METHOD OF PREPARING MODIFIED CELLULOSE PULP

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ABSTRACT

A method of preparing modified cellulose pulp using arabinoxylans is described. The method involves contacting, (i) an arabinoxylan with (ii) a cellulose pulp. The arabinoxylan of the process is in a form selected from a concentrated solution comprising arabinoxylan or a suspension comprising arabinoxylan. Also described are: a modified cellulose pulp prepared according to the present invention; and a particular arabinoxylan having on its main chain 5 to 20% arabinose substituents, and less than 5% 4-O-methylgluconic acid substituents, (the percent weights being based on the total weight of the arabinoxylan).
Figur 1

Tear Index (mN*m²/g)

Figur 2

Bulk (cm³/g)
METHOD OF PREPARING MODIFIED CELLULOSE PULP

CROSS REFERENCE TO RELATED PATENT APPLICATION


FIELD OF THE INVENTION

The present invention concerns the use of arabinoyxans as additive in paper production.

BACKGROUND OF THE INVENTION

The mechanical properties of paper are influenced by a series of different parameters of a chemical and physical nature. Several theories to explain the tear resistance properties of paper have been suggested, most of which emphasise the special relevance of fibre-fibre bonding. Amongst the most frequently cited is the theory that includes the factors of interfibre bonding force of the bonded surface and the length of the fibre.

It is generally agreed that the hemicelluloses native to the pulp improves the tear resistance and contributes to the formation of stronger fibre bonding. Depending upon the raw material and the pulping method, these hemicelluloses are modified greatly during pulp preparation and are destroyed to a considerable extent.

The use of xylans as additive in paper manufacture is known. Thus Naterova et al. (Papir a celuloza, 41, (7-8), V23-V30, 1986) describe the addition of 2% maize xylan to packaging paper. In this way the flexural strength is increased by about 172% by the addition of 2% xylan.

DE 44 09 372 A1, U.S. Pat. No. 5,810,972 and WO 2004/031477 A1 describe the addition of highly refined birch pulp and Lenzing xylan in the range of 0.005 to 0.14% (WO 2004/031477 A1) or 0.15 to 1.5% (U.S. Pat. No. 5,810,972, DE 44 09 372 A1) to tissue products. A positive effect of the xylans and xylan-rich, highly refined birch pulp on the softness of the tissue product and the behaviour of the paper web on the drying drum is described. The breaking strength was increased by 15 to 73% in the machine way and 17 to 90% transverse to the direction of travel. Allegedly the behaviour of the dry end was positively influence but not reported numerically, but assessed according to the experience of the paper maker.

In the aforementioned applications the use of xylans from the raw material wood and its secondary product pulp is discussed. In particular, the use of acetyl-4-O-methylglucuronoxylan from deciduous wood and arabin-4-O-methylglucuronoxylan from coniferous wood is cited. The examples on the use of xylans cites Lenzing xylan. This product is obtained by alkaline extraction of beech wood pulp in the viscose process and exhibits only a low degree of polymerisation of about 35.

Consequently different xylans have been investigated in respect of their attributes for the fibre properties or as paper additive. However, the work cited shows that an improvement in tear length is associated with a deterioration in other strength properties or in an unacceptable deterioration in optical properties.

There is therefore still the requirement for a cost-effective paper additive that brings about an improvement in paper properties, in particular strength, bulk and optical properties.

SUMMARY OF THE INVENTION

It has now been surprisingly found that the addition of arabinoyxans to pulp during paper production brings about a significant improvement in paper properties. By the use of arabinoylan the tear length, the tear resistance and the bulk, i.e., the volume of the paper, is improved. The improvement in the bulk improves not the strength properties and the optical properties of the paper. Surprisingly a significantly greater improvement of the paper properties is achieved in comparison to other xylans such as 4-O-methylglucuronoxylans from deciduous wood or Lenzing xylans.

In accordance with the present invention, there is provided a method of preparing a modified cellulose pulp comprising contacting,

- (i) an arabinoylan, said arabinoylan being in a form selected from the group consisting of a concentrated solution comprising arabinoylan and a suspension comprising arabinoylan, with

- (ii) a cellulose pulp.

