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GEORGE A. RICHTER, OF BERLIN, NEW HAMPSHIRE, ASSIGNOR TO BROWN COMPANY, OF BERLIN, NEW HAMPSHIRE, A CORPORATION OF MAINE

PULP OF HIGH WHITENESS AND STRENGTH AND PROCESS OF PRODUCING SAME

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This invention relates to a pulp of a whiteness similar to that of ordinary bleached sulphite pulp and of a strength similar to that of the usual kraft or "sulphate" pulp. This invention further relates to an economical process of producing the same from kraft or "sulphate" stock.

Before proceeding to a description of the present invention, certain factors which enter into the chemical treatment of kraft pulp will be briefly considered. Ordinary kraft pulp produced by the digestion of wood chips in the usual kraft or "sulphate" liquor contains about 88% to 92% total cellulose, about 5% to 10% pentosan; and, as is well known, it is exceedingly difficult to bleach such pulp. While it is possible to bleach kraft pulp with an excessive amount of bleach, say, about 50% of 35% bleach, based on the weight of bone-dry fiber, the strength of the product is relatively low, owing to the degradation of the celluloses into oxycelluloses. The commercial value of the kraft pulp is hence lowered rather than increased.

The difficulty in bleaching kraft pulp may be traced to the high percentage of ligneous and other coloring substance present in such pulp after its digestion. On the other hand, a well-cooked, unbleached sulphite pulp produced by digesting wood chips, e. g., spruce, in a suitable acid sulphite liquor, contains from 96% to 98% total cellulose, 3% to 4% pentosan, and a relatively small amount of ligneous and other coloring substance; and it may be bleached easily, that is, with a moderate amount of bleach and without greatly affecting its strength. The conclusion to be drawn from this comparison is that the liberation of fiber from wood chips with a sulphite liquor tends to produce a fairly strong pulp containing a relatively low percentage of coloring substance and a fairly low percentage of pentosan, whereas similar treatment of wood chips with a kraft or "sulphate" liquor yields a very strong pulp containing a relatively high percentage of pentosan and a very high percentage of coloring substances. Other evidence also indicates that the pentosan content of a chemical wood pulp runs parallel with its strength and bleachability: that is, the higher the percentage of pentosan and that of ligneous and other coloring substances present in such wood pulp, the stronger is the pulp but the more resistant is it to bleaching.

The object of this invention is to produce a pulp from kraft or "sulphate" pulp which will possess the whiteness inhering in bleached sulphite pulp, without affecting a substantial change of the strength of such pulp, or, in other words, to treat kraft pulp in a manner such that, while ligneous and coloring substance is removed therefrom, the pentosan content is substantially retained. I have discovered this object may be attained, briefly stated, by digesting ordinary kraft stock in an acid sulphite solution containing free SO_2 and combined SO_2 in such amounts that ligneous and other coloring substances are removed therefrom, or rendered reactive for subsequent removal, substantially without affecting its fiber strength or pentosan content, as the resulting pulp may be easily bleached to high whiteness.

The kraft pulp employed as a raw material may be produced as ordinarily, by the digestion of wood chips under the time, temperature, and pressure conditions conforming to modern practice, in the usual kraft or "sulphate" liquor containing sodium sulphide, sodium hydroxide, and a relatively slight amount of sodium sulphate. Spruce, hemlock, jack pine, long-leaf pine or any other raw cellulosic material suitable for the production of kraft pulp may be employed. After the necessary period of digestion, the digester contents are blown and the kraft pulp is washed substantially free from its black spent digesting liquor, as by passage through a counter-current washer of the type described in U. S. Letters Patent No. 1,421,664, granted July 4, 1922, to Brown et al. The washed pulp is preferably screened to remove shives, specks, and other like foreign matter, and is then thickened to the consistency desired for mixing with the acid sulphite digesting liquor. The thickened pulp is intimately mixed with a sulphurous acid solution of an alkali or an alkaline earth metal sulphite, preferably sodium sulphite, con-

