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## PULPING PROCESS

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This invention relates to an improved process for pulping lignocellulosic material such as wood.

Conventional pulping processes utilize inorganic agents such as sulphites, sulphides or alkalis. Organic pulping agents may be expected to attack the lignin fraction of wood with a degree of specificity not attainable with the usual inorganic pulping chemicals. However, an entirely satisfactory organic pulping agent has not previously been proposed.

The object of this invention is to provide a pulping process utilizing an organic pulping agent of improved effectiveness.

The foregoing is achieved in accordance with this invention by treating lignocellulosic material at an elevated temperature with an aqueous solution comprising dimethyl sulphoxide in a concentration of at least 75% by weight in the presence of an acid catalyst substantially to delignify the lignocellulosic material.

It has now been established that dimethyl sulphoxide is an effective delignifying agent both when used to treat a partially sulphonated pulp of lignocellulosic material and when used in the treatment of comminuted lignocellulosic material such as wood chips and wood shavings.

The results of a series of experiments carried out to study the effect of dimethyl sulphoxide on a partially sulphonated pulp are reproduced in Table 1. The pulp chosen was a high yield (87% yield) sodium-base sulphite pulp. The composition of the cooking liquor was 1.24% by weight free sulphur dioxide, 1.24% by weight combined sulphur dioxide and the cooking schedule was one hour during which the temperature was raised to 155° C. followed by half an hour at 155° C. A high yield pulp was used in preference to conventional low yield pulps as the latter have most of the lignin extracted. However, it would be appreciated that it is contemplated as being within the scope of this invention to treat low yield pulps for additional delignification of the latter pulps. The experiments upon which Table 1 is based were conducted in open beakers with manual stirring

Table 1

| Test No. | Raw Material                            | Treatment                                                           | K No. | Percent Klason Lignin |
|----------|-----------------------------------------|---------------------------------------------------------------------|-------|-----------------------|
| 1.....   | A high-yield (87% yield) sulphite pulp. | None.....                                                           | 67    | 24.6                  |
| 2.....   | do.....                                 | DMSO + 0.2% HCl for 3½ hrs. at 170°-175° C.                         | 19    | 1.8                   |
| 3.....   | do.....                                 | DMSO + 0.2% HCl for 3½ hrs. at 150°-160° C.                         | 13.8  | 2.6                   |
| 4.....   | do.....                                 | 0.2% HCl (without DMSO) for 3½ hrs. at the boiling temp. of 100° C. | 62    | 24.3                  |
| 5.....   | do.....                                 | DMSO for 3½ hrs. at 170°-175° C. without the acid or catalyst.      | 70    | 23.3                  |

The liquor/pulp ratio was 10:1. The percentage of the mineral acid refers to solution concentration.

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using substantially pure dimethyl sulphoxide (having a concentration in excess of 95%). The liquor/pulp ratio was 10:1 since in the absence of a digester equipped with forced circulation this high liquor ratio was necessary to keep the pulp properly wetted with dimethyl sulphoxide.

It will be apparent from Table 1 that dimethyl sulphoxide when used in a high concentration and in the presence of small amount of hydrogen ions substantially delignifies the pulp.

The results of experiments conducted with wood chips and shavings are presented in Table 2. All of the tests referred to in this section were performed under reflux except for test number 6 in which the K number (permanganate number) and the Klason lignin were determined without any prior treatment and test number 7 which was performed in an open beaker. The liquor/wood ratio (i.e. the quantity of cooking liquor per unit weight of wood) was kept at 10:1.

