ABSTRACT

Subjecting softwood chips to a mild digestion with sodium sulfite alone or sodium sulfite and a small amount of sulfur dioxide or mixtures of sodium sulfite with sodium carbonate, bicarbonate or hydroxide to obtain a Kappa number of not less than about 100, defiberizing the thus treated material, and then subjecting the defiberized material to a second digestion with an alkali in the presence of oxygen to obtain a pulp of Kappa number 20–50 for bleachable pulp or Kappa number of 70–130 for linerboard grade pulp.

9 Claims, No Drawings
1 TWO-STAGE SODIUM SULFITE-OXYGEN PULPING

This invention relates to the manufacture of pulp and particularly to a two-stage sulfite oxygen pulping process.

It has been well established that sodium hydroxide used in both kraft and alkaline sulfite pulping is responsible for the relatively low yields obtained by these two processes. Sodium sulfite used in kraft pulping causes air pollution with volatile sulfur compounds such as hydrogen sulfide and mercaptans. Alkaline sulfite pulping does not give this type of pollution due to the absence of sodium sulfite. These two known alkaline pulping processes give similar yields and strength properties at a given degree of pulping. A serious disadvantage of alkaline sulfite pulping is the very high chemical requirements compared to kraft pulping.

It has also been known for some time that lignocellulosic materials can be delignified by sodium hydroxide and an excess of oxygen under pressure. However, this pulping method suffers from penetration problems of wood chips and similar raw materials with oxygen, high alkali requirements, the need for high pressures and low product quality, i.e., similar to the acid sulfite process, and inferior to the kraft process. A more recent development in this area is oxygen bleaching, which applies alkali, oxygen and a catalyst, e.g., magnesium carbonate, for complete delignification of chemical pulps. It is stressed in patents and papers on oxygen bleaching that the catalyst must be used to reduce pulp degradation and retain product quality. Obviously, the use of a catalyst is an additional operating expense.

The main purpose of the present invention to provide a commercially acceptable alkaline pulping-type process which (a) gives superior yields and quality than kraft, alkaline sulfite or alkaline oxygen pulping (b) does not require a catalyst, and (c) does not create air pollution with volatile sulfur compounds.

With the process in accordance with this invention, alkaline sulfite pulps are obtained with extremely high yields and excellent quality when lignocellulosic material, such as wood chips, is subjected to a two-stage pulping process with the second stage being conducted in the presence of oxygen. The lignocellulosic material is first given a mild treatment under heat and pressure with sodium sulfite alone or with sodium sulfite plus sodium bicarbonate, carbonate or hydroxide, or sodium sulfite and sulfur dioxide.

The first stage digestion is carried out only to a point where it removes only some of the lignin and very little carbohydrate material compared to other pulping methods and is preferably conducted at a temperature in the range of from about 140°F to 190°F for about 15 to 150 minutes, and a sodium sulfite application of 8 to 18 percent by weight expressed as sodium oxide based on the dry weight of the lignocellulosic material. The optimum temperature of the first stage depends upon the raw material, the available reaction time, the chemical application, and the degree of pulping desired. This is well known in the art. This stage is preferably carried out at a pH value of 6 or higher. After completion of the first stage digestion, the free sulfite spent liquor is separated from the treated material and can be recycled and/or recovered for chemical regeneration.

This treated material obtained from the first stage digestion is defiberized, e.g. in a disc refiner, and is then further pulped with an alkali, such as sodium hydroxide, sodium carbonate, sodium bicarbonate or ammonia, and a large excess of oxygen under heat and pressure. It is preferable to use an alkali which is highly water soluble, because it will not lead to operating problems, such as the formation of precipitates and scales. This second stage digestion is preferably conducted at a temperature in the range of from about 95°F to 130°C for about 15 to 150 minutes, and an alkali application of 2 to 10 percent, e.g., sodium hydroxide expressed as sodium oxide based on the dry weight of the original lignocellulosic material. Oxygen is injected into the digester or any other suitable pressure reactor containing the material to be pulped as soon as the alkali is added at any convenient time during the pulping cycle. A partial oxygen pressure of 100 to 250 psig is desirable. The optimum temperature and oxygen pressure of the second stage depend on the available reaction time, quantity and concentration of alkali chosen, the degree of pulping by the first stage, and the desired lignin content of the final pulp.

