(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 239 370 A1

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
13.10.2010 Bulletin 2010/41

(51) Int Cl.:
D21H 21/18 *(2006.01)*

(21) Application number: **09450076.6**

(22) Date of filing: **09.04.2009**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA RS

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(54) **Dry and wet strength improvement of paper products with cationic tannin**

(57) The invention deals with a method of improving paper strength properties with cationic tannin and/or cationic tannin derivatives. By the method in accordance with the invention dry tensile strength of kraft paper can be improved by up to 26% by adding 1% of cationic tannin to wood pulp before the pulp is used for papermaking while other dry mechanical properties of the paper are also significantly (up to 55%) improved. In addition, paper wet tensile strength can be increased from near zero to a level corresponding to 13% of dry tensile strength. Higher cationic tannin doses yield even larger improvements in paper properties.

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Description

[0001] The large consumption and wide variety of paper products has created a great need for continuing efforts in the field of chemical additives which will impart various physical properties to the paper products. Among the more important of the strength improving chemical additives are the synthetic or starch-derived cationic polymers, oxidatively crosslinked starch xanthates (US Patent 3,160,552), starch polyethylenimino thiourethane (US Patent 3,436,305), and crosslinked starch-polyamide-polyamine interpolymers. US Patent 4,152,199). Depending on the type of paper product, there are several strength factors which must be considered when producing paper products. Important dry properties include tensile strength, tensile stretch, tensile stiffness, tear strength, burst strength, tensile energy absorption, crush resistance, and fold endurance. In terms of wet strength, tensile strength is particularly important. Most of the prior art additives will improve either the wet strength or certain dry strength properties, sometimes at the expense of other properties. One problem that often occurs is the low retention of the additives, which then end up in the white water and/or effluent, creating a removal problem.

[0002] The present invention discloses a compound that greatly increases a wide range of both wet and dry strength properties and is retained in the pulp. In accordance with the invention, the improvement in the production of paper products comprises incorporation into the paper products as wet-end additives from about 0.1% to about 2% by dry pulp weight of cationic mimosa tannin prepared from mimosa tannin by the Mannich reaction. The cationic tannin is strongly adsorbed on to the anionic pulp fibers which results in improved paper strength, possibly through better hydrogen bonding. However, since also wet strength properties are improved, other mechanisms may be involved as well.

[0003] Cationic tannin is used in the paper and other industries as a flocculant for anionic contaminants in wastewater treatment (German Patent 4,219,343). Anionic tannin together with cationic compounds such as cationic polysaccharides has been applied for paper production to improve drainage and retention in the paper machine (Canadian Patent 2,418,424).

[0004] Cationic tannin is suitable for various types of paper including products made of unbleached or partially bleached chemical (kraft, sulfite, or soda), mechanical, thermomechanical, and semichemical pulp. Since cationic tannin makes the pulp slightly darker, it may not be suitable for products made of fully bleached pulp. Papers produced from unbleached kraft pulp include brown wrapping paper, paper bags, sack paper envelopes, linerboard (kraft liner) etc.

[0005] Since many paper products are sold rather on performance per square meter basis rather than weight basis, financial savings are achieved if a product can manufactured at a lower basis weight without negatively impacting its strength properties. Another way to cut production costs is to reduce the amount of additives needed to obtain the desired dry and/or wet strength properties. For some applications such as sack paper or toilet paper, dry strength is crucial while wet strength properties are relatively unimportant or even undesirable. For other applications such as linerboard, corrugated medium, napkins, kitchen towels, and facial-pockets both dry and wet strength are important, and wet strength agents are routinely incorporated into these products. The application of cationic tannin to the manufacture of sack paper, linerboard and corrugated medium is described below as an example.

[0006] Finely divided powder products such as cement are commonly packaged in multi-wall paper sacks made from kraft paper. If the filling machine is operated at high speed it can be difficult for air to vent from the sack while it is being filled. For a two-wall paper sack, for example, it is possible to make perforations through the outer wall to allow air to vent while the sack is being filled. The inner wall should then be permeable enough to air to facilitate filling while acting as a dust barrier. Porosity (low air resistance) is thus an important property for the inner walls of sack paper in particular. Another highly important property for sack paper is the tensile energy absorption (TEA), which is a function of the tensile strength and stretch ability of paper. TEA describes the ability of a product to withstand mechanical impacts such as those cement sacks are frequently subjected to while being handled. Other dry mechanical properties such as burst and tear resistance also need to meet certain criteria.

