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PROCESS OF REFINING CELLULOSE

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In refining cellulose of wood or other origin, it is sometimes the practice to include as one of the refining treatments the subjection of the cellulose to the action of oxidants, such as chlorine water or hypochlorite bleach liquor. It has heretofore been considered desirable that the oxidant treatment be performed at comparatively low temperature, for instance the seasonal temperature of the water used in preparing the chlorine water or the hypochlorite bleach liquor.

I have found that in certain instances, and more especially when the refined cellulose is to be used for esterification purposes, it is decidedly advantageous to practise the oxidant treatment at elevated temperatures. This is particularly true when the oxidant treatment is followed by a treatment with an alkaline liquor which tends to dissolve from the cellulose such undesirable reaction products as oxycelluloses, which may have been produced by the oxidant treatment. Thus, after the cellulose has undergone the oxidant treatment, it may be subjected to the action of alkaline liquors of an alkalinity designed to enhance its alpha cellulose content beyond that possessed by the cellulose before the oxidant treatment. This result can be had when wood pulps, for example, are employed as the starting material. Assuming that unbleached cellulose, such as unbleached wood pulps, are employed as the starting material, it may be first subjected to the high temperature oxidant treatment of the present invention and then bleached in a bleach liquor which is maintained distinctly alkaline throughout the bleaching operation. Or, it may undergo an alkaline treatment after the initial high temperature oxidant treatment. The alkaline treatment may then be followed by ordinary bleaching or by bleaching in a bleach liquor containing free alkali throughout the bleaching operation. Irrespective of the combination of refining steps performed on the cellulose, I have found that by including the high temperature oxidant treatment of the present invention at an appropriate stage in the process, it is possible to improve the quality of the refined cellulose in various important respects.

While not limited thereto, the oxidant treatment of the present invention may advantageously consist in treating various forms of cellulose or cellulosic materials at temperatures of about 40° to 80° C. with chlorine water. The use of chlorine probably gives rise largely to a chlorination of the impurities associated with the cellulosic material, but inasmuch as the reaction may also be one of oxidation, I shall refer to the treatment either as one of chlorination or oxidation. When such a treatment is applied to raw sulphite pulp, for instance, and the chlorinated pulp then undergoes the refining action of alkaline liquors and a final bleaching operation, I have found it possible to realize a finished pulp which is of lower pentosan content and of higher alpha cellulose content than when the chlorination is performed at comparatively low temperature. The finished pulp is, moreover, of a brighter and more stable white color and possesses a much lower solution viscosity than when chlorination is conducted as heretofore. Wood pulps, such as kraft and soda, which are prepared by cooking wood in alkaline liquors, are especially responsive to the high temperature chlorination of the present invention, for they can be made to acquire such a low solution viscosity that they require little, if any, ageing when they are converted into cellulose xanthate. This quality of low solution viscosity may exist in a pulp which has been refined in alkaline liquor and bleached so as to acquire the high alpha cellulose content and whiteness desired for paper-making, esterification, and other purposes. The high temperature chlorination facilitates the refinement of the pulp in alkaline liquors, as well as its bleaching, and makes possible the attainment of brillant white pulps of high color stability. This is true in connection with various kinds of chemical pulps, such as sulphite, kraft, and soda, as well as mechanical wood pulp and such cellulosic materials as manila, sisal, ramie, and other leaf and bast fibers. The principles of the present invention are of value in connection with cellulose such as cotton, cotton linters, rag stock, or the like, which is of high alpha cellulose content to begin with, for such cellulose can be transformed thereby into a product of such low solution viscosity that little, if any, ageing of the product is necessary in preparing cellulose xanthate therefrom. The cellulose produced in accordance with my invention is also of great value in making other cellulose esters or derivatives, such as nitro-cellulose, characterized by their low solution viscosity when dissolved in suitable solvent media. When I speak about low solution viscosity of cellulose, I also mean that derivatives, such as the xanthate or nitrate prepared from the cellulose, can be dissolved in suitable solvent media to form solutions of comparatively low viscosity. In preparing cellulose xanthate from cellulose, it is necessary to form so-called soda cellulose and then

to treat the soda cellulose with carbon bisulphide. In order to realize substantially complete xanthation of the soda cellulose through the action of carbon bisulphide and a xanthate or viscose syrup of the proper viscosity for spinning into artificial silk or for casting into films, it is ordinarily necessary to age the soda cellulose under controlled temperature conditions over a period as long as three days before bringing about its reaction with carbon bisulphide. This ageing period, can, as already indicated, be substantially dispensed with by using cellulose produced in accordance with the present invention for the preparation of the cellulose xanthate.

