This invention has relation to high alpha cellulose fiber (i.e., pulp containing a high percentage of alpha or resistant cellulose) and a process of producing the same more especially from chemical wood pulps, such as sulphite pulp, in an economical and efficient manner.

Before proceeding to a description of the present invention, in order to give a clearer and more sufficient understanding thereof, and the results achieved thereby, it is desirable to consider the subject matter of application for U.S. Letters Patent Serial No. 72,522, filed December 1, 1925, by Milton O. Schur and myself.

In that application, it is pointed out that high alpha cellulose fiber may be produced by the purification of sulphite fiber, such as results from the digestion of wood chips in an acid sulphite liquor [as, for example, calcium bisulphite, Ca(HSO₃)₂] and which contains ordinarily about 85% to 87% alpha cellulose. That is, since the bisulphite digestion is not entirely effective in removing the ligno-celluloses contained in the wood, the resulting sulphite pulp still contains substantial amounts of the less-resistant beta and gamma celluloses, together with gums, ligneous and other coloring substances, which are undesirable constituents, if sulphite pulp is to be employed for certain purposes. In order to produce pulp which consists substantially only of alpha cellulose, it is necessary to process sulphite pulp further to eliminate, so far as is practicable, the less-resistant celluloses, together with the residual ligneous and other coloring substance contained therein. The removal of some of the undesirable constituents of sulphite pulp may be accomplished by the use of an excessive amount of bleach in the bleaching process, but this is highly detrimental, in that the alpha cellulose content of the pulp thereby suffers a material decrease by degradation into oxycellulose. Moreover, excessive bleach has the tendency to weaken the strength of the pulp. I have discovered that an alkaline liquor is effective in reacting with and dissolving the less-resistant celluloses, including ligno-cellulose and other coloring substance contained in sulphite pulp, and in the aforementioned application have described a process of producing high alpha cellulose fiber by an alkaline digestion of unbleached sulphite pulp, preferably in a caustic soda or soda ash solution. The alkaline digestion, in such case, is carried out in a dilute solution of caustic soda at an elevated temperature until the desired purification of the pulp has been effected. The purified pulp, containing, say, about 94% alpha cellulose, is washed free from the spent digesting liquor, and has a high white color after moderate bleaching. In carrying out the hot purification process of that application, a sulphite stock suspension at a consistency of about 9% to 15%, containing about 5% to 5% caustic soda, based on the weight of bone-dry fiber, is digested in open tanks under atmospheric pressure at a temperature of about 180° to 212° F., for about three to eight hours, while preferably agitating the stock and maintaining the elevated temperature by blowing live steam into the tanks.

The primary object of the present invention is to produce a high alpha cellulose fiber of substantially equal or better quality than that obtained by a hot alkaline digestion of unbleached sulphite pulp and in a more economical manner. I have discovered that this object may be attained by treating chemical wood pulp, such as sulphite pulp, with a concentrated solution of caustic soda, at room temperature (say, about 30° C.), the solution containing sufficient alkali to react with the less-resistant celluloses, ligneous, and other coloring substance contained in the pulp, but insufficient to cause a substantial mercerization of the alpha cellulose content thereof. In carrying out the cold purification of sulphite pulp, too high a concentration of caustic soda must be avoided, since otherwise the fibers will become mercerized, and in so doing will swell and acquire a coating of mercerized cellulose. Mercerization lowers the strength of the pulp; and on beating, mercerized pulp has no tendency to hydrate or gelatinize, beating merely macerating or cutting the fiber, so that paper made from the beaten mercerized fiber is extremely weak. On the other hand, if too low a caustic con-
centration is employed, a sufficient purification, or reaction of the impurities contained in the pulp with the caustic soda solution, will not take place, and the resulting pulp product will not be high enough in alpha cellulose. Consequently, the concentration of caustic soda is maintained within two limits, namely: between a maximum concentration at which mercerization takes place, and a minimum concentration at which a sufficient purification of the pulp is not effected. These limits will vary somewhat, depending upon the exact temperature employed and the characteristics of the raw stock.

After the purification, the pulp, containing preferably at least 94% alpha cellulose, is washed free from alkaline agent, and may be bleached to a high degree of whiteness with a moderate amount of hypochlorite bleach without material injury to its strength or decrease in its alpha cellulose content. If a pulp of maximum whiteness is desired, the bleached pulp may be superbleached in a chlorine solution.

