This invention relates to the manufacture from wood and kindred raw cellulosic materials of a pulp possessed of high alpha cellulose content and other desirable properties, by a novel combination of chemical pulping and refining steps.

It has been proposed to produce pulps by cooking raw cellulosic materials in non-acid sulphite solutions for instance, in a plain sodium sulphite solution or in one containing some free alkali, usually a proportion subordinate to the proportion of sodium sulphite present in the solution. Wood pulps thus produced, however, are truly raw or crude products which are capable of undergoing considerable improvement for use in the fields of high grade paper manufacture and of cellulose-derivative-making. Thus, wood pulp prepared in a straight sodium sulphite solution is invariably high in its content of pentosans and so is ill-fitted for conversion into the best grades of cellulose derivatives. So, too, paper made therefrom is harsh, brittle, and of low stability. The presence of alkali in the cooking liquor tends to improve the softness of the pulp somewhat, but the pulp is still high in pentosans and deficient in best all-round paper-making characteristics. I have found that such raw pulps lend themselves advantageously to refinement in strong alkaline solutions which can be applied at moderately low temperatures, for instance, room temperature or lower. In fact, I have found it impossible to effect the refinement of such pulps in dilute alkaline liquors, even when such liquors are used at temperatures above 150° C.—conditions under which the usual sulphite pulps produced in acid sulphite liquors containing much more free than combined SO₃ undergo a pronounced refinement and improvement in quality.

A specific example of procedure falling within the purview of the present invention may be practised substantially as follows. Chipped wood (e.g., spruce), is digested for about five hours in a solution of sodium sulphite of about 10% strength at about 250° to 375° F. These temperature conditions are comparatively high, but they must be sorted to if complete pulping is to be realized in a practical period of time, say, about five hours. The pulp thus produced is washed free of cooking liquor and when tested is found to have an alpha cellulose content of about 86%, a pentosan content of about 7% to 9%, a lignin content of about 4% to 6%, and a solution viscosity less than 1. The washed pulp is then admixed with caustic soda solution of a concentration to produce a pulp suspension of, say, 5% to 10% in a solution of, say, 5% to 10% caustic soda strength. After maintaining the mixture of pulping solution at room temperature (about 20° C.) for about four hours, the pulp may be washed free of solution. The washed pulp has an alpha cellulose content of at least 94%, a pentosan content of about 0.8%, a lignin content of about 1.9%, and a solution viscosity of about 0.5. The washed pulp can then be bleached to whiteness under conditions to preserve its alpha cellulose content, as in a bleach liquor containing, in addition to calcium or sodium hypochlorite bleach, sufficient free alkali, like caustic soda or sodium carbonate, to inhibit practically entirely any tendency to generate oxygen-celluloses throughout the bleaching operation. The resulting pulp represents, as will be appreciated by those skilled in the art, a material far more valuable for making paper and cellulose derivatives than the starting pulp.

