EUROPEAN PATENT SPECIFICATION

PROCESS FOR THE TREATMENT OF CHEMICAL PULP
VERFAHREN ZUR BEHANDLUNG VON CHEMISCHEM ZELLSTOFF
PROCEDE APPLICABLE AU TRAITEMENT DE LA PATE CHIMIQUE

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References cited:

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification.

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Description

[0001] The invention relates to a process for the bleaching or delignification of pulp, wherein, before bleaching or
delignification with an oxygen chemical, the pulp is pretreated with a chelating agent in order to eliminate the adverse
effects of any heavy metals present in the pulp.

[0002] Ever more commonly, bleaching processes using no elementary chlorine or chlorine compounds are used for
the bleaching of chemical pulp. The first-mentioned bleaching is called ECF (elementary chlorine free) bleaching and
bleaching which is entirely free of chlorine is called TCF (total chlorine free) bleaching. Especially TCF bleaching is
usually preceded by oxygen delignification. After oxygen delignification the pulp can be bleached with chlorine-free
chemicals such as ozone or hydrogen peroxide in acid or alkaline solutions in pressure-free or pressurized conditions.
Usable bleaching processes also include bleaching with peroxo compounds (such as peracetic acid, caron acid, or
mixtures of peracids), a peroxide-enhanced oxygen step, and a peroxide-enhanced oxygen-alkali step.

[0003] Such bleaching steps are most commonly preceded by the binding of heavy metals. The metals can be re-
moved by an acid wash. This is often disadvantageous, since at least some of the subsequent bleaching steps are
carried out in alkaline conditions. If heavy metals are removed at a low pH, it is necessary first to use an acid in order
to reach a low pH and in the next step an alkali to neutralize the acid. Furthermore, the acid wash removes Mg and
Ca ions, which are regarded as advantageous for bleaching. The acid wash may also reduce the strength of the pulp.

[0004] Peroxy compounds such as peracetic acid and hydrogen peroxide are highly susceptible to the catalytic action
of heavy metals.

[0005] The applicant's WO application publications 95/35406, 95/35407 and 95/35408 describe transition-metal ac-
tivated bleaching with peroxo compounds in acid conditions. The success of the bleaching presupposes the binding
of heavy metals before the bleaching and/or during the bleaching.

[0006] In the bleaching with peroxo compounds, heavy metals are bound by using agents which chelate metal ions,
for example polyaminocarboxylic acids. These include in particular ethylene diamine tetra-acetic acid and its salts
(EDTA) and diethylene triamine penta-acetic acid and its salts (DTPA). The ions the most detrimental in terms of
bleaching are manganese (Mn), iron (Fe) and copper (Cu). Also other heavy metals, such as chromium ions (Cr), etc.,
have a detrimental effect, both on the consumption of peroxo compounds and often on the bleaching result, by reducing,
for example, the viscosity of the bleached pulp. Detrimental heavy metals originate in the pulp, the treatment waters
and the pulp-treatment apparatus.

[0007] In the bleaching of chemical pulp it is usually not possible to carry out chelating in alkaline conditions, because
in such a case iron will precipitate in the form of hydroxides, oxides and oxyhydroxides, which strongly catalyze the
breaking down of peroxide compounds. For this reason, the chelating preceding peroxide bleaching is carried out in
acid conditions. Especially the removal of manganese has proved to be important in this case, since it does not form
as stable complexes as does iron and since especially a chemical pulp often contains large amounts of manganese.

[0008] In modern processes for the bleaching of chemical pulp, the bleaching is preceded by oxygen delignification.
In this process there are added to the pulp magnesium ions, the remaining of which in the pulp is important in a bleaching
with peroxide compounds, for example hydrogen peroxide. According to the article, the best Mg/Mn ratio is reached
at a pH of 4.5-5.0. For this reason the chelating should in practice be carried at a pH clearly below 6, for example at
a pH close to 5.5. In the examples of the above reference publication, the chelating was carried out at a pH of 5.3.

[0009] Effective chelating agents are often poorly biodegradable, as is DTPA, or are completely non-biodegradable,
as is EDTA. The increasing of TCF bleaching has increased the use of the said chelating agents. Therefore interest
has arisen in replacing poorly biodegradable chelating agents either in part or entirely with biodegradable chelating
agents. In order to avoid the environmental load it is additionally desirable that the biodegradable chelating agents be
preferably phosphorus-free and also contain as small an amount of nitrogen as possible.

[0010] Biodegradable complexing agents have been developed for detergent builders. They must at the same
have softening action on water, i.e. they must bind calcium ions and magnesium ions. One such sequestering agent
is ethylenediamine disuccinic acid (EDDS). This compound has three stereoisomers.

[0011] The substance is known per se from F. Pavelcek's and J. Majer's publication "New Complexanes. XXXIV.
Preparation and properties of the meso and rac forms of ethylenediamine-N,N'-disuccinic acid," Chem. Zvesti 32 (1978),
pages 37-41. FI Patent 86554 of Procter & Gamble discloses the use of this substance in detergent compositions.
Application publication WO 94/03553 of the same applicants discloses the use of the substance in bleaching liquors
as a stabilizer of peroxo compounds in the bleaching of pulp and in detergents. The more detailed description and
examples relate only to the latter. In this case the pH of the bleaching liquor must be 0.5-6.0. The publication mentions
that the compound is biodegradable. According to the patent, the S,S-isomer of EDDS is the best biodegradable.

[0012] EP patent application 556 782 discloses the use of EDDS as an iron complexer in photography chemicals.
Example 9 of the publication mentions that the ferric salts of EDTA, DTPA and HEDTA are not biodegradable. In contrast, the Fe^{2+} salt of EDDS is biodegradable. The biodegradabilities of the compounds were tested in the example by a generally approved testing method (301C Amendment MITI Test (I), OECD Chemical Substance Testing Guidelines, May 1981).

