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- **Garcia-Lindgren, Cherryleen**  
**89233 Domsjö (SE)**
- **Wännström, Sune**  
**89240 Domsjö (SE)**
- **Wågberg, Lars**  
**18130 Lidingö (SE)**
- **Gärdlund, Linda**  
**85733 Sundsvall (SE)**

(71) Applicant: **M-Real Oyj**  
**02100 Espoo (FI)**

(74) Representative: **Sundman, Patrik Christoffer et al**  
**Seppo Laine Oy**  
**Itämerenkatu 3 B**  
**00180 Helsinki (FI)**

(72) Inventors:  
• **Marklund, Ann**  
**89292 Domsjö (SE)**

(54) **Method of producing paper and board**

(57) The present invention relates to a method of producing a fibrous paper or cardboard web as well as to novel paper and board products. According to the method, the web is produced on a paper or cardboard machine from an aqueous furnish containing fibres mainly derived from a deciduous tree species, fillers and any conventional additives. The fibres are admixed in the furnish with

a polyelectrolyte complex before adding the fillers and any additives. With the invention, fibre and paper properties can be improved in combination with reduced energy consumption for refining. Furthermore, filler content can be increased while maintaining or even improving strength properties.

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## Description

**[0001]** The present invention relates to a method according to the preamble of claim 1 for producing a fibrous web on a paper or board machine.

**[0002]** According to a method of this kind, the fibrous web is formed from an aqueous furnish containing lignocellulosic fibres, mainly derived from a deciduous tree species, along with fillers and conventional additives, if any.

**[0003]** The present invention also concerns a method according to the preamble of claim 26 of producing a polyelectrolyte complex as well as novel paper and board products according to the preamble of claim 29.

**[0004]** In the production of different paper and board qualities, the paper maker has to find a compromise between different properties. For liquid packaging board, bending stiffness is one of the more important properties; for office paper dimensional stability and opacity as well as print quality are of utmost importance; for corrugated paper products compression strength is desirable, etc. The properties influence the choice of raw materials. It is well known that short fibres from hardwoods are better for opacity than long fibres. On the other hand, the long fibres of softwoods give good strength properties easier than hardwood fibres, refined or not. Therefore, the particular fibres or mixture of fibres selected for the intended fibrous product will vary depending on the desired properties of the product.

**[0005]** Furthermore, mineral fillers are incorporated into most printing papers and board products in order to improve opacity, to save fibres and improve printing results.

**[0006]** Prior to papermaking the fibres are conventionally beaten to enhance bonding and strength properties. Fibre straightening, internal and external fibrillation and fines generation contribute to improved bonding between the fibres. However, the beating process is energy consuming, gives inefficient fibre treatment and is fibre length cutting.

**[0007]** As well-known in the art, various polymeric materials can be added to the furnish for modifying the properties of the fibres, e.g. for fibre sizing. It is also known in the art to use both cationic and anionic polymers.

**[0008]** US Patent No. 5,061,346 (Betz Paperchem Inc.), titled "Papermaking using cationic starch and carboxymethyl cellulose or its additionally substituted derivatives", discloses sequential addition of cationic starch and carboxymethyl cellulose to a furnish for improved strength and filler loading.

**[0009]** JP Patent Application No. 2004250803 (Japan Maize Prod.), titled "Method for producing amphoteric starch polyion complex and method for producing paper", discloses a preproduced complex for improving drainage properties (measured as Schopper-Riegler or Standard Canadian Freeness) and filler retention.

**[0010]** Published International Patent Application WO 03087473 (Hercules Inc.), titled "Process for increasing the dry strength of paper", suggests that a premixed aqueous mixture of anionic dry strength resin and cationic starch or amphoteric starch having a net cationic charge be added to a pulp slurry to improve dry strength of papers made thereof.

**[0011]** Prof. Lars Wågberg's group has published several articles on the characterisation of polyelectrolyte complexes and its influence on strength properties for bleached spruce pulps for papermaking and high yield pulps for corrugated boardmaking (cf. for example Colloids and Surfaces A, Physicochem. Eng. Aspects 213(2003) pp. 15-25).

**[0012]** So far, nobody has addressed the question of improving the properties of pulps predominantly comprising hardwood fibres, such as uncoated and coated fine papers and board made from wood fibres, chemical and/or mechanical fibres, and inorganic filler material. Further, one particular paper property, is the bending stiffness, even if it is a quite important property not only for board products but also for papers which are printed in the form of sheets (cut-size papers). If the paper sheet exhibits good bending stiffness, this means in practice that copiers and printers can transfer the paper through the printing equipment much easier. Also the runnability on a paper machine of a web formed from short, hardwood fibres is better when the bending stiffness is high and the wet strength good.

**[0013]** The conventional way of improving (internal) bonding of fine papers is to increase beating and refining as explained above.

**[0014]** It is an aim of the present invention to provide an alternative way of producing paper and board and similar fibrous products, in particular papers, such as uncoated fine papers, predominantly formed from fibres of deciduous tree (hardwood) and mineral or polymeric fillers. Particularly, it is an aim to provide fibrous products of the above kind having good mechanical properties, such as a combination of improved bonding strength and bending stiffness, at a high bulk, said fibres being subjected to a minimum or no beating before papermaking.