The chlorination of cellulose at elevated temperature should be carried out in such a way as to ensure the proper amount of chlorine reacting with the cellulose so as to bring about the desired transformation in its characteristics. Since the solubility of chlorine in water diminishes as the temperature of the water is increased, it is desirable that the cellulose be handled as a comparatively dilute suspension in water so as to furnish as much aqueous vehicle as possible as a solvent for the chlorine. Thus, the cellulose may be treated as an aqueous suspension of about 1% to 5% cellulose concentration. The aqueous suspension may undergo treatment as a continuously flowing stream in a system which permits chlorine gas, liquid chlorine, or concentrated chlorine water to be introduced and mixed with the suspension at various points in the system. In this way, as chlorine is consumed by the cellulose in one part of the system, it is replaced by sufficient fresh chlorine at the appropriate point in the system to promote the desired reaction in another part of the system. The stream thus starts out as one substantialy saturated with chlorine at the particular elevated temperature employed, undergoes a progressive loss in chlorine by virtue of the reaction of the chlorine on the cellulosic material, and is then fortified, when the chlorine is substantially consumed, to its original chlorine content. This cycle is repeated until the cellulose has been chlorinated to the desired extent.

There are a large number of procedures which may be practised to advantage in accordance with my invention, using various kinds of cellulose as raw material and subjecting the cellulose to various combined refining steps, including that of chlorination at elevated temperatures. I shall, therefore, give a number of typical procedures.

Example 1

A raw or unbleached sulphite pulp may serve as the starting material. The pulp may be one produced as ordinarily by cooking chipped wood in an acid sulphite liquor containing calcium, sodium, or other suitable bisulphite as the fiber-liberating agent. The raw pulp delivered from the digesters may be washed and screened as ordinarily. It may then be chlorinated over a period of, say, twenty minutes to four hours, at 70° C. with about 3% to 5% chlorine, based on the weight of dry pulp. The chlorine may be added to a flowing stream of the pulp or to a batch of the pulp which is preferably maintained as a comparatively dilute, aqueous suspension, say one of a pulp content of about 5% or less. It is, of course, possible to use a pulp suspension of greater density, say one of about 10% pulp content, but this means that the chlorine must be added at more frequent intervals in order to avoid loss of chlorine on account of its comparatively low solubility under the temperature conditions employed. The solubility of chlorine in water is increased by pressure; and, accordingly, it may be advantageous to chlorinate the cellulosic material under super-atmospheric pressure, particularly when working with pulp suspensions at high densities, say from 5% to 10% or greater pulp content. In any event, the chlorine is added at intervals and in no greater amount than can be dissolved by the water of the pulp suspension. The time of the chlorinating treatment, as well as the chlorine usage, determines the extent to which the pulp will be reduced in its solution viscosity and will be freed of pentosans. The chlorinated pulp is washed free of residual or unconsumed chlorine and reaction products, whereupon it is digested in an alkaline liquor, say, one containing 8% to 10% caustic soda or equivalent alkali, based on the weight of dry pulp. The digestion of the pulp may be performed under atmospheric or under super-atmospheric pressure and at a maximum temperature attainable under the particular pressure for a period of about two to six hours. The resulting pulp, which is of distinctly higher alpha cellulose content than the pulp used as starting material, may be washed and then bleached in any suitable way to the desired whiteness. Bleaching may to advantage be performed in a hypochlorite bleach liquor containing either calcium or sodium hypochlorite and sufficient caustic soda or other alkali to maintain a condition of distinct alkalinity throughout the bleaching operation. The free alkali functions to preserve the alpha cellulose content previously developed in the pulp. The finished pulp may be one having a high alpha cellulose content, say one ranging from about 93% to 96%, a brilliant white color of high stability, and a low solution viscosity, for instance a solution viscosity permissive of the xanthation of the pulp without need of an ageing period for the soda cellulose prepared therefrom before treating the soda cellulose with carbon bisulphide to form the xanthate.

Example 2

The pulp employed as raw material may be the usual kind of raw or unbleached sulphite pulp. It may initially be subjected to the action of a hypochlorite bleach liquor containing, say, about 4% to 10% calcium or sodium hypochlorite, based on the weight of dry pulp. The bleaching may be performed under prevailing temperature conditions over a period of, say, about two to eight hours. The bleached pulp may then be washed and subjected to chlorine at a temperature of about 50° to 70° C. with about 1% to 3% chlorine, based on the weight of dry pulp. The chlorine may be applied to the pulp as described in the foregoing example and, after the chlorine has been practically consumed, the pulp may be washed. The washed pulp may then be refined in alkaline liquors, washed, and bleached to the desired whiteness, as described in the foregoing example.