The sodium sulfite is necessary in the first stage digestion, while the sodium bicarbonate, sodium carbonate, sodium hydroxide, or sulfur dioxide are used when necessary to control the pH value of this first stage in the customary manner.

The spent liquor from the second stage digestion can be recovered either together with the spent liquor from the first stage or separately in order to regenerate sodium hydroxide by well established methods.

With this process it has been found that excellent pulp yield and quality are obtained without the necessity of any catalyst or cellulose stabilizer in the second stage. It has also been found that both yield and quality are superior to those of the kraft, alkaline sulfite and alkaline oxygen pulping processes.

In addition to the above mentioned advantages, there is the very important advantage that the alkaline pulping method provided by the present invention does not cause air pollution with volatile sulfur compounds.

The present invention is illustrated by the following non-limitative examples:

EXAMPLE 1

Hemlock chips were pulped in a pressure reactor by the conventional kraft process under the following conditions:

16.3 percent active alkali based on dry wood, 20 percent sulfidity of white liquor, heating to 170°C in 105 minutes by circulating liquor through a heat exchanger, maintaining the temperature of 170°C for 120 minutes.

The following results were obtained:

Screened pulp yield, % on dry wood = 43.9
Screen rejects, % on dry wood = 0.6
Kappa number = 34.5
Unbeaten Pulp Properties:
Pulp Brightness = 23.8
Freeness, ml C.S. = 718
Mullen = 59
Breaking length, km = 4.7

EXAMPLE 2

The hemlock chips used for Example 1 were also pulped by the alkaline sulfite process under the following conditions:
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15 percent sodium sulfite expressed as Na₂O based on dry wood and 14 percent sodium hydroxide expressed as Na₂O based on dry wood, heating to 180°C in 105 minutes by circulating liquor through a heat exchanger, maintaining the temperature of 180°C for 120 minutes.

The following results were obtained:
- Screened pulp yield, % on dry wood = 43.1
- Screen rejects, % on dry wood = 1.5
- Kappa number = 39
- Unbeaten Pulp Properties:
  - Brightness = 29
  - Freeness, m. C.S. = 710
  - Mullen = 58
  - Breaking Length, km = 4.6

**EXAMPLE 3**

The hemlock chips used for Example 1 were also pulped by the prior two-stage soda oxygen process under the following conditions:
- 1st Stage: 13 percent sodium hydroxide as Na₂O based on wood, heating up to 170°C in 90 minutes, maintaining at 170°C for about 120 minutes.
- 2nd Stage: 4 percent sodium hydroxide as Na₂O based on wood, at 160 p.s.i.g. partial oxygen pressure, heating up to 115°C in 90 minutes, maintaining at 115°C for about 90 minutes.

The following results were obtained:
- Screened pulp yield, % on dry wood = 44.1
- Screen rejects, % on dry wood = 0.1
- Kappa number = 35
- Unbeaten Pulp Properties:
  - Brightness = 28.7
  - Freeness, mi C.S. = 717
  - Mullen = 58
  - Breaking Length, km = 4.5

**EXAMPLE 4**

The hemlock chips were pulped according to the process of this invention under the following time-temperature cycle:
- to 170°C in 105 minutes
- at 170°C for 120 minutes

The chemical applications are listed in the table below.