**[0015]** The present invention is based on the finding that by treating the fibres with a preformed polyelectrolyte complex before papermaking, the properties of the paper can be improved at higher filler contents and higher short fibre contents can be reached. Surprisingly, we have found that by adding a polyelectrolyte complex for example to unbeaten pulp it is possible to improve both bulk and strength properties (bending stiffness, Scott Bond and tensile strength). Furthermore, high light scattering is also maintained with the treatment of unbeaten pulp with a polyelectrolyte complex. As a result strong sheets can be obtained without loss of light scattering.

**[0016]** The method of producing a polyelectrolyte complex formed by a cationic polymer and an anionic polymer, comprises typically the step of mixing together, under turbulent mixing conditions, a first liquid flow ( $Q_1$ ) containing the anionic polymer and a second liquid flow ( $Q_2$ ) containing the anionic polymer, the turbulent mixing conditions being obtained by converging, at predetermined flow rates, the liquid flows to form integral or combined flow containing the

mixed polymers at predetermined ratios.

**[0017]** The present invention provides a fibrous product which comprises a fibrous matrix containing at least 50 % of fibres derived from deciduous tree, and further containing about 0.05 to 5.0 % of a polyelectrolyte complex, the amount being calculated on the dry weight of the paper (board).

**[0018]** More specifically, the method according to the present invention of producing fibrous webs is mainly characterized by what is stated in the characterizing part of claim 1.

**[0019]** The method of producing the polyelectrolyte complex is characterized by what is stated in the characterizing part of claim 26, and the fibrous product according to the present invention is characterized by what is stated in the characterizing part of claim 29.

**[0020]** Considerable advantages are reached by means of the present invention. Thus, as discussed above, strength properties (tensile strength, Scott Bond and bending stiffness) are maintained or improved without or with less refining of the fibres.

**[0021]** Higher filler content in paper is continuously aimed at due to cost and property benefits. So far, higher filler contents have been difficult to reach especially due to lower strength. However, the present invention makes it possible to increase filler content from 20 % to around 30 % while maintaining or even improving strength properties. Higher short fibre content (birch, aspen, mixed hardwood etc) gives better formation and printing properties, but lower strength properties. This invention makes it also possible to produce papers with higher (80-100 %) hardwood content with retained or improved strength, optical and printing properties.

**[0022]** The present invention can also be used to reduce the grammage of the paper without losing strength and optical properties, which gives economical benefits. Stock sizing is also improved.

**[0023]** A polyelectrolyte complex (PEC) treatment of fibres of the present kind, especially a treatment carried out with anionic PEC, can be utilised for improvement of fibre and paper properties combined with reduced energy consumption for refining. Increase of filler content, improvement of formation, improvement of printing properties and reduced grammage are additional benefits. PEC can be tailored to contain either a negative or a positive net charge. Good effects on retention have been observed with cationic PEC treatment, which of those being most interesting to implement is product/mill specific.

**[0024]** Next, the invention will be discussed more closely with the aid of the following detailed description and with reference to a number of working examples.

**[0025]** As discussed above, the present invention provides a method of producing a fibrous web on a paper or cardboard machine from an aqueous furnish containing fibres mainly derived from a deciduous tree species. All normal hardwoods (and softwoods) are suitable for use in the present method and will give similar results. Most interesting wood qualities for the production of hardwood-based papers are birch, beech, aspen, poplar, oak and eucalyptus. The deciduous fibres material can comprise fibres from one single wood species or a mixture of several.

**[0026]** In addition to hardwood fibres, also softwood fibres can be incorporated into the furnish. The softwood fibres are normally used for improving strength properties. Typically, fibres of pine (trees of the *Pinus* family) or spruce (trees of the *Picea* family) are used.

Usually, based on the o.d. (oven dry) weight of the fibres, the fibre composition comprises 40 to 100 % hardwood fibres and 60 to 0 % of softwood fibres.

**[0027]** According to one embodiment, at least 50 %, preferably at least 60 %, by weight of the fibres are formed by fibres of a deciduous wood species. According to another embodiment, 60 to 100 %, preferably 80 to 100 %, by weight of the fibres are comprised of deciduous wood fibres. The actual fibre composition will be selected depending on optical and mechanical properties of the paper product.

**[0028]** The fibres can be produced by mechanical, chemimechanical or chemical pulping. Groundwood, pressure groundwood, thermomechanical and chemi thermomechanical pulping are examples of suitable mechanical pulping methods. The chemical pulp can be produced by kraft, soda, sulphite or organosolv pulping.

**[0029]** In addition to fibres, the furnish typically contains particulate fillers. For example, various clay and calcium carbonate grades (including ground calcium carbonate and precipitated calcium carbonate). These fillers can be incorporated freely in amounts up to about 40 %, based on the total dry weight of the paper/board, although 5 to 35, and in particular about 8 to 30 % are conventional and about 20 % is typical. As mentioned above, the present invention allows for an increase of the filler content from about 20 to about 30 without impairing strength properties of the web, which is a surprising and rather valuable result.

**[0030]** The furnish may also contain other conventional additives, such as sizing agents and retention agents, including AKD or ASA resins, rosins and ionic and polymeric retention agents. Many of the additives in the paper furnish serve to ensure that the fibers have the required properties to attract and bond. Conventionally, the amount of such additives does not exceed 5 % by the dry weight of the paper/board, typically the amount is in the range of about 0.1 to 4 % by weight.

**[0031]** The components of the furnish are fed to the wet end of the paper machine at a consistency (of fibres) of about 0.2 to 2 % in the aqueous phase, in particular about 1 %.

