Cl. 92

Published May 4, 1943

Serial No. 299,888

ALIEN PROPERTY CUSTODIAN

PROCESSES OF MAKING HIGH-GRADE CELLULOSE

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No Drawing. Application October 17, 1939

This invention relates to processes of making high-grade cellulose, of which the following is a specification.

The making of cellulose from wood, straw or other vegetable matter by means of a process of disintegrating by alkali (sodium oxide, soda or sulphate process), as known, is only economical in case of a most extensive recovery of the alkali used in the process. In the sodium and sulphate cellulose factories, therefore, the alkali regeneration plant forms an essential part of the equipment. The size of a plant of this kind primarily depends upon the quantity of liquor required in the digesters, this quantity on its part depending again upon the "alkali-ratio" used in the cooking process, that is upon the quantity of alkali required for a certain weight of wood. By this "alkali-ratio" again the yield and especially the alpha-cellulose content of the manufactured product are determined, these quantities being greatly independent from other conditions prevailing during the cooking operation. The process of disintegrating the cellulose by means of alkali thus presents three main problems, to wit: to produce a cellulose as high-grade as possible, to secure a maximum yield of such cellulose and to use a most favorable "alkali-ratio" for the recovery of the alkali from the process.

In case of former cellulose materials made by means of an alkali disintegrating process, which cellulose had been used almost exclusively in the paper and pasteboard industry, a high-grade improvement process, especially with a view of increasing the alpha-cellulose content, and improving the properties of the product in a chemical way and mostly with respect to bleaching had been of no importance.

The problem of disintegrating cellulose by the alkali process in order to produce more valuable materials which at least regarding their chemical properties would be equivalent to the sulphite cellulose materials used in the manufacture of artificial silk has presented itself not before the demand of using sodium oxide or sulphate cellulose also in the wide field of chemical improvement processes, such as nitration, production of artificial fibres and the like. It had to be expected that this would necessitate a change in the "alkali-ratio." Thus, for instance, when using an alkali-ratio of 20:100 (that is 20 kg of NA_2O per 100 kg of wood, figuring also NA_2S with its equivalent NA_2O-value), it had been possible to produce materials having in unbleached condition an alpha-cellulose content of about 89%. Also it has soon been found that when increasing the alkali-ratio by one third of its value the alpha-cellulose content could be increased to from 93 to 94%. This, however, would require at the same time an enlarged equipment for the recovery of alkali which would result in conditions entirely impractical in economical respects.

A more favorable alkali-ratio could be expected when using one and the same liquor repeatedly for the several successive operations of cooking.

In order to reduce the costs of the process, the plain single-stage cooking process has been carried out with repeated use of the same liquor as a whole or in part, that is, in each new cooking process a greater or smaller amount of liquor from a previous cooking process had again been used. In other words, the material had been cooked with a liquor comprising a larger or smaller percentage of waste liquor from a preceding cooking process. Although in this way the consumption of alkali could be reduced and, what is more important, a waste liquor richer in organic substances was obtained, the material as such had not been in the least improved regarding its chemical constants.

On the other hand, plural-stage processes are known using the waste-liquor repeatedly for the cooking. Some time ago it appeared to be rather promising to use the combined cooking and diffusion process of Ungerer, according to which process the wood had been treated in digesters connected with each other to form a kind of diffusion battery at a temperature of 165 or 175° with a liquor increasing in strength from one to the next digester and finally with fresh liquor, the liquors being passed in succession through the digesters, commencing with the material which had already been rather extensively disintegrated and ending with the digester charged with fresh wood. (See German Patent No. 933 of July 13th 1877; see also C. Hoffmann. Handbuch der Papierfabrikation, 2nd edition, 1897, Vol. II. pages 1396–1399, as well as E. Hägglund, Natronzellstoff, 1926, pages 131–132. This process, however, could not compete with the less complicated cooking systems as had especially been stated in the last mentioned treatise of Hägglund, page 132, line 5.

In more recent time, G. A. Kienitz has described a similar process (see the Periodical "Holz als Roh- und Werkstoff", 1937, pages 33–35). In this case, the same as with Ungerer's process, the cooking liquor is intermittently conveyed from one to another digester in such a manner that the most efficiently disintegrated wood material contains the concentrated fresh liquor, while the first or initial digester, which is charged with fresh wood, is supplied with exhausted black liquor, while the second and third digester are supplied with a less exhausted liquor, until the last digester is likewise supplied with concentrated fresh liquor for the final treatment. A principal difference between the process of Klenitz and that of Ungerer consists therein that in the former process contrary to the latter the almost disintegrated cellulose is treated with the fresh liquor under very mild conditions, that is at relatively small pressure and relatively low temperature, while the fresh wood with the almost exhausted black liquor is cooked at high pressure and high temperature.

