

UNITED STATES PATENT OFFICE.

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PROCESS OF MANUFACTURING PAPER-PULP.

1,244,525.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, TSUNEYA MARUSAWA, a subject of Japan, residing at #10 Tenjin Cho, city of Fukuoka, Japan, have invented
5 new and useful Improvements in Processes of Manufacturing Paper-Pulp, of which the following is a specification.

This invention relates to improvements in process for manufacturing pulp, and consists first in cooking wood, bamboo, or any other fibrous material in a closed digester with a solution of ammonium bisulfite, or of a mixture of ammonium bisulfite, with either sulfurous acid or a soluble sulfite, thus
15 isolating fibers; and then in recovering sulfurous acid and ammonia for re-use from the exit gas of the digester and waste liquor, at the same time rendering the latter harmless. The object of this invention is to cook
20 fibrous raw material in a very short time, to obtain paper pulp of specially good qualities with high yield, and to lengthen the life of the digester.

According to my invention, one of the following three different liquors is used:—
1,— aqueous solution of ammonium bisulfite (NH_4HSO_3); 2,— mixed solution of ammonium bisulfite and sulfurous acid; and
3,— mixed solution of ammonium bisulfite and a soluble sulfite such as sulfite of ammonium, potassium, sodium, magnesium or the like. In all the cases the chief constituent of the above mentioned cooking liquors is ammonium bisulfite, which abundantly produces bisulfite ion (HSO_3'), a most powerful agent for dissolving out non-fibrous matters. The object of adding either sulfurous acid or a bisulfite is to regulate the concentration of hydrogen ion (H'), because hydrogen ion in excess is injurious, while its insufficiency will necessitate a long time of boiling and lowers the purity of the pulp. The total acidity of liquors used in my process varies between 0.4 and 0.8
45 normal, and the required concentration of hydrogen ion can be easily obtained by adding a suitable proportion of either sulfurous acid or a soluble sulfite to ammonium bisulfite solution, as will be fully explained
50 later on.

Hitherto a mixed solution of calcium bisulfite and sulfurous acid is most commonly employed for pulp manufacturing, but this liquor has several disadvantages.
55 When it is heated in a digester, according

as the temperature rises calcium sulfite or calcium sulfate deposits on the surface of the material, and consequently the cooking liquor cannot penetrate uniformly into the material, the inevitable result of which being
60 uneven cooking. Moreover, the cooking liquor gradually decomposing, the concentration of hydrogen ion becomes very great, which acting upon fibers makes them brittle, at the same time decreasing the percentage
65 of the yield of pulp. In order to remove these drawbacks as far as possible, the cooking is done at present, not with a high temperature which can be used in my process, but with a low temperature slowly and for a
70 long time.

Now, the liquors used in my process are very stable and produce no precipitates, even at very high temperature; and as the cooking can thus be effected very rapidly,
75 a greater amount of pulp with better qualities and high yield can be turned out with my process than with the process hitherto generally used. Moreover, according to my process pulp of various qualities can be
80 manufactured by simply varying the composition of the cooking liquor. Even the "kraft" pulp which has been considered impossible to manufacture by the bisulfite process hitherto in use, can easily be manufactured
85 with my process.

It has been proposed to use a cooking liquor having sulfite of soda (Na_2SO_3), or sulfite of ammonium, (NH_4) $_2\text{SO}_3$, as its chief constituent. But a solution of a sulfite has
90 only a very weak power to dissolve out non-cellulose matters. And as a solution of this kind produces by hydrolysis bisulfite ion and hydroxyl ion (OH') the latter causes the solution to become alkaline for want of
95 hydrogen ion. Moreover the concentration of bisulfite ion being very small, unless the wood or any other material be boiled for a long time at a high temperature, it is very
100 difficult in practice to decompose the structure thereof and to isolate the fiber. This process is, therefore, not efficient as an industrial process. Now, the cooking liquors used in my process are, as has been stated,
105 not only rich in bisulfite ion but also contain a suitable concentration of hydrogen ion. Consequently, they are very effective in dissolving out non-cellulose matters; and with them the cooking can be effected in a very short time. Thus my process is quite
110

different from the sulfite process mentioned above. Moreover, according to my process, the concentration of hydrogen ion never reaches during the cooking process beyond a required degree, nor is there any danger of making the fiber brittle or of corroding the material, as a bisulfite of calcium or any other alkali earth or metal does.