I have found that the time required for such cold purification, using strong solutions of caustic soda, is materially shorter than a corresponding hot treatment, so that with a given apparatus, a much higher production may be realized. Moreover, the necessity for the use of steam is avoided, thus eliminating this factor from entering into the production cost of the finished product. A further important advantage is that for a given yield of pulp, the alpha cellulose content is higher, and the pentosan content lower.

While I have indicated that the process is ordinarily and preferably carried out at room temperature, I desire to have it clearly understood that lower than room temperature, say 0° C. to 25° C., and a correspondingly suitable caustic soda concentration, may be employed to effect the purification of the sulphite pulp. Likewise, higher temperature (for example, 30° C. to 50° C.) and a correspondingly suitable concentration of caustic soda may be employed in such treatment. I have further discovered that a concentrated solution of sodium sulphide when used in lieu of a caustic soda solution will also effect a purification of sulphite pulp at relatively low temperature. However, in securing a purification equivalent to that obtained by a caustic soda solution, the sodium sulphide solution must contain about twice as much purifying sodium sulphide (by weight) as the caustic soda solution does caustic soda; and this renders the sodium sulphide treatment more expensive than the caustic soda treatment.

At any temperature, the maximum concentration of caustic soda which may be employed must be below that at which mercerization occurs, and the minimum above that at which a sufficient purification is not effected. For optimum results in respect of alpha cellulose content in a finished product produced from unbleached sulphite pulp, at a temperature of about 30° C., the minimum and maximum concentrations in a stock suspension of about 5% to 6% are, respectively, about 100% and 150% caustic soda, based on the weight of dry fiber. The alkalinity of the caustic soda solution is thus about 5% to 7½% caustic soda strength.

The cold alkaline treatment may be practiced with advantage after a portion of the ligneous and other coloring substance contained in the sulphite pulp has been removed, by treating such pulp with an oxidizing solution, preferably a solution containing chlorine. Such pretreatment is especially desirable when the sulphite pulp is undercooked, since such undercooking leaves a higher percentage of ligneous and other coloring substance than ordinarily. The oxidizing agent reacts with a portion of the impurities, forming soluble reaction products or products which are easily removable by the alkaline treatment.

In carrying out the process, wood chips (spruce, for example) are cooked in a digester in an acid sulphite liquor [as, for example, Ca(HSO₃)₂ or NaHSO₃ of a strength of about 1% combined and 5%-6% free SO₃] under the requisite time, temperature, and pressure conditions in accordance with standard modern practice. The acid digestion is especially effective in removing ligno-celluloses and coloring substance from the wood, but leaves behind a certain residual percentage thereof, together with less-resistant cellulose and some pentosan, the resulting sulphite pulp containing about 85% to 87% alpha cellulose. After digestion, the digester is "blown" into a suitable blowpit; and the sulphite pulp is separated from its digesting liquor, which may be treated, if desired, for the recovery of chemicals. The pulp is then washed substantially free of its digesting liquor and the spent products of digestion, and is preferably screened to remove specks, shives, etc., prior to the alkaline digestion. It may also be partially bleached, as hereinafter described, prior to the alkaline digestion. It is then thickened by any suitable form of pulp thickener, and intimately admixed with an alkaline solution, preferably caustic soda, to a consistency of about 5% to 6%, the suspension containing preferably about 100% to 150% caustic soda, based on the weight of dry fiber. While a lower percentage of caustic soda may be employed in cases where the resulting pulp need not contain at least 94% alpha cellulose, in the practice of the present invention, it is preferable to employ a caustic soda concentration between the limits indicated, so that a sufficient purification of the fiber may be obtained without impairing or injuring its paper-making characteristics.
material extent, or in other words, without effecting a substantial mercerization of the fiber. The alkaline treatment is carried out, preferably while stirring or agitation, so as to promote a uniform reaction, at room temperature (say, 30° C.). The treatment may require thirty minutes to two hours, depending on the characteristics of the particular stock undergoing treatment. The resulting product, which may contain from 85% to 88% alpha cellulose, is then washed substantially free from alkali. The spent liquor contains not only a very high percentage of residual unabsorbed caustic soda, but also the various organic substances removed from the sulphite pulp as indicated. The large portion of spent liquor is reemployed for the treatment of other sulphite pulp. The washed pulp is of light color, not much different in appearance from the color of ordinary unsulphite sulphite pulp.