In further accordance with the present invention, there is provided a modified cellulose pulp comprising:

- cellulose pulp; and

0.1% to 40% by weight of an arabinoylan, based on the total weight of cellulose pulp and arabinoylan.

There is also provided, in accordance with the present invention, an arabinoylan comprising, on its main chain:

- 5 to 20% arabinose substituents; and

- less than 5% 4-O-methylglucuronic acid substituents the percent weights being based on the total weight of the arabinoylan.

The subject matter of the invention relates in part to the use of arabinoyxans as additive in paper manufacture.

The features that characterize the present invention are pointed out with particularity in the claims, which are annexed to and form a part of this disclosure.

These and other features of the invention, its operating advantages and the specific objects obtained by its use will be more fully understood from the following detailed description and accompanying drawings in which preferred embodiments of the invention are illustrated and described.

Unless otherwise indicated, all numbers or expressions used in the specification and claims are understood as modified in all instances by the term “about.”

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation of plots of tear and tensile strengths of pulp samples treated with arabinoylan; and
FIG. 2 is a graphical representation of a plot of specific volume of pulp versus tensile break strength for samples of pulp treated with arabinoxylan.

DETAILED DESCRIPTION OF THE INVENTION

Suitable arabinoxylans are polysaccharides that are present in, for example, different annual plants and agricultural residues such as oat husks, straw or maize. The arabinoxylans can be obtained by different extraction techniques, e.g., with water, steam or solvents with the aid of the most different of auxiliary chemicals, as well as by enzymatic isolation and purification steps. Preferably alkali-extracted arabinoxylans are used, especially arabinoxylans from oat husks that can be obtained, for example, by extraction of oat husks with aqueous alkali solution, separation of the alkali extract and subsequent precipitation of the alkali extract in a precipitation bath of water and a water-miscible organic solvent A, with the alkali extract not neutralised before precipitation.

The special feature of the arabinoxylans from oat husks in comparison to xylans from deciduous wood and coniferous wood is that they have a comparably high number of arabinose substituents but not the 4-O-methylglucuronic acids occurring in deciduous and coniferous xylans. In comparison to xylans from pulp such as the Lenzing xylans, the arabinoxylans exhibit a much higher chain length.

Within the context of the present invention arabinoxylans are understood to be such xylans that bear 5 to 20% (w/w relative to the whole sample), preferably 7 to 15%, most preferably 8 to 13% arabinose substituents in their main chain and less than 5%, preferably less than 2%, most preferably less than 1% 4-O-methylglucuronic acid substituents (chromatographic sugar determination after acid hydrolysis).

Arabinoxylans that are obtained by extraction of oat husks with aqueous alkaline solution with isolation of an alkaline extract and subsequent precipitation of the alkaline extract in a precipitation bath of water with a water-miscible organic solvent A with the alkali extract not neutralised before precipitation are particularly preferred. Such arabinoxylans exhibit a chain length of at least 100 also after a possible bleaching stage. Usually the chain lengths of these arabinoxylans lie in the range 120 to 240.

A further subject matter of the invention is a method for the preparation of cellulose pulps comprised of contact with a concentrated solution or suspension of an arabinoxylan with pulp or stock system that contains pulp.

In one embodiment of the invention the arabinoxylan solution or suspension is added to the fibre suspension before sheet making. The action of the arabinoxylan is also carried out in combination with other paper chemicals which are added to the fibre before, after or together with the arabinoxylan. In this way the use of arabinoxylan is advantageous for the most different of products in the paper industry.

Other normal paper chemicals are for example wet-strength agents, fillers, retention agents, fixatives, defoamers, deaerators, sizing agents, optical brighteners and colorants.

A homogeneous solution or suspension of the arabinoxylan can be achieved, for example, by intense mechanical loading such as stirring, by the effect of temperature or with the help of chemicals, preferably basic chemicals such as alkali or alkaline earth hydroxides, preferably NaOH. The concentration of the arabinoxylan solution or suspension can be varied over a wide range of 0.1 to 40% (w/w). Preferred is the range of 0.1 to 25% (w/w), especially preferred is the range from 0.5% to 10% (w/w).

