Patented June 9, 1931 1,809,312

UNITED STATES PATENT OFFICE

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PROCESS OF PRODUCING WOOD PULP OF HIGH ALPHA CELLULOSE CONTENT

No Drawing. Application filed April 19, 1927. Serial No. 185,019.

This invention relates to the production of wood pulp of high alpha cellulose content, and has for its object the production of a pulp possessing optimum characteristics both for manufacture into paper and for use as a raw material for the preparation of cellulose derivatives.

Heretofore, pulp of high alpha cellulose content has been produced by the general process disclosed and claimed in our application for patent, Serial No. 716,154, filed May 27, 1924. In accordance with that process, a raw pulp, e. g., unbleached sulphite pulp, is subjected to a controlled oxidizing or chlorinating treatment which does not whiten the pulp appreciably, but, as a matter of fact, generally causes a deepening of the color of the pulp from a pale cream or light brown to a yellow or light orange, this color generation being the result of the formation of colored addition or oxidation products from the ligneous content of the pulp. The treated pulp is then digested in an alkaline liquor until a considerable portion of its non-alpha cellulose component, including the chlorinated or oxidized ligneous reaction products of the previous treatment, has been removed by dissolution, whereupon the pulp is washed and treated in a liquor containing bleach in sufficient amount to whiten it substantially to ultimate whiteness.

Inasmuch as the oxidizing or chlorinating treatment as described in said application effects what may be termed but a mild or selective reaction upon the ligneous content of the pulp, it is necessary to use 2% or more of bleach powder, based on the bone-dry weight of fiber, in the final bleaching treatment to remove sufficient ligneous and coloring content from the alkaline-digested pulp to whiten it to the desired point. Such bleach liquor, although considerably less in bleach content than that necessary to whiten sulphite pulp, yields a product usually having a copper number falling between 1.7 and 2.5, and a solubility in boiling 3% caustic solution of 5% to 7%,—indicating a low oxycellulose content as compared with the usual bleached sulphite pulp. It is desirable, however, further to reduce the copper number and soda solubility so as to enhance the suitability of the product as a raw material not only for the preparation of papers of high stability, comparable with high grade rag papers, but also for the preparation of cellulose derivatives such as nitrocellulose, cellulose acetate, cellulose xanthate, etc., as the oxycelluloses are nitrated, acetated, or xanthated along with the alpha cellulose to form unstable derivatives which may contaminate the derivative and impart inferior physical and chemical characteristics thereto.

We have found that the copper number, and accordingly the oxycellulose content of an alpha pulp, may be considerably reduced, and hence its suitability as a raw material increased, by reacting, as will be more fully hereinafter described, more completely upon the ligneous and coloring content of the raw pulp in a treatment prior to alkaline digestion, so that after alkaline digestion this content is largely removed, permitting substantially ultimate whiteness to be finally obtained in a liquor of very low bleach concentration, thus to produce a final product of low oxycellulose content. That is to say, in lieu of removing much of the ligneous content of the pulp in the final bleaching step, we effect, in accordance with our present process, the removal of most of such content by the combined effects of the initial treatment and the alkaline digestion, so that the final bleaching may be performed in liquor of relatively low bleach content. The initial treatment is carefully controlled, however, so that although the ligneous and other coloring content is thoroughly reacted upon, the pulp is not bleached or whitened prior to the alkaline digestion, since if this were attempted, it would be necessary to use considerably more bleach in the first step, this not only resulting in the production of oxycelluloses, which because of solution by subsequent alkaline digestion would be reflected in a lower yield of product, but also in a permanent loss of the desired physical and chemical characteristics of the fiber.

It is the object of the present invention to remove most of the ligneous and other coloring content from the raw pulp by the com-

bined effects of a carefully limited treatment with chlorinating and/or oxidizing agents, and of alkaline digestion, necessitating the use of but a very small quantity of bleach, usually less than 2% and frequently about 1% of 35% bleach powder based on fiber, in the final bleaching step, to bring the pulp to a high degree of whiteness. Our theory is that, even though the pulp is still highly colored after the first treating step, were it not for coloring matter adsorbed from the dark brown liquor generated during the alkaline digestion, the pulp would need no final bleaching, the coloring matter having been removed by the combined effects of the initial treatment with chlorinating and/or oxidizing agents, and by the alkaline digestion.