Example 3

A raw or unbleached sulphite pulp is initially digested in an alkaline liquor whose alkalinity is afforded by caustic soda, sodium carbonate, lime, sodium sulphide, or other suitable alkalies, alkaline compounds, or mixtures of alkalies and/or alkaline compounds capable of refining the pulp

at room or elevated temperatures. The extent to which ligneous matter, pentosans, beta and gamma celluloses, and other non-alpha cellulose components are removed from the pulp will depend upon the temperature and/or the concentration of alkali and/or alkaline compound in the liquor. The pulp thus refined to a greater or less degree is washed free of refining liquor and reaction products. It is then chlorinated at temperatures of about 40° to 60° C. with about 1% to 3% chlorine, based on the weight of dry pulp. The chlorinated pulp is then washed and may be finally bleached to the desired whiteness. While bleaching may be performed in the usual hypochlorite bleach liquor, it is distinctly advantageous to maintain free alkali in the bleach liquor throughout the bleaching operation, so as to promote the dissolution of such oxycelluloses as may have been formed during the preceding chlorination, as well as to inhibit the formation of new oxycelluloses.

Example 4

A raw or unbleached sulphite pulp may undergo the action of chlorine water or hypochlorite bleach liquor under prevailing temperature conditions. It may then be washed and refined in alkaline liquor, as described in the preceding examples. The refined pulp may then be washed and chlorinated at a temperature of, say, about 60° C. with about 1% chlorine, based on the weight of dry pulp. The chlorinated pulp may then be washed and bleached to the desired whiteness, preferably in an alkaline bleach liquor, as hereinbefore described.

Example 5

A raw or unbleached pulp may be subjected to the action of a hypochlorite bleach liquor containing, say, about 5% to 10% calcium or sodium hypochlorite at a temperature of about 60° C. If desired, a slight amount of hydrochloric or sulphuric acid may be added to the bleach liquor to liberate hypochlorous acid. It is thus seen that hypochlorite and/or hypochlorous acid may serve as the oxidants to which the pulp is subjected at elevated temperature, rather than chlorine. The oxidant-treated pulp may then be washed and refined in an alkaline liquor, as hereinbefore described. The refined pulp may then be washed and bleached to the desired whiteness, preferably in an alkaline bleaching liquor.

Example 6

A raw, unbleached sulphite pulp may be chlorinated at about 60° to 70° C. with about 1% to 3% chlorine, based on the weight of dry pulp. The chlorinated pulp may then be washed and suspended in a concentrated solution of suitable alkali, such as caustic soda and/or sodium sulphide. Thus the solution may be one containing about 4% to 18% of caustic soda, and/or sodium sulphide or equivalent alkali. A solution of such strength is capable of refining the pulp at any temperature upward of its freezing point, and so can be maintained in contact with the pulp at about room temperature to good advantage, to bring about the desired refining action. Indeed, even with caustic soda solutions of a strength of about 4%, it is possible to realize a noteworthy refining effect at a temperature not exceeding about 40° C. When the alkaline liquor is of high alkalinity, and is used at low temperature, it is desirable to add thereto a suitable oxidant which promotes a reduction in the solution viscosity of the pulp. For instance, a refining liquor containing caustic soda as the refining alkali may have added thereto sodium hypochlorite, potassium permanganate, or other suitable oxidant in amount subordinate to the alkali, thereby avoiding any tendency to form oxycelluloses. The refined pulp is then washed and then bleached to the desired whiteness, as hereinbefore described. It is possible to reverse the sequence of the first two steps given in this example, that is, to refine the pulp in the alkaline liquor before it undergoes chlorination at elevated temperature.

Example 7

A raw or unbleached kraft pulp is first treated at about 60° C. with about 4% to 7% chlorine, based on the weight of dry pulp, over a period of, say, about twenty minutes to four hours. The chlorinated pulp may then be washed and subjected to refinement in a concentrated solution of alkali at relatively low temperatures, as described in the foregoing example. Thus, the refining solution of alkali may be one containing about 10% to 18% of caustic soda and/or sodium sulphide, and be applied to the pulp at about room or lower temperatures. It is thereby possible to produce a refined pulp which not only has a low solution viscosity, but which has an alpha cellulose content as high as 98%. The fact is, that a relatively cold, concentrated solution of alkali is especially effective in removing pentosans from the pulp, and this is especially to be desired in the case of kraft pulp, which is of high initial pentosan content, usually about 7% to 10%. The refined kraft pulp is washed and bleached to the desired whiteness, preferably by applying two or more independent, distinctly alkaline bleach liquors to the pulp, and washing the pulp between the bleaching treatments. The procedure described in this example works well, not only in connection with kraft pulp, but also with other pulps, such as soda, which have been prepared by cooking wood or other raw cellulosic material in alkaline liquors.