The arabinoxylan solution or suspension can be incubated with the pulp and the desired paper auxiliaries and additives in high pulp density (solids content) of up to 20% before the pulp enters the headbox of the paper machine. Then by squeezing out the supernatant solution any unab sorbed chemicals can be used for the next batch.

In a further embodiment of the invention the pulp is mixed with the additives and the arabinoxylan solution or suspension in any desired sequence in the headbox, that is immediately before entry into the machine for paper production. The addition of the arabinoxylan in the headbox usually achieves better results than the previous incubation with the pulp.

In a further embodiment of the invention the arabinoxylan solution or suspension is added to the pulp suspension before the refinement of the pulp fibres.

Usually after achieving the optimal quantities no further increase in strength and bulk is achieved by further increase in the amount of arabinoxylan in a product formulation. The optimal amount is dependent upon which other paper auxiliaries are used in the mass so that the amount of arabinoxylan used relative to pulp can be in a wide range of 0.1% to 40% (w/w). Preferably, however, an amount between 0.5 and 10% arabinoxylan is used. Usually with the use of paper additives the optimal increase in strength is achieved at even lower arabinoxylan concentration.

The invention is illustrated but not limited in the following by a number of embodiment examples.

EXAMPLES

Unless otherwise stated in the following examples the compositions of xylans are given as % w/w relative to the whole sample, determined by chromatographic sugar determination after acid hydrolysis.

Example 1
Of the Invention

An arabinoxylan from oat husks (9.5% arabinose, <1% 4-O-methylglucuronic acid, DP ca. 160) was dissolved in water with heating with formation of a 5% solution. 20 g coniferous sulfite pulp was suspended in water and treated with the xylan solution in the amounts given in Table 1. For experiments with higher amounts of xylan solution correspondingly lower amounts of water were used in each case for suspension of the pulp. After addition of the xylan suspensions the pulp density was 7.1% in each case. The experimental batches were all incubated for 2 h at 50°C. After incubation the pulp was filtered off through a nutch.

The pulp was refined for 2.5 min in a Jokro mill in accordance with ISO 5264-3 and laboratory sheets produced
in accordance with ISO 5269-2 (rapid Köthen method). Testing for strength was carried out in accordance with ISO 1974 (DIN EN 21974).

TABLE 1

<table>
<thead>
<tr>
<th>Amount of arabinoxylan in % (w/w) rel. to pulp</th>
<th>Tear length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (reference)</td>
<td>2734</td>
</tr>
<tr>
<td>7.5</td>
<td>3473</td>
</tr>
<tr>
<td>22.5</td>
<td>3935</td>
</tr>
<tr>
<td>37.5</td>
<td>4199</td>
</tr>
</tbody>
</table>

The data in Table 1 show that in comparison with the reference pulp without xylan the pulp treated with arabinoxylan from oat husks exhibited considerably higher strength. The tear lengths increased with increasing xylan amounts. The greatest increase in tear length by addition of arabinoxylan from oat husks is 1465 m.

Example 2

Comparison Example

A 4-O-methylglucuronoxylan from birch wood (no arabinose side chains, 8.8% molar ratio 4-O-methylglucuronic acid relative to xylose units, determined by \(^1\)H NMR, DP ca. 95) was dissolved in water with heating as 5% solution. 20 g coniferous sulfite pulp was suspended in water and treated with the xylan solution. For experiments with higher amounts of xylan solution correspondingly lower amounts of water were used to suspend the pulp. After addition of the xylan suspensions the pulp density was 7.1% in each case. The experimental batches were each incubated for 2 h at 50°C. After incubation the pulp was filtered off through a nutch.

TABLE 2

<table>
<thead>
<tr>
<th>Amount of 4-O-methylglucuronoxylan in % (w/w) rel. to pulp</th>
<th>Tear length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (reference)</td>
<td>2734</td>
</tr>
<tr>
<td>7.5</td>
<td>2983</td>
</tr>
<tr>
<td>22.5</td>
<td>3126</td>
</tr>
<tr>
<td>37.5</td>
<td>3189</td>
</tr>
</tbody>
</table>

The data in Table 2 show that the 4-O-methylglucuronoxylan from birch wood can bring about only a very small increase in strength. The action of this xylan is less than 31% of the action of arabinoxylan from oat husks.