In our application, Serial No. 716,154, we stated that:

"We have noted that when unbleached chemical wood pulp is subjected to the action of an oxidizing agent, with a given proportion of the reagent during a given period of time, the first consumption of the oxidizing agent is accompanied by a rise in the proportion of alpha cellulose in the pulp, but that a critical point is reached, so that the further consumption of the oxidizing agent is accompanied by a marked decrease in the proportion of the alpha or resistant cellulose content of the pulp. We have also noted that the copper number decreases with the first consumption of the oxidizing agent up to the critical point, and thereafter rises. Consequently, in carrying on the first step of our process, we employ a relatively small amount of oxidizing agent . . . and terminate the operation when or before this critical point is reached, this taking about thirty minutes under the conditions stated in the specific example."

In the example cited, we subjected the alkaline-digested pulp to the action of 2% to 4% bleach, based on the pulp. In carrying out the process of the present invention, we pass slightly the critical point defined in that application, so that final bleaching may be effected with less than 2% bleach, based on pulp. This process requires much more operative skill than our earlier one, for if the critical point is passed to any substantial extent, the physical and chemical characteristics of the pulp suffer. On the other hand, by using the proper quantity of chlorinating and/or oxidizing agents to pass slightly the critical point so that a high degree of whiteness may be finally attained with 1% or 2% bleach, we effect a sufficient increase of stability, lowering of copper number, and reduction in soda-solubility in the product, to warrant the increased care necessary in the initial treatment.

Our new process for the manufacture of high alpha cellulose fiber represents an advance over the earlier one, for in addition to the decided and important improvement effected upon the product in its stability and in its freedom from oxycelluloses, its viscosity may be better controlled, so that a product of high viscosity and high whiteness, and which is of advantage in the preparation of cellulose esters, may be more readily prepared than by our earlier process.

The new process may be advantageously applied to hard, strong pulps prepared with a sulphite liquor high in combined sulphur dioxide, and which normally require the application of large percentages of bleach. By reacting on the ligneous and coloring matter of such pulps prior to the alkaline digestion, up to a point where but 1% to 2% bleach is required in the final bleaching step, a product having optimum characteristics is invariably obtained. Thus, the product is high in strength and tear, in alpha cellulose content, and in whiteness, yet is very low in copper number and in soda-solubility. The product is even more permanent in whiteness than is the usual alpha cellulose pulp, which latter is much more stable in this respect than the usual bleached wood pulp. For instance, alpha pulp produced by the process of the present invention yellows but little when heated at, say, 212° F. for 24 hours, or when exposed to ultra-violet light,—conditions under which sulphite pulp would turn a muddy yellow.

We have found that chlorine water is very selective in its action upon the ligneous content of the pulp, and that if such a reagent is used in sufficient strength for treating raw pulp, substantially all the ligneous content of the pulp may be reacted upon without causing material degradation of its alpha cellulose content. For instance, if raw pulp is treated with chlorine water of sufficient chlorine content, substantially all its ligneous content is reacted upon without material effect upon its final alpha cellulose content. Such treatment does not bleach or whiten the pulp, but as a matter of fact, tends to deepen its color from a pale cream or light brown to a yellow or light orange. We may, however, use an oxidizing reagent such as hypochlorite, of sufficient strength to react upon substantially all the ligneous content of the pulp, but when we so do, we find it necessary to maintain it distinctly alkaline, as under such conditions a more selective reaction is effected upon the ligneous matter, which is more selective to oxidation than the alpha cellulose. Or, we may react upon a portion of the ligneous content of the pulp by chlorine water, and upon the remaining portion by hypochlorite, or vice versa.

We have found that the reaction between raw pulp and chlorine is very rapid up to the critical point, then is very slow, so that if a moderate excess of chlorine is used for less than, say, 30 minutes in a dilute pulp

suspension, say, under 5%, at seasonable temperatures, the quantity of chlorine needed for optimum results will be consumed and the excess removed during the washing prior to the alkaline digestion. By using a moderate excess of chlorine as above described, the initial step in our process becomes more easily controllable. This, of course, is an exceedingly important advantage, especially in a continuous process, for by adjusting the chlorine input so as to maintain the desired excess in the pretreated fiber, variations in the quality of the raw stock may be closely followed with less danger of over- or under-treatment.

A specific example of procedure which may be followed in producing a product of the desired characteristics may be substantially as follows. Wood chips, e. g., spruce, may be digested in the usual acid calcium bisulphite liquor, under the usual conditions, for the necessary period of time to effect a fiber liberation. It may be preferable, however, to effect fiber liberation in liquors of other combined and free SO_2 contents, for instance in an acid alkali-metal bisulphite liquor containing, say, 1% combined SO_2 in the form of sodium bisulphite and 5% free SO_2, as such liquor yields pulp of very low ash content, this characteristic being desired by some manufacturers of cellulose derivatives. In certain instances, a cooking liquor containing a higher percentage of combined SO_2 than that usually maintained during sulphite digestion, say, one containing 2% to 4% combined SO_2 and 4% to 5% free SO_2, or one containing equal proportion of 4% or 5% combined and free SO_2, is preferably used for effecting a fiber liberation, as such high-combined liquor produces strong, hard pulp desirable for papermaking purposes. The resulting fiber is washed and screened, as usual, prior to treatment by our process.