[0007] Corrugated containers or boxes are manufactured from containerboard consisting of facings (linerboard) and the intervening fluting (corrugated medium). Linerboard is generally made of a mixture of kraft and recycled pulps and should be classified as kraft liner if it contains at least 80% virgin kraft pulp fibers or as test liner if the proportion of virgin kraft pulp fibers is below 80%. In practice, however, linerboard marketed as kraft liner may contain less than 60% virgin kraft fibers. Corrugated medium is typically made of mixed semichemical and recycled pulps. Semichemical pulps refer to pulps such as neutral sulfite semichemical pulp (NSSP) while the recycled pulp can contain fibers from old containerboards and other suitable sources. Boxboard is non-corrugated material that goes into folding cartons and trays such as shoe boxes used to package commodities.

[0008] Linerboard and corrugated medium are prepared by mixing screened and refined pulps with papermaking chemicals in the so-called stock preparation section of the manufacturing process. The pulp suspension is dewatered on the paperboard machine to form the fiber sheet and the drained water (white water) is recycled back to the process to be used for dilution of screened stock.

[0009] Corrugated containers and boxes are used for packaging and shipping of a wide range of products from foodstuffs to electronic goods. The need for their contents to be protected against mechanical damage during handling, transit, and storage sets certain requirements for their dry and wet strength properties, depending on the type of application and end-use environment. Important mechanical properties in this regard include tensile strength, tear strength, burst strength, and compression strength. Wet strength properties are particularly important for containers used for goods with high water content such as fruit or in high humidity/moisture environments. To reduce water penetration and improve wet strength, containerboards are heavily waxed or treated with sizing or wet strength agents. Most paperboard applications requiring water resistance need permanent wet strength. However, the commonly used wet strength agents imparting permanent wet strength such as aminoplast and polyamide-epichlorohydrin (PAE) resins tend to interfere with and detract from the repulpability of paper. Wet strength paper generally cannot be defibrated and repulped in neutral water without extraordinary means. Permanent resins are resistant to hydrolysis and retain their properties during repulping. The mechanism by which they provide wet strength is through bonding to or encapsulation of fibers to provide a water-resistant, hydrolytically-stable, polymer-reinforced fiber network. Paperboard treated with aminoplast resin requires high temperatures and/or low pH during repulping to be recycled. On the other hand, high pH and elevated temperatures are required to repulp PAE-treated papers. Polyamide and polyamine-epichlorohydrin (PAE) resins form difficult to break ether linkages with the hydroxyl groups available in the pulp material.

[0010] The exact amount by which paper basis weight can be reduced by the application of cationic tannin depends on the relative importance of the different strength properties for a particular product and how much these properties are improved by cationic tannin. The price of unbleached kraft pulp is approximately 450-500 euro/ton while cationic tannin is available for roughly 2000 euro/ton. Since the treatment of pulp with 1% cationic tannin in the present invention improves dry tensile strength of paper made from kraft pulp (kappa 41) by approximately 20%, the use of cationic tannin allows the basis weight of paper made from this pulp to be reduced by 15-20% (based on the dry tensile strength), saves approximately 50-60 € euro/ton of pulp if basis weight reduction is calculated based solely on dry tensile strength. Using TEA is the criterion for products such as sack paper (~ 60% TEA improvement with no change in porosity), much larger savings in pulp cost could be achieved.

[0011] As for paper products such as linerboard for which wet strength is important, the use of cationic acid reduces the amount of wet strength agent needed to achieve the desired level of wet strength; it may even not be necessary to use them at all.

[0012] An additional advantage of using cationic tannin is the fact that it is adsorbed onto the anionic fibers and thus does not end up in significant amounts in the mill white water and effluent.

[0013] An additional advantage of using cationic tannin is the fact that tannins in general are antioxidants and biocides, and may reduce odour problems during stock preparation and other production processes.

[0014] A further advantage of using cationic tannin is that pulp containing cationic tannin as a partial of complete substitute for conventional wet strength additives can be more easily repulped.

[0015] Contacting the fibers with cationic tannin can take place during stock preparation by simply adding the tannin into the stirred fiber slurry. Cationic tannin is water soluble and can thus be applied as any other paper strength agent. However, the tannin could also be added during some other part of the pulp and papermaking process.