These processes, however, likewise do not represent an optimum in a technical and economical respect. This is due to the fact that these processes require rather complicated apparatus and do not at all produce a satisfactory yield. With these processes, moreover, the yield will be smaller and smaller with increasing degrees of disintegration. According to the last-mentioned inventor (l. c. 34, right hand column), the yield varies about between from 33 to 38% in case of unbleached beach-wood cellulose.

Contrary to these known processes my new process permits production of a cellulose material of exceptionally high-grade properties. In addition, very high yields of such materials, for instance, 42% bleached or 38% highly improved pine-wood cellulose and 51% bleached or 46% highly improved beach-wood cellulose may be obtained with my new process. My new process comprises an alkali disintegrating treatment performed in two stages, the raw cellulose material being treated in the first stage of the process with a cooking liquor which for its greater part is derived as waste-liquor from a preceding final cooking (that is in the second stage) and, besides, consists for its smaller part of fresh cooking liquor, so-called white liquor, while in the second stage of the process the previously cooked cellulose material is being treated with fresh cooking liquor of dimished (that is not especially increased) concentration. As compared with the heretofore known processes using waste-liquor, my new process resides principally in an essentially different distribution of alkali with respect to fresh and already treated cellulose material, the fresh cooking material being at first, that is in the first stage, treated not exclusively with an almost exhausted black liquor of low alkali concentration from the preceding cooking stage but with a cooking liquor that had been essentially improved with respect to its alkali concentration of fresh liquor, while on the other hand the alkali content of the liquor acting in the second stage onto the previously cooked material is accordingly essentially decreased.

The extraordinary favorable effect attained by this process may be based principally on the fact that the very restriction of the process to only two stages and more especially the proper distribution of alkali will have the result of preserving the structure of the fibres to a considerable degree. This is due to the fact that the fibrous material is treated in the second stage in already extensively disintegrated and consequently more sensitive condition with respect to the action of the liquor with a quantity of alkali which, although reduced, is still sufficient to produce a highly improved material, especially as the increased alkali content of the liquor permits of carrying through the disintegrating process to an appropriate extent in the first stage. The alkali in my present process is distributed approximately in such a way that in the first stage, besides the waste-liquor from the second stage of a preceding cooking (and eventual wash waters), there will be used still about from 20–30% of the total fresh liquor required for the cooking, so that the cooking in the second stage is carried through only with about from 70 to 80% of the total quantity of fresh liquor (eventually together with alkaline wash waters).

My new process, therefore, is not dependent upon an increase of the "alkali-ratio" and, consequently, in spite of the increased yield of high-grade cellulose does not require any enlarged equipment for the recovery of alkali. A further advantage of my new process consists therein that the produced cellulose materials may be bleached with extraordinary ease permitting to reduce on the one hand the consumption of chlorine and on the other hand the loss of material during the bleaching and improving process.

Example 1

57 kg of air-dry (corresponding to 50 kg of absolutely dry) pine-wood are treated in an ordinary sodium-cellulose digester, first with a liquor composed of 100 litres of waste-liquor (having an alkali content corresponding to from 20 to 25 g of Na_2O per litre) and 55 litres wash water, both originating from the second stage of a preceding cooking operation, as well as 25 litres of fresh liquor (white liquor) with an alkali content corresponding to 2.5 kg of Na_2O (that is 100 g of Na_2O per litre). Accordingly, there is a total quantity of 180 litres of cooking liquor with an alkali content corresponding to 5 kg of Na_2O.

Heating is carried through to 155° C. for about three hours. Thereupon, from 100–120 litres of black liquor are removed and the digester immediately again filled for the second stage with preferably pre-heated cooking liquor consisting of 75 litres of 10% white liquor (with respect to Na_2O), diluted with 25 litres of wash-water from the second stage of a preceding cooking. As the alkali content of the wash-water corresponds to approximately 1% Na_2O, the total cooking liquor for the second stage will be composed of the remainder of the black liquor that had not been drawn off the first cooking stage and, in addition, of 100 litres of fresh liquor including wash-water (with an alkali content corresponding to 7.750 kg of Na_2O). Thus, assuming the remainder of the liquor from the previous cooking to be 80 litres with an alkali content corresponding to 15 g of Na_2O, this cooking liquor consists in total of 180 litres of a liquor with an alkali content corresponding approximately to 5% Na_2O.

Now heat is being applied for about one hour in order to raise the temperature to 150° and the digester is kept at this temperature for about one and one half hour. Upon completed cooking about 100 litres of liquor are let off to be used for the first stage of a subsequent cooking with fresh wood. Thereupon the digester is rinsed out with about 100 litres of hot water and the contents washed in this way are discharged into a vat. The alkaline wash-water from this washing process amounts to about 80 litres and is again used in the first and second stage of the subsequent cooking operations, as had above been mentioned. Subsequent to this, bleaching of the cellulose is carried out in known manner with chlorine water, a solution of chloride of lime or the like.

