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BLEACHING HARDWOOD PULP

George A. Richter, Berlin, N. H., assignor to Brown Company, Berlin, N. H., a corporation of Maine

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This invention relates to the production from hardwoods of the nature of birch, beech, maple, and the like of a cellulose pulp product eminently suitable for conversion into various cellulose derivatives, including such derivatives as nitrocellulose, acetylcellulose, cellulose ethers, etc.

In producing refined cellulose pulp from hardwood, one may cook hardwood to the condition of pulp in the usual chemical pulping liquors, such as acid sulphite liquor, and then refine the raw wood pulp by a series of chemical treatments designed to rid the pulp practically completely of residual lignin, which detracts seriously from the quality of cellulose derivatives prepared from the pulp. A very effective refining process, insofar as concerns eliminating lignin from hardwood pulp as well as softwood pulp, involves chlorinating the pulp with an amount of chlorine that ensures reaction with most or practically all lignin present in the pulp and then treating the pulp, preferably after washing, with an alkaline refining liquor, such as hot, dilute alkaline liquor. Upon washing and bleaching the refined pulp, one arrives at a finished product of excellent whiteness and a lignin content downwards of about 0.15%.

In carrying out a pulp-refining process of the foregoing character, I have observed that, although the finished or refined hardwood pulp is of excellent whiteness and very low lignin content, yet its residual resin content is altogether too high for preparing cellulose derivatives, such as nitrocellulose or acetylcellulose, cellulose xanthate, etc., of good or high quality. In an effort to overcome this defect in the finished pulp product, I have provided soap, such as sodium oleate, in the alkaline refining liquor and have bleached the refined pulp in distinctly alkaline bleach liquor, but even in such case the finished pulp product had a resin content, as determined by extraction with ether, of about 0.35 to 0.8%, which resin content renders the product unsuitable for nitrocellulose, acetylcellulose, cellulose ethers, cellulose xanthate, and other cellulose derivatives of good or high quality. This difficulty of removing resins from hardwood pulp does not exist in the case of softwood pulp, such as spruce sulphite pulp, which, after chlorination, refinement in alkaline liquor containing soap, and bleaching in alkaline bleach liquor, has a resin content downwards of about 0.25%.

After considerable experimentation and research, I have discovered that it is the step of chlorinating the pulp in order to remove and/or solubilize to the desired degree its lignin content that is responsible for the high residual resin content of the refined hardwood pulp. In other words, it appears that, because of the comparatively high resin content of raw hardwood pulp and/or the particular character of the resins present in such pulp, a very considerable proportion of the resins are through chlorination rendered resistant to dissolution and/or dispersion in an alkaline refining liquor even when such liquor contains dispersing agent in the form of soap or the like. I have further discovered that when the lignin content of hardwood pulp is largely or substantially completely removed and/or solubilized by the action of hypochlorite bleach liquor preparatory to the step of refining the pulp in an alkaline liquor, it is possible to avoid undesirable chlorination or insolubilization of resins present in the pulp and to arrive at a finished or refined hardwood pulp product of the desired very low resin content. Once the lignin content of the raw hardwood pulp has been largely removed and/or solubilized by the action of hypochlorite bleach liquor, the process hereof hence involves the use of a relatively small amount of chlorine for the purpose of further purging the pulp of lignin residue and thereby minimizing residual lignin in the finished pulp product while at the same time avoiding the development of chlorinated or resistant resins to such an extent as to render the finished pulp product unsuitable for its intended use in preparing good or high grade cellulose derivatives. The use of a relatively small amount of chlorine as a purging or scavenging agency for lignin residues should take place after an initial hypochlorite treatment of the pulp has done the major work of removing and/or solubilizing the lignin component of the raw pulp, for when the raw hardwood pulp is first treated with a limited or relatively small amount of chlorine designed to react only upon a subordinate proportion of the lignin content of the pulp and the chlorinated pulp then treated with hypochlorite liquor in an effort to accomplish removal or solubilization of most or practically all of the lignin present in the pulp after its chlorination, it is found that the effectiveness of such latter sequence of treatments in eliminating either lignin or resin from the pulp is poor and unsatisfactory as compared to a sequence of treatments involving the treatment of the pulp with the same relatively small amount of chlorine after the pulp has undergone a treatment with hypochlorite bleach

liquor and either before or after the pulp has been refined in an alkaline liquor.

