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PULPING PROCESS

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This invention concerns the pulping of ligno-cellulosic materials, and particularly relates to a process for the production of alpha-cellulose and other valuable products from ligno-cellulosic materials.

Of the various methods for the digestion of cellulosic materials, the soda, sulphate, and sulphite processes are the best known and most widely used. Of these, the soda and the sulphate processes are alkaline cooks, the soda cook being used primarily in digesting deciduous woods such as aspen, birch, white maple, basswood, etc., while the sulphate process is well adapted for digestion of highly resinous coniferous woods.

In the soda process the sodium hydroxide is drastic in its action on the ligno-cellulosic structure and yields a purified cellulosic fiber which is weak and possesses in general inferior chemical properties. The mixture of sodium hydroxide and sodium sulphide in the sulphate process has a milder action on cellulosic fibers but produces a pulp which contains a considerable amount of lignin and other contaminating products. Both of these processes produce a pulp having a comparatively high bleach consumption and not of a sufficiently high grade for use as chemical cellulose in making derivatives thereof.

The sulphite process is an acid cook and produces a higher grade pulp than the above alkaline digestions. The application thereof, however, is limited to the digestion of the less resinous woods, such as spruce, fir, and hemlock, since it exerts but slight action on the resinous constituents of wood and allows a high percentage of the same to pass through into the pulp, thereby creating a problem of resin removal in the later stages of fabrication.

Each of the above processes yields a waste liquor from which residual pulping agent and valuable by-products, such as lignin, are difficult of recovery, and which is not well adapted to further manufacture. At present such materials are either thrown away or used in the preparation of fertilizers, spreading or dispersing agents, and in other cheap by-products of the wood pulping industry.

Among the objects of this invention are, to provide a pulping process which (1) may be used in the treatment of any ligno-cellulosic material, (2) results in higher pulp yields than do the soda, sulphate, and sulphite processes, (3) results in a pulp having a high beater strength, and (4) yields a superior grade of pulp high in alpha cellulose, which is suitable for the preparation of cellulosic derivatives, such as ethers and esters.

Other objects will be apparent from the following detailed description of certain preferred embodiments of our invention.

We have now found that ligno-cellulosic materials can be pulped by digesting the same with pulping fluids comprising aliphatic amine compounds. The term "aliphatic amine compounds" as hereinafter employed in the specification and claims of this application refers to nitrogen-containing organic compounds such as (1) the alkylol amines, e. g. monoethanolamine, 1,3-diamino-2-hydroxypropane, etc.; (2) the alkyl amines, e. g. monomethylamine, dimethylamine, etc.; (3) the alkylene diamines, e. g. ethylene diamine, etc.; and (4) other aliphatic polyamine compounds such as 1,3-diaminopropane, etc.

In carrying out our new pulping process the ligno-cellulosic material, in a suitable state of division, is saturated with and suspended in the digesting fluid and thereafter cooked for a period of time and at temperatures and pressures varying with the type of material being pulped, the amount of aliphatic amine compound present in proportion to the cellulosic raw material being treated, and the degree of digestion desired. When the cellulosic material is sufficiently cooked, the waste liquor is recovered therefrom and the residual pulpy fiber washed, screened, and further purified by bleaching according to any of the known methods. The strength of this pulp, as shown by the beater test (Technical Association Pulp and Paper Industry official standard method No. T200M), is as high or higher than the strength of pulps otherwise obtained, and other properties such as viscosity are improved, indicating that the mild action of the organic pulping agent causes less degradation and decomposition of the cellulosic portion of the treated raw material than is caused by other pulping agents ordinarily used. The recovered treating liquor may be either (1) reutilized in the pulping of additional ligno-cellulosic material without purification, or (2) fractionally distilled to remove therefrom unreacted aliphatic amine compounds in a substantially pure state and to recover valuable ligneous residues, or (3) treated with an excess of alcohol, cyclic ether, hydroxy-ether, or dilute acid, thereby precipitating out the ligneous bodies, which may be separated, as by filtration. The lignin bodies obtainable from the above-recovered waste, or black, liquors are valuable raw materials for the preparation of various lignin-type plastics.