Example 4

Comparison Example

An arabinoxylan (9.5% arabinose, <1% 4-O-methylglucuronic acid DP ca. 160) from oat husks was dissolved in water with heating as 5% solution. A coniferous sulfite pulp was then refined for 2.5 min. in a Jokro mill in accordance with ISO 5264-3 and laboratory sheets produced in accordance with ISO 5269-2 (rapid Köthen method). Testing for strength was carried out in accordance with ISO 1974 (DIN EN 21974).

Example 5

A 4-O-methylglucuronoxylan from birch wood (no arabinose side chains, 1% 4-O-methylglucuronic acid, DP ca. 35) was dissolved in water with heating as 5% solution. 20 g coniferous sulfite pulp was suspended in water and treated with the xylan solution. For experiments with higher amounts of xylan solution correspondingly lower amounts of water used to suspend the pulp. After addition of the xylan suspensions the pulp density was 7.1% in each case. The experimental batches were each incubated for 2 h at 50°C. After incubation the pulp was filtered off through a nutch.

The pulp was refined for 2.5 min in a Jokro mill in accordance with ISO 5264-3 and laboratory sheets produced in accordance with ISO 5269-2 (rapid Köthen method). Testing for strength was carried out in accordance with ISO 1974 (DIN EN 21974).

TABLE 3

<table>
<thead>
<tr>
<th>Amount of arabinoxylan in % (w/w) rel. to pulp</th>
<th>Tear length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (reference)</td>
<td>2734</td>
</tr>
<tr>
<td>7.5</td>
<td>2983</td>
</tr>
<tr>
<td>22.5</td>
<td>3126</td>
</tr>
<tr>
<td>37.5</td>
<td>3189</td>
</tr>
</tbody>
</table>

The tear length can be improved by more than 1000 m by the addition of arabinoxylan from oat husks compared to the reference. With this method of addition the increases in strength can be achieved with low usage of arabinoxylan.
Example 5

[0051] An arabinoxylan from oat husks (9.5% arabinose, <1% 4-O-methylglucuronic acid DP ca. 160) was dissolved in water with heating as 5% solution. A coniferous sulfite pulp was then refined for 2.5 min in a Jokro mill in accordance with ISO 5264-3 and laboratory sheets prepared in accordance with ISO 5269-2 (rapid Köthen method). The xylan solutions were in each case added to the pan which is used for portioning the suspension for the individual laboratory sheets. In each pan 16 g pulp were equalised in each case in a total liquid of 6.67 l with a pulp density of 0.24%. A cationic polyamide-epichlorhydrin resin was added as paper auxiliary and stirred into the suspension for 5 min. The dosage of the paper additive corresponded constantly to a charge density of 0.013 meq/g pulp in all experiments carried out. Next the respective arabinoxylan solution was added. After 5 min portioning and preparation of the laboratory sheets was carried out.

[0052] All experiments were carried out at room temperature. Testing for strength was carried out according to ISO1974 (DIN EN 21974).

<table>
<thead>
<tr>
<th>Amount of xylan additive (g/100g pulp)</th>
<th>Tear length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>3944</td>
</tr>
<tr>
<td>0.09</td>
<td>3192</td>
</tr>
<tr>
<td>0.93</td>
<td>4698</td>
</tr>
<tr>
<td>2.3</td>
<td>5486</td>
</tr>
<tr>
<td>4.7</td>
<td>5629</td>
</tr>
<tr>
<td>7.0</td>
<td>5710</td>
</tr>
<tr>
<td>9.4</td>
<td>5728</td>
</tr>
</tbody>
</table>

[0053] The tear length can again be significantly increased by the addition of arabinoxylan compared to the reference. It can be clearly seen from the reference that through the use of the paper additive the strength generally lies at a higher level. In regard to the effect of the arabinoxylan a synergistic effect emerges in the interaction with the paper additive. The increases in the tear length are now up to as much as ca. 1800 m. The higher increases in strength are even effective at lower amounts of arabinoxylan than in the experiments without paper additive.