It is possible to deviate from the particular temperature and alkalinity conditions under which the refinement of the pulp is hereinbefore described as being effected. In any case, however, a solution of caustic soda of from about 5% to 18% or greater strength should be used at temperatures ranging from about 0° to 50° C. I am specifying operative ranges of alkalinity and temperature for the reason that the use of high temperatures with dilute alkaline solutions has little beneficial effect on raw pulps such as I am processing. For instance, were a raw pulp such as already characterized treated at 100° C. with a caustic soda solution of only about 1% to 5% strength for as long as six hours, its alpha cellulose content would still remain at about 86% and
its pentosan content would be little under 7%. Even if one went to a temperature as high as 175°C, the alpha cellulose content of such pulp would be little, if at all, affected. In practising my process, the conditions of refining treatment may be chosen to yield a product suitable for use in making both paper and cellulose derivatives, or primarily for papermaking. Thus, the use of a caustic soda solution of about 18% strength or greater at room temperature affects a mercerization as well as refinement of the pulp, so that, although the product is eminently useful for making cellulose derivatives, it cannot by itself serve as a high grade papermaking material, except for special purposes, on account of its non-hydratability when put through a beater and its tendency to form clumps or aggregates. So, too, the use of solutions weaker than 18% strength but at sufficiently low temperature to be mercerizing gives rise to a product whose field of utility consists primarily in making cellulose derivatives. On the other hand, the use of caustic soda solutions of about 6% to 12% strength at room temperature, as described in the foregoing, is conducive to a product not only serviceable for derivative-making but also of great value in the manufacture of papers possessing desirable qualities as high tear resistance, folding endurance, stability, and softness. Of importance in its applicability for making cellulose derivatives, is the quality of low solution viscosity possessed by pulps prepared in accordance with my process. Most raw pulps are of high solution viscosity, amounting to as high as 50 in the case of typical kraft pulps, but a pulp liberated by cooking wood or kindred raw cellulosic material in a non-acid sulphite solution is of very low solution viscosity, probably on account of the high temperature of cooking relied upon to accomplish pulping and the neutral or only weakly alkaline condition of the liquor. In this connection, it might be mentioned that when wood chips are digested with ordinary kraft liquor even at 375°F, the solution viscosity of the resulting pulp would be vastly greater than 1, probably on account of the fact that the liquor is strongly alkaline and that substantially only alkali is relied upon as the pulping chemical. In fact, a pulp liberated by such cooking is invariably of a solution viscosity less than 1, and can be prepared with as low a solution viscosity as 0.5, especially when the temperature at the end of the cook is raised to, say, 375° to 400° F. The refining step to which the pulp is then subjected causes a further lowering of its solution viscosity, so that the refined pulp may be characterized by a solution viscosity of as low as about 0.5, or even lower. It is hence useful, as such (i.e., without further special treatment), for esterification purposes when esters of exceedingly low solution viscosity are wanted, for instance, half-second nitrocelluloses or viscose syrups intended for spinning into artificial silks or for fabrication into films. The refining process can readily be conducted under conditions to produce a finished product of an alpha cellulose content of as high as about 97%, or even higher, and of a solution viscosity of as low as about 0.5, or even lower, which kind of product is a choice one, especially for xanthation purposes, in which connection its low solution viscosity makes possible a complete xanthation of the soda cellulose prepared therefrom without the necessity of subjecting such soda cellulose to the conventional long period of ageing under controlled temperature conditions. Because of its purity, the viscose syrups prepared therefrom may be spun into artificial silks or fabricated into films of the first quality.

