Brightness Improvement During Cold Soda Pulping

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Cold Soda Pulping

by

Harry Pratley

June 2, 1965
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Brightness Improvement during Cold Soda Pulping

The addition to cold soda pulping liquor of oxidizing agents such as sodium hypochlorite and hydrogen peroxide does improve the pulp brightness. The addition of a stabilizing agent and a surfactant appears to improve liquor penetration, however, at the expense of pulp brightness.

I. Introduction

During cold soda pulping, sodium hydroxide reacts with the lignin-carbohydrate complex to form soluble sodium lignate, and the carbohydrates are made soluble by hydrolysis (17). This lignin reaction, however, occurs only after a major portion of the caustic soda has been consumed in neutralizing the readily available acetyl and methoxyl groups and in hemicellulose dissolution. After the pulping process, the high-yield cold soda hardwood pulps exhibit a brown discoloration. A microscopic examination of the woods from which these pulps were produced (21) revealed that the brown discoloration was due to materials located in the cells of the wood. In addition it was observed that in the heartwood these substances are darker and more abundant than in the sapwood. Chemically these incrustations are not identical with lignin, but they probably develop from the same precursors.

In bleaching, the colored materials behave differently than lignin to the conventional bleaching agents. A major problem (12) of bleaching high-yield pulps is to obtain high brightness (greater than eighty brightness units) without dissolving the lignin. It was found, however, that pulps having
been discolored during the pulping operation were impossible to bleach without dissolving all the lignin (12).

According to Casey (4), the principal cause of the discoloration is the formation of carbonyl groups in the cellulose. Brown (3) reports that an experiment made on aspen sawdust to determine the cause of yellowing involved treating samples with a fifty gram per liter solution of caustic soda for two hours at atmospheric pressure after the samples had been extracted successively with ether, alcohol-benzene, and hot water (specific for the extractives). Treatment of the sawdust after each extraction produced the same characteristic yellow color as the treatment of an unextracted sample. But the color of a sample of Cross and Bevan cellulose (treatment with chlorine gas, sulfur dioxide, and sodium sulfite) prepared from the sawdust did not change after a similar treatment with caustic soda. This indicates that the color is produced by the reaction of the alkali with the lignin portion.

II. Agents that Have Been Used with Caustic Soda in Pulping

O'Brien (22) reports that the use of borohydrides (particularly "Hydrapulp-C," essentially sodium borohydride dissolved in a highly alkaline aqueous solution) in pulp cooking has improved pulp brightness, reduced brightness reversion, and subsequent bleaching with peroxide and hydrosulfite resulted in an increased brightness ceiling of five to ten points. Also, a Canadian Patent Number 609,561 (19) issued November 29, 1960, claims that the color of semichemical pulps is improved by employing a cooking liquor containing sodium or zinc hydrosulfite. In 1963 at the Forest Products Laboratory, Hyttinen
(15) found that the addition of either calcium or sodium hypochlorite to the steeping liquor in the production of hardwood cold soda pulps has resulted in pulps up to eighteen points brighter than when no hypochlorite was used and that predisintegrated chips gave greater brightness gains when steeped at atmospheric pressure than whole chip steeped at atmospheric pressure. This indicates that there is a problem of liquor penetration. Diehm (7) in an attempt to enhance penetration of cold soda liquor into hardwood explored numerous surfactants and found sodium xylene sulfonate to be most suitable. Also, Brown (3) reports that anionic surfactants added to cold soda liquor accelerates liquor penetration.

III. Agents that Have Been Used with Caustic Soda in Bleaching

According to Hooker Electrochemical Bulletin Number 200 (14), peroxide (sodium and hydrogen) has been successfully applied in a hot caustic extraction stage so that extraction and oxidation proceed simultaneously. Hawkinson (13) reports that paper is bleached as it is formed on the paper machine by applying a solution of sodium hydroxide and/or a stabilizing agent, such as sodium pyrophosphate, and subsequently subjecting the conditioned web to hydrogen peroxide vapors.

IV. Reactions of Agents on Colored Materials

Giertz (12) feels that peroxides have a specific decoloring action on wood without reacting with the lignin. Hooker Electrochemical Bulletin Number 200 (14) reports that the peroxides appear to act chiefly on the colored impurities associated with the lignin without removing the lignin from the pulp. The theory that peroxide is dissociated during bleaching into water and
oxygen and that the oxygen is the actual bleaching agent has been replaced by the concept that the bleaching effect is related to the dissociation of peroxide into ions, with the \( \text{HO}_2^- \) ion being the true bleaching agent (16). This dissociation of peroxide into \( \text{HO}_2^- \) ions becomes preferred at a high pH. It is believed that this ion selectively oxidizes and/or hydrolyzes the organic coloring compounds in the wood and does not affect the lignin and cellulose. While this bleaching effect is partially reversible, the brightness increase is more stable than when obtained with reducing agents.

Gicrutz and McPherson (12) showed that yellowing is diminished if the carbonyl groups in the cellulose are reduced to hydroxyls by the action of alkaline sodium borohydride. Luner and Supka (13) report that during the bleaching of white birch cold soda pulp with sodium borohydride in alkaline solution, borohydride is consumed by the lignin, extractives, and carbohydrates. The reduction of the lignin and extractives results in a sixteen-point brightness increment and corresponds to forty per cent of the total bleach consumed. The remainder is consumed in the reduction of the carbonyl groups formed during the alkaline degradation of the polysaccharides. According to O'Brien (22), most applications of the borohydrides are based on the ability of the borohydrides to reduce the cellulose oxidation products (aldehydes and ketones) produced in pulp cooking and bleaching processes.