According to the invention, the fibres are modified by contacting them with a polyelectrolyte complex. The modification

step comprises typically admixing, continuously or intermittently, the fibres of the furnish with a polyelectrolyte complex before adding fillers and any additives. The mixing and contacting time can amount to about 1 second to about 24 hours, typically some 10 seconds to 5 hours is sufficient and times in the range of about 1 minute to about 1 hour are preferred. The pH is in the range of 4 to 9, preferably 5 to 8, the temperature in the range of 10 to 65 °C and the pulp consistency from 0.1 to 5 %, preferably 2 to 4 %.

**[0032]** The polyelectrolyte complex (in the following also abbreviated PEC) is preformed and added as such (cf. below).

**[0033]** As a pre-treatment step, the fibres can be treated with a polymer having a net charge. According to a preferred embodiment, a portion of one of the components of the complex is used for improving attachment. The pre-treatment step is preferably carried out separately from the admixing with the PEC.

**[0034]** In particular, the treatment is carried out with a cationic polymer. Typically, the same polymer that is used as a cationic component of the complex is also employed for the pre-treatment, although it is possible to pre-treat the fibres with a first cationic component and to use a second for forming the complex. Of the total amount of cationic polymer employed during the treatment, about 10 to 95 % by weight of the polymer, preferably 20 to 90 % by weight and in particular about 20 to 60 % by weight is separately attached to the fibrous material in a pre-treatment step.

**[0035]** With the aid of a pre-treatment the affinity of the polyelectrolyte complexes for fibres is increased, in particular when the polyelectrolyte complex has a negative net charge. By treating the fibres with a cationic polymer, attachment of negatively charged polyelectrolyte complexes to the fibre surface is facilitated. With cationic polyelectrolyte complexes pre-treatment is generally not needed. Furthermore, our tests show that the pre-treatment increases the effects of the PEC. It would appear that the cationic polymer, such as polyamideamine epichlorohydrine (PAE) or other polyamine-derived polymers, which have a tertiary or quaternary amine functionality, enable increased attachment of PEC to the fibres.

**[0036]** Based on the above, according to a particularly preferred embodiment, the modification step comprises two stages, whereby in the first step, the fibres are treated with a cationic polymer component and in the second the thus obtained fibres are contacted with the preformed complex, in particular with a complex which has a predominantly anionic net charge.

**[0037]** The contacting times can be of equal length in both stages and as explained above.

**[0038]** The invention comprises three interesting embodiments with regards to the degree of beating of the fibres which are to be treated. Thus, according to a first preferred embodiment, the fibrous web is produced from fibres which have not been subjected to beating before web formation. This embodiment will save considerable amounts of energy.

**[0039]** With respect to this, a very interesting observation was that, light scattering was about the same with PEC used to unbeaten pulp as beaten pulp without PEC. In this case, strong sheets were obtained without loss of light scattering.

**[0040]** According to a second preferred embodiment, the fibrous web is produced from fibres, which have been subjected only to a moderate degree of beating amounting to less than 50 kWh/ton of fibrous material. This embodiment will provide for a reduction in beating energy and improved bonding.

**[0041]** According to a third embodiment, the fibres which are used for producing the web are subjected to beating energy input in excess of 50 kWh/ton and up to 400 kWh/ton of fibrous material. Improved bonding will be achieved.

**[0042]** According to the second embodiment above, the degree of refining for the fibres is low, preferable so low that only fibre bundles are clearly separated from each other. In the present case, the energy consumption of beating or refining can be reduced to less than 50 kWh/ton of dry fibres, preferably to between 20-50 kWh. The refining degree is, as a Schopper-Riegler (SR) number, maximally about 20 to 21 SR or less, and as CSF (Canadian Standard Freeness) between 700 and 500 ml. It is possible to use completely unbeaten fibres as part of the furnish for papermaking. As a result of the preferred embodiments of using either unbeaten or only moderately beaten fibres, drainage of the fibrous web on the paper machine is improved, which facilitates production at higher machine speeds.

**[0043]** The polyelectrolyte complex used in the present invention is a complex formed by a cationic polymer and an anionic polymer. The polyelectrolyte complex typically is charged, and in particular it has a negative net charge, but it can also have a positive net charge.

**[0044]** Generally, the cationic polymers can be selected, for example, from the group consisting of:

- cationic acrylic polymers;
- cationic polyacrylamides;
- polydiallyldialkyl-ammonium polymers;
- cationic condensation amido-amine polymers;
- condensation products formed between dicyandiamide, formaldehyde, and an ammonium salt;
- reaction products formed between epichlorohydrin or polyepichlorohydrin and ammonia, a primary amine or a secondary amine;
- polymers formed by reacting a di-tertiary amine or secondary amine and dihalo-alkanes;
- polyethylamine formed by polymerization of ethylimine; and
- polymers formed by polymerization of a N-(dialkyl-aminoalkyl)-acrylamide monomer.

**[0045]** One type of cationic polymer is formed by polyamide derivatives with tertiary and quaternary amine functionality. Another type of cationic polymer is formed by carbohydrate polymers, such as cationized starch. The anionic polymer is, for example, derived from a carbohydrate polymer having a negative net charge. Examples of such polymers are anionic cellulose derivatives, hemicellulose derivatives, starches and mixtures thereof. Synthetic anionic polymers may include polyacrylic acid, polymethacrylic acid, polyvinylamine, and polymers containing carboxyl groups, primary and secondary amine functionalities as well as mixtures of two or more of the aforementioned polymers.