Example 8

Raw cotton, rag stock, cotton linters, or similar cellulose which is initially high in alpha cellulose content, is treated at temperatures of about 40° to 60° C. with about 0.5% to 2% chlorine, based on the weight of dry fiber. Aside from the value of such treatment in reducing the solution viscosity of the fiber, it promotes the solubilization of such ligneous matter, resins, waxes, and ash as may be present in raw cotton or cotton linters. In the case of rag stock, the treatment promotes the removal of dyestuffs or other foreign matter as may be present in such stock. The chlorinated fiber is then washed and refined in any of the ways hereinbefore described. It may also receive a final bleaching treatment as hereinbefore described.

Example 9

A ground-wood pulp is treated at a temperature of about 50° to 70° C. with about 6% to 12% chlorine, based on the weight of dry pulp. In such case, a higher percentage of chlorine than that hereinbefore prescribed is used, because the pulp is associated with far more ligneous matter and other non-alpha cellulose components than chemical wood pulp, which is largely freed from non-alpha cellulose components by virtue of the chemical pulping action which it has undergone. Thus, in the ordinary

chemical pulping process, about half the wood is lost in the chemical liquor, and the lost material represents largely ligneous matter and other non-alpha cellulose components, which are, on the other hand, associated with ground-wood pulp and are capable of consuming chlorine. The chlorinated ground-wood pulp may then be refined in alkaline liquors and bleached as hereinbefore described, to produce a finished pulp of the desired high alpha cellulose content and whiteness.

As already indicated and as illustrated in the specific examples hereinbefore given, the high temperature oxidant treatment of the cellulose may be performed, not only with chlorine water, but with other oxidants, such as hypochlorite liquors. While such oxidants as permanganate solutions might be used, chlorine water or hypochlorite liquors are advantageous, not only on account of their comparatively low cost, but because they modify the cellulose in the desired way in a reasonable period of time and without causing an excessive loss of cellulose through the formation of oxycelluloses and the dissolution of the oxycelluloses in the alkaline liquors subsequently employed as refining agents. Permanganate solutions tend to cause a greater loss of cellulose than either chlorine water or hypochlorite liquors. They are rapid in their action and hence difficult to control. Chlorine water is more selective in its reaction upon ligneous matter and other non-alpha cellulose components, especially at elevated temperatures, than are hypochlorite liquors, and it is hence the preferred oxidant, particularly as it reacts quickly and smoothly until it is consumed.

The pulp produced in accordance with my invention is especially suitable for making various cellulose derivatives, in which connection its low solution viscosity as well as its purity and whiteness is of great value. It also represents a high grade paper-making material.

It is to be observed that I perform the chlorination treatment of wood pulp or other cellulosic material in the form of a flowable aqueous suspension having a consistency of, say, about 5% to 10%. Under such conditions, such heat as may be liberated by the chlorinating reaction is absorbed by and dissipated in the tremendous excess of aqueous vehicle without appreciable or sensible rise in temperature therein. It is thus seen that the elevated temperature and more particularly a temperature ranging from about 40° C. to 80° C., at which the wood pulp or other cellulosic material is chlorinated in accordance with my invention, must necessarily be an artificially created one, that is, one which is created by supplying the heat from an outside source as in the form of steam.

I claim:

1. A process which comprises treating cellulose of the character of preliberated wood pulp and cotton as a flowable aqueous suspension at artificially created elevated temperature with an oxidant, and then exposing the cellulose to the action of an alkaline refining liquor.

2. A process which comprises treating cellulose of the character preliberated wood pulp and cotton as a flowable aqueous suspension at artificially created elevated temperature with an oxidant, exposing the cellulose to the action of an alkaline refining liquor, and bleaching the cellulose in a distinctly alkaline bleaching liquor.

3. A process which comprises treating cellulose of the character of preliberated wood pulp and cotton as a flowable aqueous suspension at artificially created elevated temperature with an oxidant, and bleaching the cellulose in a distinctly alkaline bleaching liquor.