[0016] Most of the cationic tannin available on the market is produced from mimosa tannin (a "condensed", flavonoid-type tannin polymer) according to the Mannich reaction whereby cationic amino groups are introduced into the tannin polymers. Mimosa tannin is extracted mainly from mimosa bark and used in vast amounts in the leather industry which makes it a readily available starting material for cationic tannin. The current annual production of hundreds of thousands of tons of cationic tannin for its existing applications can thus easily be increased should the demand for it increase.

[0017] Although the examples presented in the present invention involved the use of cationic tannin produced from mimosa (*Acacia* sp., commonly known as wattle and acacia), any other types of condensed flavonoid-based tannin similar to mimosa tannin could also be used as raw material for cationic tannin, regardless of weather they are extracted from the bark, wood, or other components of the plant. The plants containing such suitable tannin raw material include but are not limited to other acacia species, eucalypt, fir, gambier, hickory, oak, pine, quebracho, and spruce.

[0018] The paper products from pulp supplemented with cationic tannin or its derivatives in accordance with the present invention include all types of products prepared from chemical, semichemical, mechanical, thermomechanical (TMP), and chemi thermomechanical (CTMP) pulps made from wood or other lignocellulosic raw materials such as annual or perennial plants or fibrous agricultural residues or by-products. The paper products prepared from the pulps containing cationic tannin or cationic tannin derivatives include but are not limited to: office paper, book paper, newsprint, packaging paper, sack paper, corrugated medium, linerboard, boxboard, wrapping paper, offset paper, tissue paper, kitchen towels, napkins, and paper bags.

[0019] The preparation of paper handsheets from pulp prepared with different amounts of cationic tannin is described in the examples below. The results show large increases dry and wet mechanical properties of paper.

Example 1

[0020] Fresh never-dried softwood kraft pulp (kappa 41) was obtained from the regular pulp production of an industrial pulp and paper mill and used immediately for making paper handsheets. The pulp was disintegrated and diluted to a consistency of 1.3% using a motorized stirrer. Cationic tannin powder (1% on dry pulp basis) was added to the pulp and the pH adjusted to 5 with sulfuric acid for both controls and cationic tannin. The resulting mixture was stirred (555 rpm) for 90 min at 40°C after which the pulp was used for making handsheets for testing dry strength properties (basis weight 77-82 g/m^2) and wet tensile strength (160 g/m^2). The achieved handsheet properties are summarized in Table 1.

Table 1. Properties of handsheets made with cationic tannin

	Amount of cationic tannin added to pulp, %										
	0	1	0	0.25	0.5	0.75	1.0	1.5	0	1.0	2.0
	Set 1		Set 2						Set 3		
Dry properties											
Basis weight, g/m2	82	81	79	78	77	77	80	79	77	79	81
Air resistance (Gurley), s	1.41	1.40	0.6	0.6	0.5	0.6	0.6	0.6	0.5	0.6	0.7
Tensile index, Nm/g	33.32	38.41	25.04	25.30	26.10	29.75	29.14	30.10	24.13	30.50	33.31
Stretch at break, %	1.55	1.93	1.12	1.22	1.20	1.43	1.48	1.53	1.10	1.56	1.64
Tensile stiffness, kN/m	464	472	399	378	380	387	389	397	363	391	421
Tear index, mN m^2/g	20.5	23.5	15.2	17.4	16.8	17.6	18.6	18.3	15.4	17.9	19.0
Burst index, kPa m^2/g	2.13	2.36	1.53	1.45	1.71	1.81	2.13	2.25	1.52	2.15	2.39
Tensile energy absorption, J/g	0.37	0.54	0.20	0.22	0.22	0.30	0.31	0.34	0.19	0.34	0.39
Brightness, % ISO	23.87	22.95	25.01	24.60	24.28	24.05	23.71	23.20	25.57	24.29	23.34
Wet properties (after 1h water soak)											
Basis weight, g/m^2	160	160	160	160	160	160	160	160	160	160	160
Tensile index, Nm/g	n. a.*	3.43	n. a.*	n. a.*	2.53	3.47	3.64	4.23	n. a.*	3.81	4.71
% of dry strength	n. a.*	9.32	n. a.*	n. a.*	9.1	11.2	12.0	14.1	n. a.*	12.8	14.1

*Too low to be able to be measured; lowest measurable values are - 2 Nm/g

Example 2

[0021] Paper handsheets (~ 80 g/m^2) were prepared as in example 1 except that the pH of the pulp slurry was adjusted to different values (4-8). The properties of the handsheets are listed in Table 2.

