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PROCESSING OF CELLULOSE FIBER

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This invention relates to the processing of cellulose fiber in the form of an aqueous pulp or fiber suspension to improve its suitability for use in various fields, including the papermaking and cellulose derivative industries.

There are various kinds of cellulose fibers, such as the chemical wood pulps, which are associated with a considerable amount of impurities, including lignin, resin, and beta and gamma celluloses, generally classified as non-alpha cellulose components. In order to realize best results in the use of such fibers as raw material in the papermaking and cellulose derivative industries, for example, it is necessary to refine or purify such fibers by dissolving out non-alpha cellulose components therefrom. It has been found that solutions of some alkalies such as caustic soda, sodium sulphide, sodium carbonate, and lime will, under certain conditions, react upon and dissolve impurities present in cellulose fiber, but other than by the use of such alkalies, it has been considered impossible to effect a noteworthy purification of cellulose fiber with the desired preservation of the physical characteristics of the fiber.

I discovered that there are a large number of other chemicals, notably salts and oxides, which, although they afford a substantially neutral medium when treated with water, are capable of exerting a refining action on cellulose fiber, particularly if they are used in aqueous solution or suspension at temperatures much higher than those heretofore employed in refining cellulose fiber. These salts include the sulphites, phosphates, phosphites, carbonates, borates, formates, lactates and bicarbonates. They include more specifically these salts in soluble form as when their base is sodium or other alkali metal, ammonium salts, such as ammonium sulphide, as well as in insoluble form, as when their base is magnesium, calcium, barium, or other metal. The oxides include zinc oxide, aluminum oxide, or other oxides of the heavy metals, although there is greater difficulty in securing a product of high alpha cellulose content with such oxides. I have found that the chemicals enumerated are relatively inert, so far as concerns purifying cellulose fiber, if they are used at temperatures below about 150° C., but when they are used at temperatures above about 150° C., for instance at 200° C., or at higher temperatures, they bring about a sharp increase in the alpha cellulose content of fibers susceptible to refinement, without, however, substantially injuring their physical, papermaking, or esterification characteristics. Aside from their ability in refining pulps at such temperatures, I have discovered that such chemicals cause a pronounced lowering of the solution viscosity of the fiber, by which I mean that derivatives, such as nitrocellulose, prepared from the resulting fiber form solutions of low viscosity in suitable solvent media. So, too, cuprammonium cellulose solutions prepared from the fiber have low viscosity. I have found it advantageous to digest refined fibers, including cotton linters, in solutions or suspensions of such chemicals, for not only do such solutions or suspensions maintain or even augment the refined condition of the fiber by dissolving pentosans, waxes, and ash, but they have the effect of bringing about a lowering of the solution viscosity of such fibers so that they are suited for conversion into xanthates or nitrocelluloses of low solution viscosity.

The chemicals hereinbefore mentioned seem to have the common feature of forming a low hydroxyl ion concentration in the liquor during the entire refining operation. It is apparently the hydroxyl ion which makes possible the purification of the fiber, for if the fiber is treated with water alone at about 200° C., or at higher temperature, the product is of relatively low alpha cellulose content. Evidently at about 200° C., or at higher temperatures, water hydrolyzes the pentosans and less-resistant celluloses present in the fiber to form organic acids, which if permitted to remain in the sphere of reaction hydrolyze the fiber. If, however, there is the buffer chemical present in the sphere of reaction to furnish progressively hydroxyl ions to neutralize the acids, the fiber is refined to high alpha cellulose content. Some of the chemicals, such as the sulphites and insoluble carbonates which furnish an ex-

tremely low hydroxyl ion concentration, are more effective in lowering the solution viscosity of the fiber than chemicals such as the borates or the phosphates. The sulphites are further advantageous, in that they serve as delignifying agents.

I shall now give examples of procedure falling within the purview of the present invention, in which the sulphites and carbonates were employed as the agents for modifying the composition and/or characteristics of the fiber.