The alkali oxygen treatment was carried out under the following conditions:
- to 115°C in 85 minutes
- at 115°C for 90 minutes
  - partial oxygen pressure = 160 psig (at 20°C)

The alkali applications are listed in the table below.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Stage (alkaline sulfite) Chemicals, % on BD Wood</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₃ as Na₂O</td>
<td>16.0</td>
<td>16.0</td>
<td>12.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaHCO₃ as Na₂O</td>
<td>0</td>
<td>0</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulp Yield, % on BD Wood</td>
<td>72.8</td>
<td>79.7</td>
<td>75.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kappa No.</td>
<td>141</td>
<td>147</td>
<td>146</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*175°C maximum temperature 2nd Stage (Oxygen alkali)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH as Na₂O, % on BD Wood</td>
<td>7.9</td>
<td>10.1</td>
<td>9.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Results:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kappa No.</td>
<td>34.5</td>
<td>41</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulp Yield, % on BD Wood</td>
<td>50.7</td>
<td>54.3</td>
<td>52.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brightness</td>
<td>37.2</td>
<td>36.5</td>
<td>36.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freeness, m. C.S.</td>
<td>685</td>
<td>675</td>
<td>679</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mullen</td>
<td>125</td>
<td>113</td>
<td>125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Breaking Length, km</td>
<td>8.8</td>
<td>8.1</td>
<td>8.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A comparison of these results with the data given in Examples 1, 2 and 3 shows clearly that at a comparable lignin content, the present two-stage process gives 6.0 to 10 percent higher yields of bleachable pulps with 8 to 10 points higher brightness and double the mullen and breaking length of conventional kraft, alkaline sulfite and alkaline oxygen pulps without beating. It is surprising that the pulps resulting from this process give these high pulp yields despite the strongly alkaline conditions in the oxygen pulping stage and without the use of a catalyst.

**EXAMPLE 5**

The hemlock chips were pulped by the conventional kraft process under the following conditions to prepare linerboard pulps:
- 15 percent active alkali based on dry wood, 20 percent sulfidity of white liquor, the same time-temperature cycle as described in Example 1.

The following results were obtained:
- Total pulp yield, % on BD Wood = 50.9
- Kappa No. = 87
- Brightness = 16.4

In the laboratory, 26 lb. duplex linerboard handsheets were also prepared and these had the following properties:
- Mullen = 85
- Ring Crush = 58
- Breaking Length, km = 8.2
- Brightness = 15.2

**EXAMPLE 6**

The hemlock chips used for example 5 were also pulped by the present two-stage alkaline sulfite oxygen process under the time-temperature cycle described in Example 4. The chemical applications and results were as follows:

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Stage Chemicals, % on BD Wood Na₂SO₃ as Na₂O</td>
<td>11.0</td>
<td>10.0</td>
<td>11.0</td>
<td>11.0</td>
</tr>
<tr>
<td>NaHCO₃ as Na₂O</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Na₂CO₃ as Na₂O</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>NaOH as Na₂O</td>
<td>11.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Total pulp yield, % on BD Wood</td>
<td>80.7</td>
<td>78.9</td>
<td>78.1</td>
<td>71.7</td>
</tr>
<tr>
<td>Pulp Yield, % on BD Wood</td>
<td>80.7</td>
<td>78.9</td>
<td>78.1</td>
<td>71.7</td>
</tr>
<tr>
<td>Kappa No.</td>
<td>142</td>
<td>151</td>
<td>150</td>
<td>155</td>
</tr>
<tr>
<td>Brightness</td>
<td>169</td>
<td>169</td>
<td>169</td>
<td>169</td>
</tr>
</tbody>
</table>

A comparison of these results with those given in Example 5 show clearly that, at a given lignin content, those two-stage pulps were obtained with up to 13 percent higher yields based on wood and significantly higher strength properties and brightness of duplex linerboards than the comparable conventional kraft pulp.

It is unexpected that despite the significant lignin removal (from 22.5 percent to 12.7 percent lignin in the
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pulps) in the alkaline oxygen stage, the pulp yields and properties were considerably superior to those of a comparable kraft pulp.

