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PRODUCTION OF HIGH GRADE CHEMICAL PULPS

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This invention relates to the production of cellulose pulps or kindred raw cellulosic material, being more particularly concerned with the so-called chemical pulps in the production of which chemical liquors are employed to dissolve the cementitious constituents which bind together the fibers of the raw wood. Various chemical liquors, both of acid character, e. g., bisulphite liquors, and of alkaline character, e. g., kraft or soda liquors, have been employed for this purpose to produce chemical pulps. The various kinds of pulp vary considerably in their compositions and in their physical characteristics, as the different chemical liquors do not act in the same way upon the non-fibrous or upon the fibrous constituent of the wood. The acid liquors containing bisulphites are more selective in their action on the pentosans than are the alkaline liquors, but the resulting pulp in either case has a substantial residue of pentosans,—amounting to as high as 3% to 4% in the usual commercial sulphite pulps and to as high as 8% to 10% in the usual commercial kraft and soda pulps. It is possible to remove pentosans from wood pulps by chemical refining processes which include the step of treating the raw pulp under suitable conditions with solutions of alkalies, but such solutions are not especialy effective or complete in their action even over considerable periods of time.

The production of wood pulps low in pentosan content and other non-alpha cellulose components is highly desirable when such pulps are to be used in the preparation of cellulose derivatives such as the nitrate, acetate, and xanthate, and in the manufacture of high grade papers, as it has been found that the freer the wood fiber is from non-alpha cellulose components including pentosans, the better is the quality, color and stability of its derivatives, and the more nearly do papers made therefrom approach the qualities of new-rag papers.

I have found that if wood chips, e. g., spruce, or kindred raw cellulosic material is initially treated with a solution of a mineral acid, and more particularly one which is highly ionized in water, and is then cooked at elevated temperature and under pressure in a solution of a suitable alkali, for instance in the usual kraft or soda liquors, it is possible to produce cellulose pulps of high alpha cellulose content and of exceedingly low pentosan content. The resulting product may have an alpha cellulose content of from 94% to 98% and a pentosan content of less than 1%, depending upon the particular conditions under which the initial treatment with acid solution and the subsequent cooking in alkaline liquor are carried out. In bleached condition, the product is eminently suitable for use in the papermaking and derivative industries. One of the major advantages of the process is that it may be controlled to produce a product of unusually low solution viscosity, as some derivatives, such as the lower nitrocelluloses intended for lacquer manufacture, must have low solution viscosity. Whereas it is necessary to subject the usual fibers or derivatives to special chemical treatments designed to bring about a lowering of solution viscosity, the product of the present process need not require such treatment. I do not, however, herein claim the product, as this subject matter has been described more fully and claimed in my application Serial No. 435,962, filed March 14, 1930.

Evidently the use of mineral acid solutions in the initial treatment causes a substantially complete hydrolysis of the pentosans into soluble sugars and other reaction products which are readily soluble in alkaline cooking liquors. The initial treatment is not in the nature of a fiber-liberating operation, since even when sulphurous acid solutions are used, they should be substantially free from bisulphites, which promote fiber liberation by reacting upon and dissolving the ligneous matter in the wood. The presence of bisulphites in substantial amount, as in the usual sulphite cooking liquor, evidently so represses the ionization of the free sulphurous acid of the liquor as to diminish greatly the hydrolysis of pentosans. Inasmuch as once fiber liberation is effected the pulp undergoes serious chemical injury when in contact with a strongly acid liquor, it is essential that the

initial treatment with strong acid solution be effected while the wood fibers are bound together and are associated with more reactive constituents, which evidently protect the fibers from degradation by undergoing reaction themselves. The initial acid treatment may also transform the alpha cellulose to a form profoundly different from that present in wood pulp, such as sulphite or kraft, for not only may the final product be of surprisingly low solution viscosity when tested by the usual cuprammonium cellulose solution standard, but other derivatives, such as the nitrocelluloses prepared therefrom, have even lower solution viscosity than similar derivatives prepared from other fibers whose cuprammonium cellulose solution viscosity has been lowered by one or more special treatments to the same value as that possessed by a cuprammonium cellulose solution prepared therefrom.

In the initial treatment of the wood chips with an acid solution, various acids and or acid salts and various conditions of treatment may be used. The acids or acid salts employed, however, should be comparatively strong or highly ionized in aqueous solution and to this end mineral acids such as sulphuric, sulphurous, nitric, and hydrochloric, or acid salts of these acids, are suitable, since they effect the desired reaction upon the pentosan content of the wood. The use of involatile mineral acids such as sulphuric is particularly advantageous, inasmuch as there is no liberation of obnoxious gas from the solution even when the treatment is carried out at boiling temperatures in open tanks. If desired, a sufficiently strong solution of such mineral acids may be used so that the desired reaction takes place under room temperature conditions, under which conditions the use of special apparatus and steam is avoided. For instance, when using concentrated acid solutions of from 15% to 35% acid content, the treatment may be carried out under atmospheric pressure conditions of, say, from 20° to 40° C. for a period of about one hour, but the use of dilute acid solutions of, say, an acid content of about 1% makes necessary the use of much higher temperatures, for instance, 100° C., or higher, and a period of treatment of about two hours.