While our process is particularly adapted to utilize the aliphatic amine compounds in sub-

stantially pure form, we have found that the crude commercial mixtures of the above, such as are obtained by the reaction of aliphatic halides, halo-ethers, olefine oxides, or chlorohydrins with ammonia, may be advantageously employed as pulping agents. The presence in the treating liquor of water or other inert solvent for the active pulping agent is not prejudicial to satisfactory pulping. Other pulping agents, such as sodium hydroxide, sodium sulphide, etc., may be used in combination with the aliphatic amine compounds, but are not necessary for the carrying out of the reaction. The concentration of aliphatic amine compound in the treating liquor varies with the specific aliphatic amine employed. For example, the alkylamines and alkylene amines are generally employed at a concentration of at least 15 per cent by weight of the amine in the treating liquor, while best results have been obtained with alkylol amines by employing said compounds at concentrations between approximately 70 per cent and 100 per cent by weight of the liquor. The above concentrations are, however, only illustrative of those found preferable in our process, and it is not our intention to limit ourselves thereby, since treating liquors containing aliphatic amine compounds in amounts other than those specified have been found satisfactory for pulping under the proper conditions of temperature and pressure. The amount of such aliphatic amine compound composition preferably used by us in a pulping run is inversely proportional to the concentration of the aliphatic amine compound therein. We frequently use 4 to 5 pounds of aliphatic amine compounds per pound of treated material, in order to cover or suspend the lignocellulosic material therein completely. Only a small proportion of the treating fluid is, however, used up in such case, and the recovered liquor may be re-utilized a number of times, i. e. until no free aliphatic amine compound remains therein, to give a satisfactory pulping action. There is no theoretical upper limit on the amount of aliphatic amine compound which may be present, since the waste liquors from one run, as pointed out above, may be repeatedly re-cycled in the process. Practical considerations will determine the economical ratio.

In applying our process to the preparation of a high grade cellulose pulp, the wood, preferably in the form of dried chips, is introduced into a suitable pressure cooking vessel and the treating liquor added thereto. The cooking vessel is then sealed and the contents gradually heated to, and maintained at, the desired digestion temperature, generally between room temperature and 200° C., under the vapor pressure of the reactants at such temperature, until the desired degree of digestion is obtained. We generally prefer a digestion temperature of 100° to 180° C., although at temperatures as low as 25° C. appreciable pulping action has been observed. The wood is usually completely pulped in from 4 to 20 hours, although the time of reaction varies with the amount and concentration of aliphatic amine compound present in the treating liquor, the type and degree of division of wood being pulped, and the temperature at which cooking is carried out. When the wood is properly cooked, the charge is blown or otherwise removed from the reactor into a suitable draining or filtering device, e. g. a wash pit, wherein the liquor is removed from the solid product. The resulting fibrous pulp is washed free of liquor, screened,

and may thereafter be bleached if desired. Prior to the bleaching step, the crude pulp may be washed with a dilute aqueous inorganic acid, e. g. 5 per cent hydrochloric acid, which step insures a more complete and efficient bleaching action than is obtained if the bleaching step be carried out without such wash. The pulp is then ready for further manufacture into any desired cellulosic product, such as ethyl cellulose, cellulose acetate, cellulose xanthate, or regenerated cellulose. If the primary waste liquor is to be used for further digestion it should be diluted as little as possible with wash liquors.

The following examples are illustrative of various ways in which we have applied the principle of our invention, but are not to be construed as limiting the same.

Example 1

3 pounds of dried poplar chips and 15 pounds of substantially pure monoethanolamine were charged into a pressure cooker equipped with suitable means for repeatedly circulating the treating liquor through and over the mass of chips. The temperature of the reaction mixture was gradually raised to 180° C. and maintained thereat under a pressure of 30 pounds gauge for 5½ hours, after which the charge was blown into a wash pit and the waste liquor recovered therefrom. The resultant crude cellulosic pulp was washed with an excess of hot water to remove residual cooking liquors, screened, thereby removing 0.1 per cent by weight of the wet pulp as undigested chip fragments, and dried. The product consisted of 2.17 pounds of unbleached fibrous material, which represented a yield of 69.1 per cent, based on the weight of the dried poplar chips treated. This unbleached pulp contained 84.54 per cent of alpha cellulose, 0.34 per cent of lignin bodies, and had a "beater strength" of 114 in terms of points/100 pounds ream.

The recovered treating liquor, comprising the major portion of the monoethanolamine in unreacted form, contained approximately 30 per cent by weight of the wood constituents dissolved therein, and was adapted to be used as a pulping agent in later runs.

Example 2

3 pounds of dried spruce chips was digested, as described in Example 1, with 15 pounds of monoethanolamine for 5 hours, the maximum temperature being 180° C. 1.89 pounds of dry unbleached pulp was recovered therefrom, having an alpha-cellulose content of 84.28 and containing only 0.9 per cent of lignin.

