selected from the group consisting of benzoic acid, salicylic acid, xylenesulfonic acid, cymenesulfonic acid, phenolsulfonic acid, toluenesulfonic acid and their alkali metal salts at from 95° C. to 100° C. until from 1/3 to 1/2 of the original pentosan content is removed.

9. The process of claim 8 wherein the time of cooking is a plurality of hours.

10. The process of claim 8 wherein the hydrotropic compound is sodium xylenesulfonate.

11. The process of claim 10 wherein the lignocellulose material is bagasse.

12. The process of claim 10 wherein the lignocellulose material is wood.

13. The process of claim 8 wherein the cooking of the lignocellulose material is done by moving said material continuously through said aqueous cooking solution until 1/3 to 1/2 of the pentosan content of the lignocellulose material is removed, and thereafter removing the so

cooked material continuously from said cooking solution.

14. The process of claim 13 wherein the cooking is done in an open vessel and wherein dilute aqueous cooking solution is added continuously to said vessel to make up for solution losses due to removal of cooked material from said vessel.

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