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ACID-ALKALI PROCESS FOR THE PREPARATION OF CELLULOSE FIBERS

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This invention relates to the preparation of cellulose fibers from bagasse. Consisting principally of the fibrous residue of sugar cane after extraction of the juice, bagasse is a waste material available in enormous quantities at sugar mills, and is commonly used as fuel at the mills for lack of a better method of disposal. It is the principal object of the invention to provide a process whereby the cellulose fibers in bagasse may be economically liberated and further purified to produce a high grade pulp suitable for use in paper making, in the manufacture of cellulose products and derivatives such as viscose and cuprammonium rayon, also cellulose ethers and esters, and for use in various other fields which have heretofore been supplied solely by pulp derived from other and more expensive sources.

Extensive efforts have been made over many years to devise a satisfactory process for producing cellulose from bagasse. Treatment of bagasse both with nitric acid and with caustic soda is now employed but these efforts have achieved nothing more than the production on a small scale of pulp for low grades of wrapping paper and paper board. So far as we are aware, no pulp produced by prior methods is suitable for use in high class paper, and even a good quality of paper stock is far from sufficiently pure for the rayon trade. By means of the present invention, however, we are enabled to obtain from bagasse a cellulose pulp having certain qualities and characteristics comparable to those exhibited by pulp derived from cotton linters, and suitable for use not only in the manufacture of the best grade of paper, but in viscose rayon. Furthermore, these results are achieved by employing a novel sequence of processing steps which involve no appreciable increase in cost over methods heretofore proposed for the treatment of bagasse.

In general, our process is based on conventional nitric acid processing, which comprises treatment with nitric acid, followed by alkaline digestion and bleaching. It differs, however, in several respects which we have found to be essential to the production of high grade pulp. Thus the present process may consist essentially of the following steps, taken in the order named:

1. The bagasse, as received from the sugar mill, is mechanically processed to effect reduction in size, and mud is removed by washing.

2. The finely divided bagasse is treated with nitric acid at an elevated temperature, the acid drained, and the material washed.

3. The material is subjected to alkaline digestion at elevated temperature.

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4. The resulting pulp is then violently agitated to break up fiber bundles and washed.

5. A second treatment with alkali at elevated temperature is applied.

6. After washing and screening, the pulp is chlorinated, and again washed.

7. The chlorinated pulp is steeped in alkali without substantial heating.

8. The pulp is rebleached and soured in accordance with known procedures, formed into sheets, and dried.

While the selection of appropriate conditions for each processing step is of importance in determining the character of the final product, these conditions are, in general, not critical and may be varied within fairly wide ranges. The sequence of operations is, however, quite important; of special significance is the treatment which immediately follows the nitration, namely steps numbered 3 to 5 above, which are believed to be responsible in large part for the excellent qualities of the cellulose produced by our method. The steps which follow the repeated alkaline extraction are, for the most part, conventional, but the effect of this later processing is probably greatly altered by the unique alkaline treatment and agitation to which the pulp is subjected following the nitric acid treatment. The several steps of the process will now be described in more detail.

1. *Mechanical disintegration and washing.*—The purpose of this step is to reduce the bagasse to smaller size to facilitate handling and to accelerate the subsequent chemical reaction. The removal of mud and other entrained substances is more readily effected when the bagasse is in a more finely divided state than as customarily received from the sugar mill.

Any conventional means may be employed to subdivide the bagasse, such as a hammer mill or a beater; the operation should be continued until the particles are reduced to a length of not more than one-half inch and preferably smaller.

2. *Nitric acid treatment.*—This is a common step in previously proposed methods of liberating fibers from bagasse, and exerts a threefold action on the material: (a) Part of the encrusting material, probably lignin, is nitrated. (b) Other encrusting materials, such as xylans, are hydrolyzed by the acid. (c) Oxidation of part of the encrustants is effected, as evidenced by evolution of NO.

We prefer to employ a dilute nitric acid solution, for instance 2%, in the ratio of 9 parts of treating solution to one part of bagasse by weight, ordinarily sufficient to insure complete immersion of the solids, and the reaction may be allowed to continue for about one hour at a tem-

perature between 80° C. and 110° C., for instance 95° C. Stronger acid is unnecessary, and therefore uneconomical, as is longer time or higher temperature. The action does not start well at temperatures below 90° C., but once initiated is slightly exothermic for about 10 minutes, after which applied heat may again be necessary to maintain the selected temperature. Used acid seems to be more effective than fresh acid, and may therefore be employed in somewhat less concentration, for instance 1.5%. Thus it is desirable to drain and wash the acid from the treated bagasse, to introduce a sufficient amount of fresh acid to restore the strength of the solution, and to re-use the same for the treatment of succeeding batches of bagasse.

3. *First alkaline extraction.*—In this treatment the humins, nitro compounds, and other materials such as hemicelluloses are either wholly or partly dissolved.

