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PROCESSING OF RAW CELLULOSIC MATERIALS

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In the manufacture of cellulose pulp, it is the practice to cook raw cellulosic material such as wood in chemical liquors which react upon and dissolve the substances which bind the fibers together, thereby liberating the fibers. The composition and characteristics of the resulting pulp depend largely upon the type of chemical liquor employed for fiber liberation, it being possible to produce pulps of widely varying compositions and characteristics from one type of raw material.

In accordance with the process of the present invention, I accomplish a liberation of cellulose pulp from suitable raw material in a liquor which is initially acid, for instance in a sulphurous acid liquor, and which is rendered alkaline during the cooking operation. By such a process, it is possible to produce a finished pulp of higher alpha cellulose content than that present in the usual chemical wood pulps, as cooking in both acid and alkaline liquors results in a removal from the raw material of non-alpha cellulose constituents which might otherwise survive cooking in either acid or alkaline liquors alone. In carrying out the process of the present invention, the raw material is cooked in a sulphurous acid liquor, preferably short of complete fiber liberation, as it is thereby possible to avoid the loss in yield and injury to the fibers occurring when the isolated fibers are digested in acid liquors. After cooking to the desired extent has been effected in the acid liquor, the liquor is converted, preferably while hot, to an alkaline liquor the alkalinity of which is afforded, at least in part, by sodium sulphide. By continuing the cooking operation until fiber liberation is complete in an alkaline liquor containing sodium sulphide, it is possible to produce a finished pulp not only of high alpha cellulose content but having physical characteristics superior to those possessed by products produced in alkaline liquors in which caustic soda alone is used as a fiber-liberating chemical. The superior characteristics of the finished pulp are attributable to the mild action of the sodium sulphide on the fibers, as compared with alkalies such as caustic soda. It is doubtless because of the mild action of sodium sulphide that kraft pulp, so called, which is produced in sodium-sulphide-containing alkaline liquor is superior in its physical characteristics to soda pulp, so called, which is produced in a cooking liquor containing practically only caustic soda.

When converting the sulphurous acid liquor to an alkaline condition in accordance with the process of the present invention, the sulphur constituent present in the liquor is maintained combined in the form of water-soluble compounds. This result may be realized if the acid liquor is neutralized with suitable alkaline compounds such as caustic soda or sodium carbonate, as these alkalies react with the acid groups present in the liquor to form water-soluble sodium-sulphur salts. After such neutralization, a suitable amount of sodium sulphide or mixture of caustic soda and sodium sulphide may be added without danger of precipitating sulphur, such as occurs when sodium sulphide is added to an acid liquor. The precipitation of sulphur is highly undesirable, in that it contaminates the resulting pulp and is difficult to remove by washing. While the precipitated sulphur may redissolve in the resulting alkaline liquor to produce thiosulphates, the thiosulphate, too, is undesirable, in that under the temperature conditions of cooking it may decompose and precipitate sulphur, which will contaminate the resulting pulp unless a sulphidity sufficiently high to dissolve such sulphur is maintained in the liquor, such a sulphidity being so high as to be impractical and uneconomical.

Acid cooking liquors of various compositions may be employed in the process of the present invention, depending upon the characteristics desired in the finished product. When a finished pulp especially low in pentosans is desired, the acid cooking liquor is preferably one containing sulphurous acid alone or together with another acid 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 liquor to give sodium sulphite. After cooking in the sulphurous acid liquor under the desired conditions for a suitable period of time, it is preferable to release or exhaust free SO_2 from the hot 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 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. In order to avoid the formation of sodium thiosulphate and the precipitation of sulphur, non-reducing alkalies such as caustic soda and/or sodium carbonate, may be added in amount sufficient to neutralize the liquor. When sodium carbonate is employed, carbon dioxide is liberated during the neutralizing reaction, so that it is necessary to permit the escape of this gas through a suitable relief valve. After neutralization has been effected, sodium sulphide and/or caustic soda may be added to produce the desired alkalinity in the 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 95%, 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 apparently less.

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 preliminary neutralization 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 alkali is necessary to neutralize residual sulphurous acid groups in the liquor. After the release of sulphur dioxide from the liquor, a suitable alkali such as caustic soda may be introduced into the digester. The amount of caustic soda 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 caustic soda 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 usual liquor heater to the top of the digester, to ensure a uniform diffusion of the alkali through the liquor. When sodium carbonate is employed as the alkali, carbon dioxide generated through the neutralization reaction may be allowed to escape from the digester through a suitable relief valve.

After the neutralization reaction has been

completed, the desired amount of alkali may be added to the digester, as in the form of a solution of sodium sulphide and caustic soda 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 to 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 from which sodium carbonate may be selectively crystallized for use in neutralizing other spent acid liquor, or which may be causticized with lime to produce an alkaline liquor containing caustic soda and sodium sulphide. When sodium carbonate has been selectively crystallized from the smelt solution, the mother liquor is rich in sodium sulphide and may be added to good advantage to the neutralized or slightly alkaline cooking liquor. The causticized smelt liquor may also be used to good advantage in rendering the neutralized cooking liquor more distinctly alkaline, as it contains both caustic soda and sodium sulphide, 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 desired cooking step has been carried out in a liquor containing sodium compounds, it will be seen that the sodium constituent present during both acid and alkaline cooking is accumulated in a single aqueous liquor, from which recovery is effected. The neutralizing agent being 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 cooking raw cellulosic material in a sulphurous acid liquor, neutralizing the liquor while maintaining the sulphur constituent in combined state, adding alkali including sodium sulphide to the liquor to render it alkaline, and continuing the cooking of the cellulosic material.

2. A process which comprises cooking raw cellulosic material in a sulphurous acid liquor short of complete fiber liberation, releasing free sulphur dioxide from the hot liquor, adding non-reducing sodium base alkaline compounds to such liquor to neutralize residual sulphurous acid groups therein, adding alkali including sodium sulphide to the liquor to render it alkaline, and continuing the cooking of the raw cellulosic material to complete fiber liberation.

3. A process which comprises cooking raw cellulosic material in a sulphurous acid liquor, neutralizing the hot liquor with non-reducing sodium base alkaline compounds, adding alkali including sodium sulphide to the liquor to render it alkaline, continuing the cooking of the cellulosic material, separating the resulting pulp from the spent liquor, and recovering the sodium constituent of the spent liquor in the form of alkaline compounds for use in again practising one or more steps of the process.

4. A process which comprises cooking raw cellulosic material in a sulphurous acid liquor, adding non-reducing sodium base alkaline compounds to the hot liquor to react upon residual sulphurous acid groups therein, adding caustic soda and sodium sulphide to the liquor to render it distinctly alkaline,

continuing the cooking of the cellulosic material, separating the resulting pulp from the spent liquor, smelting the sodium constituent of the spent liquor in a reducing atmosphere to produce sodium carbonate and sodium sulphide, causticizing the sodium carbonate, and using the caustic soda and sodium sulphide for again producing distinctly alkaline liquor.

5. A process which comprises cooking raw cellulosic material in a sulphurous acid liquor, adding sodium carbonate to the hot liquor to react upon residual sulphurous acid groups therein, adding alkali including sodium sulphide to the liquor to render it alkaline, continuing the cooking of the cellulosic material, separating the resulting pulp from the spent liquor, smelting the sodium constituent of the spent liquor in a reducing atmosphere to produce sodium carbonate and sodium sulphide, selectively crystallizing sodium carbonate from the smelt for use in again reacting upon residual sulphurous acid groups, and using the rest of the smelt for again producing alkaline liquor.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.