

UNITED STATES PATENT OFFICE

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PULP REFINING PROCESS

No Drawing.

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In preparing refined cellulose pulps from what may be termed crude pulps, such as obtained from wood or other raw cellulosic material, it has been the practice to digest the pulp in solutions of comparatively strong alkalis, such as caustic soda, sodium sulphide, sodium carbonate, or the like, as such solutions are effective in extracting from the pulp its non-alpha cellulose components, including beta and gamma celluloses, oxycelluloses, ligneous matter, resins, etc.

I have discovered that water containing a volatile alkali, preferably ammonia, is an efficient pulp refining agent, more particularly at elevated temperatures, at which there is a strong tendency to expel the volatile alkali from solution. In fact, whereas ammoniated water is practically inert so far as concerns refining pulps at room temperature, I have found that it is highly active for this purpose at elevated temperatures, preferably above about 150° C. the activity of ammoniated water at such high temperatures is such that when crude pulps are digested therein for a comparatively short period of time, they undergo a marked increase in alpha cellulose content. The resulting refined product is useful as a raw material in making high grade papers and cellulose derivatives comparing favorably with those obtainable from new rags or cotton fiber.

In applying my discovery, it is necessary that the pulp used as a raw material and the ammoniated water with which it is treated be confined in a digester before heating, in order to permit the attainment of temperatures above atmospheric boiling, as well as to prevent the escape of ammonia into the atmosphere. The pulp may be in an unbleached, partially bleached, or completely bleached condition when it is subjected to the action of the ammoniated water, which may consist of a weak or strong ammoniacal liquor. The digesting operation may be carried out in a steel digester such as used in the so-called sulphate or soda processes of fiber liberation, but it should be of sufficient strength to withstand not only the vapor pressure of the water at the digesting temperature, but also that of the ammonia. In

order to avoid the generation of excessive pressures in the digester, particularly when using strong solutions of ammonia, the vapors present in the vapor space of the digester may be allowed to escape therefrom by providing the digester with a relief valve similar to that with which the usual acid sulphite digester is equipped. The vapors, including steam and ammonia, released from the digester, may be passed to a suitable recovery system, for instance, through a scrubbing tower in countercurrent contact with cold water, which serves to condense the steam and to absorb the ammonia, or into a refrigerating unit which serves to condense the steam and, if desired, to liquefy the ammonia. Even when a dilute ammoniacal solution is employed, it is desirable to relieve the digester after the completion of the refining operation, in order to recover the ammonia, but in such case, the digester need not be relieved until the refining operation has been completed. The ammonia recovered as an ammoniacal liquor or as gaseous or liquid ammonia may be employed in preparing the ammoniacal solutions for succeeding pulp refining operations.

The refined pulp associated with spent or residual liquor may be separated from the liquor as by straining and/or washing.

This separation of pulp from liquor may be accomplished before recovering the last or residual portion of ammonia in the liquor. Ammonia which has been partly fixed and which may be present in the form of complex organic compounds may not be liberated when relieving the digester in which the pulp and liquor is contained. This last portion of ammonia may be liberated and recovered in part by subjecting the separated spent liquor to a higher temperature than that to which it is desirable to subject the pulp undergoing refinement, thereby permitting greater leeway in the temperatures and pressures at which the refining operation in the digester is carried out. The separated spent liquor may be concentrated to higher solids content by evaporation before its subjection to the final high temperature to expel ammonia to be recovered therefrom. The separated liq-

uor containing a comparatively small amount of residual ammonia in the form of ammonium organic compounds, such as acetates or oxalates, may, on the other hand, be evaporated to dryness and the dried residuum used as a fertilizer, because of its fixed nitrogen content. If desired, however, the ammonium organic compounds present in the spent liquor may be decomposed as by the addition of caustic soda and the ammonia liberated thereby recovered for reuse. Or the ammonia may be liberated and recovered from the liquor by evaporating it to dryness and then heating the dried residuum to decompose the ammonium organic compounds, which undergo dry decomposition quite readily. The ammonia may further be recovered from the spent liquor in the form of sulphite liquors such as used in the production of sulphite pulps, for when treated with sulphur dioxide or other acid solutions, the ammonium organic compounds undergo metathesis to form ammonium sulphite or other salts with the precipitation of organic matter which may be removed from the solution as by settling and/or filtration. It is thus seen that the refining process of the present invention is further advantageous, in that it makes possible an easy recovery of the volatile refining agent for reuse in the repetition of the refining process. This is in marked contrast to what is called for in the case of involatile refining agents, such as caustic soda, which, when consumed by the refining reaction must be subjected to recovery operations, including smelting and causticization, which involve comparatively expensive apparatus and the consumption of lime.