The raw hardwood pulp to be refined by the process hereof may be prepared by cooking or pulping chips of hardwood, e. g. birch, beech, maple, or the like, in a chemical pulping liquor, preferably an acid sulphite liquor. Typically, the acid-sulphite liquor may contain about 1% combined SO_2 and 5% free SO_2 and chips of the usual size cooked therein with a liquor to dry wood ratio of about 6 to 1 for a period of about 9 to 10 hours under a maximum temperature of about 285° F., which temperature may be attained gradually over a period of about 3 to 5 hours. The hardwood sulphite pulp as thus produced and washed has a lignin content of about 1% and a resin content, as determined by extraction with ether, upwards of about 0.7%. Indeed, when such pulp is prepared from hardwood consisting largely or essentially only of white birch, which is notably high in resin, the resin content of such pulp may be as high as about 2%. A raw pulp having a resin content ranging from about 0.7 to 2.0% may hence constitute the material to be transformed into the finished pulp product hereof.

Example I

A raw or unbleached hardwood sulphite pulp is (*a*) treated at a stock density of about 4% and at about 20° C. for about 1 to 3 hours with hypochlorite bleach liquor containing about 6% to 8% bleach, based on the weight of dry pulp, calculated in the usual terms of an available chlorine content of 35%. The pulp is then washed and (*b*) treated at about 4% stock density and at about 20° C. for about 1 hour with about 1% chlorine, based on the dry weight of pulp. The pulp is then washed and (*c*) cooked at a stock density of about 8% and at about 80° C. for about 2 to 6 hours in a refining liquor to which about 4% caustic soda and about 0.5% oleic acid, based on the dry weight of pulp, has been added. The cooked or refined pulp is then washed and (*d*) treated at about 10% stock density and at about 38° C. for about 6 hours with distinctly alkaline hypochlorite bleach and about 0.7% caustic soda, based on the dry weight of pulp. Upon washing the pulp and testing it, it exhibits a lignin content of about 0.08% and a resin content, as determined by extraction with ether, of only about 0.10 to 0.2%. It is also very white and of an alpha cellulose content, 91%+, notably higher than that, about 87%, of the raw hardwood sulphite pulp used as the starting material. Because of the extremely low resin content, the extremely low lignin content, the supernormal alpha cellulose content, and the high whiteness of the hardwood pulp product hereof, it is eminently suitable for preparing high-grode nitrocellulose, cellulose acetate, cellulose ethers, and other cellulose derivatives. It is also useful as high-grade papermaking material, since its very low resin and lignin contents as well as its supernormal alpha cellulose content bespeak the realization therefrom of paper products having high color-stability even under heat. In this latter connection, it might be noted that papers made from pulps of high resin content tend to "yellow" upon aging, being especially sensitive to color-change upon being heated. Again, the substantially resin-free hardwood pulp product hereof does not tend to cause fouling or "gumming" of the cylinder, wire, or felts of a papermaking machine as is true of a hardwood pulp product of comparatively high residual resin content.

Example II

The procedure of this example was similar to that of Example I, excepting that the chlorination of the pulp was performed after the pulp had undergone treatment with hot alkaline refining liquor. In other words, steps (*b*) and (*c*) of Example I were practiced in reverse order. The finished pulp product was so similar to that of Example I that its characteristics need hardly be enumerated.

Example III

The procedure of this example was also similar to that of Example I, excepting that the step of chlorinating the pulp was entirely omitted and the pulp subjected after its initial treatment with hypochlorite bleach liquor to the action of the hot alkaline refining liquor and finally to the action of distinctly hypochlorite bleach liquor. In other words, the pulp was subjected simply to treatments (*a*), (*c*), and (*d*) of Example I. Although the finished pulp product had a resin content of only about 0.2% and other characteristics practically on a par with those of the product of Example I, its lignin content was comparatively high, namely, upwards of 0.2%. This Example III, which is outside the purview of the present invention, hence shows the value of including a chlorinating treatment in the refining process hereof for the purpose of minimizing lignin residue in the finished pulp product, provided that hypochlorite bleach liquor is relied upon, preparatory to chlorination and/or refinement of the pulp in the alkaline liquor, for removing and/or solubilizing most of the lignin content of the raw pulp.

