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PROCESSING OF RAW CELLULOSIC MATERIALS

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This invention relates to the processing of raw cellulosic materials such as wood, its general object being to provide a process which may be economically practised to produce cellulose pulps valuable as a raw material both for papermaking and for conversion into cellulose derivatives and have an alpha cellulose content greater than that present in the usual chemical wood pulps such as sulphite, kraft, or soda.

When raw cellulosic material such as wood is cooked in an acid liquor and the liquor is then converted into an alkaline liquor by the addition of alkali and cooking is then carried out in the alkaline liquor, it is possible so to control the compositions of the acid and alkaline liquors and the time, temperature and other conditions of cooking as to produce a finished pulp of high alpha cellulose content.

In accordance with the process of the present invention, the initial step of cooking is carried out in an acid liquor short of complete fiber liberation, and the subsequent step of cooking is carried out in an alkaline liquor, the alkalinity of which is preferably afforded at least in part by sodium sulphide. By terminating the acid cook short of complete fiber liberation, it is possible to avoid the loss in yield and injury to the fibers occurring when the isolated fibers are digested in acid liquors. By carrying out the second cooking step in an alkaline liquor containing sodium sulphide, not only is it possible to complete fiber liberation and to produce a finished pulp of high alpha cellulose content, but, because of the mild action of the sodium sulphide on the fibers as compared with alkalies such as caustic soda, it is possible to produce a product having physical characteristics superior to those possessed by products produced by cooking in alkaline liquors in which caustic soda alone is used as a fiber-liberating chemical.

Acid cooking liquors of various compositions may be employed in carrying out the initial cooking step, depending upon the characteristics desired in the finished product. When a finished pulp especially low in pentosans is desired, the cooking liquor is preferably one containing sulphurous acid alone or together with another acid reagent such as sulphuric acid. Evidently such a liquor effects more pronounced hydrolysis of the pentosans present in the raw cellulosic material, producing water-soluble reaction products. A finished pulp of low pentosan content is especially desirable when it is to be used as a raw material for the production of cellulose derivatives such as the acetate, as pentosans appear to impart undesirable characteristics such as opaqueness and cloudiness to lacquers or films produced from the derivative. If, however, the finished pulp is to be used as a raw material for papermaking, it may be preferable to employ an acid cooking liquor containing SO_2 combined in the form of sodium sulphite or containing sodium salts such as sodium bisulphate, sodium sulphate, or sodium borate, which undergo metathesis in a sulphurous acid solution to give sodium sulphite. After cooking in the sulphurous acid liquor to the desired degree, it is preferable to release or exhaust the free SO_2 content of the hot spent liquor, so that alkali need not be consumed in reacting upon such SO_2 to produce sodium sulphite, which is of comparatively little value in the subsequent step of alkaline cooking.

The spent acid liquor contains residual sulphurous acid groups existing as sulphurous acid or combined in the form of loose, complex organic compounds. If sodium sulphide be added to the hot charge in the digester, not only is neutralization of the free acid effected, but reaction takes place to produce sodium thiosulphate and free sulphur. Some of the free sulphur may redissolve in the alkaline liquor to produce sodium thiosulphate, but this compound may decompose

to precipitate sulphur under the high temperature conditions maintained during the step of alkaline cooking. In order to avoid the formation of sodium thiosuphate and the precipitation of sulphur, which is difficult to remove from the resulting pulp, the sulphurous acid groups are preferably oxidized to sulphuric acid or sodium sulphate by a suitable oxidizing agent and the addition of alkali. This oxidation may be effected to advantage when only caustic soda is to be added to produce an alkaline liquor, although it is particularly advantageous when alkali including sodium sulphide is added, since, as previously stated, a better quality pulp is produced in an alkaline cooking liquor containing sodium sulphide, and at the same time the formation of sulphites, thiosulphates, and sulphur is avoided by reaction of the sodium sulphide with the sulphurous acid groups. Various oxidizing agents, such as sodium hypochlorite, sodium peroxide, sodium perborate, or chlorine water, may be employed, oxidation occurring rapidly by the use of such agents and resulting in the conversion of the sulphurous acid groups to sulphuric acid or sodium sulphate. It is also possible to effect oxidation by the use of oxygen or air, under pressure, although such oxidation takes place much more slowly than when water-soluble oxidizing chemicals are used. After oxidation has been effected, alkali may be added to the digester in the form of a solution of caustic soda or a mixture of caustic soda and sodium sulphide to produce an alkaline liquor, whereupon cooking may be continued in the resulting alkaline liquor until fiber liberation has been completed. The alkaline liquor in which fiber liberation is completed may be of sufficiently high alkalinity to produce a finished pulp of high alpha cellulose content, say 92% to 96%, or even higher, although, if desired, the alkalinity of the liquor may be lower, such as to produce a pulp having an alpha cellulose content of, say, only 89% to 90%.