Another known biodegradable complexing agent is 2,2'-iminodisuccinic acid (ISA). The use of this compound in alkaline detergents is disclosed in EP patent application 509 382. The patent application mentions the use of 2,2'-iminodisuccinic acid as a stabilizer of peroxide compounds, in particular in alkaline detergent compositions which contain hydrogen peroxide and its derivatives. In the examples of the application, only perborate is used. Since perborate releases hydrogen peroxide only slowly, no far-reaching conclusions can be drawn from the examples of the patent regarding the stabilization of hydrogen peroxide in similar detergent compositions.

Another known biodegradable complexing agent is 2,2'-iminodisuccinic acid (ISA). The use of this compound in alkaline detergents is disclosed in EP patent application 509 382. The patent application mentions the use of 2,2'-iminodisuccinic acid as a stabilizer of peroxide compounds, in particular in alkaline detergent compositions which contain hydrogen peroxide and its derivatives. In the examples of the application, only perborate is used. Since perborate releases hydrogen peroxide only slowly, no far-reaching conclusions can be drawn from the examples of the patent regarding the stabilization of hydrogen peroxide in similar detergent compositions.

DE patent application 4 216 363 discloses the use of ISA as a stabilizer of tensides. There is no mention of the use of a peroxide compound. EP patent application 513 948 mentions the use of the substance in detergents which are intended for hard surfaces and contain an organic solvent boiling at approx. 90 °C. There is no mention of the use of a peroxide compound.

DE patent application 4 340 043 discloses the use of ISA as a bleaching agent in the bleaching of groundwood pulp. According to the publication, the purpose of ISA is the stabilization of hydrogen peroxide, and the examples show that at a pH of 10 it is a better stabilizer than DTPA. There is no demonstration in the publication of the action of ISA on heavy metals, nor of any bleaching results.

The object of the present invention is to eliminate the adverse effects of heavy metals in the bleaching and delignification of chemical pulp. It is also an object to obtain a biodegradable effective chelating agent which yields a good bleaching result.

The characteristics of the invention are given in accompanying Claims 1-15.

In the process according to the invention, compounds according to Formula I, known per se, are used

\[
\text{COOR}_1 \quad \begin{array}{c}
\text{H} \\
\text{N} \\
\text{CH}_2 \text{CH}_2 \text{N}^+ \\
\text{CH} \end{array} \quad \text{COOR}_3
\]

\[
\text{COOR}_2 \quad \text{COOR}_4
\]

where
- \( n \) is 1-3
- \( m \) is 0-3
- \( p \) is 1-3
- \( R_1, R_2, R_3 \) and \( R_4 \) are \( H, \text{Na, K, Ca or Mg} \)
- \( R_5 \) and \( R_6 \) are \( H, \text{CH}_2 \text{OH, CH}_2\text{CH}_2 \text{OH or CH}_2\text{O(CH}_2\text{CH}_2\text{O})_{1-10} \text{CH}_2\text{CH}_2 \text{OH} \).

DTPA, which is commonly used in the bleaching of pulp, chelates heavy metals best at a pH of approx. 5.

It has now been observed, surprisingly, that compounds according to Formula I can be used advantageously, at a higher pH than can DTPA, as chelating agents in a pretreatment step preceding the bleaching or delignification of pulp. Suitable pH values in the use of the compounds in accordance with the invention for the pretreatment of pulp are pH 4-8, preferably pH 5.0-7.5 and most preferably pH 6.5-7.5. If the compounds are also used in the actual bleaching or delignification step, the suitable pH values are respectively pH 4-8, preferably pH 4-6 and most preferably pH 4-5. Since chelating can be carried out at a higher pH value, the consumption of alkali in the subsequent step is not as high as when the chelating is carried out at a lower pH. This is a clear advantage over, for example, DTPA.

The process according to the invention can be used for all known chemical pulps. These include alkaline and neutral sulfite pulps, soda pulps, sulfate pulps (kraft pulps) and oxygen-delignified (oxygen cooking) sulfate pulps. Furthermore, the process can be used in the bleaching of so-called organosolv pulps in which alcohols or organic acids have been used as the cooking solvent, for example Milox cooking in formic acid. The chelating process according to the invention may also be used when polysulfides or, for example, anthraquinone, have/has been used in sulfate cooking.

The treatment can be carried out on pulp cooked from different fiber raw materials, such as softwood, hardwood or reed, straw or other raw material of vegetable origin.
The chelating process according to the invention, with compounds of Formula I, e.g. EDDS and ISA, is used as a pretreatment before bleaching or delignification with oxygen chemicals. Chelating agents according to Formula I, such as EDDS and ISA, can also be used as a chelating agent in bleaching or delignification with oxygen chemicals. These include bleaching with peracetic acid, bleaching with mixtures of peracids, bleaching with hydrogen peroxide, bleaching with mixtures of hydrogen peroxide and peracids, transition-metal catalyzed hydrogen peroxide bleaching within the acid pH range, developed by the applicant, alkaline peroxide bleaching, and combinations of all these, as well as oxygen delignification, peroxide-enhanced oxygen-alkali steps and pressurized peroxide steps and, in conjunction with these, optional treatments with enzymes, ozone or chloride dioxide.

The chelating process according to the invention can be used as a pretreatment for pulp bleaching or delignification in acid conditions and possibly also in the bleaching or delignification step itself.

The pH control of an acid chelating step can be carried out using conventional mineral acids, such as sulfuric acid, sulfur dioxide or an aqueous solution thereof, carbon dioxide, or organic acids such as formic acid and acetic acid.