EXAMPLE 7

Hemlock chips were pulped by the present process to Kappa numbers of 94 to 107 under the following conditions:

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Stage*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH as NaO, % on BD Wood</td>
<td>16.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Pulp Yield, % on BD Wood</td>
<td>78.9</td>
<td>78.9</td>
</tr>
<tr>
<td>Kappa No.</td>
<td>151</td>
<td>151</td>
</tr>
</tbody>
</table>

| 2nd Stage*     |   |   |
| NaOH as NaO, % on BD Wood | 4.2 | 2.8 |

*Time-temperature cycles and oxygen pressures were identical with those given in Example 4.

A comparison of these data with the results reported in Example 5 show clearly that up to 18.5 percent higher pulp yields based on wood and significantly better linerboard properties were obtained by the two-stage alkaline sulfite oxygen process than by kraft pulp-
ing to a lower Kappa number (85 vs 94 and 107). These conclusions are entirely unexpected because, normally, pulping to higher Kappa numbers in the range covered has adverse effects on pulp quality, especially mullen, breaking length and brightness. It can probably also be concluded that, in the oxygen pulping stage, the ligno-sulfonates, which are formed in the alkaline sulfite stage and remain in the pulp, are changed chemically and thus contribute to the improved pulp properties at these very high yield increases. This is an entirely new way of utilizing chemically modified lignin in high yield pulps. Obviously, the benefits of this new principle are two fold: (a) increased pulp yield, and (b) increased pulp quality.

A major difference between the second stage of this novel process and oxygen bleaching is that, in the latter method, pulps are delignified completely whereas in the present process the pulp is only partially delignified and lignin is modified chemically to make it respond more favorably to subsequent papermaking.

Hemlock chips were used in the above tests, but the same tests were made with other wood species; such as Western red cedar and Douglas fir, and similar results were obtained.

With the process of this invention the lignocellulosic material can be pulped in the first stage of digestion to Kappa numbers 100 to 200, and in the second stage of digestion to Kappa numbers 20 to 50 for bleachable pulps. The linerboard grade pulps can in the second stage of digestion by pulped to Kappa numbers 70 to 130.

We claim:

1. An alkaline pulping process which comprises subjecting softwood chips to a first mild digestion with soda-
mium sulfite alone or sodium sulfite in combination with one or more chemical compounds selected from the group consisting of sulfur dioxide, sodium bicar-
bonate, sodium carbonate, and sodium hydroxide, under conditions of temperature, pressure and time to produce pulp with high residual lignin content while re-
moving little carbohydrate material, the pulp so pro-
duced having Kappa number of not less than about 100, defiber the thus treated material, and then sub-
jecting the defibered material to a second digestion with an alkali in the presence of an excess of oxygen under conditions of temperature, pressure and time to produce a high yield and quality pulp of Kappa number 20–50 for bleachable pulp or Kappa number 70–130 for linerboard grade pulp.

2. A process as claimed in claim 1 wherein the alkali used in the second digestion is selected from the group consisting of sodium bicarbonate, sodium carbonate and ammonia.

3. A process according to claim 1 wherein the first digestion is conducted at a temperature in the range of 140° to 190°C.

4. A process according to claim 1 wherein the Kappa number of softwood pulp from the first digestion is from about 100 to about 200.

5. A process according to claim 1 wherein the pulp from the second digestion is bleachable pulp.

6. A process according to claim 1 wherein the pulp from the second digestion is linerboard grade pulp.

7. A process according to claim 1 wherein the sodium sulfite or sodium sulfite in combination with the selected chemical compound in the first digestion is from 8 to 18 percent by weight based on the dry weight of the cellulose material.

8. A process according to claim 1 wherein the second digestion is carried on at a temperature of from about 95° to 130°C for from about 15 to 150 minutes at a pressure from about 100 to 250 p.s.i.g.

9. A process according to claim 1 wherein the alkali in the second digestion is from about 2 to 10 percent by weight based on the dry weight of the original ligno-
cellulosic material.