A process such as described makes possible the realization of many advantages, among which may be enumerated the following:

1. It permits the production of a finished pulp of the desired alpha cellulose content with a comparatively small amount of sodium base chemicals, as the initial step of cooking in an acid liquor may be carried out in a liquor containing little, if any, sodium base compounds. Subsequent alkaline cooking may be effected in an alkaline liquor of a sodium base compound concentration not in excess of that employed in the usual kraft process, and often appreciably lower.

2. It makes possible the conservation of the heat associated with the spent acid liquor and cellulosic material after cooking.

3. The step of washing the cellulosic material after acid digestion may be avoided, the same apparatus being used from the start to the finish of the pulping operation.

4. The oxidation of the spent acid liquor permits cooking in a sodium-sulphide-containing alkaline liquor and results in a finished pulp having excellent physical and papermaking characteristics.

5. The entire process need require no more time than that of the usual sulphite process, as each of the cooking steps is of short duration, compared with the usual sulphite process, for example.

While various specific procedures may be adopted in accordance with the present invention, the following example will serve as an illustration of a procedure intended for the production of finished pulp of high alpha cellulose but low pentosan content. Any suitable raw cellulosic material, such as spruce chips, may be placed in the usual acid sulphite digester, together with a sulphurous acid solution containing, say, 5% free SO_2. The digester charge may be confined and slowly heated to a temperature of about 250° F., say in about two hours, at which temperature it may be maintained for a period of about two hours, whereupon the temperature may be raised quickly and the relief valve of the digester opened to release sulphur dioxide from the liquor into a suitable cooling and absorption system designed for the preparation of fresh acid cooking liquor. While releasing SO_2 from the liquor, the pressure in the digester may be lowered, and this may in some cases be carried out until substantially atmospheric pressure is reached and a comparatively small amount of oxidizing agent is necessary to oxidize residual sulphurous acid groups in the liquor. After the release of sulphur dioxide from the liquor, a suitable oxidizing agent such as sodium hypochlorite may be introduced into the digester. The amount of sodium hydrochlorite introduced is based upon the amount of sulphurous acid groups present in the liquor in the digester, this being ascertained by analyzing a sample of the liquor. The sodium hypochlorite in the form of a strong solution may be introduced near the bottom of the digester, so that natural circulation of the liquor will result in a diffusion of the solution through the liquor, although if indirect cooking is being practiced, the liquor may be pumped from the bottom of the digester, through the liquor heater, to the top of the digester, to ensure a uniform diffusion of the oxidizing agent through the liquor. Any oxygen gas generated during the oxidizing reaction may be allowed to escape from the digester through a suitable relief valve.

After the oxidizing reaction has been completed, the desired amount of alkali may be added to the digester, as in the form of a solution containing 15% to 18% caustic soda equivalent. The amount of alkali added to

the digester may vary, depending upon the alpha cellulose content desired in the finished pulp. If a finished product of, say, about 92% alpha cellulose content is desired, sufficient alkaline solution should be added to the digester to produce a liquor containing 1.5 pounds of active Na_2O per cubic foot. If, however, a product of unusually high alpha cellulose content is desired, the alkali concentration produced in the liquor may correspond to 2.5 pounds of active Na_2O per cubic foot. Preferably about 40% or more of the alkali exists in the form of sodium sulphide, as the presence of sodium sulphide is advantageous, particularly in the production of a pulp which is to be finally bleached and employed in papermaking. After the addition of alkali, the liquor contains caustic soda, sodium sulphide, sodium sulphate, and possibly slight residues of sodium sulphite. The hot liquor together with the previously cooked chips may then be heated to a temperature of about 335° F. and maintained at this temperature for two or three hours to complete fiber liberation, but this temperature may be varied somewhat, depending upon factors such as the period of cooking and the alkali content of the liquor.