**[0046]** According to one working embodiment, the polyelectrolyte complex comprises polyamide amine epichlorohydrine (PAE) or cationized starch and carboxymethyl cellulose (CMC) or a similar cellulose derivative. Other polymer combinations have also been tested and proven to work. Thus, the PEC can be made by adding a polyamide amine epichlorohydrine resin (PAE) to carboxymethyl cellulose (CMC) having a degree of substitution between 0.4 and 1.3 and preferably forming that PEC in water. (See Colloid and Surfaces A: Physicochem. Eng. Aspects 213 (2003) 15-25), the content of which is herewith incorporated by reference). Generally, molar ratios of PAE to CMC of about 1:1 to 1:5 can be used. But preferably, a proportion based on charge density is used. The charge ratio (meq/g of cationic polymer/meq/g of anionic polymer as absolute value) most often used is in the range of 0.3 to 1.5.

**[0047]** Similar proportions can be used with starch derivatives.

**[0048]** It is preferred to contact the components of the PEC at turbulent conditions, e.g., under intensive agitation by dynamic or static mixers. Alternatively, the turbulence can be generated by utilizing the velocity differences of two feeds flowing at different flow rates. The contacting can be carried out in a continuous operation or batch-wise or semibatch-wise, although continuous or semibatch operation is preferred.

**[0049]** According to one, non-limiting embodiment, polymer complexes are prepared in a mixing chamber by combining two converging flows, one with the cationic component and one with the anionic component, at predetermined flow rates. Preferably, the flow rate of one component,  $Q_1$ , is greater than that of the other component,  $Q_2$ . Depending on the aimed character of the complex (anionic/cationic) either the anionic or the cationic component should have a greater flow rate - if the complex should be anionic, then the anionic component should have a greater flow rate and vice versa. The ratio  $Q_1$  to  $Q_2$  can vary in the range of approximately 1 to 50, although a ratio of about 2 to 20 and in particular about 6 to 10 has been found satisfactory. Experiments have been carried out with a ratio of about 8.

**[0050]** In this embodiment, the converging flow streams can be accomplished by injecting the flow of one component into another. To produce an anionic complex, the cationic component, flowing at a smaller flow rate, is injected into the flow of the anionic component, and vice versa for a cationic complex. Preferably the flows are concurrent or at least essentially concurrent. In one experimental setup, which can be used on larger scale, the two components are combined by arranging the feed conduits of the components inside each other. Thus, the feed conduit of a first component can be arranged inside the feed conduit of a second component with the feed nozzle of the first component opening into the feed conduit of the second component. In this way, the first component, at a lower flow rate, is fed or injected into the flow of the second component. It is also possible to have several injection points for the first component arranged inside the feed conduit of the second component.

**[0051]** The feeds can be recirculated by recovering the flow of the second component after the addition of the first component and then recycle that flow for injection of more of the first component until the desired ratio between the two components is reached. Thus, a continuous or semicontinuous (semibatch) operation is achieved. The above arrangement allows for cost efficient, on-site production of PEC. By the described operation mode, which is not the only way to produce the complex, the storage volumes can be reduced and there is no greater risk for PEC deterioration. But other configurations aside from the one described above, are possible in producing polyelectrolyte complexes in a large scale.

**[0052]** As described above, the PEC should have a net charge. In case of an anionic complex, the net anionic charge is preferably at least -0.1 meq/g, typically about -0.4 to -4.0 meq/g. Similarly, for a cationic complex, the net cationic charge is preferably at least 0.1 meq/g, typically about 0.4 to 4.0 meq/g. Cryoscopic transmission electron microscopy images of PEC show a size range of 1-500 nm in diameter.

**[0053]** The effect of the PEC is found already at 0.01 % of paper dry weight and amounts in excess of 10 wt-% do not significantly further improve any property. Normally the best addition amount is found to be 0.05 to 5 wt-% based on paper dry weight.

**[0054]** In practice, it is possible to proceed by preproducing the polyelectrolyte complex at room temperature (about 20 degrees, but generally at about 10 to 65 degrees C) and with turbulent, mixing and by feeding the complex, in a preselected amount of about 0.01 to 10 wt-%, preferably 0.05 to 5 wt-%, to a pulp slurry, which may first be treated with 0.01 to 10 wt-%, preferably 0.05 to 5 wt-%, PAE, the percentages being calculated on the dry weight of the paper/board.

**[0055]** After contacting with the polyelectrolyte complex at a retention time, of about 1 to 60 minutes, typically about 10 to 30 minutes, a filler in an amount of 1 to 50 wt-% based on dry paper/board weight, preferably about 5 to 40 wt-%, in particular about 20 to 30 wt-%, and other paper chemicals are added to the pulp slurry, which is then fed to the paper machine.

**[0056]** Other PECs based on other polymers will work similarly. Cost/effect optimisation are needed to find the best system.

**[0057]** The present invention provides considerable advantages as was explained above. To reiterate briefly, it allows for - with maintained or even improved mechanical and optical properties - one or several of the following improvements:

- increased filler content,
- higher content of short hardwood fibres,
- lower grammage, and
- reduction in refining energy,
- along with reduction in demand of sizing chemicals.

**[0058]** The examples above show that according to the new invention refining can be reduced, which gives higher bulk, dimensional stability, and decreased costs for refining. Thus, paper can be made with less beating the fibres and utilizing more short fibre furnish than earlier. The filler content can be increased which gives improved optical and printing properties, and reduced production costs, as can the hardwood content which leads to improved formation and printing properties of the web. In fact, the hardwood content can be increased even up to 100 %. Additional benefits, and important options, are reduced grammage, decreased costs for sizing and retention chemicals.