Example 1.—A raw or unbleached sulphite pulp having an alpha cellulose content of 89%, a lignin content of 2%, a pentosan content of 3.5%, and a solution viscosity of 21.2, was used as a raw material. The pulp was digested for two hours in a 1% solution of sodium sulphite at 200° C. The product, after washing free of sulphite solution, had an alpha cellulose content of 95.6%, a lignin content of 0.75%, a pentosan content of 1.37%, and a solution viscosity of 0.77. If, on the other hand, the unbleached sulphite pulp is digested for four hours in a 1% solution of sodium sulphite at 125° C., the washed product has an alpha cellulose content of 90.2%, a pentosan content of 3.35%, and a viscosity of 22. It is thus seen that temperature is an all-important factor in refining cellulose pulp and reducing its solution viscosity in a sodium sulphite solution.

Example 2.—The procedure was similar to that of Example 1, except that the solution employed was a 2% solution of sodium sulphite. The washed product had an alpha cellulose content of 96.5%, a lignin content of 0.97%, a pentosan content of 1.4%, and a solution viscosity of 0.38.

Example 3.—The pulp was digested at 5% consistency for three hours in an aqueous suspension of magnesium carbonate at 190° C., containing 10% magnesium carbonate, based on the weight of dry pulp. The washed product had an alpha cellulose content of 94.1% and a pentosan content of 1.25%.

Example 4.—The pulp was digested under the same conditions as in the previous example in an aqueous suspension of calcium carbonate containing 10% calcium carbonate, based on the weight of dry pulp. The washed product had an alpha cellulose content of 92.6%, which value indicates that magnesium carbonate is a better refining chemical than calcium carbonate under the same time and temperature conditions. If, however, digestion is carried out at a temperature of 200° C. for about five hours, the resulting product has an alpha cellulose content of about 94%. If, on the other hand, the pulp is digested for four hours in an aqueous suspension of calcium carbonate at 150° C., containing 10% calcium carbonate, based on the weight of dry pulp, the washed product has an alpha cellulose content of 88.9%, a pentosan content of 3.45%, and a solution viscosity of 21. This indicates that calcium carbonate is relatively inactive on cellulose fiber at temperatures even as high as 150° C.

In both Examples 3 and 4, the residual or spent liquor from the digesting operation is clear, despite the fact that the fresh or initial liquor was of marked turbidity because of the suspension of relatively insoluble carbonate therein. The loss of turbidity by the liquor indicates that the insoluble carbonate is progressively dissolved as the refining reaction continues, and that the hydroxyl ions consumed by the reaction with acids permit undissolved carbonate to go into solution to form more hydroxyl ions. In preparing the suspension of insoluble carbonate, it is preferable to employ carbonate in extremely fine particle size, for instance carbonate such as produced by precipitation, for carbonate in such condition is more effective in its refining action than coarse carbonate, because of the much larger surface which is exposed to the liquor and pulp. The precipitated carbonate which is produced may advantageously be that which is produced as a by-product in causticizing the so-called smelt solutions containing sodium carbonate, which are produced in the operation of soda or kraft pulp mills. In such case, lime is added to the smelt solutions to convert the sodium carbonate into caustic soda, thereby precipitating calcium carbonate, which is filtered out as a so-called lime sludge. The lime sludge may be freed from organic or other impurities by suitable treatment, for example, by the treatment disclosed in U. S. Patent No. 1,587,679, issued June 8, 1926, to George A. Richter and Sanford L. Swasey.

Example 5.—An unbleached sulphite pulp of the type previously described was digested for four hours in a 1% aqueous suspension of magnesium sulphite at 200° C. The washed pulp had an alpha cellulose content of 95.5%, a pentosan content of 1.2%, and a solution viscosity of 3.0. If the same procedure is carried out at 150° C., the resulting washed product has an alpha cellulose content of 89%, a pentosan content of 3.0%, and a solution viscosity of 8.2. This example again demonstrates the importance of the temperature factor in producing the desired refinement of the pulp.