There are various supplemental treatments or steps which might be introduced into the main combination of steps heretofore outlined as constituting my process. Or the main steps themselves might be modified somewhat. For instance, the alkalinity of the refining solution might be furnished in part by sodium sulphide, but in any case the alkalinity of the solution as furnished by both the sodium sulphide and caustic soda should be equivalent to that which must be had when caustic soda alone is used. I am referring specifically to refining liquors containing sodium sulphide as well as caustic soda as the refining chemical, in view of the fact that such a liquor is economically available in a kraft mill as the so-called white liquor. The sodium sulphide is also a potent refining chemical, especially in so far as concerns its activity upon ligneous matter contained in the pulp. In some kraft mills, the sulphidity of the white liquor may run as high as 40%; that is, about 40% of the active alkali may be present as sodium sulphide. The presence of sodium sulphide in the liquor favors the production of a refined pulp having superior papermaking characteristics. When caustic soda alone is used in the refining liquor, a relatively small amount of oxidant, such as hypochlorite or permanganate, may advantageously be added to the liquor to enhance both the refining action and the reduction of solution viscosity effected upon the pulp. The oxidant does not appreciably attack the alpha cellulose, because it is inhibited from so doing by the large excess of alkali. It does, however, attack and dissolve ligneous and coloring matter as well as promote a reduction of the solution viscosity of the pulp. Thus, the use of a small amount of calcium or sodium hypochlorite or other suitable oxidant in the refining liquor not only improves the color of the pulp while attaining a given alpha cellulose content, but
promotes the reduction of the solution viscosity of the pulp to values of as low as 0.2 to 0.1, especially when the concentration of caustic soda in the liquor amounts to about 15% or higher and is in itself conducive to a drastic lowering of the solution viscosity of the pulp, as well as its refinement and activation for xanthation or other esterifying operation. An oxidant should not be used in a refining liquor containing sodium sulphide, because it would react upon and consume the sodium sulphide, rather than favorably affecting the fiber. In addition to or instead of bleaching the refined pulp as hereinbefore described, the raw pulp may be treated with a suitable bleaching agent, like chlorine water or hypochlorite bleach, to remove ligneous and coloring matter theretofrom and/or to facilitate subsequent removal of ligneous and coloring residues by the alkaline refining liquor. This preliminary treatment need not necessarily whiten the pulp. In fact, it can be carried out to advantage with chlorine water under conditions merely to chlorinate the ligneous matter and deepen the color of the pulp to a yellow or orange, the chlorinated ligneous reaction products being easily dissolved subsequently in the strongly alkaline refining liquor. The refining treatment may, however, be performed on a fully or completely pre-bleached pulp. Before the pulp undergoes the action of the strongly alkaline refining liquor, its pentosan content may be put in condition for ready solution by subjecting the pulp to a high temperature hydrolyzing treatment in water or in weak solutions of salts or basic or acid chemicals. These hydrolyzing treatments can be conducted without degrading the alpha cellulose content of the pulp if water solution is used or if the water is rendered only faintly basic or acid or is maintained neutral by suitable chemical addition. The temperature of the treatment may be 400° F. or even higher, under which conditions the pentosans present in the pulp are conditioned for subsequent removal and the fiber itself is lowered in solution viscosity, thus leaving less work to be done subsequently by the strongly alkaline refining liquor. The same result may be realized by concluding the non-acid sulphite cooking of paper cellulose material at higher temperature than that maintained during the main cooking or pulping period. For instance, although the main cook to produce pulp may be conducted at 350° to 375° F., the pulped material may be given a final stage treatment in the digester at, say, 400° F., or at higher temperature, for only a short period of time, say, ½ hour or so. These high temperature treatments do not remove appreciably pentosans from the pulp, but they do activate them, as already indicated, for subsequent removal in the strongly alkaline refining liquors.

I have hereinbefore also talked about the solution-viscosity characteristics of pulp in terms of specific values. The solution viscosity of fiber is herein given in absolute c. g. s. units, and is determined by measuring the viscosity of a solution of 6 grams of dry fiber in a cuprammonium solution composed of 225 cc. of 28% ammonia water containing 9 grams of cuprous oxide. The c. g. s. unit is employed because it is definite, denoting a viscosity 100 times that of water at 20° C., wherefore a cuprammonium cellulose solution prepared from a certain type of fiber and by means of which such fiber is identified as having a solution viscosity of 10, is 1000 times as viscous as water at 20° C.

What I claim is:

1. A process which comprises pulping raw cellulosic material in a non-acid sulphite cooking liquor, subjecting the resulting pulp to the action of an alkaline refining liquor of at least about 5% alkalinity, calculated in terms of caustic soda equivalent, and washing the refined pulp.

2. A process which comprises pulping raw cellulosic material at a temperature of at least about 350° F. in a non-acid sulphite cooking liquor, subjecting the resulting pulp to the action of an alkaline refining liquor of at least about 5% alkalinity, calculated in terms of caustic soda equivalent, and washing the refined pulp.

3. A process which comprises pulping raw cellulosic material at a temperature of at least about 350° F. in a non-acid sulphite cooking liquor, subjecting the resulting pulp to the action of caustic soda refining solutions of at least about 5% strength and up to and beyond 18% strength and at temperatures of from about 0° to 50° C., and washing the refined pulp.

4. A process which comprises pulping chipped wood at a temperature of at least about 350° F. in a substantially neutral solution of sodium sulphite of at least about 10% strength, subjecting the resulting pulp to the action of an alkaline refining liquor of at least about 5% alkalinity, calculated in terms of caustic soda equivalent and at temperatures of from about 0° to 60° C., and washing the refined pulp.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.