Example IV

The procedure of this example was similar to that of Example I, excepting that the chlorination of the pulp preceded the first treatment of the pulp with hypochlorite bleach liquor. In other words, treatments (*a*) and (*b*) of Example I were performed in reverse order. The finished pulp product was generally similar to that of Example I, excepting that its resin content was markedly higher, namely, about 0.35%, and its lignin content also definitely higher, namely, about 0.16%. This Example IV, which is also outside the purview of the present invention, demonstrates that it is distinctly advantageous to chlorinate the pulp with a comparatively small amount of chlorine after the pulp has undergone an initial hypochlorite treatment with sufficient hypochlorite to remove and/or solubilize most of the lignin present in the raw pulp. It is evidently the case that, once the hypochlorite has reacted with and solubilized most of the lignin present in the raw pulp, a comparatively small amount of chlorine can be advantageously used to promote elimination of residual lignin while minimizing undesirable modification of the resins present in the pulp, whereas, on the other hand, the use of the same amount of chlorine on the raw pulp preparatory to its treatment with the hypochlorite entails to an appreciable extent undesirable modification of the resins and the hypochlorite subsequently used is not so effective in purging the pulp of lignin.

That the procedures of the present invention, namely those of Examples I and II, are surprisingly effective in eliminating resin as well as

lignin from raw hardwood pulp is at once apparent not only from Examples III and IV but also from the results realized when only chlorine is employed as the reagent for eliminating lignin from the raw pulp. Thus, when the procedure of Example I is performed excepting that the pulp is, preparatory to its refinement in the alkaline liquor, treated with sufficient chlorine to ensure a finished pulp product of the desired freedom from lignin, it is found that such product is of comparatively very high resin content. Specifically, when steps (*a*) and (*b*) of Example I were supplanted by a single treatment of the pulp with 3% chlorine, based on pulp, but the pulp otherwise processed as in Example I, it was found that the finished pulp product, although of a whiteness quality, alpha cellulose content, and lignin content substantially similar to the product of Example I, had a resin content ranging from 0.4% to 0.6%. Such a product is thus even far less satisfactory for conversion into cellulose derivatives than is the product of Example IV.

An important advantage of the present invention is that it makes available enormous supplies of comparatively inexpensive hardwoods for producing refined wood pulps as satisfactory as and in some respects excelling the refined softwood pulps for conversion into nitrocellulose, acetylcellulose, cellulose ethers, and other cellulose derivatives. Besides being characterized by a highly desirable and novel combination of low lignin content, namely, downwards of 0.20% and very low resin content, namely, downwards of about 0.20%, the hardwood pulp product hereof, by virtue of its short-fibered character, lends itself to formation into tissues or papers of very uniform texture even when they are used in only lightly or substantially unbeaten condition. The uniformly textured tissues or papers thus made from the hardwood pulp product hereof are highly absorbent, especially when formed from substantially unbeaten pulp; and they are quickly penetrated by and smoothly reacted upon by the usual nitrating, acetylating, and other reagents employed in preparing cellulose derivatives. The refined hardwood pulps hereof, although derived from a comparatively low-cost source, thus excel in some respects the refined softwood pulps, such as refined spruce pulp, which are comparatively long-fibered.

In some instances, a portion of the relatively small amount of chlorine used for purging the hardwood pulp as far as possible of residual lignin may be applied to the pulp after its first hypochlorite treatment but before it has been purified in the alkaline refining liquor, preferably containing soap; and another portion of such chlorine may be applied to the pulp after it has been purified in the alkaline refining liquor but before its second hypochlorite treatment, preferably in the presence of sufficient free caustic soda or other alkali to ensure a condition of distinct alkalinity throughout the second hypochlorite treatment. By such a refining process, it is possible to produce a finished pulp product of even lower residual lignin content than when the pulp undergoes a single chlorination either immediately before or after its purification in the alkaline refining liquor. After the chemical treatment, the pulp is preferably washed as in the examples of procedure hereinbefore described.

