CONTINUOUS ACIDULATION AND COAGULATION OF LIGNIN IN BLACK LIQUOR

FIG. 1.

FIG. 2.

INVENTORS
FRANK J. BALL
WILLIAM G. VARDELL

ATTORNEYS.
Our present invention relates to improved processes of lignin recovery from black liquors by precipitation and coagulation of the sodium lignate content therein. It is well-known that when wood is cooked by the alkaline process—whether soda or kraft—the lignin present in the wood is dissolved in the alkaline liquor as sodium lignate. In the paper industry this liquor after completion of the cook is termed black liquor. To recover the sodium lignate therefrom, black liquor containing the sodium lignate, is usually treated with sulfuric acid. However in some instances, it has been found possible to use concentrated sulfuric acid, i.e., 60% Bé, as the neutralizing agent. Heretofore it was thought impracticable to use sulfuric acid of this concentration for the reason that local concentrations of the strong acid would give rise to release of acid gases such as carbon dioxide and hydrogen sulfide, foaming difficulties, etc. Furthermore, advantage is taken of the fact that handling of strong acid involves less of a corrosion problem than does that of a weak acid.

A still further and important advantage of the improved process lies in the fact that it enables one to use black liquor of a higher concentration than heretofore.

Lignin yields from black liquors acidulated to the same pH value, increase steadily as the solids concentration of the black liquor increases. At pH 9.7, for example, the yield of sodium lignate (the precipitated lignate salt after the occluded materials have been removed) was found to increase on the order from 200 to over 320 pounds per 1000 pounds of black liquor solids corresponding to an increase from about 55 to about 85 percent of the available sodium lignate in the liquor as the liquor concentration was increased from 25 percent to 50 percent solids. This is shown graphically in FIGURE 2. Unfortunately, in commercial production a disadvantage of using the higher solids black liquor appeared to be insurmountable. When black liquor of a solids content substantially in excess of 30% is acidified at below coagulation temperatures, the solution becomes so viscous that it cannot be handled in the ordinary paper plant operations. However, with acidification and simultaneous coagulation at the higher temperatures used, there is no difficulty in handling the resulting coagulated lignate.

Black liquor acidulated at the coagulation temperature does not completely coagulate instantaneously, such coagulation taking place however in a matter of seconds thereafter. Preferably, therefore, the liquor acidulated at temperatures around 180° F. and above will be held at that temperature for a brief interval on the order of from 20 to 30 seconds before cooling. However, the process is operative even though no conscious effort is made to hold the liquor acidulated at 180° F. or above for the reason that the liquor begins to coagulate in an instantaneous, whereby time is afforded for the necessary coagulation. However, better results are to be had if the liquor immediately following acidulation, is held for a few seconds, say 20 to 30, before cooling.

When the liquor is acidulated to pH 9 not lower than say 10.3, the coagulation proceeds with greater difficulty, leading to greater difficulty in filtration and in washing the filter cake.

Our invention will be best understood by reference to the following specific examples, and to the annexed drawing in which

FIGURE 1 illustrates diagrammatically apparatus suitable for carrying out such examples, and

FIGURE 2 consists of a graph showing the yield of sodium lignate with concentration of black liquor started with.

EXAMPLE 1

Skimmed black liquor from the kraft cooking of pine wood taken from the evaporator (not shown) at a solids content of 25% is contained in the tank 10 and is continuously pumped theretofrom by means of pump 11, through heater 12 in which its temperature is raised to that desired for coagulation; thence it passes to mixer 13. Immediately before it reaches said mixer it meets sulfuric acid, preferably of 60° Bé from tank 14. From tank 14 the sulfuric acid passes through pipe 15, regulating valve 16 to inlet 16a of said mixer 13. In mixer 13, it is thoroughly mixed with the heated liquor. Thence the mixture passes to dwell tank 17, wherein
time is allowed for complete coagulation. To be able to vary the interval that the liquor is held in said tank, a series of valved outlets 17a, 17b, 17c, etc. of varying height are provided. From tank 17, the coagulated liquor passes through cooler 18, and thence to the filter 19, preferably of a continuous type, the mother liquor being collected in tank 20, and the lignate in container 21.

The following runs were made:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>205</td>
<td>9.7</td>
<td>0</td>
<td>135</td>
<td>15</td>
<td>45</td>
<td>29.4</td>
</tr>
<tr>
<td>2</td>
<td>205</td>
<td>9.4</td>
<td>1</td>
<td>130</td>
<td>15</td>
<td>45</td>
<td>26.4</td>
</tr>
<tr>
<td>3</td>
<td>205</td>
<td>9.7</td>
<td>2</td>
<td>135</td>
<td>15</td>
<td>45</td>
<td>26.8</td>
</tr>
<tr>
<td>4</td>
<td>224</td>
<td>9.9</td>
<td>3</td>
<td>135</td>
<td>15</td>
<td>45</td>
<td>26.7</td>
</tr>
<tr>
<td>5</td>
<td>224</td>
<td>9.7</td>
<td>3</td>
<td>135</td>
<td>15</td>
<td>45</td>
<td>26.2</td>
</tr>
<tr>
<td>6</td>
<td>224</td>
<td>9.5</td>
<td>10</td>
<td>135</td>
<td>15</td>
<td>45</td>
<td>26.0</td>
</tr>
</tbody>
</table>