The washed pulp is then treated at about 4% to 5% stock density at about room temperature with chlorine water containing about 2% to 4% (all chemical percentages herein given are based upon weight of dry fiber) chlorine, depending upon the degree to which the raw stock has been cooked. The chlorine reacts rapidly upon substantially all the ligneous content of the pulp,—that is, to the extent necessary for the realization of optimum results, but without materially degrading its alpha cellulose content. In lieu of treating the pulp with chlorine water, we may treat it at a stock density of about 10%, at about room temperature or lower, with bleach liquor of sufficient strength to pass the critical point only slightly. When so treating, however, the bleach liquor must be maintained alkaline during the entire treatment, as this apparently represses the oxidizing reaction,—that is, renders it more selective upon the ligneous matter, which is more susceptible to oxidation than the cellulose, so that treatment slightly beyond the critical point becomes more easily controllable. This may be accomplished by the addition of a suitable proportion of an alkali, say, about 1% to 2% caustic soda, to the bleach liquor. The effect desired may also be realized by reacting upon a portion of the ligneous content of the pulp by chlorination, and another portion by oxidation, during which oxidation treatment an alkaline condition may be maintained to promote a greater selectivity of reaction upon the ligneous matter, as hereinbefore described. For instance, the raw pulp when undercooked may first be treated at ordinary temperatures at a 4% density with about 2½% chlorine in water, until practically all the chlorine is consumed, then washed, and treated at a 10% stock density with a liquor containing 4% sodium or calcium base bleach, which may contain ½% to 1% caustic soda, based on fiber, until practically all the bleach is consumed. Or the order of the chlorine and bleach treatments may be reversed, or the chlorinating and oxidizing treatments may be simultaneously carried out, but it is preferable to separate the steps, because of the easier control and more gentle treatment thereby realized.

After the chlorinating and/or oxidizing treatment, substantially all the ligneous content of the pulp has been reacted upon to produce products soluble in the alkaline digestion which is to follow. The pulp is washed and then treated with an alkaline solution under conditions to effect a dissolution and removal of its non-alpha cellulose component, including less-resistant celluloses and the reaction products of the chlorinating and/or oxidizing treatment. The alkaline treatment may be carried out with various reagents and under various conditions. For instance, it may be carried out at a stock density of about 10% in a liquor containing about 7% caustic soda at atmospheric-boiling temperature. Such treatment is complete in about six hours, yielding a pulp of high alpha cellulose content. The treatment may also be carried out at a stock density of about 10% in a liquor containing 100% caustic soda or its equivalent in the form of sodium sulphide, at about room temperature. Such latter treatment is accompanied by a higher rate of reaction, the treatment being complete in about two hours. Again, the treating liquor may be one containing about 10% lime. Treatment in lime liquor should be carried out in about five to eight hours at about atmospheric-boiling temperature.

Most of the ligneous and other coloring content of the pulp is removed by the initial and the alkaline treatments. The alkaline-digested pulp is then washed and treated with a relatively weak bleach liquor, which serves to whiten it substantially to ultimate

whiteness,—that is, to the point desired for paper manufacture or for conversion into cellulose derivatives. Bleaching may be effected in a liquor containing 1% sodium or calcium bleach, preferably made distinctly alkaline by the addition of about ½% to 1% caustic soda, as bleaching under an alkaline condition prevents contamination of the bleached product with oxycelluloses, so that it is more permanent in whiteness and more satisfactory for the preparation of cellulose derivatives. The bleached pulp is washed and treated with an anti-chlor, e. g., sodium bisulphite solution, to neutralize residual bleach and alkali. The fiber is again washed and, after dilution to the proper consistency, may be run off on a paper machine into "drier sheet," so called, in which form the pulp may be marketed for use as a raw material in the manufacture of paper, rayon, or other cellulose derivatives or products.

In some cases, particularly in preparing high alpha cellulose fiber of exceptional freedom from coloring matter and hence preferable for conversion into esters and other cellulose products of high quality, it is expedient purposely to use an excess of bleach in the final treatment, say, 4% or 5%, even though a high whiteness can be obtained with but 1% or 2%, for the use of excess bleach ensures the removal of traces of coloring matter evident only after the pulp has been esterified. In order to prevent contamination of the bleached product with oxycelluloses, ½% or more of free caustic soda should be present during the final bleaching step.