As indicated, it may be desirable to treat the sulphite pulp with a solution of an oxidizing agent prior to the alkaline treatment, especially when such pulp is of a "refractory" or undercooked nature and thus has a higher lignin content than ordinarily. In such cases, the pulp is treated, approximately at room temperature at a stock concentration of 5% for about 1/2 to 1 hour, preferably in a solution containing 1% to 3% chlorine or 2% to 5% of 35% lime bleach (Ca(OCl)2), based on the dry weight of fiber. The solution reacts with the ligninous and coloring substances contained in the pulp, forming soluble reaction products easily or products removable by the subsequent alkaline treatment. The pretreated stock is then treated in a concentrated solution of caustic soda, as hereinbefore described.

Subsequent to, or during the washing of the alkaline treated stock, it may be desirable to add a small amount of bisulphite or sulphurous acid solution, to neutralize and thereby remove any last traces of alkali which the washing does not eliminate,—the addition of weak acid being especially desirable if the washing is incomplete, in which case such a treatment is apt to be an appreciable quantity of caustic soda present, which would otherwise cause an alkaline condition in the bleaching. If alkali is necessary in the bleaching operation, it is better to provide alkali for the purpose, as will subsequently appear, rather than to depend on the alkali present in an incompletely washed pulp. In actual practice, the bisulphite or sulphurous acid may or may not be used prior to bleaching, according to economic expediency.

Since the alkaline treatment has removed from the original fiber a substantial amount of ligneous and other coloring matter, together with less-resistant beta and gamma celluloses, the bleaching of the fiber may be accomplished with less hypochlorite bleach than is ordinarily required in the production of a white product. The stock is treated at a consistency of about 10% to 16% with about 5% to 10% of 35% lime bleach (Ca(OCl)2), based on the dry weight of pulp. Precautions must be taken to maintain a temperature not exceeding 30° F. In the bleaching tanks, in order to preserve the maximum strength of fiber. If desired, a certain small proportion of caustic soda liquor may be added to the bleach liquor and pulp within the bleachery, to retard the bleaching and thereby avoid the possibility of lowering the alpha cellulose content or injuring the strength of the stock due to too-violent bleaching. The bleaching period ranges from eight to twenty hours, depending upon the characteristics of the fiber undergoing treatment; and at its conclusion the stock has a color of 95 to 100. The bleached high alpha cellulose fiber has approximately the following characteristics:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength (Mullen)</td>
<td>35-50</td>
</tr>
<tr>
<td>Sloewness (min.)</td>
<td>8-10</td>
</tr>
<tr>
<td>Tear</td>
<td>220-350</td>
</tr>
<tr>
<td>Pentossan</td>
<td>1.5-2.0%</td>
</tr>
<tr>
<td>Yield (from unbleached sulphite)</td>
<td>89-92%</td>
</tr>
<tr>
<td>Alpha cellulose</td>
<td>94-98%</td>
</tr>
<tr>
<td>Average fiber length</td>
<td>1.1 - 1.2 min.</td>
</tr>
</tbody>
</table>

The stock thus bleached may be improved by a superbleaching operation. In superbleaching, the preferably washed and bleached high alpha cellulose fiber is treated at a stock consistency of from 4% to 6%, with about 0.2% to 0.5% chlorine, based on the weight of bone-dry fiber. No effort need be made to control the temperature in superbleaching, which may approximate the temperature of water available at the time. If it is desired to increase the rate of superbleaching, the temperature may be increased to not higher than 90° F. After superbleaching, the stock is treated with an antichlor, as for example, a bisulphite solution, which serves to react with and to neutralize any residual traces of chlorine or hydrochloric acid present in the stock. The stock is then washed substantially free from reaction products. The superbleaching may be carried out on stock which has not been washed after its main bleaching operation, but this is not altogether a satisfactory mode of operation, due to the high chlorine consumption resulting from the reaction of the chlorine with the products of reaction of the original bleach. The superbleaching requires 1 to 2 hours, and yields a stock having a color of 106 to 108.

The bleached or superbleached stock is then diluted to about 2% to 4%, and is delivered over a set of rifflers, which removes from the stock a substantial per cent of heavy impurities, such as cinders, cement, or iron rust, which may be present therein in small
quantities. It may then be sent to a classifier, which removes from it a certain proportion (1% to 20%, depending on the degree of refining to which it is desired to subject it) of very short and broken fibers, as well as fibrille and specks which are not removed by screening or riffling. The pulp is then sent to a wet machine and finally taken off in sheet form, ready for shipment.

Due to its properties and the particular treatment which it has received as described hereinbefore, high alpha cellulose produced by the practice of my invention may be employed instead of rag fiber in the manufacture of high grade bond and ledger papers, as a substitute for cotton fiber in the manufacture of the cellulose esters and the cellulose ethers, and for any other purpose where a substantially pure cellulose fiber is required.