The hot digester contents may be blown as usual from the digester into a pit, and the pulp separated from the spent cooking liquor as by washing. The spent cooking liquor may then be concentrated to the desired consistency, as in multiple effect evaporators, and the concentrated liquor then delivered into a furnace, where the organic combustible material is burned and the inorganic sodium constituent is smelted preferably under reducing conditions to produce a smelt consisting of sodium sulphide and sodium carbonate. The smelted compounds may then be dissolved in water to produce a solution which may be causticized with lime to produce an alkaline liquor containing caustic soda and sodium sulphide. The causticized liquor may be used in rendering the spent acid cooking liquor alkaline, as previously described. The washed pulp may be bleached, if desired, to produce a white product suitable for use as a raw material either for papermaking or for conversion into cellulose derivatives.

If the acid cooking step has been carried out in a liquor containing sodium compounds, it will be seen that the sodium constituent present in both the acid cooking step and in the alkaline cooking step is accumulated in a single aqueous liquor, from which recovery is effected. When the oxidizing agent is a sodium compound, sulphurous acid residues remaining in the spent cooking liquor are changed into sodium-sulphur compounds which, after smelting, appear in the smelt as sodium sulphide, thereby resulting in the recovery of sulphur constituent, which is ordinarily lost in the water employed for washing cellulosic material after acid sulphite digestion. The organic matter extracted from the raw cellulosic material during acid and alkaline cooking is accumulated in a single aqueous liquor, so that when smelting is effected in a combined boiler and smelter furnace, for instance of the general type described in Patent No. 1,326,414, issued December 30, 1919, to Hugh K. Moore and John T. Quinn, a higher fuel value than ordinarily is realized.

I claim:

1. A process which comprises digesting raw cellulosic material at elevated temperature in a sulphurous acid liquor, oxidizing residual sulphurous acid groups in the liquor, adding sufficient alkali to the liquor to render it alkaline, and digesting at elevated temperature in the alkaline liquor.

2. A process which comprises digesting raw cellulosic material at elevated temperature in a sulphurous acid liquor short of fiber liberation, adding alkali including sodium sulphide in amount sufficient to render the liquor alkaline, and digesting at elevated temperature in the alkaline liquor until fiber liberation is complete.

3. A process which comprises digesting raw cellulosic material at elevated temperature in a sulphurous acid liquor, releasing sulphurous acid from the hot liquor, oxidizing residual sulphurous acid groups in such liquor, adding alkali including sodium sulphide in amount sufficient to render such liquor alkaline, and digesting in the alkaline liquor.

4. A process which comprises digesting raw cellulosic material at elevated temperature in a sodium base acid sulphite liquor short of complete fiber liberation, adding a sodium base oxidizing agent to the hot liquor to oxidize sulphurous acid groups therein, adding sodium base alkaline compounds including sodium sulphide in amount sufficient to render the liquor distinctly alkaline, and digesting at elevated temperature in the alkaline liquor until fiber liberation is complete.

5. A process which comprises the following steps: (*a*) digesting raw cellulosic material at elevated temperature in a sulphurous acid liquor; (*b*) adding a sodium base oxidizing agent to the hot liquor; (*c*) adding sodium base alkaline compounds thereto to render the liquor alkaline; (*d*) digesting at elevated temperature in the alkaline liquor; (*e*) separating the resulting pulp from the spent liquor; (*f*) and recovering the inorganic content of the spent liquor in the form of alkaline compounds for use in again carrying out step (*c*).

6. A process which comprises the following steps: (*a*) digesting raw cellulosic material at elevated temperature in a sulphur-

ous acid liquor; (*b*) adding a sodium base oxidizing agent to the hot liquor; (*c*) adding sodium base alkaline compounds including caustic soda and sodium sulphide thereto to render the liquor alkaline; (*d*) digesting at elevated temperature in the alkaline liquor; (*e*) separating the resulting pulp from the spent liquor; (*f*) smelting the inorganic content of the spent liquor in a reducing atmosphere; (*g*) and causticizing the smelted compounds for use in again carrying out step (*c*).

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.