**[0059]** One particularly interesting aspect of the invention is that it, at a given light scattering, is possible to get a stronger and stiffer sheet compared to by beating.

**[0060]** The invention is particularly well suited for the production of generally any kind of paper and board, e.g. printing and graphic papers and cartoon boards. Examples of suitable paper qualities include any kind of coated and uncoated wood free and wood containing papers.

**[0061]** The following non-limiting examples illustrate the invention:

#### Example 1

**[0062]** PAE was charged, in an amount of 2.0 wt-% based on total dry weight of paper, to a pulp slurry at 3 % pulp consistency. The pulp slurry consisting of 80 % bleached birch kraft pulp (refined to 20 SR) and 20 % bleached softwood kraft pulp (refined to 24 SR). After a few minutes, 2.0 wt-% of the complex PAE+CMC (PEC) was added and the slurry was stirred vigorously. After further 5-30 minutes the filler (20 and 28 wt-% PCC), 0.2 % stock starch, 0.16 % ASA-size and retention aids (consisting of polyacrylamide and bentonite) were added and the slurry was fed to a small laboratory paper machine and an 80 g/m<sup>2</sup> paper was made. The strength properties were compared with a paper from a non-pretreated pulp furnish.

**[0063]** The results are shown in Table 1 below:

**Table 1: 80/20 Birch kraft pulp/Softwood kraft pulp. Birch pulp refined to 20 SR and the softwood pulp to 24 SR.**

| Trial | Filler PCC, % | PAE+PEC, % | Bulk, cm <sup>3</sup> /g | Tensile index, (geometr average) Nm/g | Tear index, (geometr average) mN m <sup>2</sup> /g | Scott Bond, J/m <sup>2</sup> | Tensile stiffness index, MD/CD MNm/kg | Bending stiffness MD/CD mNm |
|-------|---------------|------------|--------------------------|---------------------------------------|----------------------------------------------------|------------------------------|---------------------------------------|-----------------------------|
| 1.1   | 20            | 0          | 1.45                     | 26                                    | 5.7                                                | 119                          | 5.6/2,3                               | 0.36/0.18                   |
| 1.2   | 20            | 2+2        | 1.48                     | 44                                    | 7.1                                                | 291                          | 6.5/3,1                               | 0.42/0.22                   |
| 1.3   | 28            | 0          | 1.44                     | 20                                    | 4.8                                                | 89                           | 4.5/1,8                               | 0.27/0.13                   |
| 1.4   | 28            | 2+2        | 1.46                     | 34                                    | 6.2                                                | 228                          | 5.4/2,5                               | 0.31/0.18                   |

**[0064]** As apparent from Table 1, the PAE and PEC treated pulp slurry gave a paper with superior strength properties compared to untreated pulp slurry.

**[0065]** Conventionally, an increase of the filler level from 20 to about 28 % reduced all strength properties, as can be seen from a comparison of Trials 1.1 and 1.3. However, when the pulp slurry was treated with PAE+PEC the strength properties were improved even at this high filler level, which can be seen by comparing Trials 1.1 and 1.4.

**[0066]** The pretreatment procedure can also be used to significantly improve the strength properties at the lower filler level. This feature is evident from a comparison of Trials 1.1 and 1.2.

**Example 2**

**[0067]** PAE was charged, in an amount of 2.0 wt-% based on total dry weight of paper to a pulp slurry at 3 % pulp consistency. The pulp slurry consisting of 80 wt-% birch kraft pulp and to a second slurry consisting of 100 wt-% birch kraft pulp. In both cases, the birch pulp was bleached kraft pulp refined to 20 SR. The first slurry contained 20 wt-% (and the second 0 %) bleached softwood kraft pulp refined to 24 SR. After a few minutes 2.0 wt-% of the complex PAE+CMC (PEC) was added and the slurry was stirred vigorously. After a further 5 - 30 minutes, the filler (20 % PCC) and conventional additives comprising 0.2 % stock starch, 0.16 % ASA-size and retention aids (consisting of polyacrylamide and bentonite) were added and the slurry was fed to a small laboratory paper machine and an 80 g/m<sup>2</sup> paper was made.

**[0068]** The strength properties of the papers made from PEC treated fibres were compared with a paper from an untreated furnish, and the results appear from Table 2:

**Table 2: 80 and 100 % birch kraft pulp/20 and 0 % softwood kraft pulp. The birch pulp refined to 20 SR and the softwood pulp to 24 SR. 20 % PCC.**

| Trial | Birch content,<br>% | PAE+PEC,<br>% | Bulk,<br>cm <sup>3</sup> /g | Tensile index,<br>(geometr average)<br>Nm/g | Tear index,<br>(geometr average)<br>mN m <sup>2</sup> /g | Scott Bond,<br>J/m <sup>2</sup> | Tensile stiffness index,<br>MD/CD<br>MNm/kg | Bending stiffness<br>MD/CD<br>MNm |
|-------|---------------------|---------------|-----------------------------|---------------------------------------------|----------------------------------------------------------|---------------------------------|---------------------------------------------|-----------------------------------|
| 2.1   | 80                  | 0             | 1.45                        | 26                                          | 5.7                                                      | 119                             | 5.6/2.3                                     | 0.36/0.18                         |
| 2.2   | 80                  | 2+2           | 1.48                        | 44                                          | 7.1                                                      | 291                             | 6.5/3.1                                     | 0.42/0.22                         |
| 2.5   | 100                 | 0             | 1.49                        | 21                                          | 3.8                                                      | 82                              | 4.8/2.1                                     | 0.33/0.16                         |
| 2.6   | 100                 | 2+2           | 1.48                        | 40                                          | 6.0                                                      | 223                             | 5.9/2.9                                     | 0.44/0.23                         |

**[0069]** Increasing the birch pulp content from 80 to 100 % decreased the strength properties, as can be seen from a comparison of Trials 2.1 and 2.5. When the pulp slurry was treated with PAE and PEC the strength properties improved considerably (cf. Trials 2.1 and 2.6). This example shows that it is possible, with the PEC pretreatment, to increase the shortfibre content in the paper up to 100 % and get better strength properties than an untreated slurry with 80 % birch pulp.

