CHELATING AGENTS IN

Eucalyptus KRAFT PULPS

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I. PHOSPHONATES IN PULPING AND BROWN STOCK WASHING
Introduction

TCF vs. ECF
- Environment
- Strength
- Costs

Hydroxyl radical (HO•), extremely reactive and indiscriminate.
- Generated by peroxide decomposition.
- Catalyzed by metallic ions present in pulps.
Introduction

- Hydrogen peroxide is an intermediate in the stepwise reduction of $O_2$ in oxygen delignification.
- The hydroxyl radical can also be produced in this stage.
Introduction

- Process loses selectivity, attacking the carbohydrates.
- Controlling organic peroxides formation and reaction will promote better brightness and physical properties of pulps.
- Since wood itself contains Mn\(^{+2}\); Fe\(^{+3}\) and Cu\(^{+2}\), metal management in an early stage of pulp production or handling could be advantageous.
A pretreatment of pulp in a Q separate stage is usually performed to eliminate heavy metals, and prevent peroxide decomposition. But chelating agents may be added at several points in a TCF sequence.
Introduction

- An aspect to consider in chelating agent selection is pulp pH.
- An important cost reduction could be achieved if the intermediate acidification is eliminated.
- While EDTA requires acid conditions, most phosphonates function well in strong alkaline medium, supporting Kraft process high pH and temperatures.
Experimental

*Eucalyptus spp.* air dried chips from Celulosa Argentina, Capitán Bermúdez mill, were used as raw material.

Phosphonates were provided by Solutia Inc.

- **DTPMPA**: (diethylene triamine penta (methylene phosphonic acid))
- **SPAP** (Sodium salt solution of Polyaminophosphonic acids) is currently almost unknown for these uses.

DTPMPA and SPAP were added in cooking and brown stock washing.

Chelant agent charge of each stage was 0.1% (active acid base) on oven dry weight of chips or pulp respectively.
Scheme of the experiences
$2^2$ factorial design

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Q in cooking</th>
<th>Q in brown stock washing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without Q</td>
<td>Without Q</td>
</tr>
<tr>
<td>2</td>
<td>Without Q</td>
<td>With Q</td>
</tr>
<tr>
<td>3</td>
<td>With Q</td>
<td>Without Q</td>
</tr>
<tr>
<td>4</td>
<td>With Q</td>
<td>With Q</td>
</tr>
</tbody>
</table>
Results DTPMPA - SPAP
Results DTPMPA - SPAP
Results DTPMPA
Results DTPMPA - SPAP

Means and Standard Errors (pooled s)

Brightness (%E known)

Treatment (DTPMPA)

Means and Standard Errors (pooled s)

Brightness (%E known)

Treatment (SPAP)

C

C+Q

W

W+Q
Results DTPMPA
Results DTPMPA
Conclusions

- Chelant agents do not perform in the same way concerning *Eucalyptus spp.* Kraft pulps.

- Depending on mills particularities, and their diverse metallic ions concentration in wood and pulps, different strategies of metal management could be applied.
Conclusions

- Adding phosphonates in cooking or in brown stock washing is a valid alternative to remove harmful ions.

- This option involves the use of new products that undergo high temperatures and pH.
Conclusions

- Results show that metallic ions could be almost eliminated previous to the oxygen stage.
- DTPMPA addition in the cooking stage reduces Mn to a very low level, preserving or increasing physical properties.
- It is effective to reduce metallic ions when applied in brown stock washing, producing better levels of physical properties referred to the control (without any treatment).
Conclusions

- SPAP shows a good performance in physical properties when applied in cooking with usual washing (without chelant), but metals are best removed when dosed in brown stock washing.
- In both cases, manganese is reduced to a very low level at the very beginning of the bleaching sequence.
- Mn levels after 0.1% of DTPMPA or SPAP addition in brown stock washing would be less than 2ppm.
- SPAP is more effective than DTPMPA in iron reduction and in magnesium preservation, resulting in highest viscosity levels.
II. DIFFERENT CHELANT AGENTS ADDITION IN BROWN STOCK WASHING
Introduction

Most popular chelating agents in the pulp and paper industry are:
- EDTA (ethylene diamine tetraacetic acid)
- DTPA (diethylene triamine pentaacetic acid).

Other sequesters included more recently are:
- HEDTA (Hidroxyethylene diamine tetraacetic acid)
- PHOSPHONATES:
  - DTPMPA: (diethylene triamine penta (methylene phosphonic acid))
  - HEDP (1-Hydroxy ethylidene diamine (1, 1-diphosphonic acid)).
  - SPAP (Sodium salt solution of Polyaminophosphonic acids) is currently almost unknown for these uses.
Introduction

An important aspect to consider in chelating agent selection is pulp pH.

- EDTA requires acid conditions
- DTPA, DTPMPA and HEDP function in alkaline medium.
Introduction

Hexenuronic acid groups, which consume electrophilic bleaching chemicals (chlorine dioxide, ozone and peracides), are usually eliminated using an acid treatment. They are however unreactive in alkaline oxygen and peroxide bleaching stages. In this case, the intermediate acid stage removal can reduce costs greatly. Hexenuronic acid groups can originate the low brightness stability of TCF pulps, so color reversal should be kept under observation.
Introduction

This work shows alternatives of chelant application in *Eucalyptus* Kraft brown stock washing, preceding oxygen delignification and TCF bleaching.

Phosphonates chelating agents known as DTPMPA, HEDP and SPAP were applied using EDTA and an acid stage as controls.
Experimental

- Conditions were similar to those of part I.
- The work was carried out dividing one pulp in fractions, to assure equal starting conditions.
- Unscreened pulp yield was 50.6%.
- Washing was standardized to obtain similar COD values before de oxygen stage.
- Washing was accomplished in three stages.
- DTPMPA, SPAP, and HEDP, were added in the second brown stock washing stage.
- Acid treatments were applied in the third washing stage.
Results
Results
Results
Results
Results

Means and Standard Errors (pooled s)

Mg (ppm)

1 2_DTPMPA 2_HEDP
2_Acid 2_EDTA 2_SPAP
Results

Means and Standard Errors (pooled s)

Mn (ppm)

1 2_DTPMPA 2_HEDP
2_Acid 2_EDTA 2_SPAP
Results

Means and Standard Errors (pooled s)

Cu (ppm)

0
0.1
0.2
0.3
0.4
0.5
1 2_DTPMPA 2_HEDP 2_Acid 2_EDTA 2_SPAP
Results

Means and Standard Errors (pooled s)

Fe (ppm)

1 2_DTPMPA 2_HEDP 2_Acid 2_EDTA 2_SPAP
Conclusions

Chelant agents do not perform in the same way concerning *Eucalyptus* *spp.* kraft pulps.

Depending on the particular problem of the mill and its different metallic ions concentration, diverse strategies of metal management could be applied.

Phosphonates incorporation in brown stock washing is a valid choice.

Results show that metallic ions could be almost eliminated before the oxygen stage.
Conclusions

- Acidic treatments require an intermediate stage involving sulfuric acid addition.
- The consequence is supplementary manipulation and equipment costs, including special materials.
- These reasons make expensive its utilization.
Conclusions

- Even though an acidic washing at pH= 2 seem to have benefits in ions reduction, lignin precipitation onto fibers makes unviable its application.
- In this case, washing efficiency reduces, as revealed by Kappa number increase and COD reduction.
- This effect could be harmful to the following oxygen stage.
Acknowledgements

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