In the process according to the invention, an especially suitable chelating agent according to Formula I may be ethylenediamine-N,N'-disuccinic acid, its various isomers and its alkali metal salts, such as sodium and potassium salts, and its earth-alkali metal salts, such as calcium and magnesium salts. It is also possible to use ethylenediamine-N,N'-disuccinic acid together with calcium sulfate and/or magnesium sulfate. Another particularly suitable chelating agent is 2,2'-iminodisuccinic acid, its various isomers and its alkali metal salts, such as sodium and potassium salts, and its earth-alkali metal salts, such as calcium and magnesium salts. It is also possible to use 2,2'-iminodisuccinic acid together with calcium sulfate and/or magnesium sulfate.

Usable chelating agents also include N-(1,2-dicarboxyethyl)-N-(2-hydroxyethyl)aspartamic acid, its various isomers and its alkali metal salts and earth-alkali metal salts. The acid may also be used together with potassium sulfate or magnesium sulfate.

The chelating agent may be added in an amount of 0.1-5 kg, preferably 0.5-2 kg per metric ton of dry pulp.

It has also been observed that EDDS and ISA can be used together with hydroxycarboxylic acids without the bleaching result being worsened. EDDS and ISA may in part be replaced with chelating agents which do not contain nitrogen, such as hydroxycarboxylic acids having the general formula II:

\[ R_1C_nH_m(OH)_p(COOH)_qR_2 \]  

(II)

where

\[ n \text{ is } 1-8, \]
\[ m \text{ is } 0-2n, \]
\[ p \text{ is } 0-n, \]
\[ q \text{ is } 0-2, \]
\[ R_1 \text{ is COOH, and} \]
\[ R_2 \text{ is H, CH}_2\text{OH or COOH.} \]

The detrimental nitrogen load in effluents from bleaching can thus be reduced. Conventional carboxylic acids, hydroxycarboxylic acids, polyhydroxycarboxylic acids and hydroxypolycarboxylic acids according to Formula II, such as citric acid, tartaric acid, lactic acid, pimelic acid, glutamic acid, glucoheptonic acid, ascorbic acid, glycolic acid, glutaric acid, adipic acid, succinic acid or malonic acid, can be used as replacement chelating agents.

It is quite surprising that hydroxy acids can be used as chelating agents in bleaching. The said substances are quite poor binders of heavy metals, but bind well calcium and magnesium. Especially citric acid has been used as a replacement for phosphates in phosphate-free detergents and cleansing agents, in which the substances are required to bind calcium and magnesium. Especially the binding of magnesium should be disadvantageous in terms of bleaching.

The invention is illustrated below with examples, which do not, however, limit the invention to relate only to the examples presented here.

Example 1

To investigate the chelating of heavy metals and earth alkali metals, an oxygen-delignified chemical pulp was washed with aqueous solutions containing EDDS. The metal contents of the washing solution were analyzed after the
washed. Thereby the transfer of iron (Fe), manganese (Mn), calcium (Ca) and magnesium (Mg) into the washing waters was investigated. The transfer of iron and manganese into the washing solutions is advantageous for bleaching. In contrast, the transfer of calcium and magnesium into the washing solutions is disadvantageous for bleaching. In the reference tests the pulp was washed with DTPA or EDTA solutions. The chelating agent concentrations and the pH during the wash are indicated in Table 1.

In Table 1, Na₅DTPA stands for the pentasodium salt of DTPA, Na₄EDTA stands for the tetrasodium salt of EDTA, and H₄EDDS stands for the acid form of EDDS. However, the pH used will determine how the chelating agents are dissociated, i.e. in which form they actually appear in the treatment. The H₄EDDS (reaction mixture) mentioned in the table refers to experiments in which the chelating agent used was an unpurified reaction product directly from the process for the preparation of EDDS.

Example 2

Table 2 shows the results of washing experiments similar to those described in Example 1, when EDDS was diluted with certain hydroxy acids.
In the chelating step, DTPA is usually dosed into a softwood pulp at a rate of approx. 2 kg/tp. In the second series of experiments (Table 2), the effect of the DTPA dose on the chelating of metals was first investigated. Chelating was clearly less when the dose of EDDS was reduced from a rate of 2.0 kg/tp to a rate of 1.0 kg/tp or 0.5 kg/tp. In the previous series of experiments (Table 1) it was observed that when Na₅EDDS was used at a rate of 1.5 kg/tp, chelating was as complete as when Na₅DTPA was used at a rate of 2.0 kg/tp.

Practical experience and the above results of experiments indicate that DTPA must be used in the chelating step at a rate of approx. 2.0 kg/tp and EDDS at a rate of approx. 1.5 kg/tp in order for the heavy metals to be chelated sufficiently completely for bleaching. When sodium salts of citric acid or gluconic acid were used as a chelating agent alongside EDDS, it was possible to reduce the dose of EDDS significantly. Even though the dose of EDDS had been lowered to a rate of 1.0 kg/tp, the chelating of metals in these experiments was as complete as when EDDS was used at a rate of 1.5 kg/tp. By the use of, for example, salts of hydroxyacarboxylic acids together with EDDS as the chelating agent, the nitrogen load in the effluents from the chelating step can be reduced significantly, while the chelating of the metals is still sufficiently complete for bleaching.

It can be observed from Table 2 that a water wash has no effect as regards the chelating of metals. Likewise, citric acid used alone does not remove heavy metals. Citric acid chelates only earth-alkali metals, which is not desirable for bleaching. This indicates that a good chelating result is achieved through the joint effect of EDDS and, for example, citric acid.

Example 3

An oxygen-delignified pulp was chelated and bleached with an alkaline hydrogen peroxide. The chelating agent used was EDDS or DTPA. The results are compiled in Table 3. The bleaching result can be evaluated on the basis of the consumption of peroxide, the brightness achieved, and the viscosity of the pulp.
In a reference experiment the chelating was carried out with DTPA before bleaching (Experiment 1). When the chelating with EDDS was carried out at a pH of 5.5, the bleaching result was poor (Experiment 5). In contrast, when the chelating with EDDS was carried out at a pH of 6.6 (Experiment 6), the bleaching result was better than in the reference experiment (Experiment 2).