**Example 3**

**[0070]** 2.0 wt-% PAE (based on total dry weight of paper) was charged to a pulp slurry at 3 % pulp consistency. The pulp slurry consisting of 80 % bleached birch kraft pulp (not refined with 16 SR or refined to 20 SR) and 20 % bleached softwood kraft pulp (refined to 24 SR). After a few minutes 2.0 wt-% of the complex PAE+CMC (PEC) was added and the slurry was stirred vigorously. After a further 5-30 minutes, the filler (20 % PCC), 0.2 % stock starch, 0.16% ASA-size and retention aids (consisting of polyacrylamide and bentonite) were added and the slurry was fed to a small laboratory paper machine and a paper having the grammage 80 g/m<sup>2</sup> was made.

**[0071]** Strength properties were compared with paper from an untreated furnish, and the results are given in Table 3:

**Table 3: 80/20 Birch kraft pulp/Softwood kraft pulp. The birch pulp unrefined (16 SR) and refined (20 SR). The softwood kraft refined to 24 SR. 20 % PCC.**

| Trial | Dewatering resistance<br>SR | PAE+PEC,<br>% | Bulk,<br>cm <sup>3</sup> /g | Tensile index,<br>(geometr average)<br>Nm/g | Tear index,<br>(geometr average)<br>mN m <sup>2</sup> /g | Scott Bond,<br>J/m <sup>2</sup> | Tensile stiffness index,<br>MD/CD<br>MNm/kg | Bending stiffness<br>MD/CD<br>mNm |
|-------|-----------------------------|---------------|-----------------------------|---------------------------------------------|----------------------------------------------------------|---------------------------------|---------------------------------------------|-----------------------------------|
| 3.1   | 20 (refined)                | 0             | 1.45                        | 26                                          | 5.7                                                      | 119                             | 5.6/2.3                                     | 0.36/0.18                         |
| 3.2   | 20 (refined)                | 2+2           | 1.48                        | 44                                          | 7.1                                                      | 291                             | 6.5/3.1                                     | 0.42/0.22                         |

(continued)

| Trial | Dewatering resistance<br>SR | PAE+PEC,<br>% | Bulk,<br>cm <sup>3</sup> /g | Tensile index,<br>(geometrical average)<br>Nm/g | Tear index,<br>(geometrical average)<br>mN m <sup>2</sup> /g | Scott Bond,<br>J/m <sup>2</sup> | Tensile stiffness index,<br>MD/CD<br>MNm/kg | Bending stiffness<br>MD/CD<br>mNm |
|-------|-----------------------------|---------------|-----------------------------|-------------------------------------------------|--------------------------------------------------------------|---------------------------------|---------------------------------------------|-----------------------------------|
| 3.7   | 16                          | 0             | 1.56                        | 18                                              | 4.5                                                          | 68                              | 4.2/1.9                                     | 0.32/0.16                         |
| 3.8   | 16                          | 2+2           | 1.52                        | 38                                              | 7.1                                                          | 195                             | 5.7/2.8                                     | 0.38/0.24                         |

**[0072]** As evident, by omitting the refining of the birch pulp energy can be saved and the bulk of the paper increased (compare the results of Trials 3.1 and 3.7). However, the strength properties decreased considerably.

**[0073]** A comparison of Trials 3.1 and 3.8 reveals that by treatment of the pulp slurry with PAE and PEC it is possible to restore or even to improve the strength properties at a higher bulk.

#### Example 4

**[0074]** PAE was charged, in an amount of 0.5-2.0 wt-% based on dry weight of paper, to a pulp slurry at 3 % pulp consistency. The pulp slurry consisting of 70 % bleached mixed hardwood pulp (refined to 22 SR) and 30 % bleached softwood kraft pulp (refined to 24 SR). After a few minutes, 0.5-2.0 wt-% of the anionic complex PEC:A1-3 (PAE+CMC) was added and the slurry was stirred vigorously. After further 5-30 minutes 25 % PCC, AKD sizing and retention agents were added. The cationic complex PEC:C1-3 (cationic starch DS 0.17+CMC) was added, without pre-treatment, in an amount of 0.5-2.0 wt-% based on dry weight of paper. Filler, sizing and retention agents were added in the same way as with PEC:A1-3. Except for trial PEC:C2\*, where no retention agents were added. The slurry was fed to a small laboratory paper machine and 80 g/m<sup>2</sup> paper was made. The strength properties were compared with a non-pretreated reference. The results are shown in Table 4 below:

**Table 4: Anionic PEC:A1-3 (PAE+CMC) and cationic PEC:C1-3 (cationic starch+CMC) complexes. 70/30 Mixed hardwood/softwood kraft pulp. The mixed hardwood pulp refined to 22 SR and the softwood kraft pulp to 24 SR. 25 % PCC filler. The geometrical average of the strength data is given.**

| Trial     | PAE<br>% | PEC:A<br>% | PEC:C<br>% | Bulk<br>cm <sup>3</sup> /g | Tensile index<br>Nm/g | Tear index<br>mN m <sup>2</sup> /g | Scott Bond<br>J/m <sup>2</sup> | Tensile stiffness index<br>MNm/kg |
|-----------|----------|------------|------------|----------------------------|-----------------------|------------------------------------|--------------------------------|-----------------------------------|
| Untreated | -        | -          | -          | 1.56                       | 15.6                  | 4.9                                | 66                             | 3.1                               |
| PEC: A1   | 0.5      | 0.5        | -          | 1.57                       | 22.6                  | 5.9                                | 119                            | 3.6                               |
| PEC: A2   | 1.0      | 1.0        | -          | 1.54                       | 26.2                  | 6.6                                | 159                            | 3.9                               |
| PEC: A3   | 2.0      | 2.0        | -          | 1.55                       | 31.4                  | 6.4                                | 226                            | 4.3                               |
| PEC: C 1  | -        | -          | 0.5        | 1.56                       | 16.0                  | 5.6                                | 90                             | 3.2                               |
| PEC: C 2  | -        | -          | 1.0        | 1.56                       | 17.2                  | 5.6                                | 106                            | 3.3                               |
| PEC: C 3  | -        | -          | 2.0        | 1.54                       | 19.9                  | 6.3                                | 133                            | 3.5                               |
| PEC: C2*  | -        | -          | 2.0        | 1.56                       | 21.2                  | 6.5                                | 140                            | 3.6                               |

**[0075]** As can be seen, at the same chemical charge, 0.5 %, the anionic complex PEC:A gave better strength properties than the cationic complex PEC:C. The cationic complex gave, however, higher tear index and Scott Bond than the untreated reference.

## Example 5

**[0076]** An experimental paper machine (XPM) trial was performed. A fibre furnish consisting of 80 % unbeaten birch kraft pulp and 20 % beaten (270SR) softwood kraft pulp was used. The furnish was pre-treated (unless otherwise stated) with PAE and allowed to stand with vigorous stirring for 15 minutes. The anionic PEC was then added and allowed to stand with vigorous stirring for at least 15 minutes. The targeted filler (PCC) level and grammage were 25 % and 80 g/m<sup>2</sup>, respectively. 0.2 % stock starch, 0.16% ASA-size and retention aids (consisting of polyacrylamide and bentonite) were added prior to the headbox.

**[0077]** The results of the tested papers are as follows:

**Table 5: 80/20 Birch kraft/softwood kraft. The birch kraft pulp was unrefined (20 SR) and the softwood kraft refined to 24 SR. 25% PCC**

|                     | % PAE as pre-treatment | Wetstrength kN/m | Tensile index Nm/g | Tear index mNm <sup>2</sup> /g | Scott Bond J/m <sup>2</sup> | Tensile stiffness index MNm/kg |
|---------------------|------------------------|------------------|--------------------|--------------------------------|-----------------------------|--------------------------------|
| Untreated reference | -                      | 0.11             | 18.4               | 4.7                            | 82                          | 2.3                            |
| 0.2 % PEC           | 0.2                    | 0.33             | 21.3               | 5.2                            | 88                          | 2.5                            |
| 0.5 % PEC           | 0.5                    | 0.53             | 24.4               | 5.8                            | 126                         | 2.7                            |
| 0.5 % PEC           | -                      | 0.36             | 22.0               | 5.5                            | 91                          | 2.6                            |
| 1.5 % PEC           | 1.5                    | 0.80             | 30.5               | 6.3                            | 182                         | 3.1                            |

**[0078]** The positive effects of the PEC treatment as compared to the reference are evident in all the strength parameters shown above. Moreover, the increase in all the strength properties is proportional to the amount of PEC added. Additionally, PEC without PAE pre-treatment, also showed an increase in all the properties mentioned, but not as high as with PAE pre-treatment. This indicates that the anionic PEC used also had an affinity to the paper web despite the fact that fibres are usually considered to be negatively charged. Pretreatment with the cationic polymer is necessary in order to maximize the effects of PEC. But depending on the application and economic considerations, pretreatment may also be eliminated.

## Claims

1. A method of producing a fibrous web on a paper or cardboard machine from an aqueous furnish containing fibres mainly derived from a deciduous tree species, fillers and any conventional additives, **characterized by** admixing the fibres of the furnish with a polyelectrolyte complex before adding the fillers and any additives.
2. The method according to claim 1, wherein the fibrous web is produced from fibres which have not been subjected to beating before web formation.
3. The method according to claim 1, wherein the fibrous web is produced from fibres which have been subjected to a moderate degree of beating amounting to less than 50 kWh/t of fibrous material.
4. The method according to any of claims 1 to 3, wherein the fibres exhibit a degree of beating of 20 SR or less.
5. The method according to claim 1, wherein the fibrous web is produced from fibres which have been subjected to a degree of beating amounting to approximately 50 to 400 kWh/t of fibrous material.
6. The method according to any of claims 1 to 5, wherein at least 40 %, preferably at least 60 %, by weight of the fibres are formed by fibres of a deciduous wood species.
7. The method according to any of claims 1 to 6, wherein 60 to 100 %, preferably 80 to 100 %, by weight of the fibres are comprised of deciduous wood fibres.