Example 6

[0054] An arabinoxylan from oat husks (9.5% arabinose, <1% 4-O-methylglucuronic acid DP ca. 160) was dissolved in water with heating as 5% solution. A beech wood sulfite pulp was then refined for 2.5 min, 5 min, 10 min, 15 min and 20 min in a Jokro mill in accordance with ISO 5264-3 and laboratory sheets prepared in accordance with ISO 5269-2 (rapid Köthen method). The arabinoxylan solutions at 9.4% (relative to pulp) were in each case added to the pan which is used for portioning the suspension for the individual laboratory sheets. In each pan 16 g pulp were equalised in each case in a total liquid of 6.67 l with a pulp density of 0.24%. 5 Min after addition of the arabinoxylan solution portioning and preparation of the laboratory sheets was carried out. All experiments were carried out at room temperature. Testing for strength was carried out according to ISO1974 (DIN EN 21974). Light scattering coefficients were determined according to Instruction SCAN C 27:76.

[0055] The experiments showed that not only the tensile strength of the pulp was increase by arabinoxylan addition, but also the tear strength. The tear-tensile plot allows combined viewing of the tensile strength and tear strength of all samples from the refinement series (FIG. 1). Effect of arabinoxylan from oat husks (9.38% relative to pulp) on the tear-tensile plot of beech sulfite pulp. It is obvious that the samples show clearly better values in both strengths by the addition of the arabinoxylan such that the whole curve is displaced to a higher level.

[0056] The specific volume of the pulp is characterised by the bulk, which is plotted in FIG. 2 against the tensile breaking strength (Effect of arabinoxylan from oat husks (9.38% relative to pulp) on the bulk-tensile plot of beech sulfite pulp). It is clear that the curve for the different points of the degree of refinement is displaced to higher bulk values. In order to produce a product with the desired strength a higher sheet volume can be produced by the addition of the arabinoxylan. The increased bulk leads to an increase in the light scattering coefficients and thus to improved optical properties.

[0057] Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

What is claimed is

1. A method of preparing a modified cellulose pulp comprising contacting,

   (i) an arabinoxylan, said arabinoxylan being in a form selected from the group consisting of a concentrated solution comprising arabinoxylan and a suspension comprising arabinoxylan, with

   (ii) a cellulose pulp,

2. The method of claim 1 wherein 0.1 and 40% by weight of said arabinoxylan is contacted with said cellulose pulp, based on the total weight of arabinoxylan and cellulose pulp.

3. The method of claim 1 further comprising:

   incubating the arabinoxylan with the cellulose pulp at a cellulose pulp concentration of a positive amount up to 20% by weight, based on the total weight of arabinoxylan and cellulose pulp, thereby forming an incubated composition comprising arabinoxylan and cellulose pulp; and

   adding at least one paper additive to said incubated composition.

4. The method of claim 1 further comprising:

   adding at least one paper additive, thereby forming a composition comprising arabinoxylan, cellulose pulp and said additive; and

   incubating the composition comprising arabinoxylan, cellulose pulp and said additive, wherein said cellulose
pulp is present in a positive amount of up to 20% by weight, based on the total weight of arabinoxylan and cellulose pulp.

5. The method of claim 1 further comprising:
providing a paper making machine comprising a head box; and
introducing said arabinoxylan and said cellulose pulp into the head box of said paper making machine after contacting said arabinoxylan with said cellulose pulp.

6. The method of claim 1 further comprising refining a composition formed by contacting said arabinoxylan with said cellulose pulp in a refiner.

7. A modified cellulose pulp comprising:
cellulose pulp; and
0.1% to 40% by weight of an arabinoxylan, based on the total weight of cellulose pulp and arabinoxylan.

8. The modified cellulose pulp of claim 7 wherein the arabinoxylan comprises, on its main chain:
5 to 20% arabinose substituents; and
less than 5% 4-O-methylglucuronic acid substituents, the percent weights being based on the total weight of the arabinoxylan.

9. An arabinoxylan comprising, on its main chain:
5 to 20% arabinose substituents; and
less that 5% 4-O-methylglucuronic acid substituents the percent weights being based on the total weight of the arabinoxylan.

10. Paper comprising the modified cellulose of claim 1.

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