The relatively small per cent of short fiber high alpha cellulose obtained in classification may be used to advantage in the preparation of cellulose derivatives.

Another advantage following from the practice of the herein described process lies in the fact that, with the high alpha cellulose fiber obtained therefrom, a solution of cellulose or cellulose esters may be obtained of lower viscosity than it is possible to produce either with ordinary cotton fiber or with high alpha cellulose produced by the hot process. That is, with a given amount of cellulose in solution, a solution of high alpha cellulose produced by the cold method is of a materially lower viscosity than a solution of cotton, and of considerably lower viscosity than a solution of high alpha cellulose produced by the hot process. Consequently, when solutions of cellulose or cellulose esters are employed in operations where a high concentration of cellulose together with a low viscosity is desirable, and when the concentration to be employed is limited by the viscosity of the solution, the high alpha cellulose fiber as herein produced may be employed at a much higher concentration and with more advantageous result than cotton or high alpha cellulose produced by the hot process.

As previously indicated, while high alpha cellulose fiber may be produced by a cold caustic soda solution treatment of sulphite pulp, formed either by the acid digestion of wood chips in a sodium bisulphite liquor or in a calcium bisulphite liquor, I preferably employ sulphite pulp resulting from the sodium base liquor, because of the more desirable physical characteristics in the final product. In this connection, it may be stated that while the high alpha cellulose fiber produced from the sulphite pulp liberated from wood chips by a sodium base acid liquor possesses an alpha cellulose content substantially the same as that produced from a calcium base acid liquor, its physical characteristics, including strength, tear and folding endurance, are materially higher. This is undoubtedly due to the fact that the unbleached sulphite pulp resulting from a sodium base sulphite liquor is superior in quality to a pulp obtained from a calcium base sulphite liquor because of its greater fiber length. The greater length of fiber and better strength are believed in great measure to be due to the more thorough penetration of a sodium base sulphite liquor and the lower maximum temperature of digestion required for conversion of the wood chips to pulp. The superior physical characteristics of the sodium base fiber carry through the various treatments, including the cold alkaline treatment, to the finished high alpha cellulose stock. In fact, its tear test is increased relatively by the cold alkaline treatment to a much greater extent than the increase in the tear test of a pulp produced in an acid calcium bisulphite liquor.

While I have confined myself to a description of the purification of unbleached sulphite pulp, I have also discovered that the characteristics of pulps of various other derivations may be favorably modified by treatment with a concentrated caustic soda solution in the cold. For example, as disclosed in my application, Serial No. 73,193, filed December 4, 1925, kraft or “sulphate” pulp may be similarly treated, or as disclosed in my application Serial No. 72,602 filed December 1, 1926, a “4-4” pulp, i.e., a pulp which has been produced by digestion in an acid sulphite liquor containing approximately 4% combined and 4% free SO₂, may be similarly treated. In each case a product possessing certain desirable characteristics is produced. I do not herein claim broadly a process wherein pulp is treated with an alkaline reagent, specifically a hot sodium caustic soda, as specified in application, Serial No. 72,528, filed by Milton O. Schur and myself on December 1, 1925; nor do I claim herein the process or parts thereof generically or specifically claimed therein.

What I claim is:

1. A process which comprises treating sulphite pulp admixed with a solution of caustic soda to a stock consistency of about 5% to 6% at about room temperature for about thirty minutes to two hours, said solution containing 100% to 150% caustic soda based on the weight of dry fiber.

2. A process which comprises treating sulphite pulp at about room temperature with a concentrated caustic soda solution containing caustic soda in amount sufficient to react with and render soluble less-resistant celluloses and ligneous matter contained therein, but insufficient to cause substantial mercerization of the alpha cellulose content thereof, washing the treated pulp substantially free of its alkaline liquor and the entrained prod.
ucts of reaction, bleaching the washed product, and superbleaching the bleached pulp.

3. A process which comprises treating sulfate pulp with a solution containing chlorite to remove ligninous and other color- ing substance contained therein, washing said pulp free from said solution, and treating said washed pulp at about room temperature with a concentrated caustic soda solution containing caustic soda in amount sufficient to react with and render soluble less-resistant cellulosic and ligninous matter contained therein, but insufficient to cause a substantial mercerization of the alpha cellulose content thereof.

4. A process which comprises treating sulfate pulp at approximately room temperature at a stock density of about 5% in a solution containing 1% to 2% chlorine based on the dry weight of fiber, washing said pulp free from said solution, and treating said washed pulp at a stock density of 5% to 8% at about room temperature in a solution containing about 100% to 150% caustic soda based on the dry weight of fiber.