It is to be noted that, in the reference experiments, appropriate bleaching results were obtained only when DTPA was used in the chelating at a rate of at minimum 2 kg/metric ton of pulp (Ref. Experiment 3). In contrast, when the chelating was carried out by using EDDS at a rate of only 0.6 kg/tp, a good bleaching result was obtained (Experiment 9). This means a considerable reduction in the consumption of chemicals in bleaching. The use of magnesium sulfate as an additive in chelating, alongside EDDS, is also advantageous in terms of bleaching (Experiment 8).

Example 4

In this experiment, the effect of EDDS and the salts of hydroxycarboxylic acids on chelating was investigated. Pretreated softwood pulp described in Example 3 was used in the experiment. The chelating of the pulp and the alkaline peroxide bleaching were carried out in conditions described in Table 4.
In the reference experiments the chelating was carried out with DTPA and EDDS. When sodium citrate alone was used in the chelating step, the bleaching result was poor (Experiment 9). In contrast, in experiments in which sodium gluconate or Na citrate was used together with EDDS in the chelating, the bleaching results were good.

When biodegradable auxiliary agents which did not contain nitrogen, such as Na gluconate or Na citrate, were used together with EDDS in the chelating, the dose of EDDS could be reduced even down to a rate of 0.25 kg/tp without the bleaching result being worsened. This is a significant result, for example in terms of the treatment of effluents. By the use of chelating agent mixtures described above, the nitrogen load in the effluents from bleaching can be reduced significantly.

Example 5

As a reference experiment, chelating and an alkaline peroxide bleaching were carried out on a softwood pulp which had been delignified with peracetic acid after oxygen delignification. The conditions of the chelating and the bleaching are described in Table 5. In the reference experiments the chelating was carried out with DTPA.
No chelating was performed in Experiment 5. This led to a poor bleaching result. In particular, the viscosity of the pulp was considerably reduced. After chelating steps at a pH of 5 and at a pH of 6.5, the bleaching results achieved were better in experiments in which EDDS was used than in experiments in which DTPA was used. Judged on the basis of viscosity and brightness, the best bleaching result was achieved when the chelating step had been carried out by using EDDS at a pH of 6.4. The dissociation of hydrogen peroxide was considerably less in this experiment than in a reference experiment in which the chelating had been carried out with DTPA. It is to be noted that in these experiments, also, the amount of EDDS used (1.5 kg/tp) was considerably lower than the amount of DTPA used (2.0 kg/tp).

In this experiment, an oxygen-delignified softwood pulp was bleached with an alkaline hydrogen peroxide by
adding the chelating agent directly to the bleaching liquor. In reference experiments the chelating was carried out with DTPA or EDDS before the bleaching. The pulp used in the reference experiments was also pre-bleached with peracetic acid before the chelating. The conditions and results of the experiments are compiled in Table 6.

Table 6

<table>
<thead>
<tr>
<th>Softwood sulfate pulp</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>777 dm³/kg</td>
</tr>
<tr>
<td>Kappa</td>
<td>6.7</td>
</tr>
<tr>
<td>Brightness</td>
<td>65.7 % ISO</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O₂ delignification</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chelating</strong></td>
<td></td>
</tr>
<tr>
<td>t, min</td>
<td>60</td>
</tr>
<tr>
<td>T, °C</td>
<td>75</td>
</tr>
<tr>
<td>CS, %</td>
<td>12</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
</tr>
<tr>
<td>Chelate kg/tp</td>
<td>0</td>
</tr>
<tr>
<td>PAA delignification</td>
<td></td>
</tr>
<tr>
<td><strong>Bleaching</strong></td>
<td></td>
</tr>
<tr>
<td>t, min</td>
<td>180</td>
</tr>
<tr>
<td>T, °C</td>
<td>90</td>
</tr>
<tr>
<td>CS, %</td>
<td>12</td>
</tr>
<tr>
<td>pH</td>
<td>10.4</td>
</tr>
<tr>
<td>H₂O₂, kg/tp</td>
<td>20</td>
</tr>
<tr>
<td>Residual H₂O₂, kg/tp</td>
<td>2.5</td>
</tr>
<tr>
<td>Residual H₂O₂, %</td>
<td>12.5</td>
</tr>
<tr>
<td>Kappa</td>
<td>2.3</td>
</tr>
<tr>
<td>Viscosity, dm³/kg</td>
<td>449</td>
</tr>
<tr>
<td>Change in viscosity, %</td>
<td>29</td>
</tr>
<tr>
<td>Brightness, % ISO</td>
<td>88.5</td>
</tr>
</tbody>
</table>

[0052] It is to be noted that the pulp used in these experiments was considerably bright already after the pretreatment. When the chelating agents were added directly to the bleaching liquor, the bleaching results were similar when DTPA was used at a rate of 2.0 kg/tp and when EDDS was used at 1.5 kg/tp. In experiments in which the chelating was carried out before the bleaching, a better pulp brightness was achieved. Judging from this, in terms of the bleaching
results it is more advantageous to carry out a separate chelating than to add the chelating agents to the bleaching liquor.

Example 7

[0054] In this experiment, a softwood pulp was chelated and delignified in acid conditions with molybdate-activated hydrogen peroxide (mP step). In the reference experiment, DTPA was used for the chelating. The chelating was carried out at a pH of 6.0-6.5.