Table 2

| Test No.   | Raw Material                       | Treatment                                                                                           | K No.                   | Percent Klason Lignin |
|------------|------------------------------------|-----------------------------------------------------------------------------------------------------|-------------------------|-----------------------|
| 25 6.....  | Black spruce wood.                 | None.....                                                                                           | 50                      | 29                    |
| 7.....     | Black spruce shavings.             | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 2½ hrs. at 150°-160° C.                            | 11.8                    | 3.6                   |
| 8.....     | do.....                            | 95% DMSO for 5 hrs. at 172°-174° C. without acid catalyst.                                          | No pulping accomplished | 2.2                   |
| 9.....     | The uncooked shavings from test 8. | Added H <sub>2</sub> SO <sub>4</sub> so as to have 0.2% H <sub>2</sub> SO <sub>4</sub> in solution. | 8.6                     |                       |
| 10.....    | Black spruce shavings.             | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 5 hrs. at 100° C., then 3 hrs. at 140° C.          | 25.3                    | 8.1                   |
| 35 11..... | Black spruce chips.                | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 5½ hrs. at 160° C.                                 | 21.2                    | 5.4                   |
| 12.....    | do.....                            | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 1½ hrs. at 130° C., then 6½ hrs. at 155° C.        | 3.9                     | 1.1                   |
| 13.....    | do.....                            | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 5½ hrs. at 165° C.                                 | 4.2                     | 2.0                   |
| 40 14..... | do.....                            | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 6½ hrs. at 160° C.                                 | 6.3                     | 2.0                   |
| 15.....    | Black spruce shavings.             | 75% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 13 hrs. at 126° C.                                 | 23.1                    | 8.1                   |
| 16.....    | do.....                            | 50% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 90 hrs. at 108° C.                                 | 45.5                    | 28.4                  |
| 17.....    | do.....                            | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 3½ hrs. at 165° C.                                 | 5.7                     | 3.1                   |
| 45 18..... | do.....                            | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 2½ hrs. at 165° C.                                 | 13.6                    | 3.9                   |
| 19.....    | do.....                            | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 1½ hrs. at 165° C.                                 | 30.7                    | 8.0                   |
| 20.....    | do.....                            | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 2 hrs. at 170° C.                                  | 8.0                     | 2.1                   |
| 50 21..... | do.....                            | 95% DMSO + 0.2% H <sub>2</sub> SO <sub>4</sub> ; 3 hrs. at 170° C.                                  | 4.1                     | 1.2                   |

The liquor/wood ratio was kept at 10:1.  
The percentage of the mineral acid refers to solution concentration.  
The yields were determined exactly for the last five cooks and they were (in order) 43%, 46%, 49%, 44%, and 40%.

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It will be noted that although good pulping and delignification was achieved with a high concentration of dimethyl sulphoxide and in the presence of an acid catalyst such as sulphuric acid, no pulping was accomplished even after five hours of cooking at 170°-174° C. in the absence of the acid catalyst. The shavings retained their original shape and could not be defibered in a Waring Blendor. However, when a small amount of sulphuric acid was added to the cook and the cooking continued for another four hours at 150°-160° C. the shavings were smoothly pulped and the pulp had a K number of 8.6 and a Klason lignin content of 2.2%. With high temperatures the rate of delignification is greater. With low temperatures longer cooking times are required for satisfactory delignification. Tests 15 and 16 show that for practical purposes a concentration of not less than 75% dimethyl sulphoxide should be used if the cooking is to be per-

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formed under normal atmospheric pressures. Cook 15 was performed with 75% dimethyl sulphoxide in water and cook 16 with 50% dimethyl sulphoxide in water. The cooking temperatures were 126° C. and 108° C. respectively, since these are the normal boiling points of 75% and 50% dimethyl sulphoxide in water and could not be raised without super-atmospheric pressures. Even with 75% dimethyl sulphoxide a cooking time of 13 hours was needed for reasonably good pulping. With 50% dimethyl sulphoxide practically no delignification was accomplished even after 90 hours.

The pulps, when given a washing with dimethyl sulphoxide prior to washing by water had a colour similar to that of sulphite pulps in the same yield range. However, if the washing with dimethyl sulphoxide was omitted, the ligneous material from the solvent still residing in the pulp was precipitated out on contact with water and absorbed on the fibres producing a dark-coloured pulp. The pulps had a low pentosan (furfural yielding components) content. The percentage of pentosan was determined for tests numbered 11 to 15 inclusive and 17 to 21 inclusive in Table 2 and the results were respectively 0.95, 1.2, 0.27, 0.65, and 3.26 for tests 11 to 15 inclusive and 0.29, 1.52, 1.75, 1.65, and 0.61 for test 17 to 21 inclusive. Three of the pulps, namely tests numbers 12, 13 and 14, were analysed for  $\alpha$ -cellulose (17.5% sodium hydroxide) and the  $\alpha$ -cellulose contents of the raw pulps were, in order, 94.6%, 91% and 91%. It appears that most of the hemicellulose fraction is removed by pulping with dimethyl sulphoxide.

Where the process is continued to the point of substantial completion, that is to say about 1% lignin, the pulp is a highly purified material which is higher in  $\alpha$ -cellulose and lower in pentosans than ordinary sulphite pulp of the same lignin content. There is no strong attachment of the pulping agent to the lignin or the cellulose and the pulps at any lignin content showed only traces of sulphur. In comparison, a high yield sulphite pulp obtained without using dimethyl sulphoxide has a sulphur content approaching 1% due to sulphonation of the lignin.