When free alkali is present during the final step, it is advantageous in some cases to use a high temperature in order further to reduce the beta and gamma celluloses and residual coloring matter. Excellent results may be obtained by raising the temperature to above, say, 150° F., preferably after most of the bleach has been exhausted. In some cases it is expedient to hasten the further removal of beta and gamma celluloses and of residual coloring matter in the last step by using, say, 1% to 4% bleach in the presence of a large excess of caustic.

We present herewith a table showing the average value of certain characteristics of a pulp prior to and after treatment by our process:

	Unbleached sulphite pulp	Bleached alpha fiber
Tear	150	290-300
Color	Pale cream.	105
Alpha cellulose	86%	94%+
Cellulose content	94%	98-99%
Copper number	3	1-1.3
Soda solubility (3% boiling NaOH solution for 1 hour)	16%	3% to 5%

The paramount advantage of the process herein described over our previous process, is that we are enabled to produce a product bleached substantially to ultimate whiteness and of minimum oxycellulose content, as attested by its very low copper number, its low soda solubility, higher cuprammonium viscosity for a given degree of whiteness, and high color stability. Such a product is eminently satisfactory for conversion into high grade papers of marked permanency and into cellulose derivatives such as nitrocelluloses, cellulose xanthate, and other esters.

While the reagents and conditions of the treatments herein given are subject to variation, the initial treatment in any case should be carried out in a manner to effect a selective reaction upon substantially all the ligneous content of the pulp, but without materially degrading its alpha cellulose content, so that final bleaching may be accomplished under conditions to produce a white alpha pulp of very low oxycellulose content. The pretreated pulp will still contain material quantities of coloring matter prior to the alkaline digestion, but these will be largely removed by the alkali, so that a very white pulp can be finally realized through the use of small quantities of bleaching agent. In the various treatments, sodium or calcium base chemicals, either alone or in admixture, may be used, and the density of the pulp and the temperature of the various treatments may be controlled to produce the desired product. The bleached pulp may, in certain instances, be advantageously selected or classified into a long fiber portion and a short fiber portion,—the latter portion containing the short and broken fiber and the fabrillae, which usually entrain therewith colloidal and coloring substance. We have found that the longer fiber portion is of particular advantage, not only for the manufacture of fine grade writing papers, but also for the preparation of cellulose derivatives of preeminent purity and freedom from color. Such fiber, for instance, when nitrated or acetated and dissolved in suitable solvents, yields films, lacquers, and other products of exceptional clarity, freedom from coloring matter, strength, and stretch, and which in these respects are practically equal to or better than similar products prepared from a good grade of cotton linters. The shorter fiber may be employed in a furnish to be used for the manufacture of relatively cheap paper. In certain instances, this selection or classification may be performed on the raw stock, and the long-fibered portion processed as hereinbefore described. After processing, the long-fibered product may, if desired, be again subjected to classification, to ensure the separation of its less desirable portion.

Owing to the lack of a better generic term, by the use of the term "lignin-reactive reagent" in the appended claims, we mean

chlorine water and/or bleach or equivalent reagents capable of reacting with the ligneous and other coloring material in raw pulp.

We claim:

1. A process which comprises separating from raw pulp its long fiber portion, treating the separated portion of pulp with a lignin-reactive reagent and terminating the treatment slightly after a critical point is reached at which further consumption of the reagent is accompanied by a marked decrease in alpha cellulose and an increase in copper number, digesting the treated pulp in alkaline liquor, bleaching the alkaline-digested pulp, and classifying the bleached pulp into long fiber and short fiber portions.

2. A process which comprises separating from raw pulp its long fiber portion, treating the separated portion of pulp with a lignin-reactive reagent and terminating the treatment slightly after a critical point is reached at which further consumption of the reagent is accompanied by a marked decrease in alpha cellulose and an increase in copper number, digesting the treated pulp in alkaline liquor, and bleaching the alkaline-digested pulp.

3. A process which comprises treating raw pulp with a lignin-reactive reagent and terminating the treatment slightly after a critical point is reached at which further consumption of the reagent is accompanied by a marked decrease in alpha cellulose and an increase in copper number, digesting the treated pulp in alkaline liquor, bleaching the alkaline-digested pulp, and classifying the bleached pulp into long fiber and short fiber portions.

In testimony whereof we have affixed our signatures.

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