4. A step which comprises subjecting cellulosic material to chlorination as a flowable aqueous suspension at elevated temperature created by supplying heat from an outside source.

5. A step which comprises chlorinating cellulosic material in admixture with chlorine water as a flowable mixture under pressure and at elevated temperature created by supplying heat from an outside source.

6. A step which comprises subjecting cellulosic material to chlorination as a flowable aqueous suspension at temperatures not less than about 40° C. created by supplying heat from an outside source.

7. In the treatment of cellulosic material, those steps which comprise maintaining a progressively flowing aqueous stream of such material at elevated temperatures created by supplying heat from an outside source, and adding chlorine at intervals to said heated stream.

8. In the treatment of cellulosic material, those steps which comprise maintaining a progressively flowing aqueous stream of such material at elevated temperatures created by supplying heat from an outside source, and adding chlorine at intervals to said heated stream in amount not materially in excess of the chlorine-saturating point at said temperature.

9. In the treatment of cellulosic material, that step which comprises chlorinating a flowable aqueous suspension of such material at artificially created elevated temperature by adding the chlorine as increments none of which are materially in excess of the chlorine-saturating point of the suspension at said temperature.

10. In the treatment of cellulosic material, that step which comprises chlorinating a flowable aqueous suspension of such material at artificially created temperatures of about 40° to 80° C. by adding the chlorine as increments, none of which are materially in excess of the chlorine-saturating point of the suspension at such temperatures.

11. In the treatment of cellulose of the character of preliberated wood pulp and cotton, that step which comprises chlorinating a flowable aqueous suspension of such cellulose at a cellulose content downward of about 5% and at an artificially created temperature upward of about 40° C.

12. In the treatment of cellulose of the character of preliberated wood pulp and cotton, those steps which comprise chlorinating a flowable aqueous suspension of such cellulose at elevated temperature created artificially by supplying heat from an outside source, and then exposing the cellulose to the action of an alkaline refining liquor.

13. In the treatment of cellulose of the character of preliberated wood pulp and cotton, those steps which comprise chlorinating a flowable aqueous suspension of such cellulose at elevated temperature created artificially by supplying heat from an outside source, exposing the cellulose to the action of an alkaline refining liquor, and bleaching the cellulose in a distinctly alkaline bleaching liquor.

14. In the treatment of cellulose of the character of preliberated wood pulp and cotton, those steps which comprise chlorinating a flowable aqueous suspension of such cellulose at elevated temperature created artificially by supplying heat

from an outside source, and bleaching the cellulose in a distinctly alkaline bleaching liquor.

15. In the treatment of cellulose of the character of unbleached wood pulp, those steps which comprise chlorinating a flowable aqueous suspension of such pulp at artificialy created temperatures of about 40° to 80° C., and bleaching the pulp.

16. In the treatment of cellulose of the character of unbleached wood pulp, those steps which comprise chlorinating a flowable aqueous suspension of such pulp at an artificially created temperature upward of about 40° C., and bleaching the pulp in a distinctly alkaline bleach liquor.

17. In the treatment of cellulose of the character of unbleached wood pulp, those steps which comprise chlorinating a flowable aqueous suspension of such pulp at an artificially created temperature upward of about 40° C., exposing the pulp to the action of an alkaline refining liquor, and bleaching the refined pulp.

18. In the treatment of cellulose of the character of unbleached wood pulp, those steps which comprise chlorinating a flowable aqueous suspension of such pulp at an artificially created temperature upward of about 40° C., exposing the pulp to the action of an alkaline refining liquor, and bleaching the refined pulp in a distinctly alkaline bleach liquor.

19. In a process which involves refining preliberated wood pulp in an alkaline liquor and bleaching, that step which comprises chlorinating a flowable aqueous suspension of the pulp at artificially created elevated temperature at any stage of the process prior to bleaching.

20. In a process which involves refining preliberated wood pulp in an alkaline liquor and bleaching in a distinctly alkaline bleach liquor, that step which comprises chlorinating a flowable aqueous suspension of the pulp at an artificially created temperature upward of about 40° C. at any stage of the process prior to bleaching.

21. In the treatment of chemical wood pulp, that step which comprises chlorinating such wood pulp as a flowable aqueous suspension at a temperature ranging from about 40° to 80° C., created artificially by supplying heat from an outside source.

22. In the treatment of sulphite wood pulp, that step which comprises chlorinating such sulphite pulp as an aqueous suspension of about 5% to 10% pulp content at a temperature ranging from about 40° C. to 80° C., created artificially by supplying heat from an outside source.

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