In addition to the delignification achieved with the use of dimethyl sulphoxide as exemplified by the tests reproduced in Tables 1 and 2, dimethyl sulphoxide has advantages in comparison with other organic pulping agents. In the first place dimethyl sulphoxide is completely indifferent to cellulose whereas this is not true of some of the organic pulping agents suggested in the literature such as, for example, chloro-substituted organic acids. Dimethyl sulphoxide also has a high boiling point (189° C.) which will permit a wide variation of cooking temperatures depending upon the composition of the pulp desired without it being necessary to use pressure vessels. An additional advantage is that dimethyl sulphoxide does not form an azeotrope with water and can, therefore, easily be recovered from the liquor by fractional distillation. This has been verified by distilling the spent liquor from one of the test cooks. The ligneous material can readily be precipitated from the spent cooking liquor by merely diluting with water. This together with the probability that the waste lignin is in a form which can more readily be utilized for other purposes gives rise to the possibility of the economical recovery of the lignin as a by-product.

The spent liquors from the dimethyl sulphoxide cooks were of a dark colour and possessed a peculiarly unpleasant odour. On dilution with water the ligneous material precipitated out of the spent liquor as a bulky brown precipitate. The yield of the precipitate which was obtained from Cook No. 21 (Table 2) was meas-

ured. The precipitate was washed with large amounts of warm water, dried at 50° C., and the moisture content was determined by drying a sample at 105° C. The yield (on a bone-dry basis) was 12.50 gm. from 50 gm. of B.D. wood. Assuming that black spruce contains about 27% lignin, it appears that over 90% of the "lignin" can be recovered from the dimethyl sulphoxide-spent liquors.

The ligneous material was insoluble in ether, benzene, and carbon tetrachloride; the first two solvents turned slightly yellowish, but no dissolution appeared to have taken place. The material was sparingly soluble in chloroform and ethanol; 100 ml. of the latter solvent, on vigorous shaking, dissolved only 0.6 gm. (out of 1 gm.) of the substance at room temperature. Acetone and ethylene glycol effected a complete solution, the rate of dissolution in the latter solvent being substantially lower than in the former. The solutions were of an intense brown colour. The substance was readily soluble in formamide and also in dioxane. The material could be precipitated in ether (as a flocculent brown precipitate) from the dioxane solution and this afforded a good method for its purification. The purified material was carbohydrate-free (Molisch reaction) and showed no sign of melting even at 200° C. The material was insoluble in sodium bicarbonate but was readily dissolved by 1% sodium hydroxide producing a bright yellow solution. This was an indication of the presence of one or more phenolic groups, as the substance contained no nitrogen which precluded the possibility of imides, nitro-compounds, etc. The usual qualitative tests for phenols were inconclusive, indicating the phenol was a complex one.

It was determined by qualitative ultraviolet absorption data on the alcoholic solution of the purified ligneous material, using the solvent as standard, that the alcoholic solution exhibited the characteristic lignin absorption maximum around 280 m $\mu$ . The ligneous material had a methoxyl content of 12.2%.

I claim:

1. A process for pulping lignocellulosic material comprising the step of treating said lignocellulosic material at an elevated temperature with an aqueous solution comprising dimethyl sulphoxide in a concentration of at least 75% by weight in the presence of an acid catalyst substantially to delignify said lignocellulosic material.
2. A process as in claim 1 in which said step is conducted at a temperature of between about 126° C. and about 175° C.
3. A process as in claim 1 in which said acid catalyst is selected from the group consisting of sulphuric acid and hydrochloric acid.
4. A process as in claim 1 in which the solution concentration of said acid catalyst is about 0.2%.
5. A process as in claim 1 in which said lignocellulosic material comprises comminuted wood.
6. A process as in claim 1 in which said lignocellulosic material comprises a partially sulphonated pulp.
7. A process for pulping lignocellulosic material comprising the step of treating said lignocellulosic material at an elevated temperature with an aqueous solution comprising dimethyl sulphoxide at a concentration sufficient to provide a substantial rate of delignification at the pressure and temperature at which said step is conducted, in the presence of a catalyst adapted to provide hydrogen ions in said aqueous solution.

References Cited in the file of this patent

- "Handbook of Chemistry and Physics," 32d edition, 70 Hodgman, page 998, June 20, 1951, Division 25.