The acid liquor associated with the wood after the treatment is of dark brown color as a result of the solution of organic matter and the hydrolysis of pentosans present in the wood to soluble sugars. When a strong sulphuric or other acid solution is initially employed, it may be drained or otherwise separated from the wood and employed wholly or in part for the treatment of other raw wood, but if too dilute or contaminated for reuse, its sulphur content, in the case of sulphurous or sulphuric acid solutions, may be recovered by mixing it with the spent alkaline liquor recovered from the second cooking step before the latter is subjected to the well-known recovery treatment practised in the kraft process. The use of sulphuric acid solutions or of niter cake solutions in the acid treatment of the wood is not only advantageous for those reasons already given, but because these chemicals are comparatively inexpensive and furnish a high concentration of hydrogen ion, which evidently favors the desired hydrolyzing action on the pentosans. These chemicals are further advantageous, in that the sulphur content of the spent acid liquor may be recovered along with the sodium constituents of the spent alkaline liquor by the usual recovery operations, which include the steps of concentrating the mixed liquors as by multiple effect evaporation, and of smelting the inorganic constituents of the concentrated liquor under reducing conditions to produce a smelt containing sodium sulphide. The smelted compounds, which may be of high sulphidity, may be advantageously employed in the production of the alkaline cooking liquor for the second step of my process, as it is preferable to use one containing sodium sulphide, because the resulting pulp has better physical characteristics and is more easily bleachable.

The acid-treated wood is of much darker color than the raw wood, usually being of a reddish hue. While it may be readily crushed at this stage into fragments, nevertheless it is so high in ligneous matter that it does not lend itself to ready disintegration into a pulp suitable for conversion into paper or derivatives. The wood is preferably washed free of residual spent acid liquor before it is subjected to cooking in an alkaline liquor which, as previously stated, preferably consists of a solution of sodium hydroxide and sodium sulphide and may be of a concentration and composition similar to that used in the kraft process. The chips may, for example, be cooked in a liquor containing about 1.5 pounds of alkali per cubic foot, both in the form of caustic soda and sodium sulphite, the alkali compound being calculated as active Na_2O. The sulphidity of the liquor may amount to about 40%, which corresponds to the sulphidity of a typical kraft liquor. The cooking operation may be carried out in the usual alkaline digester and the digester contents may be heated to a maximum temperature of from 300° to 335° F. in two hours, after which the digester contents may be maintained at this temperature with a corresponding steam pressure of about 100 pounds for about two hours. At the end of this cooking operation, the wood has been converted into a pulp, so that the digester may be blown as usual and the pulp washed free of spent liquor. The pulp may be converted to a product of high whiteness by the use of hypochlorite bleach liquor, but to

facilitate bleaching it may be preliminarily subjected to mild chemical refining. For instance, the pulp may be initially treated at a suitable stock consistency with about 1% chlorine, based on the weight of dry pulp, whereupon it may then be washed, digested in a solution containing 1% caustic soda, based on the weight of dry pulp, and again washed. Thereupon it may be bleached to a high degree of whiteness with only about 2% hypochlorite bleach, based on the weight of dry pulp. In order to preserve the high alpha cellulose content of the pulp during the bleaching operation, it is preferable to effect bleaching in a hypochlorite liquor containing a slight amount of free alkali, such as caustic soda, and to maintain such liquor at a temperature of between 70° and 120° F. In lieu of hypochlorite bleach, other bleaches, such as permanganates, peroxides, perborates, or the like, may be employed.

In the initial treatment of the raw cellulosic material with a mineral acid solution, it may be desirable to add a small amount of suitable oxidizing or reducing agent to the solution when the acid itself does not act as such, as the presence of such agents often accelerates the desired modification in the raw material and, in the case of reducing agents, sometimes improves the papermaking characteristics of the finished product. For instance, when a solution of sulphuric acid is employed, an oxidizing agent such as permanganate may be added thereto, but no such addition need be made to a solution of nitric acid, which itself is an oxidizing agent.

One of the major advantages residing in a process such as described is that it is possible to produce a product having the desirable characteristics mentioned, by the use of comparatively inexpensive chemicals and by rapid treatment in inexpensive apparatus. In producing refined pulps from wood or kindred raw cellulosic materials, it has heretofore been the practice to prepare a raw wood pulp such as sulphite or kraft, and then to dissolve non-alpha cellulose components from such pulp by the use of alkaline liquors. Aside from the fact that such a process does not result in a product of minimum pentosan content or of exceedingly low solution viscosity, strong alkalies, such as caustic soda, are much more expensive than acids such as sulphuric, and it is generally necessary to consume, as much, if not more, of such alkali to produce a given weight of finished pulp.

I claim:

1. A process which comprises treating chipped raw wood with a solution of sulphuric acid to effect reaction more particularly upon the pentosan content of the wood, and then cooking the wood at elevated temperature and under pressure in an alkaline liquor to effect fiber liberation into a pulp of high alpha cellulose content and low solution viscosity.

2. A process which comprises treating chipped raw wood with a hot, dilute solution of sulphuric acid to effect reaction more particularly upon the pentosan content of the wood, and then cooking the wood in an alkaline liquor under pressure to effect fiber liberation into a pulp of high alpha cellulose content and low solution viscosity.

3. A process which comprises treating chipped raw wood with a solution of sulphuric acid to effect reaction more particularly upon the pentosan content of the wood, washing the wood, and then cooking the washed wood in an alkaline liquor under pressure to effect fiber liberation into a pulp of high alpha cellulose content and low solution viscosity.

4. A process which comprises treating chipped wood with a solution of niter cake to effect reaction more particularly upon the pentosan content of the wood, and then cooking the wood in an alkaline liquor to effect fiber liberation.

5. A process which comprises treating chipped wood with a solution of sulphuric acid to effect reaction more particularly upon the pentosan content of the wood, and then cooking the wood to effect fiber liberation in an alkaline liquor containing sodium sulphide.

6. A process which comprises treating chipped raw wood with a solution of sulphuric acid to effect reaction more particularly upon the pentosan content of the wood, and then cooking the wood at elevated temperature and under pressure in an alkaline liquor containing sodium sulphide to effect fiber liberation into a high grade paper-making pulp of high alpha cellulose content and low solution viscosity.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.