It is possible to vary the causticity or alkalinity of the alkaline refining liquor in Example I for the purpose of varying, as may be desired, the degree of refinement or purification of the pulp to an alpha cellulose content upwards of that (about 87%) of the raw hardwood sulphite pulp. For instance, by increasing the causticity of the liquor of Example I to about 10% to 12% caustic soda, based on the weight of the pulp, it is possible to produce by that example of procedure a pulp product of an alpha cellulose content of at least about 94%. Indeed, by providing an alkaline refining liquor of even greater alkalinity or causticity, it is possible to arrive at finished hardwood pulp products of an alpha cellulose content greater than 94%. The refined hardwood pulp product hereof is thus characterized by a lignin content not greater than 0.2% and ether-soluble constituents or resin content not greater than 0.25%; and its alpha cellulose content is greater than 87%, for instance, ranges from about 87% to about 94% or more. Because of the extremely low lignin and resin contents of the hardwood pulp product hereof, such product is satisfactory for preparing cellulose derivatives of good grade even at an alpha cellulose content of about 87% to 92%, that is, when it is prepared by a process involving a comparatively inexpensive refining treatment with an alkaline liquor of relatively low strength or causticity.

I claim:

1. A process of refining preliberated hardwood pulp to low lignin and resin contents, which comprises subjecting the pulp to sequential treatments with hypochlorite liquor, chlorine, alkaline refining liquor, chlorine, and hypochlorite liquor, said first treatment with hypochlorite liquor being performed with sufficient hypochlorite to effect reaction upon most, if not practically all, of the lignin content of the pulp.

2. A process of refining preliberated hardwood pulp to low lignin and resin contents, which comprises subjecting the pulp to sequential treatments with hypochlorite liquor, chlorine, alkaline refining liquor, and hypochlorite liquor, said first treatment with hypochlorite liquor being performed with sufficient hypochlorite to effect reaction upon most, if not practicaally all, of the lignin content of the pulp.

3. A process of refining preliberated hardwood pulp to low lignin and resin contents, which comprises subjecting the pulp to sequential treatments with hypochlorite liquor, alkaline refining liquor, chlorine, and hypochlorite liquor, said first treatment with hypochlorite liquor being performed with sufficient hypochlorite to effect reaction upon most, if not practically all, of the lignin content of the pulp.

4. A process of refining preliberated hardwood sulphite pulp to low lignin and resin contents, which comprises subjecting such pulp to sequential treatments with hypochlorite liquor, chlorine water, hot dilute alkaline liquor containing soap, chlorine water and hypochlorite liquor containing sufficient free alkali to maintain it distinctly alkaline throughout the treatment of the pulp, each of said treatments being succeeded by washing of the pulp and said first treatment with hypochlorite liquor being performed with sufficient hypochlorite to effect reaction upon most, if not practically all, of the lignin content of the pulp.

5. A process of refining preliberated hardwood sulphite pulp to low lignin and resin contents, which comprises subjecting such pulp to sequential treatments with hypochlorite liquor, chlorine water, hot dilute alkaline liquor containing soap, and hypochlorite liquor containing sufficient free

alkali to maintain it distinctly alkaline throughout the treatment of the pulp, each of said treatments being succeeded by washing of the pulp and said first treatment with hypochlorite liquor being performed with sufficient hypochlorite to effect reaction upon most, if not practically all, of the lignin content of the pulp.

6. A process of refining preliberated hardwood sulphite pulp to low lignin and resin contents, which comprises subjecting such pulp to sequential treatments with hypochlorite liquor, hot dilute alkaline liquor containing soap, chlorine water, and hypochlorite liquor containing sufficient free alkali to maintain it distinctly alkaline throughout the treatment of the pulp, each of said treatments being succeeded by washing of the pulp and said first treatment with hypochlorite liquor being performed with sufficient hypochlorite to effect reaction upon most, if not practically all, of the lignin content of the pulp.

GEORGE A. RICHTER.