taining free SO_2 in such quantity that the strength of the pulp remains substantially unimpaired and its pentosan content is preserved. I have discovered that such digesting liquor must contain more combined SO_2 than free SO_2 if the desired results are to be obtained. If a digesting liquor containing a higher free than combined SO_2 content is used, the stock loses materially in strength probably owing to the reaction upon and removal of the pentosan and to the degradation of the cellulose at such higher sulphurous acid or hydrogen ion concentration. For best results, the digesting liquor should contain about one-half as much free as combined SO_2 and at least .5% combined and .25% free SO_2. The percentage may vary between these limits, depending upon the characteristics of the particular kraft pulp undergoing digestion and upon the temperature and time of digestion. In other words, during the digestion of the kraft pulp in the acid sulphite liquor the hydrogen ion concentration must be maintained at a value such that a reaction with the pulp or the pentosan content thereof is not favored, whereas a reaction with the ligneous and other coloring substances is promoted. The presence of alkali, metal, or alkaline earth metal sulphite in the digesting liquor in amount to furnish combined SO_2 in excess of the free SO_2 evidently serves to maintain therein the desired concentration of hydrogen ion and thus to make selective the removal of ligneous and other coloring substance from the pulp.

The digestion of the kraft pulp is carried out in an open tank at atmospheric pressure at an elevated temperature, the pulp being stirred and intimately mixed with the digesting liquor to insure a uniform reaction and a uniform product. The liquor reacts with the coloring substances contained in the pulp, forming soluble reaction products or products which are easily removable by subsequent treatment, the reaction being a selective one, in that the strength of the pulp and its pentosan content are substantially unaffected. After the necessary period of digestion, the pulp is washed substantially free from spent liquor and the entrained products of reaction, as by passing it through a counter-current washer of the type indicated. The resultant spent liquor is of a yellow color and may be treated for the recovery of valuable inorganic compounds. The digested and washed pulp is of a lighter color than the initial kraft pulp.

The washed pulp may then be easily bleached to a cream color resembling that of unbleached sulphite pulp or to a distinct whiteness, a moderate amount of bleach being employed and not at all seriously affecting the strength of the product. If it is desired to increase the whiteness of the bleached pulp, it may be superbleached in a chlorine solution substantially without effect upon its strength.

It may occur that the kraft pulp undergoing treatment possesses extremely refractory properties, that is, has an unusually high ligneous and coloring matter content. Such pulps which usually result from an undercooking of the wood chips in the kraft digesters, when treated by my process, might still tend to retain their color and be difficult to bleach. In such cases, the excess ligneous matter present in the pulp as a result of undercooking should be eliminated prior to digestion in the acid sulphite liquor. This may be accomplished by pretreating the kraft pulp with an oxidizing or lignin-removing agent, preferably chlorine. The kraft pulp is accordingly treated with a solution of chlorine or hypochlorite bleach ($CaOCl_2$) for a few minutes at room temperature, the chlorine reacting with some of the ligneous and coloring impurites present in the pulp to form soluble reaction products or other products which are removed during subsequent treatment substantially without effect upon the strength or the pentosan content of the pulp. The pulp is then washed substantially free from oxidizing solution and the soluble products of reaction, is digested in the acid sulphite solution, and is finally bleached, as hereinbefore described in connection with ordinary kraft stock.

I shall now supplement the foregoing general disclosure of my invention with a representative example of procedure and the results obtained therefrom.

A washed and preferably screened kraft stock is digested with agitation at a stock density of about 10% and at a temperature of about 180°–210° F. in open tanks under atmospheric pressure in a sulphurous acid solution of an alkali or alkaline earth metal sulphite, preferably sodium sulphite, containing approximately 1.0% combined and 0.5% free SO_2. The stock is digested from about 2 to 6 hours, depending upon the characteristics of the stock undergoing treatment, the temperature of digestion, and the strength of acid sulphite liquor employed. It may be stated that while I have found it to be more economical to digest the kraft stock in open tanks under atmospheric pressure, the digestion could be carried out in digesters at higher temperatures and pressures. After the digestion has been effected, the stock is washed substantially free of its digesting liquor and the entrained products of reaction. The washed stock may then be bleached, without injuring its strength, to a high degree of whiteness by subjecting it from five to ten hours at a stock density of about 10%, preferably at room temperature, to a hypochlorite bleach solution containing about 15% to 25% of 35% bleach ($CaOCl_2$)

based on the bone-dry weight of fiber. If a cream-colored product similar in color to unbleached sulphite pulp is desired, the pulp is subjected to a hypochlorite solution containing a lower percentage of bleach, say, about 6%–12% of 35% bleach based on the bone-dry weight of fiber. The bleached pulp is then washed substantially free of reaction products and may be treated with a solution of antichlor, as for example sodium bisulphite solution, to react with and neutralize the last traces of bleach. The neutral pulp may then be washed substantially free of reaction products. The washed pulp, if subjected to the full amount of bleach (15%–25%), has a color of about 102 to 104, and a substantially increased total cellulose content over the initial kraft stock. In certain cases it may be desirable to increase the whiteness of the pulp without injury thereto. This may be accomplished by treating the bleached pulp, preferably at room temperature and at a stock density of about 6%–8%, for about two to six hours with a chlorine solution containing 0.3% chlorine based on the bone-dry weight of fiber. Such superbleaching treatment increases the color to about 104 to 106.

