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PULPING LIGNOCELLULOSE WITH SODIUM ALUMINATE

John Henry Fisher, Quebec, Quebec, and Bruce Ronald Mead, Saint Catharines, Ontario, Canada, assignors to The Ontario Paper Company Limited, Thorold, Ontario, Canada

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This invention relates to the production of fibrous material from ligno-cellulose material including wood.

In particular, the invention relates to the manufacture of a fibrous pulp by a new alkaline pulping process capable of producing a product, whose properties may be generally predetermined according to the specific conditions of pulping, and useful in a wide variety of pulp and paper applications.

A further object of our invention is to obtain a pulp at high yield from ligno-cellulose material.

A further object of our invention is to provide an alkaline pulping process of such character that the recovery of chemicals for reuse therein is improved.

The treatment of ligno-cellulose materials including wood by alkaline solutions is the basis of certain well known processes for preparing pulps utilized in the pulp and paper industry. The kraft or sulfate process, in which the alkali employed is essentially a sodium hydroxide-sodium sulphide mixture, and the soda process, in which the alkali employed is essentially sodium hydroxide, are the two best known and commercially developed examples of this art. In each of them the properties of the product are dependent on the conditions of temperature, pressure and concentration of chemicals used in the pulping operation. These conditions are predetermined to promote desired properties in the product. In both of these processes the residual liquors at the end of digestion are separated, concentrated and burned. During combustion of the organic residue contained in the liquors, heat values are released which may be recovered. A substantial portion of the original chemicals used may be recovered from the residue from combustion, followed by such chemical processes as are necessary to reconvert the said residue to a form which is useful in subsequent pulping operations. For example in the soda process the sodium is present in the said residue essentially as carbonate and this is treated with lime to causticize or convert the carbonate to sodium hydroxide.

In the above mentioned applications of the general principle of pulping ligno-cellulose materials in an alkaline medium, the character of the resulting pulp depends on the chemicals employed. For example, kraft pulp and soda pulp have entirely different characteristics, and are used for essentially different purposes in the pulp and paper making industry. As produced, kraft pulp is brown, and typically long-fibred and strong, whereas soda pulp is characteristically grey-white, and of low strength. Thus while the character of either kraft or soda pulp may be

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modified by variation of the conditions in its own process, each pulping process yields a product having its own special characteristics.

The cost of the process is also dependent on the different chemicals employed, on the yield and quality of pulp obtained, and on the ease and efficiency of chemical recovery.

Our invention as described herein discloses the basis of a new alkaline pulping process and, therefore, capable of yielding a product of specific qualities not heretofore available, which product may itself be modified over a wide range of yield and quality according to the conditions of pulping and, in addition, possessing certain unique features in connection with the recovery of chemicals therefrom, all as hereinafter described.

We have ascertained that ligno-cellulose materials may be pulped using an alkaline medium comprising a solution of sodium aluminate or a solution of certain modified sodium aluminates, e. g. sodium phospho-aluminate; or solutions comprising mixtures of sodium hydroxide with the before mentioned aluminates. We have also discovered that a pluping action is obtained not only in an aqueous medium, although this is the preferred embodiment of our invention, but also can be effected when the medium is composed in part of a hydroxyl containing organic material, e. g. ethyl alcohol.

As is the case with all pulping processes for treatment of ligno-cellulose material, the result obtained is dependent on the time, temperature, pressure and concentrations of chemicals employed. The selection of any particular set of conditions will be dependent upon the result desired. For example, if it is desired to increase the yield of pulp from a given quantity of ligno-cellulose material, one or more, or some combination, of the factors of lower temperature, lower pressure, shorter time, lower concentration of chemicals, lower liquor to chip ratio will be employed. Coincident with such higher yields the resultant pulp will normally be less modified from its original woody condition and will have those properties which will normally be associated with such lower modification. Correspondingly, use of higher temperature, higher pressure, longer time, higher concentration of chemicals and greater liquor to chip ratio will tend toward the production of pulp at lower yield and with corresponding modification to the quality of the pulp produced. The presence of sodium hydroxide additional to sodium aluminate promotes a stronger pulping action than the aluminate alone and, in general, when mixtures of sodium hydroxide with the before mentioned aluminates are employed, pulp will be produced at lower yield and the corre-

sponding characteristics. It will be apparent from the preceding that a wide range of conditions is available for pulping procedures in accordance with our invention and that in any particular instance a selection of conditions will be made in accordance with the result desired.