The yield of bleached material amounts to 42% of the used wood, this material containing from 93 to 94% alpha-cellulose and from 4 to 5% pentosane. From this material a high-grade cellulose was obtained by means of an improvement process carried through in known manner with a liquor of caustic soda, the yield of this cellulose being about 6% higher than the yield of a material of the same chemical properties which had been improved in exactly the same way by the known single-stage process.

Example 2

In case of leaf-wood my new process will be especially efficient inasmuch as the disintegrating is carried through in a manner widely preserving the structure of the fibre and attaining an essentially greater chemical purity of the product. For instance, beach-wood can be disintegrated in the same manner as had been described in Example 1, the cooking temperature in both stages, however, may be kept from 8 to 10° lower, that is the temperature may be about 145° in both stages. Also, washing and further treatment is carried through in the same manner as according to Example 1. Thus a material is obtained containing from 93 to 95% alpha-cellulose and from 10 to 11% pentosane, the yield being about 51%. The improving process carried through in known manner with a liquor of caustic soda has resulted in the present case in a yield of high-grade cellulose about 12% higher than the yield in case of a material which had been made according to the known one-stage process and improved in exactly the same manner

Example 3

In case of straw and similar raw materials a relatively somewhat greater quantity of liquor must be applied, or what is the same, a like quantity of liquor must be used for a smaller quantity of raw material as compared with the process of disintegrating wood. On the other hand the composition of the liquor may remain unchanged in both cooking stages.

For instance, 35 kg of air-dry straw, corresponding to 50 kg of absolutely dry straw, are cooked in the first stage with 180 litres of liquor of about the same consistency as in Example 1, that is with a total alkali content corresponding to about 5 kg of Na_2O. Heat is applied for about threc hours and the temperature raised to about 150° C, whereupon a quantity from 100 to 120 litres of liquor is let off and the digester immediately filled again with the liquor for the second stage, 100 litres of liquor being taken in this case with an alkali content corresponding to about 8 kg of Na_2O. Now heat is applied for about one hour to raise the temperature to 155° C, while the material is kept at this temperature for about two and one half hours. Subsequent washing and further treatment are carried out in the same manner as in case of Example 1.

In this way there is produced a yield of straw-cellulose of about 41% containing in unbleached condition about 10% wood-gum. Bleaching carried through in the usual manner has resulted in a yield of 40.5% (figured with respect to the quantity of used wood). This material contained 88% alpha-cellulose and 10% wood-gum. Upon improving with about 5% cold sodium oxide liquor a cellulose was obtained with 95% alpha-cellulose and 3% wood-gum and a yield of 37% (figured with respect to straw).

Example 4

The ratio of the quantities of liquor and cellulose raw material and the composition of the liquor are the same as had been stated in connection with Example 3.

38 kg of air-dry esparto-grass (alpha-grass), corresponding to 35 kg of absolutely dry esparto-grass, were heated together with 180 litres cooking liquor with an alkali content corresponding to about 5 kg of Na_2O for about three hours up to a tempertaure of about 145° C. After letting-off about 100 litres of black liquor the digester is immediately again filled with the liquor for the second cooking, about 100 litres of this liquor having an alkali content corresponding to about 8 kg of Na_2O being taken. Thereupon the temperature is raised for about one hour up to about 150° C and constantly kept at this value for about from two or three hours in accordance with the behavior of the raw material. Cooking, washing and further treatment of the material is thereupon carried out in the manner stated in connection with Example 1.

In this manner there is obtained a yield of cellulose of 40% comprising in unbleached condition 93% alpha-cellulose and 8% wood-gum. Upon bleaching in the usual manner with hypochlorite the material was composed of 95% alpha-cellulose and 3% wood-gum. Improving with a 5% sodium oxide liquor has resulted in a yield of 35% (figured with respect to wood) of high-grade cellulose with 99% alpha-cellulose and 1% wood-gum.

The great advantages of my new process may be seen from the below Table showing a comparison of the quantites of the bleached and improved materials with those materials which can be produced with the usual one-stage cooking and subsequent improvement processes with the same degree of disintegration and the same consumption of alkali.

TABLE

	Yield		Alpha-cellulose		Wood rubber	
	One stage process	New process	One stage process	New process	One stage process	New process
Pine-wood, bleached	40	42	89	92	8	5
Pine-wood, improved	36	38	98	98	3	2
Leaf-wood, bleached	49	51	89	94	21	10
Leaf-wood, improved	41	46	98	98	3	3
Straw, bleached	38	40,5	82	88	17	10
Straw, improvod	31	37	95	95	3	3
Esparto, bleached	38,5	39.5	90	96	15	3
Esparto, improved	33	36,5	98	99	3	1

This Table shows that by my new process there may be obtained either cellulose of higher grades (that is with a greater alpha-cellulose content and smaller wood content) or in some cases higher yields of materials of the same properties.

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