Table 2. Properties of handsheets prepared at different pH levels with 1% cationic tannin at 40°C

	Control (pH5)	pH4	pH5	pH6	pH7	pH8
Dry properties						
Basis weight, g/m^2	76	76	74	75	73	74
Air resistance (Gurley), s	0.7	0.7	0.7	0.9	1.33	1.37
Tensile index, Nm/g	29.45	33.19	35.50	38.44	38.55	40.76
Stretch at break, %	1.45	1.86	1.94	2.02	1.89	2.04
Tensile stiffness, kN/m	397	388	403	434	440	446
Tear index, mN m^2/g	20.9	22.1	20.4	20.6	25.7	24.8
Burst index, kPa m^2/g	1.96	2.15	2.35	2.48	2.73	2.78
Tensile energy absorption, J/g	0.31	0.45	0.50	0.57	0.53	0.60
Brightness, % ISO	23.80	22.98	22.96	22.20	21.87	21.76
Wet properties						
Basis weight, g/m^2	160	160	160	160	160	160
Tensile index, Nm/g	n.a.*	4.36	4.33	4.59	4.46	4.31
% of dry strength	n.a.*	12.92	12.45	11.74	11.57	10.67

*Too low to be able to be measured; lowest measurable values are - 2 Nm/g

Claims

1. A method of improving the dry and wet strength properties of paper and paper products by incorporating cationic tannin or its derivatives into a lignocellulosic or cellulosic pulp before the pulp is used for papermaking.

2. The method according to claim 1, wherein the pulp is contacted with the cationic tannin or its derivative at any time before the pulp is used for papermaking.

3. The method according to claim 1, wherein the pulp is contacted with the cationic tannin or its derivative during stock preparation or pulp storage.

4. The method according to any of the claims 1-3, wherein the pulp is obtained from wood or other lignocellulosic material by chemical pulping (kraft, sulfite, soda, or organosolv pulping).

5. The method according to any of the claims 1-3, wherein the pulp is obtained from wood or other lignocellulosic material by mechanical, thermomechanical, chemi thermomechanical, or semichemical pulping.

6. The method according to claim 5, wherein the pulp is unbleached, partially bleached, or fully bleached cellulosic or lignocellulosic pulp.

7. The method according to any of the claims 1-6, wherein the cationic tannin added to the pulp is produced from the bark, wood, pods, nutshells, or other components of wood or other lignocellulosic or woody plants.

8. The method according to claim 7, wherein the cationic tannin added to the pulp is produced from mimosa tannin.

9. The method according to claims 7 and 8, wherein a derivative of the corresponding cationic tannin is added to the pulp.

10. The method according to claim 1, wherein the amount of cationic tannin or cationic tannin derivative added to the pulp is 0.1-20% based on dry pulp weight.

11. The method according to claim 1, wherein the amount of cationic tannin or cationic tannin derivative added to the pulp is 0.5-5% based on dry pulp weight.

12. A paper or paper product obtained by the method of any of the claims 1-11, wherein the paper product made from the pulp is one selected from the group consisting of: office paper, offset paper, newsprint, linerboard (e.g. kraft

liner), corrugated medium, boxboard, sack paper, paper bag, wrapping paper, packaging paper, toilet paper, napkin paper, paper towels, book paper, and magazine paper

13. A paper or paper product obtained by the method of any of the claims 1-11, wherein the dry strength properties such as tensile index, stretch before breaking, tensile energy absorption, tear index, and burst index of a paper product of a certain basis weight are substantially (more than 5%) improved by the use of cationic tannin or cationic tannin derivative

14. A paper or paper product obtained by the method of any of the claims 1-11, wherein the wet strength tensile index expressed as a percentage of the corresponding dry tensile strength is substantially (from near zero to at least 3% and up to more than 20%) improved by the use of cationic tannin or cationic tannin derivative

15. A paper or paper product obtained by the method of any of the claims 1-11, wherein the amount of conventional dry strength, wet strength or sizing agents such as starch, alkyl ketene dimer (AKD), aminoplast resin, polyamide-epichlorohydrin (PAE) resin, or wax used to impart dry or wet strength to the paper product can be eliminated or their amount substantially reduced by the use of cationic tannin or cationic tannin derivative.

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	1 September 2009	Karlsson, Lennart

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