The preferred alkaline agent is sodium hydroxide, which may be employed in the form of a dilute solution, for instance 1% to 3%, the reaction being continued for about one hour at a temperature between 80° and 110° C., preferably about 95° C. As in various other steps of the process, we find it convenient to use a 9:1 ratio of solution to solid material. Other alkaline agents may be employed to replace all or part of the caustic soda, in most instances with less economy when used in quantity sufficient to effect results comparable to those achieved by caustic soda, for instance alkaline carbonates and sulphites, or any of the various alkaline agents heretofore suggested for use in the liberation of fibers from cellulosic materials. The conditions of the reaction are not critical and may be varied over a considerable range, as is evidenced by the earlier literature on this subject.

It is in the course of this step that the bagasse is first truly pulped, the fiber bundles being reduced in size so as to approach individual fiber dimensions.

4. *Mechanical agitation.*—The mechanical disintegration of the pulp at this stage, followed by further alkaline treatment, is important to successful practice of the invention. The effect of the agitation is to break up further the fiber bundles in order that the caustic treatment may be more effective and complete, whereby the soda soluble value may be lowered without any accompanying degradation of the cellulose. The apparatus employed in this step may vary widely and may be selected from the many devices capable of violently agitating slurry. Following agitation, the material is preferably washed.

5. *Second alkaline extraction.*—Further treatment with alkali at this point is necessary in order to complete the treatment initiated in step 3. This step also tends to lower the soda soluble value and to reduce the consumption of chemicals in the subsequent bleaching operation by removing easily oxidizable hemi-cellulosis from the pulp.

As in step 3, conventional alkaline agents may be employed, the preferred agent being sodium hydroxide, of which 1% concentration is usually sufficient, although solutions of less or greater strength may be employed. A convenient liquid to solids ratio is 9:1, and the reaction may be carried out under conditions similar to those used in the first alkaline digestion for a period of about one hour. The conditions are not critical and substantial variations, suggested in the

literature for caustic treatment of pulp, may be followed.

At the conclusion of the treatment, the pulp may be agitated somewhat more to effect complete reduction of the fiber bundles to suitable size, and is washed. The amount of dirt in the pulp is reduced by screening through a pulp screen of about 0.008 inch slots, to insure that the bleach will not be wasted on improperly purified pulp.

6. *Chlorination.*—The principal effect of this processing step is to effect chlorination of remaining encrustants, especially those of the lignin type which are readily susceptible. Conventional agents and processing conditions may be employed, such as are common in the paper and related industries. Thus we may employ an acid hypochlorite bleach for one hour at room temperature (about 25° C.), or we may use a straight chlorination step with direct chlorine at high density. The details of this processing step form no part of the instant invention. Following the chlorination, the pulp is washed.

7. *Alkali steep.*—Treatment at this stage is preferably carried out at room temperature (25° C.), since the low temperature steeping promotes swelling of the fibers and renders the remaining encrustants more accessible to further treatment. Chlorinated lignins and hemicelluloses are also removed. We prefer to employ sodium hydroxide, but other alkaline agents known to be useful in this field may be used. Solutions of caustic soda of concentration varying from 5% to 14% may be satisfactorily employed, the actual concentration being substantially less, due to the presence of water in the pulp. For instance, we prefer 9% sodium hydroxide to facilitate re-use as hereinafter mentioned; the actual concentration is then about 5.6%. Actual concentrations of the order of 10% to 12% of caustic solution tend to result in "pilly" pulp, due to easy mercerization of the pulp, and such high concentrations are unnecessary in any event. Operation at reduced temperatures effects some slight improvement of the fiber, but is hardly worth the added expense. Treatment for about one hour is usually entirely adequate.

The treated pulp is washed, and the wash liquors may be re-used in the digesting steps 3 and 5 by suitable adjustment of the concentration.

8. *Rebleaching.*—This step is also one which is practiced in accordance with established procedures and with conventional agents such as chlorine or an agent yielding chlorine. It is preferably carried out in the presence of a slight excess of alkali, as is usually practiced in known processes.

Following the rebleach, the pulp is soured and washed in accordance with conventional procedure, and is then formed in sheets and dried, as is customary in the pulp industry.

While we prefer to carry out steps 6, 7, and 8 in the order named, this sequence of operations is subject to considerable variation. Thus the strong alkaline steep of step 7 may precede step 6, or may be omitted altogether for the manufacture of paper, with resultant increase in yield. Again, the alkaline steep may be employed both before and after each bleach step, or may follow either the chlorination or rebleach steps. As hereinbefore pointed out, these stages of the process are of much less significance in producing high grade pulp than are the successive mild alkaline treatments and mechanical agitation

which immediately follow the treatment with nitric acid.

Highly successful results have been achieved by processing bagasse in the manner now briefly outlined and given by way of example.