Example 3

3 pounds of dried spruce chips, 12 pounds of monoethanolamine and 3 pounds of water were charged into a pressure cooking vessel and reacted together at a temperature of 175° C. and under a pressure of 95 pounds gauge for approximately 5 hours. The waste treating liquor was separated from the solid products of reaction as described above and the crude pulp washed to remove residual liquor. The finely divided product was then screened and dried, yielding 2 pounds of unbleached fibrous material having an alpha-cellulose content of 88.69 per cent.

Example 4

3 pounds of dried poplar chips was digested, as described in Example 1, with a treating solution consisting of 14.4 pounds of 1.3-diamino-2-hy-

droxypropane and 3.6 pounds of water at a temperature of 162° C. and a pressure of 110 pounds gauge for approximately 5 hours. 2.28 pounds of dry unbleached pulp was recovered therefrom, having an alpha-cellulose content of 89.53 per cent by weight and containing only 0.07 per cent by weight of lignin bodies. Screenings from the above cook amounted to 0.57 per cent based upon the unscreened pulp.

Example 5

2.08 pounds of dried poplar chips, 8.3 pounds of monoethanolamine, 2.08 pounds of water, 0.105 pound of sodium hydroxide, and 0.035 pound of sodium sulphide were charged into a pressure cooking vessel and reacted together at a temperature of 180° C. and under a pressure of 115 pounds gauge for 5 hours. The resultant crude reaction mixture was worked up substantially as described in Example 1, resulting in the isolation of 1.33 pounds of dry unbleached pulp having an alpha-cellulose content of 89.56 per cent, containing 0.28 per cent of lignin, and which, after acid washing, required treatment with only 4 per cent of chlorine to produce a high white pulp (77.5).

Example 6

2 grams of 60-80 mesh poplar sawdust was refluxed for 5 hours at 180° C. with 200 grams of triethanolamine. The suspended solids were then separated from the liquor by filtration, washed successively with hot triethanolamine, hot water, alcohol, and ether, and dried, yielding 1.511 grams of dry unbleached pulp high in alpha-cellulose and low in lignin.

Example 7

0.939 pound of dried poplar chips, 6.58 pounds of a high-boiling still residue obtained in the fractional distillation of the crude reaction product of glycerol dichlorohydrin (alpha) and ammonia, and 1.65 pounds of water were charged into a pressure cooker and reacted together at a temperature of 165° C. and under a pressure of 110 pounds gauge for 5 hours. The resultant crude reaction mixture was worked up substantially as described in Example 1, resulting in the isolation of 0.43 pound of dry unbleached pulp high in alpha-cellulose and low in lignin content.

Example 8

6.939 pound of dried poplar chips, 5.34 pounds of ethylene diamine, and 2.51 pounds of water were charged into a rotary autoclave and reacted together at a temperature of 175° C. and under a pressure of 95 pounds gauge for approximately 6 hours. The waste treating liquor was separated from the solid products of reaction as described in Example 1 and the crude pulp washed to remove residual liquor. The resulting pulp was screened, washed with 5 per cent hydrochloric acid, and dried, yielding 0.448 pound of unbleached fibrous material. This unbleached acid-washed pulp contained 92 per cent of alpha-cellulose and required only 4.24 per cent of chlorine to produce a high white pulp.

Example 9

0.939 pound of dry poplar chips was digested in a rotary autoclave with 7.12 pounds of a 29.41 per cent by weight aqueous solution of monomethylamine. The autoclave was heated until the pressure on the reaction mixture was approximately 200 pounds gauge and the reaction

maintained under such conditions for a period of 7 hours. The digester charge was then blown into a wash pit to remove the waste liquor, and the crude pulp separated thereby screened, washed with 5 per cent hydrochloric acid, and dried, yielding 0.5612 pound of unbleached fibrous material high in alpha-cellulose and low in lignin bodies. This cellulose product required only 3.62 per cent of chlorine for bleaching to a satisfactory whiteness.

The recovered treating liquor, comprising a major portion of the monomethylamine, was adapted to be used as a pulping agent in later runs.

Example 10

In a similar manner 0.911 pound of dry poplar chips was digested with 7.3 pounds of a 24.77 per cent by weight solution of dimethylamine in water. The yield of unbleached fibrous material so obtained amounted to 0.557 pound.

If desired, the digestion process may be interrupted prior to the complete delignification of the treated material as described in the foregoing examples. The resulting semi-refined cellulosic bodies have been found to be useful in the preparation of manufactured articles such as ropes, mats, etc., where the presence of a certain amount of lignin in the finished product is not objectionable.