As hereinbefore indicated, if the kraft pulp is of an undercooked or refractory nature, it is pretreated with an oxidizing solution to remove the ligneous and other coloring matter present therein. This is accomplished by treating the raw pulp from 10 to 30 minutes at a stock density of about 10% with a chlorine solution containing about 1% to 3% chlorine, or with a hypochlorite solution containing about 3% to 8% of 35% lime bleach ($CaOCl_2$), based on the weight of dry pulp. The reaction with the oxidizing solution is a mild and selective one, the ligneous and other coloring substance contained in the pulp reacting to form soluble reaction products or products which are easily removed during the subsequent digestion, but the pentosan content and also the strength of the pulp remaining substantially unchanged. The pretreated pulp is washed substantially free of the oxidizing solution and the entrained products of reaction and is then digested in an acid sulphite solution and bleached under conditions similar to those employed in connection with a normal kraft stock, the resultant pulp being of a whiteness and strength equivalent to the product resulting from normal kraft stock.

Pulp produced in accordance with this invention has a Mullen or bursting strength equal to that of ordinary kraft pulp, namely, about 150 to 175, and a color equal to that of ordinary bleached or superbleached sulphite pulp, namely, about 98 to 105, and a pentosan content of from 6%–10%, depending upon the characteristics of the initial kraft stock. Inasmuch as the finished pulp has substantially the same fiber length, strength, and tear resistance of unbleached kraft pulp derived from similar wood and subjected to the same degree of beating, it thus possesses the most valuable and important characteristics of both kraft and sulphite pulps; and hence, when beaten and sized, may be converted into high-grade bond and ledger papers of extraordinary strength. The paper does not change color upon ageing in the air or upon exposure to light any more appreciably than does a bleached sulphite pulp. Because of the relative cheapness of unbleached kraft pulp, even after treatment of such pulp in accordance with this invention, the resultant pulp may, in some instances, cost less than high grade, bleached sulphite pulp. Another impor ant advantage of the hereindescribed process is the high yield of finished pulp obtainable thereby, which may amount to about 95% of the initial kraft stock. It may be further noted that my invention makes available substantially all woods employed in the production of kraft pulp, for the manufacture of high-grade writing paper of superior strength.

What I claim is:

1. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, that step which comprises digesting said kraft pulp at an elevated temperature in an acid sulphite liquor containing free SO_2 in such amount but not exceeding combined SO_2 that the strength of the digested pulp remains substantially unchanged.

2. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, that step which comprises digesting said kraft pulp from two to six hours at an elevated temperature in an acid sulphite liquor containing at least ½% combined SO_2 and ¼% free SO_2, but with the free SO_2 in smaller proportion than the combined SO_2.

3. In the treatment of undercooked kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, a process which comprises treating said kraft pulp with an oxidizing agent, washing said treated pulp, digesting said washed pulp at an elevated temperature in an acid sulphite liquor containing free SO_2 in such amount but not exceeding combined SO_2 that the strength of the digested pulp remains substantially unchanged, washing said digested pulp, and bleaching said digested and washed pulp.

4. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, that step which comprises digesting said kraft pulp at an elevated temperature in a sulphurous acid solution of an alkali or alkaline earth metal sulphite containing free

SO_2 in such amount but not exceeding combined SO_2 that the strength of the digested pulp remains substantially unchanged.

5. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, that step which comprises digesting said kraft pulp at an elevated temperature in a sulphurous acid solution of sodium sulphite containing free SO_2 in such amount but not exceeding combined SO_2 that the strength of the digested pulp remains substantially unchanged.

6. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, a process which comprises digesting said kraft pulp at an elevated temperature in an acid sulphite liquor containing free SO_2 in such amount but not exceeding combined SO_2 that the strength of the digested pulp remains substantially unchanged, washing said digested pulp, bleaching said washed pulp, and superbleaching said bleached product.

7. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, a process which comprises digesting said kraft pulp at an elevated temperature in a sulphurous acid solution of sodium sulphite containing free SO_2 in such amount but not exceeding combined SO_2 that the strength of the digested pulp remains substantially unchanged, washing said digested pulp, bleaching said washed pulp in calcium hypochlorite bleaching liquor, and superbleaching said bleached product in a chlorine solution.

8. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, a process which comprises treating said kraft pulp with a chlorine solution, washing said treated pulp, digesting said washed pulp at an elevated temperature in a sulphurous acid solution of sodium sulphite containing free SO_2 in such amount but not exceeding combined SO_2 that the strength of the digested pulp remains substantially unchanged, washing said digested pulp, and bleaching said digested and washed pulp.

9. In the treatment of a kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, that step which comprises digesting said kraft pulp at an elevated temperature in an acid sulphite liquor having a combined SO_2 content not less than its free SO_2 content, and containing free SO_2 in such amount that the strength of the digested pulp remains substantially unchanged.

10. In the treatment of a kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, that step which comprises digesting said kraft pulp at an elevated temperature in an acid sulphite liquor having a combined SO_2 content of about twice its free SO_2 content, and containing free SO_2 in such amount that the strength of the digested pulp remains substantially unchanged.

11. In the treatment of a kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, that step which comprises digesting said kraft pulp at an elevated temperature in a sulphurous acid solution of sodium sulphite containing about 1.0% combined and 0.5% free SO_2.

12. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, a process which comprises digesting said kraft pulp at an elevated temperature from about 2 to 6 hours in a sulphurous acid solution of sodium sulphite containing about 1.0% combined and 0.5% free SO_2, washing said digested pulp, bleaching said washed pulp in calcium hypochlorite bleaching liquor containing about 15% to 25% of 35% bleach based on the bone-dry weight of fiber at about room temperature from about five to ten hours, and washing said bleached pulp.

13. In the treatment of kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, a process which comprises digesting said kraft pulp at an elevated temperature from about two to six hours in a sulphurous acid solution of sodium sulphite containing about 1.0% combined and 0.5% free SO_2, washing said digested pulp, bleaching said washed pulp in calcium hypochlorite bleaching liquor containing about 15% to 25% of 35% bleach based on the bone-dry weight at about room temperature from 5 to 10 hours, washing said bleached pulp, and superbleaching said washed and bleached pulp in a chlorine solution containing about .3% chlorine based on the bone-dry weight of fiber for about two hours.

14. In the treatment of undercooked kraft or "sulphate" pulp for the production of a pulp characterized by its whiteness and high strength, a process which comprises treating such pulp with a chlorine solution containing about 1%–3% chlorine based on the weight of fiber for about ten to thirty minutes, washing said treated pulp, digesting said washed pulp at an elevated temperature from about two to six hours in a sulphurous acid solution of sodium sulphite containing about 1.0% combined and 0.5% free SO_2, washing said digested pulp, bleaching said washed pulp in calcium hypochlorite bleaching liquor containing about 15% to 25% of 35% bleach based on the bone-dry weight of fiber from about two to six hours and washing said bleached pulp.

15. In the treatment of kraft or "sulphate"

pulp for the production of a pulp characterized by its whiteness and high strength, a process which comprises digesting said kraft pulp at an elevated temperature in an acid sulphite liquor containing free SO_2 in such amount but not exceeding combined SO_2 that the strength of the digested pulp remains substantially unchanged, washing said digested pulp, and bleaching said digested and washed pulp, said entire treatment giving a yield of finished pulp amounting to about 95% of said initial kraft or "sulphate" pulp.

16. A process of producing pulp characterized by its whiteness and high strength, which comprises digesting kraft pulp at atmospheric pressure and at an elevated temperature in a sulphurous acid solution of an alkali metal or alkaline earth metal sulphite of such free SO_2 content, but not exceeding combined SO_2 content, that the strength of the digested pulp remains substantially unchanged.

17. Chemical wood pulp having substantially the same average fiber length, strength, and tear resistance of unbleached kraft pulp derived from similar wood and subjected to the same degree of beating or hydration, said pulp being further characterized by the whitness qualities of a completely bleached sulphite pulp including permanency against ageing in air and against exposure to light.

18. A white chemical wood pulp having those physical characteristics and composition resulting from the digestion of the kraft pulp at elevated temperature in a sulphurous acid solution of a sulphite having a free SO_2 content not in excess of its combined SO_2 content.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.