A specific example of procedure falling within the purview of the present invention may be carried out substantially as follows. An unbleached sulphite pulp having an alpha cellulose content of 87% and a pentosan content of 3.9%, which represents a typical commercial raw sulphite pulp, may be used as a raw material. This pulp may be digested at a consistency of, say, 5% to 10%, in a 0.5% solution of ammonia at 200° C. for three hours under a maximum pressure not exceeding 200 pounds gauge. The resulting product, when washed, has an alpha cellulose content of 94.5% and a pentosan content of 1.7%; and its yield is 85%, based on the weight of dry pulp used as a raw material.

If the concentration of ammonia in the refining liquor is increased to, say 1%, the product and yield vary little from that described. This shows that it is unnecessary to use concentrated ammoniacal liquors for the refining operation. My theory is that the ammonia itself plays little direct part in bringing about the extraction or dissolution of the non-alpha cellulose components from the pulp, but merely serves to neutralize pro-

gressively the organic acids formed by the hydrolysis of the non-alpha cellulose components effected by the highly heated water. This version seems to be borne out by the fact that the digestion of a raw pulp in highly heated water alone is accompanied by a marked elimination of pentosans and loss of raw material, even though the resulting product is injured physically and is not of high alpha cellulose content, doubtless because of the hydrolyzing effect of the organic acid reaction products on the alpha cellulose content of the pulp. The ammonia evidently checks hydrolysis of the alpha cellulose content of the pulp by neutralizing the organic acid reaction products progressively as they are formed, thereby rendering the refining reaction selective or preferential upon the more easily hydrolyzable non-alpha cellulose components of the pulp.

The refined pulp produced by the process hereinbefore described is bleachable to whiteness with a smaller consumption of bleaching agent, such as hypochlorite, than that necessary when the raw pulp is bleached directly to a similar degree of whiteness. As already indicated, the raw pulp may be partially or completely bleached before the refining operation, in which case the refined product consumes even less bleach in being brought to pure whiteness than a stock which has not been subjected to preliminary bleaching. A low bleach usage in the final bleaching step is desirable in that the refined pulp suffers little if any, degradation into oxycelluloses, particularly when free alkali is present in the bleach liquor throughout the final bleaching operation. The initial bleaching of the stock may be advantageously effected with chlorine water, although hypochlorite bleach liquor may also be used for this purpose. In the case of a raw sulphite pulp, a partial bleaching may be accomplished with chlorine water containing, say, about 3% chlorine, based on the dry weight of pulp, or with bleach liquor containing, say, about 3% to 5% hypochlorite bleach, based on the dry weight of pulp.

If desired, ammonium salts and substitution ammonia products, such as ammonium sulphide, ammonium carbonate or the amines and hydroxylamines, may be used in place of part or all the ammonia in the ammoniacal refining liquor. I have found that such salts function more or less as does ammonia, perhaps because under the high temperature conditions employed, the salts are decomposed considerably and furnish ammonia, which may be recovered as previously described during and/or after the refining reaction. There appears to be some advantage in using ammonium sulphide in lieu of ammonia, for the reason that ammonium sulphide is more reactive upon the ligneous content of the pulp, and accordingly tends to

produce a more easily bleachable refined product. By the expression "ammoniacal liquor" or "ammoniated water," as used in this specification and claims, I mean to include not only solutions of ammonia, but also
5 of ammonium salts and substitution ammonia products, which behave more or less like ammonia in promoting a refinement or purification of pulp, particularly at elevated temperature conditions, as hereinbefore described. When volatile alkalies other than
10 ammonia, such as the amines, are employed, the digesting operation is carried out with the pulp suspension in the refining liquor confined in the digester and with the recovery of the volatile alkali during or after the operation.

In some cases, the pulp may initially be treated with a concentrated solution of ammonia at relatively low temperatures and then to bring the suspension of pulp in the solution to a much higher temperature while releasing and recovering most of the ammonia from the solution as the temperature
25 is raised. For instance, the treatment of the suspension may commence at as low as room temperature or even lower with a solution containing as much as 20% to 30% or more ammonia. This procedure tends to
30 produce a very soft and fluffy fiber because of the action of the strong ammonia liquor at low temperatures.

I claim:

1. A process which comprises digesting a
35 suspension of pre-liberated wood pulp in ammoniated water at elevated temperature until said pulp acquires a high alpha cellulose content.

2. A process which comprises digesting a
40 suspension of pre-liberated, chemical wood pulp in an ammoniacal solution under confinement at elevated temperature until such pulp acquires a high alpha cellulose content.

3. A process which comprises digesting a
45 suspension of pre-liberated sulphite pulp in an ammoniacal solution under confinement at a temperature above about 150° C. until such pulp acquires an alpha cellulose content of at least about 94.5%.

50 4. A process of refining pre-liberated cellulose pulp to high alpha cellulose content, which comprises digesting a suspension of such pulp in an aqueous liquor containing a volatile alkali at temperatures above 150°
55 C. until such pulp acquires an alpha cellulose content of at least about 94.5%.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.