5. A process which comprises treating sulfate pulp with a caustic soda liquor containing from 5% to 8% caustic soda at about room temperature for about thirty minutes to two hours, thereby effecting a solution of a substantial proportion of the non-alpha cellulose content of such pulp.

6. A process which comprises treating sulfate pulp at approximately room temperature at a stock density of about 5% in a solution containing 1% to 2% chlorine based on the dry weight of fiber, washing said pulp free from said solution and treating said washed pulp with a caustic soda liquor containing from 5% to 8% caustic soda at about room temperature.

7. A process which comprises treating cellulose pulp liberated from raw cellulose material at a temperature considerably below 180° F., with alkaline solution of sufficient alkalinity to effect a solution of a substantial proportion of the non-alpha cellulose content of such pulp without deleteriously affecting its papermaking characteristics.

8. A process which comprises treating pulp liberated from raw cellulose material at about room temperature with a caustic soda solution of sufficient alkalinity to react upon and render soluble a substantial portion of the non-alpha cellulose content of the pulp, but of insufficient alkalinity to mercerize the pulp.

9. A process which comprises treating chemical wood pulp at about room temperature with a caustic soda solution of sufficient alkalinity to react upon and render soluble a substantial proportion of the non-alpha cellulose content of the pulp, but of insufficient alkalinity to mercerize the pulp, washing the pulp substantially free of the solution and dissolved reaction products, and bleaching the washed pulp.

10. A process which comprises treating pulp liberated from raw cellulose material at about room temperature with an alkaline solution of sufficient alkalinity to effect a solution of a substantial proportion of the non-alpha cellulose content of such pulp but without deleteriously affecting its papermaking characteristics.

11. A process which comprises treating chemical wood pulp at about room temperature with an alkaline solution containing caustic soda and sodium sulfide in amount sufficient to effect a solution of a substantial proportion of the non-alpha cellulose content of such pulp but without deleteriously affecting its papermaking characteristics.

12. In purifying unbleached chemical wood pulp, the sequence of operations which comprises partially bleaching the pulp, treating the partially bleached pulp with a solution of caustic alkali, the pulp and solution being brought together in such amounts and concentrations as to give a resulting suspension having an alkalinity equivalent to that of a caustic soda solution of at least about 5% strength but below mercerizing strength, continuing the treatment for the desired period of time, separating caustic alkali solution from the so-treated pulp and washing the latter, subjecting the treated and washed pulp to a second stage of bleaching treatment, and washing the resulting finally bleached pulp.

13. In purifying unbleached chemical wood pulp, the sequence of operations which comprises partially bleaching the pulp, treating the partially bleached pulp with a solution of caustic alkali, the pulp and solution being brought together in such amounts and concentrations as to give a resulting suspension having an alkalinity equivalent to that of a caustic soda solution of at least about 5% strength but below mercerizing strength, continuing the treatment for the desired period of time at a temperature less than the boiling point of water, separating caustic alkali solution from the so-treated pulp and washing the latter, subjecting the treated and washed pulp in aqueous suspension to a second stage of bleaching treatment, thereafter treating the pulp with an antichlor, and washing the resulting finally bleached pulp.

14. In purifying unbleached chemical wood pulp, the sequence of operations which comprises partially bleaching the pulp, treating the partially bleached and washed pulp with a solution of caustic alkali, the pulp and caustic alkali solution being brought together in such amounts and concentrations as to give a resulting suspension having an alkalinity equivalent to that of a caustic soda solution of at least about 5% strength but below mercerizing strength, continuing the treat-
ment for the desired period of time at a temperature below 212°F., separating caustic alkali solution from the so-treated pulp and washing the latter, subjecting the treated and washed pulp in aqueous suspension to a second stage of bleaching treatment, and washing the resulting finally bleached pulp.

15. In purifying unbleached chemical wood pulp, the sequence of operations which comprises partially bleaching the pulp, thickening the same, treating the thickened pulp with a solution of caustic alkali, the pulp and caustic alkali solution being brought together in such amounts and concentrations as to give a resulting suspension having an alkalinity equivalent to that of caustic soda solution of at least about 5% strength but below mercerizing strength, continuing the treatment at a temperature below 212°F. for the desired period of time, separating caustic alkali solution from the so-treated pulp and washing the latter, subjecting the treated and washed pulp to a second stage of bleaching treatment, and washing the resulting finally bleached pulp.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.