Hooker Electrochemical Bulletin Number 200 (14) reports that hypochlorite may react with the cellulose as well as with
the impurities associated with the cellulose. To minimize the cellulose degradation, the pH should not fall below seven and five tenths. The rate of bleaching, however, is retarded at a high initial pH.

V. Experimental Program

Oxidizing agents, reducing agents, a surfactant, and a stabilizing agent were added (singly or in combination) along with the caustic soda during the cold soda pulping process. The agents or combination of reagents were prepared and added to the caustic soda solution prior to addition to the aspen wood chips.

The pulping process consisted of a two hour retention period with a caustic concentration of forty grams per liter and a liquor to wood (oven dry) ratio of four to one. The liquor and wood combination were mixed constantly at room temperature. After pulping, the wood chips were passed through a disc refiner. Pulp yield and brightness were determined.

The following experiments were performed:

1. A control cold soda pulping process using the conditions stated above.

2. A cold soda pulp produced with the addition of Na₄P₂O₇ (1%).

3. A cold soda pulp produced with the addition of NaClO (10%) and Na₄P₂O₇ (1%).

4. A cold soda pulp produced with the addition of NaClO (10%) and NaSO₃C₃H₈₀ (1%).

5. A cold soda pulp produced with the addition of NaBH₄ (1%) and Na₄P₂O₇ (1%).

6. A cold soda pulp produced with the addition of NaBH₄ (1%) and NaSO₃C₃H₈₀ (1%).
7. A cold soda pulp produced with the addition of \( \text{H}_2\text{O}_2 \) (10\%) and \( \text{Na}_4\text{P}_2\text{O}_7 \) (1\%).

8. A cold soda pulp produced with the addition of \( \text{Na}_3\text{O}_3\text{C}_8\text{H}_10 \) (1\%).

9. A cold soda pulp produced with the addition of \( \text{Na}_2\text{S}_2\text{O}_4\cdot\text{H}_2\text{O} \) (1\%) and \( \text{Na}_4\text{P}_2\text{O}_7 \) (1\%).

VI. Discussion and Conclusions

The addition of sodium xylene sulfonate (surfactant) resulted in a slight increase in pulp yield. This same effect was observed with the addition of sodium pyrophosphate (stabilizer). The increase in both cases amounted to approximately eight-tenths per cent.

A brightness decrease was noted when sodium xylene sulfonate or sodium pyrophosphate was added to the pulping liquor. This possibly indicates a better penetration of the liquor into the wood chips and more complete discoloration of the "fibers" by the caustic soda. The sodium xylene sulfonate addition showed a brightness decrease of six and seven tenths brightness points, while the sodium pyrophosphate addition decreased only two and two tenths brightness points. (See table.) Other reagents which showed a brightness decrease were: 1. the addition of sodium xylene sulfonate and sodium borohydride, which amounted to four tenths brightness points; and 2. the addition of sodium pyrophosphate and sodium hydrosulfite, which amounted to four and seven tenths brightness points. It appears from the last two cases mentioned that the reducing agents are not effective in overcoming the brightness decrease caused by the surfactant and stabilizing agent.
A brightness increase was observed with the addition to the steeping liquor of oxidizing agents and a surfactant or stabilizing agent. The effective oxidizing agents were sodium hypochlorite and hydrogen peroxide, with the brightness increase being three and seven tenths and four and six tenths points, respectively.

The use of sodium pyrophosphate is more effective than sodium xylene sulfonate in aiding the bleaching agent for brightness improvement. This was particularly evident with sodium hypochlorite where the brightness difference between the sodium pyrophosphate and the sodium xylene sulfonate additions was one and six tenths brightness points. This difference was also noted with sodium borohydride and was one and eight tenths brightness points.
### Data

<table>
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<tr>
<th>Run #</th>
<th>Reagents Used</th>
<th>Yield (%)</th>
<th>Brightness</th>
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<tr>
<td>1</td>
<td>NaOH</td>
<td>92.4</td>
<td>46.1</td>
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<td>2</td>
<td>NaOH + Na₄P₂O₇</td>
<td>93.0</td>
<td>43.9</td>
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<td>86.8</td>
<td>49.8</td>
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<td>NaOH + Na₅O₃C₈H₁₀</td>
<td>88.6</td>
<td>48.2</td>
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<td>NaOH + Na₄P₂O₇ + NaBH₄</td>
<td>91.1</td>
<td>47.5</td>
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<td>7</td>
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<td>50.7</td>
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<td>11</td>
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<td>74.6</td>
<td>41.4</td>
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Table--Brightness Differences from Control

<table>
<thead>
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<th>Increase*</th>
<th>Decrease*</th>
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<td>2.2</td>
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<td>4</td>
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<td>NaOH + Na₅O₃C₈H₁₀ + NaClO</td>
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<td>11</td>
<td>NaOH + Na₄P₂O₇ + Na₂S₄O₄·2H₂O</td>
<td>---</td>
<td>4.7</td>
</tr>
</tbody>
</table>

*Increase or decrease in brightness from the control which showed a brightness of 46.1.
LITERATURE


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