Table 7

| Softwood sulfate pulp | Kappa | 13.1 | Viscosity | 878 dm³/kg |

<table>
<thead>
<tr>
<th>Chelating</th>
<th>t, min</th>
<th>T, C</th>
<th>CS, %</th>
<th>Chelate</th>
<th>kg/tp</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>45</td>
<td>60</td>
<td>12</td>
<td>None</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>60</td>
<td>12</td>
<td>Na₂DTPA</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>60</td>
<td>12</td>
<td>Na₂EDDS</td>
<td>1.5</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>mP delignification</th>
<th>t, min</th>
<th>T, C</th>
<th>CS, %</th>
<th>H₂O₂, kg/tp</th>
<th>Mo, kg/tp</th>
<th>pH</th>
<th>Residual H₂O₂, kg/tp</th>
<th>Residual H₂O₂, %</th>
<th>Kappa</th>
<th>Brightness, % ISO</th>
<th>Viscosity, de³/kg</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>180</td>
<td>90</td>
<td>12</td>
<td>15</td>
<td>0.45</td>
<td>5</td>
<td>2.6</td>
<td>17.3</td>
<td>6.4</td>
<td>62.4</td>
<td>789</td>
</tr>
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<td>180</td>
<td>90</td>
<td>12</td>
<td>15</td>
<td>0.45</td>
<td>5</td>
<td>6.7</td>
<td>44.7</td>
<td>6.3</td>
<td>61.4</td>
<td>820</td>
</tr>
</tbody>
</table>

Example 8

[0055] The results (Table 7) show that without a pretreatment the peroxide consumption in the mP step was greater than it was for pretreated pulps. Likewise, the viscosity of the pulp after delignification was higher in the experiments in which chelating had been performed. The peroxide consumption of EDDS-chelated pulp in the mP step was smaller than that of a DTPA-chelated pulp.

Example 8

[0056] To investigate the chelating of heavy metals and earth-alkali metals, an oxygen-delignified chemical pulp was
washed with aqueous solutions containing ISA. The metal contents of the washing solution were analyzed after the wash. Thus the transfer of iron (Fe), manganese (Mn), calcium (Ca) and magnesium (Mg) into the washing waters was investigated. The transfer of iron and manganese into the washing solutions is advantageous for bleaching. In contrast, the transfer of calcium and magnesium into the washing solutions is disadvantageous for bleaching. In the reference experiments the pulp was washed with DTPA or EDTA solutions. The chelating agent concentrations and the pH during the wash are shown in Table 9.

Table 8

<table>
<thead>
<tr>
<th>Softwood sulfate pulp</th>
<th>Chelating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kappa number</td>
<td>16.9</td>
</tr>
<tr>
<td>Viscosity</td>
<td>963 dm³/kg</td>
</tr>
<tr>
<td>Brightness</td>
<td>39.6 % ISO</td>
</tr>
<tr>
<td>Time</td>
<td>60 min</td>
</tr>
<tr>
<td>Temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Consistency</td>
<td>12 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Dose</th>
<th>pH</th>
<th>Metal contents in the filtrate (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg/tp</td>
<td></td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Na₅DTPA</td>
<td>1</td>
<td>6.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Na₅DTPA</td>
<td>2</td>
<td>6.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Na₅DTPA</td>
<td>2</td>
<td>5.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Na₅DTPA</td>
<td>0.5</td>
<td>6.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Na₅EDTA</td>
<td>0.5</td>
<td>6.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Water wash</td>
<td>6.0</td>
<td>6.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Water wash</td>
<td>7.0</td>
<td>7.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Na₃ citrate</td>
<td>1</td>
<td>6.3</td>
<td>0.0</td>
</tr>
<tr>
<td>ISA</td>
<td>1.5</td>
<td>5.8</td>
<td>1.1</td>
</tr>
<tr>
<td>ISA</td>
<td>1.5</td>
<td>8.9</td>
<td>0.0</td>
</tr>
<tr>
<td>ISA + Na citrate</td>
<td>1/1</td>
<td>7.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

[0057] In Table 8, Na₅DTPA stands for the pentasodium salt of DTPA, Na₄EDTA stands for the tetrasodium salt of EDTA, and ISA stands for the acid form of iminodisuccinic acid of ISA. However, it is the pH used that determines how the chelating agents are dissociated, i.e. in which form they actually are present in the treatment.

[0058] It can be observed that in the water wash carried out as a reference experiment, iron and manganese dissolved poorly in water at both a pH of 6.0 and a pH of 7.0. In a more alkaline solution, more magnesium and calcium was dissolved in the washing water. A wash with a sodium salt of citric acid was also ineffective in removing iron and manganese. In contrast, in this experiment earth-alkali metals were removed to some degree, which is disadvantageous for bleaching. EDTA and DTPA chelated iron and manganese with approximately the same efficiency at a pH of 6.5.

[0059] ISA chelated iron and manganese well at a pH of 5.8. It is to be noted that ISA removed very little magnesium from the pulp at a pH of 5.8. This is advantageous for bleaching. Chelating in an alkaline solution at a pH of 8.9 was also very successful. It is to be noted that at this pH iron is precipitated. This explains the small iron contents in the filtrate.

[0060] Chelating with a mixture of ISA and the sodium salt of citric acid was also successful, considering that the chelating was carried out at a pH of 7.7.

[0061] It is to be noted that a conclusion regarding the bleaching result cannot be drawn directly from washing experiments of the type described above. Therefore the effect of corresponding chelating steps on an alkaline hydrogen peroxide bleaching was investigated.

Example 9

[0062] An oxygen-delignified pulp pretreated with a molybdate-catalyzed peroxide was chelated and bleached with an alkaline hydrogen peroxide. The chelating agent used was ISA or DTPA.

[0063] The results are compiled in Table 9. The bleaching result can be assessed on the basis of peroxide consumption and the achieved brightness and pulp viscosity.
When a relatively ample ISA dose of 0.5 kg/tp of pulp was used in the chelating, the bleaching result was very good as compared with the bleaching result after DTPA chelating. On the other hand, when ISA was used in very low concentrations, as low as 0.25 kg/tp pulp in chelating together with the sodium salt of citric acid, a good bleaching result was obtained. This is a significant improvement over chelating with DTPA. The nitrogen load in effluents from bleaching can be reduced significantly by using this bleaching process.