Year-old Louisiana bagasse is washed and slightly disintegrated in a beater. The washed bagasse is then cooked in 2% nitric acid at 9:1 ratio at 95° C. for one hour. The material is washed, and then cooked in 2% sodium hydroxide at 9:1 ratio at 95° C. for one hour. The fiber is then disintegrated by mechanical agitation, washed, and again cooked in sodium hydroxide under the same conditions. After washing, further mechanical disintegration, and screening, the pulp is steeped in 9% sodium hydroxide at a ratio of 4.5:1 at 20° C. for one hour. The pulp is washed, bleached with chlorine solution at 9:1 ratio and under acid conditions, and again steeped for two hours in 9% sodium hydroxide at 20° C. Following further washing and rebleaching with a hypochlorite solution with excess alkalinity, the pulp is soured, washed, formed into sheets, and air-dried to 7% moisture.

When only one caustic steep is employed in the foregoing example, the chlorine bleaching and the succeeding operations are conducted immediately following the step of screening.

It will be observed that each reaction step may be carried out by simple immersion of the solid material in the treating solution, and that elevated pressures are not required. Thus the method lends itself readily either to continuous, semi-continuous, or batch processing with unusual economy.

Sheet pulp produced by our process is somewhat more dense than standard cotton linters pulp, and while not like board, is somewhat stiffer than cotton linters pulp. It swells considerably more than cotton linters pulp during steeping for viscose. The alpha cellulose content is high, often exceeding 96.5%. Filtration of viscose prepared from the pulp is reasonably good, and far exceeds that of pulp liberated from bagasse by prior methods.

The pulp from bagasse may be used in blends of pulps for various purposes. For example, in banknote paper and bond paper it improves the "rattle": it will increase the weight of board; and will also add opacity to a sheet, since the fibers are so fine. The alpha cellulose will depend on the exact process used, which will depend in turn on the end use for which the pulp is intended.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. A process for liberating and purifying fibers from bagasse which consists in immersing the bagasse, prior to alkaline treatment thereof, in dilute nitric acid solution having a concentration of about 2% at elevated temperature between 80° C. and 110° C. for a period of about one hour, removing the acid solution and washing the bagasse, thereafter immersing the bagasse in dilute sodium hydroxide solution having a concentration of about 1% to 3% at about 95° C. for a period of about one hour to reduce the size of fiber bundles and form a pulp, mechanically and violently agitating the pulp before washing to break up the fiber bundles, thereafter

washing the pulp, again immersing the pulp in dilute sodium hydroxide solution at about 95° C. for a period of about one hour, chlorinating the pulp to effect bleaching and removal of encrustants, steeping the pulp in the cold in 5% to 14% sodium hydroxide solution for a period of about one hour, and rebleaching the pulp in a hypochlorite solution with excess alkalinity.

2. A process for liberating and purifying fibers from bagasse which consists in immersing the bagasse, prior to alkaline treatment thereof in 2% nitric acid solution at about 95° C. for a period of about one hour, removing the acid solution and washing the bagasse, thereafter immersing the bagasse in 2% sodium hydroxide solution at about 95° C. for a period of about one hour to reduce the size of fiber bundles and form a pulp, mechanically and violently agitating the pulp before washing to break up the fiber bundles, thereafter washing the pulp, again immersing the pulp in 2% sodium hydroxide solution at about 95° C. for a period of about one hour, further mechanically agitating and washing the pulp, steeping the pulp in 9% sodium hydroxide solution without substantial heating, and thereafter bleaching the pulp.

3. A process for liberating and purifying fibers from bagasse which consists in immersing the bagasse, prior to alkaline treatment thereof, in 2% nitric acid solution at about 95° C. for a period of about one hour, removing the acid solution and washing the bagasse, thereafter immersing the bagasse in 2% sodium hydroxide solution at about 95° C. for a period of about one hour to reduce the size of fiber bundles and form a pulp, mechanically and violently agitating the pulp to break up the fiber bundles, again immersing the pulp in 2% sodium hydroxide solution at about 95° C. for a period of about one hour, further mechanically agitating and washing the pulp, and thereafter bleaching the pulp.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,690,954	Spencer	Nov. 6, 1928
1,829,852	Darling	Nov. 3, 1931
1,840,162	Heimann et al.	Jan. 5, 1932
1,987,195	Kipper	Jan. 8, 1935
2,013,042	Foster	Sept. 3, 1935
2,183,643	Dreyfus	Dec. 19, 1939
2,301,314	Montonna	Nov. 10, 1942

FOREIGN PATENTS

Number	Country	Date
14,988	Great Britain	of 1884

OTHER REFERENCES

- Industrial and Engineering Chemistry, vol. 30, pages 1192 and 1198 (1938).
- Industrial and Engineering Chemistry, November 1932, pages 1249 to 1254.
- Industrial and Engineering Chemistry, December 1934, pages 1339 to 1341.
- Paper World, April 1939, pages 41 to 48.
- Paper World, June 1939, pages 335 to 343.