While the above examples describe only the treatment of poplar and spruce, our process is equally useful in the pulping of other deciduous and coniferous woods such as birch, white maple, basswood, fir, pine, etc. It is also adapted to produce cellulose from such cellulose-containing raw materials as corn stalks, cotton linters, wheat straw, and other agricultural waste products.

In a similar manner cellulose may be prepared by the digestion of ligno-cellulosic materials with other aliphatic amine compounds, solutions of the same in an inert solvent such as water, and mixtures and/or combinations of the same with known pulping agents. Among the aliphatic amine compounds which may be so employed are the mono-, di-, and tri-ethylamines, the propylamines, the butylamines, propylene diamine, butylene diamine, di-ethanolamine, the propanolamines, the pentanolamines, 1,2-diamino-3-hydroxypropane, 1,2-dihydroxy-3-amino-propane, 1,3-diamino-butane, 1,3-diamino-3-methyl-propane, the crude reaction products of ammonia with aliphatic halide compounds such as ethylene chlorohydrin, glycerol dichlorohydrin, ethylene dichloride, ethyl chloride, propyl bromide, butylene chloride, mixtures of the above, etc.

Our method of pulping ligno-cellulosic materials has, among others, the following advantages: (1) it may be applied to the preparation of cellulose and valuable by-products from any ligno-cellulosic material, (2) the yields of pulp are high and the pulp is stronger, i. e. it has a higher beater strength than that obtained from other well known processes (3) the so-called waste liquors are valuable for reutilization in the process or for the preparation of resinous bodies, (4) our method may utilize as a pulping agent cheap and comparatively crude aliphatic amine compound mixtures without the separation therefrom of their constituents, (5) it produces a pulp having a high alpha-cellulose content, (6) the pulp so produced has unusually desirable characteristics as a starting material for the preparation of cellulosic derivatives, such as ethers, es-

ters, etc., and (7) the mild action of the pulping agent causes less degradation and decomposition of the cellulose in the treated raw material than in processes ordinarily used, and therefore results in a high yield of desired product relatively free from cellulose decomposition products, such as sugars, etc., which would tend to reduce its value for chemical use.

Our copending application, Serial No. 107,144, now Patent 2,192,202, particularly concerns the use of the alkylolamines in the delignification of ligno-cellulosic materials.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the methods herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:

1. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of an aliphatic amine compound.

2. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of an alkylamine.

3. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent not less than 15 per cent by weight of an alkylamine at temperatures not in excess of 180° C. and under the vapor pressure of the reaction at such temperature.

4. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of a methylamine.

5. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent not less than 15 per cent by weight of a methylamine at temperatures not in excess of 180° C. and under the vapor pressure of the reaction at such temperature.

6. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of mono-methylamine.

7. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent not less than 15 per cent by weight of mono-methylamine, and thereafter recovering the digestive liquors from the solid products of reaction and reutilizing such recovered liquors in the digestion of additional cellulose raw materials.

8. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent not less than 15 per cent by weight of mono-methylamine at temperatures not in excess of 180° C. and under the vapor pressure of the reaction at such temperature.

9. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as

an active pulping agent at least 15 per cent by weight of an alkylene diamine.

10. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent from not less than 15 per cent by weight of an alkylene diamine.

11. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of an alkylene diamine.

12. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of an alkylene diamine at temperatures not in excess of 180° C. and under the vapor pressure of the reaction at such temperature.

13. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of ethylene diamine.

14. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent not less than 15 per cent by weight of ethylene diamine, and thereafter recovering the digestive liquors from the solid products of reaction and reutilizing such recovered liquors in the digestion of additional cellulose raw materials.

15. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of ethylene diamine at temperatures not in excess of 180° C. and under the vapor pressure of the reaction at such temperature.

16. In a process for pulping raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of the product resulting from the reaction of an aliphatic halogen derivative with ammonia.

17. In a process for removing lignin bodies from raw ligno-cellulosic materials, the step which consists in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of dimethylamine.

18. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of an aliphatic amine compound, and thereafter recovering the digestive liquors from the solid products of reaction and re-utilizing recovered liquors in the digestion of additional cellulose materials.

19. In a process for pulping raw ligno-cellulosic materials, the steps which consist in digesting the same with a treating liquor comprising as an active pulping agent at least 15 per cent by weight of an aliphatic amine compound, separating the crude pulp therefrom, screening the same, washing the screened pulp with dilute inorganic acid, and thereafter bleaching the washed pulp.

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