In employing our invention, the ligno-cellulose material is separated by chipping or other suitable means, charged into a digester and cooked under pressure following a predetermined temperature and pressure time cycle with the pulping solution containing sodium aluminate or a modified sodium aluminate, as an active ingredient thereof. We have employed concentrations of sodium aluminate in aqueous solution in the concentration range from 2%–15%. We have also employed pulping solutions containing sodium aluminate and as an additional active agent therein sodium hydroxide, the latter ranging in concentration from 4% downward. We have also varied the liquor to chip ratio over a wide range from the high ratio of 10:1 downward. In commercial pulping practice a low liquor to chip ratio is normally preferred for economic reasons and the preferred embodiment of our invention would therefore involve substantially lower ratios than the maximum ratio hereinbefore stated. In the temperature-time cycle employed by us for digestion of the ligno-cellulose material we have followed the procedure of raising the temperature to the maximum desired as rapidly as can be accomplished by the heating means at hand. This is in accordance with established procedure for alkaline pulping. We have employed final temperatures in a range up to 200° C. and, with digesting time at maximum temperature up to 16 hours. The pressure employed in the digesting process was that normally developed by the other predetermined conditions. It will be obvious to anyone skilled in the art that to obtain a required result with higher concentration of chemicals and/or higher temperatures, digestion will require shorter time periods. In experiments performed in which the maximum temperature was in the range 185–200° C. the digestion time at maximum temperatures was typically 2½ to 3 hours.

The pulp produced according to our invention is typically a brown, free-draining pulp of high initial tearing strength and capable of substantial mullen strength development on beating. To illustrate the characteristics of the product which may be obtained by application of our invention, the following may be cited.

Example 1

1,660 grams equivalent oven dried weight of spruce wood chips (38.7% moisture) were immersed in an aqueous solution containing 720 grams commercial sodium aluminate (of approximately 75% $Na_2Al_2O_4$) and 240 g. sodium hydroxide and the total volume of water present adjusted to 12,000 grams. This mixture was sealed in a bomb which was immersed in a hot oil bath and was heated therein to a temperature of 185–190° C. over a period of three hours and maintained at this temperature for an additional three hours. The bomb and its contents were then cooled rapidly in a water bath and the solid product separated from the liquor. As the digester had not been blown, this solid portion was still substantially in chip form or in the form of large fibre bundles which retained such liquor as was impregnated therein. It was washed with water and an aliquot portion dried and weighed which indicated the recovery of solid product, including unremoved impregnated liquor, of 59% of the original weight to the wood chips.

The above product was then disintegrated into fibres in a laboratory beater of the general type described in Official Standard T 200*m*–43 of The Technical Association of The Pulp & Paper Industry but without weight on the lever arm and after such disintegration washed thoroughly with water on a screening plate. The final washed pulp amounted to 48% of the original weight of the wood used.

The pulp as above was a brown pulp of free draining character and high tearing strength which was also capable of considerable mullen strength development on beating. The pulp had an initial freeness (Canadian standard) of 758 for the unbeaten pulp which decreased to 670, 508, 295, 139, after 20, 40, 60, 80 minutes beating respectively. The initial unbeaten tearing strength of handsheets prepared from the pulp diminished from 236 grams to 137 grams after 80 minutes beating. The mullen strength developed from an initial unbeaten test of 67% pts. per lb. for the unbeaten stock through a maximum of 119% pts. per lb. at 40 minutes beating.

Example 2

505 pounds equivalent oven dried weight of spruce chips containing 18.5% moisture were charged into a 65 cu. ft. digester. To this was added 427 U. S. gallons of a 9.1% solution of commercial sodium phospho aluminate which by titration at room temperature was of an alkalinity corresponding to that of 4.75% sodium hydroxide. The digester was provided with a circulation system whereby the liquors were continually drawn from the center of the digester and readmitted at both the top and bottom thereof. The liquors were heated indirectly by passage through a suitable heat exchanger during the course of their cycle external to the digester. By such heating means the temperature of the charge was raised to 175° in 55 minutes and was thereafter maintained substantially thereat for an additional two hours and thirty minutes. The pressure on the digester was then relieved to 60 lbs. per sq. in gauge and the digester blown. The solid material as blown was still substantially in chip or large fibre bundle form and was given a single pass through an attrition mill which reduced the chips and large fibre bundles to a pulp form. The latter was washed and the yield determined after washing. This amounted to 83% of the original weight of the wood substance charged to digester.

The resulting brown pulp was very free draining having a freeness test (Canadian standard) of 775, was very long fibred and, as would be expected from the high yield, very woody in texture.