My invention is carried into effect as follows:—

According to my invention, (1) solution of bisulfite of ammonium is prepared by causing sulfur dioxide gas to be absorbed in a solution of bisulfite of ammonium, or in a solution of ammonia, or sulfite or carbonate of ammonium; (2) mixed solution of bisulfite of ammonium and sulfurous acid, either by passing a further quantity of sulfur dioxide through ammonium bisulfite solution prepared as described in (1), or by causing chemical reaction to take place by adding thereto a calculated quantity of a strong acid, such as hydrochloric or sulfuric acid; and (3) mixed solution of ammonium bisulfite and a soluble sulfite of various bases, by causing a suitable amount of sulfur dioxide gas to be absorbed in an aqueous solution of any of such various bases or its sulfite or carbonate, or by adding to a solution of ammonium bisulfite any of such bases or its sulfite or carbonate. In every case the acidity of liquors must not be less than about 0.4 normal.

The cooking operation in my process may be described as follows:—First, charge the digester, tightly closed, with the material previously cut into chips and add thereto the cooking liquor about 4 to 5 times by weight of the material, and then, heat them either by direct or by indirect steaming. The strength of the cooking liquor used differs according to the quantity of non-cellulose matters contained in the material, but the sulfur dioxide contained therein ranges between 2.5 and 5 per cent. The rate of composition of the cooking liquor greatly differs, as will be described later on, according to the kind and quality of the pulp to be manufactured. With regard to heating, however, it consists in every case of two stages: viz. "preliminary heating" and "final heating." During the preliminary heating, the temperature within the digester is maintained for two or three hours at 110° C., and during this time the cooking liquor is made to penetrate into the material fully and uniformly, thus uneven cooking, or so-called over-boiling, being most effectively avoided. Then the temperature is gradually raised until the required maximum degree is attained, and then the contents of the digester are subjected to the final heating for a required time. The temperature and duration of the final heating vary according to the kind and quality of the pulp

to be manufactured and the rate of composition of the cooking liquor used. In order to make my invention clearly understood, I give here a few examples.

Example 1: To manufacture a strong pulp which is faintly colored but can be used in unbleached condition for manufacturing most kinds of paper, ammonium bisulfite solution which contains free hydrogen ion at a rate of about 1/1000 mol. in 1 liter of the liquor at ordinary temperature. After the preliminary heating of about two hours, the temperature is raised and the charge is subjected to the final heating for a required time. The temperature of the final heating should never exceed 170° C., and below this limit, the higher the temperature is, the shorter time it takes to effect cooking. Thus at 140° C., it takes about 7 hours; at 150° C., about 3 to 4 hours; at 160° C., about 2 hours; and at 170° C., about one hour, to effect cooking. Several temperatures are given here in order to show that any temperature below 170° C. can be used and the same object can be attained, provided that the boiling is continued for the time corresponding to the temperature used. A temperature should thus be chosen taking into consideration the strength of the digester, the pressure of steam available, and such other circumstances.

The paper pulp thus obtained is faintly colored, very strong and contains over 90% of pure cellulose, with a very high yield. It may be used for manufacture of most kinds of paper.

Example 2: To manufacture easily bleachable pulp of a very superior quality, a mixed solution of ammonium bisulfite and sulfurous acid is used. The suitable proportions of ammonium bisulfite to sulfurous acid in this mixture are 1.5 to 3 mols. of the former to 1 mol. of the latter, although in some cases the proportion of ammonium bisulfite is to be made greater than 3 mols.; and the free hydrogen ion in 1 liter of the solution should be not more than 2/100 mols. at ordinary temperatures. After the preliminary heating of from 2 to 3 hours at the temperature of 110° C., the temperature is raised and the charge is subjected to the final heating at a temperature in this case not higher than 160° C. As in Example 1 the time required for cooking varies with the intensity of temperature used, but in this case it can generally be shortened from 30 minutes to 1 hour compared with the time required in Example 1. This time required for cooking may also be shortened even when the total quantity of sulfurous acid in the liquor is the same, by increasing the rate of free sulfurous acid gas in the cooking liquor. However, when using this kind of cooking liquor containing sulfurous acid in excess, not only is it difficult