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<th>No.</th>
<th>1</th>
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<tr>
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</tbody>
</table>
Example 10

[0065] In order to determine how ISA functions when bleaching is carried out in acid conditions, chelating was carried out as a pretreatment for an acid peroxide bleaching step. This latter step was the transition-metal catalyzed bleaching according to the applicant's previous invention.

| Table 10 |
| Softwood sulfate pulp |
| Kappa | 13.1 |
| Viscosity | 878 dm³/kg |

<table>
<thead>
<tr>
<th>Chelating</th>
<th>t, min</th>
<th>45</th>
<th>45</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>t, C</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>CS, %</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Chelate kg/tp</td>
<td>None</td>
<td>DTPA</td>
<td>ISA</td>
<td></td>
</tr>
<tr>
<td>mP delignification</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td></td>
</tr>
<tr>
<td>t, min</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>t, C</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>CS, %</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>H₂O₂, kg/tp</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>No, kg/tp</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Residual H₂O₂, kg/tp</td>
<td>2.6</td>
<td>5.7</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>Residual H₂O₂, %</td>
<td>17.3</td>
<td>38.0</td>
<td>34.7</td>
<td></td>
</tr>
<tr>
<td>Kappa</td>
<td>6.4</td>
<td>6.3</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>Brightness, % ISO</td>
<td>62.4</td>
<td>63.4</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Viscosity, dm³/kg</td>
<td>789</td>
<td>825</td>
<td>810</td>
<td></td>
</tr>
</tbody>
</table>

[0066] The results show that without a pretreatment the consumption of peroxide in the mP step was considerably higher if no pretreatment with DTPA or ISA was performed. The viscosity of the pulp was higher if a pretreatment had been performed.

Claims

1. A process for the bleaching or delignification of a chemical pulp, in which process the pulp is pretreated, before a bleaching or delignification with an oxygen chemical, with a chelating agent in order to bind into a chelate complex the heavy metals present in the pulp, characterized in that the chelating agent used is a compound having the formula (I)
1. \[ \text{where} \]

| n is 1-3  
| m is 0-3  
| p is 1-3  
| R₁, R₂, R₃ and R₄ are H, Na, K, Ca or Mg  
| R₅ and R₆ are H, CH₂OH, CH₂CH₂OH or CH₂O(CH₂CH₂O)₁₋₁₀CH₂CH₂OH.  

2. A process according to Claim 1, \textit{characterized in that} the chelating agent is ethylenediamine-N,N'-disuccinic acid and/or an alkali metal salt or earth-alkali metal salt thereof.

3. A process according to Claim 1 or 2, \textit{characterized in that} the chelating agent used is a sodium, calcium or magnesium salt of ethylenediamine-N,N'-disuccinic acid or ethylenediamine-N,N'-disuccinic acid and calcium sulfate and/or magnesium sulfate.

4. A process according to Claim 1, \textit{characterized in that} the chelating agent used is 2,2'-iminodisuccinic acid and/or an alkali metal salt and/or earth-alkali metal salt thereof.

5. A process according to Claim 1 or 4, \textit{characterized in that} the chelating agent used is a sodium, calcium or magnesium salt of 2,2'-iminodisuccinic acid or 2,2'-iminodisuccinic acid and calcium sulfate and/or magnesium sulfate.

6. A process according to Claim 1, \textit{characterized in that} the pretreatment of the pulp is carried out at a pH of 4-8, preferably at a pH of 5.0-7.5 and most preferably at a pH of 6.5-7.5.

7. A process according to Claim 1 or 6, \textit{characterized in that} the pretreatment with a chelating agent constitutes a step directly preceding a bleaching or delignification with an oxygen chemical.

8. A process according to any of Claims 1, 6 and 7, \textit{characterized in that} the pretreatment is carried out once or several times.

9. A process according to Claim 1 or 7, \textit{characterized in that} the oxygen chemical bleaching or delignification comprises bleaching with a peracetic acid, bleaching with a peracid mixture, bleaching with peroxides as such or as mixtures, either alone or as a mixture with peracids, a transition-metal catalyzed hydrogen peroxide bleaching within the acid pH range, an alkaline peroxide bleaching and combinations of all of these, as well as oxygen delignification, a peroxide-enhanced oxygen-alkali step and pressurized peroxide steps, and combined with these optional treatments with enzymes, ozone or chlorine dioxide.

10. A process according to Claim 1 or 9, \textit{characterized in that} the chelating treatment is carried out also in the oxygen chemical bleaching or delignification step.

11. A process according to any of Claims 1, 9 and 10, \textit{characterized in that} the oxygen chemical bleaching or delignification is carried out at a pH of 4-8, preferably at a pH of 4-6, and most preferably at a pH of 4-5.

12. A process according to any of Claims 1 and 9-11, \textit{characterized in that} the oxygen chemical treatment is carried out once or several times.

13. A process according to any of Claims 1 and 9-12, \textit{characterized in that} the oxygen chemical treatment of the
pulp is carried out simultaneously with a peroxide and a peracid.

14. A process according to any of Claims 1 and 9-13, characterized in that the peroxide treatment of the pulp is carried out with hydrogen peroxide, with a mixture of hydrogen peroxide and oxygen gas, or with organic peroxy compounds.

15. A process according to any of Claims 1 and 9-14, characterized in that the peracid treatment of the pulp is carried out with peracetic, performic, perpropionic or caron acid or with a transition-metal activated peracetic, performic, perpropionic or caron acid or a combination of these.

16. A process according to any of Claims 1-15, characterized in that the chelating agent is used at a rate of 0.1-5 kg/metric ton of dry pulp.