The foregoing table, amongst other things, indicates in the columns headed "Filter Temperatures" and "Filter Time," the effect of the dwell of the liquor in the tank 17, such data referring to the time required for filtration of a 200 ml aliquot. Thus when the dwell time was held to one minute the filter time was approximately halved. Furthermore, even when held as long as ten minutes, the filtration time was even less. The column headed "ash" refers to the ash content of the recovered lignate, and is a measure of the cleanliness of separation of the precipitate from the mother liquor which is highly charged with sodium sulfate and other solids. However, maintaining the coagulated but unfiltered liquor at appreciably longer times, gives rise to the difficulty that the coagulated lignates fuse and lump, which will increase, rather than decrease, the ease of filtration. When the acidification temperature is dropped to 180° F, the liquor is difficultly filterable with a comparative filtration time of 85 seconds at 120° C. The sulfuric acid used was 60° Bé.

**EXAMPLE 2**

In this example a black liquor of 50.3% solids of the same origin as in Example 1 is used in the same apparatus as previously described. It is pumped at 2.1 pounds per minute and heated under pressure to selected temperatures near the boiling point. The data of the runs made are as follows:

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp., °F</th>
<th>Black Liqu.</th>
<th>pH</th>
<th>Vol., ml</th>
<th>Temp., °F</th>
<th>Time, Sec.</th>
<th>Ash, Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>205</td>
<td>9.1</td>
<td>200</td>
<td>140</td>
<td>15</td>
<td>32.2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>205</td>
<td>9.7</td>
<td>100</td>
<td>120</td>
<td>15</td>
<td>33.4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>205</td>
<td>8.4</td>
<td>100</td>
<td>120</td>
<td>15</td>
<td>32.7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>205</td>
<td>10.26</td>
<td>100</td>
<td>140</td>
<td>16</td>
<td>33.7</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>205</td>
<td>8.2</td>
<td>100</td>
<td>140</td>
<td>16</td>
<td>38.1</td>
<td></td>
</tr>
</tbody>
</table>

100 ml aliquot.

The acid used was 61.1° Bé sulfuric acid. A most significant aspect of this example is that it shows that it is feasible to use black liquor in excess of 50% solids. If it were attempted to recover lignin from black liquor of this high degree of solids in the ordinary way, i.e., without acidification at 180° or above, it would be found that the liquor became so viscous as to make handling thereof impracticable. Although the ash content of the crude filter cake is shown to be higher in this example than in Example 1, this drawback is overcome by washing the filter cake with hot water or hot brine. The temperature range of 195-205° F. was chosen so that assuming 6° F. temperature rise due to the heat of neutralization, the black liquor would be just below the boiling point after mixing with the acid.

In run 2, the filter cake of the crude solids was washed with 0.69 pound water per pound of crude cake solids to give a refined cake containing 357 pounds per thousand pounds of black liquor solids started with, with an ash content reduced from around 35% to 21%.

It was further found that when the black liquor is acidified to a pH much higher than 9.7 as for example 10.35 as in run #4, the precipitate filtered readily, but it could not be readily washed.

While the purity of the lignate cake could be increased by further washing, this is had at the expense of the yield, since the lignate is to some extent soluble in the wash water. Black liquors having a solids content from 14% or below to substantially above 51.5% may be processed similarly to the foregoing.

We claim:

1. In the method of recovering sodium lignate from black liquor having a solids content in excess of 30% and a pH in excess of 10.4, the steps which consist in:

   (a) continuously adding concentrated sulfuric acid to black liquor which has a temperature sufficient to yield a precipitation temperature in excess of the temperature of lignin coagulation of around 180° F., said acid being added in an amount to effect a substantial precipitation of sodium lignate.

   (b) thoroughly and continuously mixing said heated black liquor and said acid to bring about the precipitation of sodium lignate with commencement of substantially simultaneous coagulation thereof.

   (c) maintaining the coagulating black liquor in a dwell stage at the precipitation temperature for a period of from 20 seconds to 10 minutes to complete the coagulation thereof, and

   (d) continuously separating the coagulated lignate from the mother liquor.

2. The method according to claim 1 in which the acidification of the black liquor is carried out with avoidance of boiling of the liquor.

3. The method according to claim 1 in which the temperature of said black liquor, just prior to the addition of the concentrated sulfuric acid, is in the range of 195-205° F.

4. The method according to claim 1 in which the concentrated sulfuric acid is of a strength of approximately 60° Bé.

5. The method according to claim 1 in which the black liquor started with has a solids content in the approximate range 30-50% by weight.

6. The method according to claim 1 in which the temperature of filtration will vary from that of coagulation to 125° F.

7. The method according to claim 1 in which the crude lignate cake obtained is filtered and water-washed to reduce the ash content of the lignate.

**References**

Cited in the file of this patent

**UNITED STATES PATENTS**

2,623,040 Kellen ---------------- Dec. 23, 1952
2,640,622 Stoddard -------------- May 26, 1953