8. The method according to any of the preceding claims, wherein the polyelectrolyte complex is a complex formed by a cationic polymer and an anionic polymer.
9. The method according to claim 8, wherein the polyelectrolyte complex has a negative net charge.
10. The method according to claim 9, wherein polyelectrolyte complex has a negative net charge of at least -0.1 meq/g, preferably about -0.4 to -4.0 meq/g .
11. The method according to claim 8, wherein the polyelectrolyte complex has a positive net charge.
12. The method according to claim 11, wherein the polyelectrolyte complex has a positive net charge of at least 0.1 meq/g, preferably about 0.4 to 4 meq/g.
13. The method according to any of the preceding claims, wherein the polyelectrolyte complex comprises a cationic polymer and an anionic polymer derived from a carbohydrate polymer.
14. The method according to claim 13, wherein the anionic carbohydrate based polymer is selected from the group of anionic derivatives of starch, hemicellulose, cellulose and mixtures thereof
15. The method according to claim 14, wherein the anionic polymer is carboxymethyl cellulose (CMC).
16. The method according to any of claims 1 to 12, wherein the polyelectrolyte complex comprises an anionic polymer selected from the group of synthetic anionic polymers, including polyacrylic acid, polymethacrylic acid, polyvinylamine, and polymers containing carboxyl groups, primary and secondary amine functionalities, as well as mixtures thereof.
17. The method according to any of the preceding claims, wherein the cationic polymer is selected from the group of:
  - cationic acrylic polymers;
  - cationic polyacrylamides;
  - polydiallyldialkyl-ammonium polymers;
  - cationic condensation amido-amine polymers;
  - condensation products formed between dicyandiamide, formaldehyde, and an ammonium salt;
  - reaction products formed between epichlorohydrin or polyepichlorohydrin and ammonia, a primary amine or a secondary amine;
  - polymers formed by reacting a di-tertiary amine or secondary amine and dihalo-alkanes;
  - polyethylamine formed by polymerization of ethylimine; and
  - polymers formed by polymerization of a N-(dialkyl-aminoalkyl)-acrylamide monomer.
18. The method according to claim 17, wherein the cationic polymer is a synthetic cationic polymer selected from the group of polyamide derivatives having amine functionality, such as polyamide amine epichlorohydrine (PAE).
19. The method according to any of claims 1 to 16, wherein the cationic polymer is a polymer derived from a carbohydrate polymer.
20. The method according to any of claims 1 to 19, wherein the polyelectrolyte complex is reproduced under turbulent mixing and the complex is fed, in an amount of about 0.01 to 10 wt-%, preferably 0.05 to 5 wt-%, to a pulp slurry.
21. The method according to any of claims 1 to 20, wherein the fibres of the pulp slurry are first treated with a polymer.
22. The method according to claim 21, wherein the fibres are treated with a polymer in order to cationize a significant part.
23. The method according to claim 21 or 22, wherein the fibres are treated with 0.01 to 10 wt-%, preferably 0.05 to 5 wt-%, of a polyamide derivative having a tertiary or quaternary amine functionality, the percentages being calculated on the dry weight of the paper or board.
24. The method according to any of claims 21 to 23, wherein the fibres are pretreated with a portion of the same or another cationic polymer used for producing the polyelectrolyte complex.

25. The method according to any of claims 1 to 24, wherein after contacting with the polyelectrolyte complex after a retention time, of about 1 to 60 minutes, typically about 10 to 30 minutes, a filler in an amount of 1 to 50 wt-%, preferably about 5 to 40 wt-%, in particular about 10 to 30 wt-% based on the dry weight of the paper or board, and other paper chemicals are added, as usual, to the pulp slurry, which is then fed to the paper or board machine.

26. A method of producing a polyelectrolyte complex formed by a cationic polymer and an anionic polymer, comprising the step of

- mixing together under turbulent mixing conditions a first liquid flow ( $Q_1$ ) containing the anionic polymer and a second liquid flow ( $Q_2$ ) containing the anionic polymer,

the turbulent mixing conditions being obtained by converging the liquid flows at predetermined flow rates.

27. The method according to claim 26, wherein the ratio between the flow rates  $Q_1/Q_2$  is being selected depending on the anionic or cationic character of the complex to be prepared.

28. The method according to claim 27, wherein the ratio of the flow rates  $Q_1/Q_2$  or  $Q_2/Q_1$ , respectively, is approximately 1 to 50, preferably about 2 to 20 and in particular about 6 to 10.

29. A paper or board which comprises a fibrous matrix containing at least 50 % of fibres derived from deciduous tree, and further containing about 0.05 to 5.0 % of a polyelectrolyte complex, the amount being calculated on the dry weight of the paper or board, said paper or board being obtained by any of the methods according to claims 1 to 21.

30. The paper or board according to claim 29, which is produced from a fibrous raw material containing at least 40 %, preferably 80 to 100 % of hardwood fibres.

31. The paper according to claim 29 or 30, which is used as a printing and speciality paper or board.

32. The use of a method according to any of claims 1 to 25 for improving at least one property of a filler containing paper or board, said property being selected from the group of mechanical strength, stiffness, formation, retention, opacity and brightness.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 06 39 6017

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                                                                                                                                                                        |                                                          |                                                          |
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| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                                                                                                        |                                                          |                                                          |
| Place of search<br><b>Munich</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                        | Date of completion of the search<br><b>13 April 2007</b> | Examiner<br><b>Settele, Ulrika</b>                       |
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EPO FORM 1503 03.82 (P04C01)



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# EUROPEAN SEARCH REPORT

Application Number  
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| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                       |                                                          |                                         |
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## EUROPEAN SEARCH REPORT

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EPO FORM 1503 03 02 (P04C01)

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EP 06 39 6017

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