Patentansprüche

1. Verfahren zum Bleichen oder Delignifizieren eines chemischen Zellstoffs, bei welchem Verfahren der Zellstoff vor dem Bleichen oder Delignifizieren mittels einer Sauerstoff-Chemikalie mit einem Chelatbildner vorbehandelt wird, um die in dem Zellstoff vorhandenen Schwermetalle in einen Chelatkomplex zu binden, durchgeführt, dass der verwendete Chelatbildner eine Verbindung mit der Formel (I) ist:

\[
\begin{align*}
&\text{COOR}_1 \\
&(\text{CH}_2)_n \text{R}_5 \\
&\text{HC} \rightleftharpoons \text{N} \rightarrow (\text{CH}_2\text{CH}_2\text{N})_m \rightarrow \text{CH} \\
&\text{COOR}_2 \\
&(\text{CH}_2)_p \\
&\text{COOR}_3 \\
&R_5 \text{ und } R_6 \\
&\text{wobei:} \\
n &1 - 3 \text{ ist,} \\
m &0 - 3 \text{ ist,} \\
p &1 - 3 \text{ ist,} \\
R_1, R_2, R_3 \text{ und } R_4 &\text{H, Na, K, Ca oder Mg sind,} \\
R_5 \text{ und } R_6 &\text{H, CH}_2\text{OH, CH}_2\text{CH}_2\text{OH oder CH}_2\text{O(CH}_2\text{CH}_2\text{O})_{1-10}\text{CH}_2\text{CH}_2\text{OH sind.}
\end{align*}
\]

2. Verfahren nach Anspruch 1, durchgeführt, dass der Chelatbildner Ethylendiamin-N,N'-dibernsteinsäure und/oder ein Alkalimetallsalz oder Erdalkalimetallsalz derselben ist.

3. Verfahren nach Anspruch 1 oder 2, durchgeführt, dass der verwendete Chelatbildner ein Natrium-, Calcium- oder Magnesiumsalz der Ethylendiamin-N,N'-dibernstein säure oder Ethylendiamin-N,N'-dibernstein säure und Calciumsulfat und/oder Magnesiumsulfat ist.

4. Verfahren nach Anspruch 1, durchgeführt, dass der verwendete Chelatbildner 2,2'-Iminodibernsteinsäure und/oder ein Alkalimetallsalz und/oder Erdalkalimetallsalz derselben ist.

5. Verfahren nach Anspruch 1 oder 4, durchgeführt, dass der verwendete Chelatbildner ein Natrium-, Calcium- oder Magnesiumsalz der 2,2'-Iminodibernsteinsäure oder
2,2'-Iminodibenzsteinsäure und Calciumsulfat und/oder Magnesiumsulfat ist.

6. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, dass
   die Vorbehandlung des Zellstoffs bei einem pH-Wert von 4 - 8, vorzugsweise bei einem pH-Wert von 5,0 - 7,5 und am bevorzugtesten bei einem pH-Wert von 6,5 - 7,5 ausgeführt wird.

7. Verfahren nach Anspruch 1 oder 6, **dadurch gekennzeichnet**, dass
   die Vorbehandlung mit einem Chelatbildner einen Schritt darstellt, der dem Bleichen oder Delignifizieren mittels einer Sauerstoff-Chemikaliele unmittelbar vorausgeht.

8. Verfahren nach einem der Ansprüche 1, 6 und 7, **dadurch gekennzeichnet**, dass
   die Vorbehandlung einmal oder mehrmals ausgeführt wird.

9. Verfahren nach Anspruch 1 oder 7, **dadurch gekennzeichnet**, dass

10. Verfahren nach Anspruch 1 oder 9, **dadurch gekennzeichnet**, dass
    die Chelatbildungs-Behandlung ebenfalls in dem Schritt des Bleichens oder Delignifizierens mittels einer Sauerstoff-Chemikaliele ausgeführt wird.

11. Verfahren nach einem der Ansprüche 1, 9 oder 10, **dadurch gekennzeichnet**, dass
    das Bleichen oder Delignifizieren mittels einer Sauerstoff-Chemikaliele bei einem pH-Wert von 4 - 8, vorzugsweise bei einem pH-Wert von 4 - 6 und am bevorzugtesten bei einem pH-Wert von 4 -5 ausgeführt wird.

12. Verfahren nach einem der Ansprüche 1 und 9 - 11, **dadurch gekennzeichnet**, dass
    die Behandlung mit einer Sauerstoff-Chemikaliele einmal oder mehrmals ausgeführt wird.

13. Verfahren nach einem der Ansprüche 1 und 9 - 12, **dadurch gekennzeichnet**, dass
    die Behandlung des Zellstoffs mittels einer Sauerstoff-Chemikaliele gleichzeitig mit einem Peroxid und einer Persäure ausgeführt wird.

14. Verfahren nach einem der Ansprüche 1 und 9 - 13, **dadurch gekennzeichnet**, dass
    die Peroxid-Behandlung des Zellstoffs mit Wasserstoffperoxid, mit einer Mischung aus Wasserstoffperoxid und Sauerstoffgas oder mit organischen Peroxyverbindungen ausgeführt wird.

15. Verfahren nach einem der Ansprüche 1 und 9 - 14, **dadurch gekennzeichnet**, dass
    die Persäure-Behandlung des Zellstoffs mit Peressigsäure, Perameisensäure, Perpropionsäure oder Caroscher Säure oder mit mittels eines Übergangsmetalls aktivierter Peressigsäure, Perameisensäure, Perpropionsäure oder Caroscher Säure oder einer Kombination dieser erfolgt.