Rather than starting with an unrefined pulp as a raw material, I may start with a refined pulp and digest it in a solution of, for example, an insoluble sulphite of carbonate, primarily to lower its solution viscosity. I shall now give examples involving the use of a refined wood fiber; or refined fibers of other origins, such as cotton linters, linen, or the like, may be employed.

Example 6.—A refined sulphite pulp having an alpha cellulose content of 94.7%, a pentosan content of 1.92%, and a solution

viscosity of 4.75, was employed as a raw material. The fiber was digested for two hours at a consistency of 5% in an aqueous suspension of calcium carbonate at 190° C., containing 10% calcium carbonate, based on the dry weight of fiber. The washed fiber had an alpha cellulose content of 95.1%, a pentosan content of 1.40%, and a solution viscosity of 0.86.

Example 7.—The same procedure was followed as in the previous example, except that barium carbonate was used in place of calcium carbonate. The washed fiber had an alpha cellulose content of 93.2%, a pentosan content of 1.19% and a solution viscosity of 0.53.

Example 8.—In this example, a suspension of calcium sulphite was employed under the same conditions as in the previous example, with the result that the washed fiber had an alpha cellulose content of 94.4%, a pentosan content of 1.12%, and a solution viscosity of 0.59. These results indicate that calcium sulphite has refining ability equal to that of calcium carbonate and superior to that of barium carbonate; but that it is superior to calcium carbonate in lowering the solution viscosity of the fiber, in which respect it is similar to barium carbonate.

In the examples hereinbefore given, borates such as sodium borate, or phosphates such as disodium or trisodium phosphate, may be employed. In such case, however, the solution-viscosity-lowering effect on the fiber is not as marked as when the sulphites or carbonates are employed. They are, however, excellent refining agents under the conditions given in the examples. It is of course possible, as already indicated, to use various types of fibers as a raw material. While in the first four examples given, an unbleached or raw pulp was cited as the raw material, if desired, the raw material may be a partly or completely bleached pulp, for instance a pulp which has been treated with chlorine water or bleach liquor in amount sufficient to react upon its ligneous content without, however, whitening the pulp, or a pulp which has been converted to a pure white condition, in which case, unless precaution is used in the bleaching operation, the bleached pulp will contain a considerable amount of oxycellulose. When a completely bleached or whitened pulp containing oxycelluloses is refined in accordance with the present invention, the refining liquor dissolves out oxycelluloses, as well as other classes of non-alpha cellulose impurities.

It is thus seen that the process of my invention makes possible the application of a large number of chemicals which have heretofore been considered entirely unsuitable. Most of these chemicals, such as the carbonates, phosphates, and borates, are far less expensive than the alkalies as refining agents. In fact, as already noted, calcium carbonate, which gives such good results, may be a waste product. In addition to their ability as refining agents, their effect on reducing the solution viscosity of the fiber is of especial importance when the finished product is to be employed in the manufacture of derivatives, such as nitrocellulose or cellulose xanthate, which yield, for some purposes, solutions of low viscosity. The usual fibers employed in the viscose industry, for example, even when they have a solution viscosity of as low as 5, require from 60 to 96 hours ageing after they have been converted into cellulose, and before they are ready for xanthation. The procedures hereinbefore given which yield fibers of a solution viscosity of less than 1 are of especial value in the viscose industry, as fibers of such low solution viscosity may be xanthated directly, that is, without the necessity of subjecting the cellulose prepared therefrom to an ageing period. In carrying out the high temperature digestions herein described, the digesters employed must be constructed to withstand pressures of about 200 to 230 pounds. The heating of the liquor may be carried out by providing a circulating system for the digester such as is employed in the so-called indirect cook in pulp making, in which case the liquor is drawn from the bottom of the digester through a screen, is passed through a heater, and returned to the top of the digester. Or, if desired, screened liquor may be removed from the top of the digester, passed through a heater, and introduced into the bottom of the digester, in order to induce a more positive circulation within the digester. If desired, however, the pulp and liquor may be passed through a heater and thus do away with the necessity of screening. Where high pressure steam is unavailable for the heater, it may be desirable to bring the digester charge to as high a temperature as is possible with the available steam, and then to raise the charge to the highest temperature by a suitable electric heating unit, for instance, an electric heater strapped about the digester. Because of the lack of a generic definition which includes the various chemicals which I employ as refining agents in my process, I shall provide such a definition for the appended claims. These claims may be defined as being "buffers" against the generation of acids in the liquor in which they are dissolved or suspended when cellulose fiber is digested in such liquor, particularly at temperatures above about 150° C., at which temperatures considerable non-alpha cellulose components in the fiber are hydrolyzed to form acids and the solution viscosity of the fiber is lowered. The term "buffer" as thus used is meant to exclude alkalies, such as caustic soda, sodium sulphide, sodium carbonate, and lime, which afford a compara-