to raise the temperature of the fluid to a high degree by direct steaming, but self-decomposition of sulfurous acid which takes place at a high temperature, has very injurious effects. The use of liquor containing sulfurous acid in excess is therefore disadvantageous. When the material is wood, the cooking liquor to be used should contain sulfurous acid and ammonium bisulfite at a rate of 1 mol. of the former to 3 mols. of the latter (the rate of total sulfurous acid being about 3.5% in the form of sulfur dioxide); and when the material is subjected to the final heating for two hours and a half, the cooking will be completed. The pulp obtained by this process is a little inferior in the yield to pulp obtained by the process described in Example 1, but it is almost pure white, contains over 97% of pure cellulose, is very easily bleachable, and is suitable for manufacture of paper of very superior quality.

Example 3: To manufacture "kraft" pulp, which is best adapted as material for making wrapping paper, a mixture of ammonium bisulfite and a soluble sulfite is used. The proportions of these two ingredients differ more or less according to the kind of the material to be cooked, but the one considered best is 1 mol. of the former to not more than 0.3 mols. of the latter. The amount of free hydrogen ion should not be less than 1/100,000 mols. at ordinary temperature in one liter. In this case the material should be subjected to the preliminary heating for about two hours. Then the temperature is gradually raised until it reaches to 180° C., which should be maintained for a required length of time. The duration of the final heating varies according to the intensity of temperature used, just as in the cases of Examples 1 and 2, but generally speaking in the case of the Example 3, a somewhat longer time is required for the final heating to effect cooking. For instance, when to cook common wood with the liquor which contains ammonium bisulfite and a sulfite at a rate of 1 mol. of the former to 0.2 mols. of the latter (the total sulfurous acid, about 4% as sulfur dioxide), it takes about six hours at 150° C., and about 2 hours at 160° C., of the final heating to effect the cooking. The pulp manufactured according to Example 3 has special luster, is of beautiful yellowish color, and is very strong and tough, and its yield is very high, being about 60% of the raw material. It contains about 15% of non-cellulose matters, but part of these impuri-

ties serving as cementing agent of fibers, they make the finished paper more tough.

During the cooking or after the cooking is over, the gas contained in the tightly closed digester is made to escape, and sulfurous acid gas, or ammonia, contained therein according to the composition of the cooking liquor used, is recovered for re-use by any suitable means. The waste cooking liquor and the liquid in which the pulp has been washed are led into any suitable distilling apparatus, and by adding thereto caustic lime and heating same, ammonia is distilled for further use.

Having now particularly described my said invention, what I claim and desire to have protected by Letters Patent is as follows:

1. A process to manufacture paper pulp characterized by cooking vegetable fibrous materials with a solution of ammonium bisulfite, substantially as and for the purposes hereinbefore set forth.

2. A process to manufacture paper pulp characterized by cooking vegetable fibrous materials with a solution containing ammonium bisulfite and sulfurous acid, the acidity of which being from 0.4 to 0.8 normal, and the concentration of hydrogen ion of which being in ordinary temperature not more than 2/100 mols. in 1 liter of the liquor, substantially as and for the purposes hereinbefore set forth.

3. A process to manufacture paper pulp characterized by cooking vegetable fibrous materials with a solution containing ammonium bisulfite and a soluble sulfite, the acidity of which being 0.4 to 0.8 normal, and the concentration of hydrogen ion of which being in ordinary temperature not less than 1/100,000 mols. in 1 liter of the liquor, substantially as and for the purposes hereinbefore set forth.

4. A process of manufacturing paper pulp characterized by the use as cooking liquor ammonium bisulfite or its mixture with sulfurous acid or a soluble sulfite, maintaining acidity of from 0.4 to 0.8 normal and effecting the cooking by the two stages of preliminary heating and final heating, substantially as and for the purposes hereinbefore set forth.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

TSUNEYA MARUSAWA.

Witnesses:

YOSHIKA IKEDA,
H. F. HAWLEY.