16. Verfahren nach einem der Ansprüche 1 - 15, **dadurch gekennzeichnet**, dass
    der Chelatbildner in einem Verhältnis von 0,1 - 5 kg pro Tonne trockenen Zellstoffs verwendet wird.
Revendications

1. Procédé pour le blanchiment ou la délignification d'une pâte chimique, procédé dans lequel la pâte est pré-traitée, avant un blanchiment ou une délignification avec un composé chimique oxygéné, avec un agent chélatant, pour lier dans un complexe chélate les métaux lourds présents dans la pâte, caractérisé en ce que l'agent chélatant utilisé est un composé ayant la Formule (I)

\[
\begin{align*}
\text{COOR}_1 & \quad \text{COOR}_3 \\
(\text{CH}_2)_n & \quad (\text{CH}_2)_p \\
\text{R}_5 & \quad \text{R}_6 \\
\text{HC} - \text{N} - (\text{CH}_2\text{CH}_2\text{N})_m - \text{CH} & \quad \text{COOR}_4
\end{align*}
\]

(I)

dans laquelle

- \( n \) vaut de 1 à 3
- \( m \) vaut de 0 à 3
- \( p \) vaut de 1 à 3
- \( R_1, R_2, R_3 \) et \( R_4 \) sont H, Na, K, Ca ou Mg
- \( R_5 \) et \( R_6 \) sont H, CH\(_2\)OH, CH\(_2\)CH\(_2\)OH ou CH\(_2\)O(\text{CH}_2\text{CH}_2\text{O})\text{t-10} \text{CH}_2\text{CH}_2\text{OH}.

2. Procédé selon la revendication 1, caractérisé en ce que l'agent chélatant est l'acide éthylénediamine-N,N'-disuccinique et/ou un sel d'un métal alcalin ou un sel d'un métal alcalino-terreux de ce dernier.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'agent chélatant utilisé est un sel de sodium, de calcium ou de magnésium de l'acide éthylénediamine-N,N'-disuccinique ou l'acide éthylénediamine-N,N'-disuccinique et le sulfate de calcium et/ou le sulfate de magnésium.

4. Procédé selon la revendication 1, caractérisé en ce que l'agent chélatant utilisé est l'acide 2,2'-iminodisuccinique et/ou un sel de sodium, de calcium ou de magnésium de l'acide 2,2'-iminodisuccinique ou l'acide 2,2'-iminodisuccinique et le sulfate de calcium et/ou le sulfate de magnésium.

5. Procédé selon la revendication 1 ou 4, caractérisé en ce que l'agent chélatant utilisé est un sel de sodium, de calcium ou de magnésium de l'acide 2,2'-iminodisuccinique ou l'acide 2,2'-iminodisuccinique et le sulfate de calcium et/ou le sulfate de magnésium.

6. Procédé selon la revendication 1, caractérisé en ce que le pré-traitement de la pâte est mis en œuvre à un pH de 4 à 8, de préférence à un pH de 5,0 à 7,5 et de façon la plus préférée à un pH de 6,5 à 7,5.

7. Procédé selon la revendication 1 ou 6, caractérisé en ce que le pré-traitement avec un agent chélatant constitue une étape qui précède directement un blanchiment ou une délignification avec un produit chimique oxygéné.

8. Procédé selon l'une quelconque des revendications 1, 6 et 7, caractérisé en ce que le pré-traitement est mis en œuvre en une fois ou plusieurs fois.

9. Procédé selon la revendication 1 ou 7, caractérisé en ce que le blanchiment ou la délignification par un produit chimique oxygéné comprend le blanchiment avec un acide peracétique, le blanchiment avec un mélange de peracides, le blanchiment avec des peroxydes en l'état ou sous forme de mélanges, seuls ou sous forme d'un mélange avec des peracides, un blanchiment par du peroxyde d'hydrogène catalysé par un métal de transition, dans la plage de pH acides, un blanchiment par un peroxyde d'un métal alcalin, et les combinaisons de tous ces procédés, ainsi que la délignification à l'oxygène, une étape oxygène-alcali renforcée par un peroxyde et des étapes utilisant des peroxydes sous pression, et en combinaison avec ceux-ci des traitements facultatifs avec des enzymes, de l'ozone ou du dioxyde de chlore.
10. Procédé selon la revendication 1 ou 9, caractérisé en ce que le traitement chélatant est mis en oeuvre aussi dans l'étape de blanchiment ou de délignification par un produit chimique oxygéné.

11. Procédé selon l'une quelconque des revendications 1, 9 et 10, caractérisé en ce que le blanchiment ou la délignification par un produit chimique oxygéné est réalisé à un pH de 4 à 8, de préférence à un pH de 4 à 6 et de façon la plus préférée à un pH de 4 à 5.

12. Procédé selon l'une quelconque des revendications 1 et 9 à 11, caractérisé en ce que le traitement par un produit chimique oxygéné est mis en oeuvre une fois ou en plusieurs fois.

13. Procédé selon l'une quelconque des revendications 1 et 9 à 12, caractérisé en ce que le traitement de la pâte par un procédé chimique oxygéné est mis en oeuvre simultanément avec un peroxyde et avec un peracide.

14. Procédé selon l'une quelconque des revendications 1 et 9 à 13, caractérisé en ce que le traitement de la pâte par un peroxyde est mis en oeuvre avec du peroxyde d'hydrogène, avec un mélange de peroxyde d'hydrogène et d'oxygène gazeux, ou avec des composés peroxy organiques.

15. Procédé selon l'une quelconque des revendications 1 et 9 à 14, caractérisé en ce que le traitement de la pâte par un peracide est mis en oeuvre avec de l'acide peracétique, performique, perpropionique ou de Caro, ou avec un acide peracétique, performique, perpropionique ou de Caro activé par un métal de transition ou une combinaison de ces derniers.

16. Procédé selon l'une quelconque des revendications 1 à 15, caractérisé en ce que l'agent chélatant est utilisé à raison de 0,1 à 5 kg/tonne métrique de pâte sèche.