tively high concentration of hydroxyl ions in water.

I present herein a list of a large number of genus chemicals and species falling within the genue, which may be employed in the process of my invention, but this list is not meant to be exhaustive of all the chemicals falling within the purview of my invention and the scope of the appended claims.

Sulphites,
Na_2SO_3
$CaSO_3$
$MgSO_3$
Phosphates,
Na_2HPO_4
$Ca_3(PO_4)_2$
$Mg_3(PO_4)_2$
Complex phosphates
Carbonates,
$CaCO_3$
$BaCO_3$
$MgCO_3$
Hydroxides,
$Ba(OH)_2$
$Al(OH)_3$
Oxides,
ZnO
Al_2O_3
Silicates,
Na_2SiO_3
Phosphites,
Formates,
Lactates,
Benzoates,
Phenolates,
Bicarbonates,
Aluminates,
Zincates,
Soaps.

What I claim is:

1. A process which comprises digesting cellulose fiber at temperatures above 150° C. in a substantially neutral aqueous liquor containing a buffer against the generation of acids.

2. A process which comprises digesting cellulose fiber at temperatures above about 150° C., in substantially neutral water containing a buffer against the generation of acids.

3. A process which comprises digesting chemical wood pulp at temperatures above about 150° C., in substantially neutral water containing a buffer against the generation of acid to increase materially the alpha cellulose content of such pulp, as well as to reduce its solution viscosity.

4. A process which comprises digesting a refined pulp at temperatures above about 150° C., in substantially neutral water containing a buffer against the generation of acids to reduce its solution viscosity.

5. A process which comprises digesting cellulose fiber at temperatures above 150° C., in a solution of substantially neutral sulphite.

6. A process which comprises digesting sulphite pulp at temperatures above about 150° C., in a solution of sodium sulphite.

7. A process which comprises digesting cellulose fiber at elevated temperature in water containing insoluble carbonate in suspension therein.

8. A process which comprises digesting cellulose fiber at temperatures above about 150° C., in water containing insoluble carbonate in suspension therein.

9. A process which comprises digesting chemical wood pulp at temperatures above about 150° C., in water containing calcium carbonate in suspension therein.

10. A process which comprises digesting cellulose fiber at a temperature above about 150° C., in water containing precipitated calcium carbonate in suspension therein.

11. A process which comprises digesting cellulose fiber at elevated temperature in water containing phosphate.

12. A process which comprises digesting an unrefined chemical wood pulp at temperatures above about 150° C., in water containing phosphates to increase materially the alpha cellulose content of such pulp.

13. A process which comprises digesting chemical wood pulp of the character of sulphite and kraft at temperatures above about 150° C. in water containing an insoluble phosphate like calcium phosphate in suspension therein.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.