The felting qualities of the above pulp were substantially improved either by additional passes through an attrition mill or by beating. The development of properties of this high yield pulp upon laboratory beating is shown in the table below

Beating Time	0 Min.	30 Min.	60 Min.	90 Min.
Freeness Canadian Standard	775	653	309	76
Mullen Per Cent pts./lb	13	72	87	78
Tensile kg./15 mm	2.6	12.8	15.0	14.8
Tear, grams	124	162	117	99
Porosity, seconds	0	7	115	635

The use of sodium aluminate as an active pulping agent constitutes a novel alkaline pulping process. In the established alkaline processes the presence of small quantities of "sodium aluminate" have been noted. Such small quantities arise chiefly from alumina-containing refractory materials used in the recovery system. Under normal operating conditions in the heretofore known alkaline pulping processes, the presence of such "aluminate" is disregarded. Our invention does not relate to such an incidental and normally disregarded presence of "aluminate" as occurs due to contamination of the pulping liquors in the conventional alkaline pulping processes. In the presence of such incidental quantities only the conventional alkaline pulps are obtained.

The tendency of solutions containing sodium aluminate to decompose with formation of a precipitate usually in the form of aluminum hydroxide is well known. The presence of free sodium hydroxide in the pulping liquors acts to prevent such precipitation and this is obviously desirable so as to prepare a pulp which is free from such a precipitate and so as to improve recovery of the chemical materials used in pulping. We have found that the addition of as small a quantity of sodium hydroxide as corresponds to 1% concentration in the cooking liquor will usually serve to substantially prevent the afore-mentioned precipitation. This quantity is subject to some modification dependent on the actual cooking conditions. The use of any other alkali for a similar purpose falls equally within the scope of our invention. Certain alternative methods are also used to limit or prevent the precipitation from solutions of aluminates under certain specific conditions. Examples of materials used for such purposes include organic compounds containing hydroxyl groupings such as ethylene glycol, glycerine, or similar poly-hydroxy alcohols, also sodium tartarate, sodium oxalate or the like, also tannin containing materials, and mixtures of such classes of compounds. The use of sodium phospho aluminate illustrates the use of a modified aluminate whose characteristics of precipitation are favourably modified under certain conditions. Some precipitation occurred during the course of the digestion described in example 2 and the use of the modified aluminate was therefore not a complete answer to the precipitation problem under the stated experimental conditions.

The above are cited as representative methods by which the undesirable precipitation may be minimized. Under the cooking conditions which we have employed, we have found the use of sodium hydroxide to be the most satisfactory means of preventing precipitation.

In the processes herein described the active chemicals in the liquors residual to pulping may be recovered. When sodium aluminate is used as the pulping agent its recovery may be effected by concentrating the liquor to a point suitable for combustion, burning and then treating the residual ash with water. The resulting alkaline aluminate solution may be reused directly in subsequent pulping procedures and only requires such make-up of chemicals as are inherent as losses in the entire recovery system. It will be noted in this case that the step of causticization of alkali common to the sulfate process and the soda process is eliminated, and the recovery process thereby simplified.

When mixtures of sodium aluminate and sodium hydroxide are employed, a causticizing process will be included to regenerate the sodium hydroxide. When sodium aluminate is admixed with other active pulping agents, the details of the recovery process must be dependent on the nature of the co-present pulping agents. Unless the products formed from co-pulping agents introduce complications by reactions with aluminate, the aluminate portion of the pulping agent will present a relatively simple recovery problem and to this extent will simplify the recovery.

What we claim as our invention is:

1. In the manufacture of pulp from fibrous ligno-cellulose materials, the step which comprises digesting under autogenous pressure the said ligno-cellulose materials with an aqueous solution containing sodium aluminate as the active pulping agent, the said aluminate being initially present in the cooking liquor in a concentration not less than two percent nor more than fifteen percent, at temperatures in the range 185° to 200° C. and a time of not more than 3 hours nor less than 2½ hours.

2. In the manufacture of pulp from fibrous ligno-cellulose materials, the step which comprises digesting under autogenous pressure the said ligno-cellulose materials with an aqueous solution containing sodium aluminate as an active pulping agent and sodium hydroxide to limit the precipitation of alumina which may occur under pulping conditions, the said sodium hydroxide being initially present at a concentration in the pulping liquor of not more than four percent and not less than one percent and the said aluminate being initially present in the cooking liquor in a concentration not less than two percent nor more than fifteen percent, at temperatures in the range 185° to 200° C. and a time of not more than 3 hours nor less than 2½ hours.

JOHN HENRY FISHER.
BRUCE RONALD MEAD.

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