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(54) **Use of ozone for increasing the wet strength of paper and nonwoven**

(57) The present invention relates to the use of a treatment sequence comprising ozonation under acidic conditions followed by an acidic wash for enhancing the wet strength of a cellulosic fibrous material, as well as the corresponding process. Preferably the ozone treatment and the acidic wash are followed by a second ozonation step under acidic conditions.

The present invention further concerns a fibrous cellulosic material obtainable by this treatment sequence which preferably has a breaking length of at least 100 m.

The present invention thus allows increasing the wet strength of a cellulosic fibrous material (e.g. pulp), paper or nonwoven without the use of additives, such as wet strength agents. This use of ozone is very simple and efficient, and leads to highly pure products. The use of ozone as the only treatment chemical in particular avoids the introduction of so-called "non-process elements" (NPE) into the treatment system, for instance metal oxides such as MgO, which are frequently used in the oxidative treatment of pulps.

EP 1 316 639 A1

Description

[0001] The present invention relates to the use of ozone for enhancing the wet strength of a cellulosic fibrous material, e.g. pulp, and paper or nonwoven made from this cellulosic material.

BACKGROUND ART

[0002] Papers and paper products are often exposed to extremely varied strength requirements in the wet and dry states. For instance, it must be ensured in the case of packaging paper that it also retains its strength at least for a specific period of time when exposed to rainwater. On the other hand, toilet paper should dissolve in water - some time after use - in order to prevent the sewage systems from clogging up. At the same time, toilet paper must not immediately lose its strength properties during use, i.e. whenever it has just briefly come into contact with the moisture from excrement.

[0003] Similarly, kitchen paper should not lose their strength properties when moistened with water and other primarily aqueous liquids, which frequently happens during their use in the kitchen.

[0004] To describe the strength properties of paper, the prior art therefore often draws a distinction between a paper's "dry strength", "initial wet strength", "temporary" and "permanent" wet strength. This also applies to tissue paper and tissue products.

[0005] Dry strength is generally determined in a similar manner, in the case of paper usually based on DIN EN ISO 1924-2, Paper and Board, Determination of properties under tensile load. Part 2: method at a constant rate of elongation, April 1995, (ISO 1924-2 : 1994). In the case of tissue paper and tissue products, tests are performed on the basis of DIN EN 12625 - 4, Tissue Paper and Tissue Products - Part 4: determination of width-related breaking strength, elongation at break and the tensile energy absorption, January 1999.

[0006] The initial wet strength originally characterized the strength after sheet formation, and particularly refers to the strength of the initially formed moist paper web at the time of the first free transfer, e.g. from the screen section to a subsequent press section.

[0007] More recent prior art defines initial wet strength more broadly than earlier prior art. This definition essentially acts as a parameter for characterizing the strength behavior of remoistened paper, paper products, tissue paper and tissue products. It is ascertained as the tensile strength of paper soaked over a specific period of time.

[0008] In this way, WO 97/36052 and WO 97/36054 do indeed define the initial wet strength by means of the normal wet strength determination employed in comparable measuring techniques. Yet the so-called initial wet strength here corresponds to the wet strength of a sample (test strip) from a test sheet exhibiting a predetermined basis weight and produced under standardized conditions, calculated - after previously soaking the test strip - using a standardized tensile testing device under standardized test conditions.

[0009] In addition to the initial wet strength, the aforementioned documents introduce and use the terms "temporary" and "permanent" wet strength as further criteria for evaluating the strength of a product after it has been remoistened (wet strength) and hence as criteria for its suitability in everyday practice (for example the dissolving properties of toilet paper after it has been used in order to avoid clogging up the pipes). The soaking duration and decrease in wet strength over time are used in these documents as criteria to differentiate between initial, temporary and permanent wet strength.

[0010] In these documents, a rate of decrease is mathematically determined on the basis of measured values as a criterion for the evaluation of temporary wet strength in that the difference is formed from the so-called initial wet strength as the wet strength after 5 s soaking duration and the wet strength after 30 min soaking duration for samples that were somehow pretreated e.g. by addition of a wet-strength agent or by modification of the fibrous material in order to increase wet strength. The difference of the corresponding measurements for untreated samples is calculated in a similar way. The difference of the strengths of the treated samples is then placed in proportion to the difference of the strengths of the untreated samples and expressed as a percentage.

[0011] In simplified terms, this means that temporary wet strength should be defined as the drop in strength of a sheet of paper or tissue paper or of a tissue product; after remoistening the paper, tissue paper or tissue product after expiry of an interval of the action of moisture (soaking) to be specified by definition, this drop can be determined in terms of measurement technology by means of a standard test method.

In contrast, the permanent wet strength should be defined as the maintenance of strength even after moisture has exerted its influence for a fairly long time upon remoistening, e.g. for a period of 30 min.

[0012] In the present invention, the term "wet strength" refers to remoistened samples which were soaked into water for only a few seconds as described in the section "test methods". In the case of paper samples, the soaking period before tensile testing was fixed as 30 sec. From the breaking strength (N/15 mm) obtained thereby, it is possible to calculate the wet breaking length (in m), and the relative wet strength, which is the ratio of breaking length (wet)/breaking length (dry).

[0013] The same applies to nonwovens and products made thereof.

[0014] A paper of an untreated cellulose-containing fibrous material usually loses 95 % to 97 % of its dry strength when saturated with water, so that it normally cannot be used in the moistened or wet states. This is due to the fact that the paper and/or paper products to an extent develop a dry strength as a result of inter-fiber hydrogen bonds. If the paper is moistened, the water breaks up the hydrogen bonds and therefore reduces the strength of the paper.

[0015] There are three important techniques for increasing the wet strength of paper that have already been in use for some time.

[0016] The first technique prevents the water from reaching and breaking up the hydrogen bonds, e.g. by applying a water-repellent material to the fibers.

[0017] The second approach is to provide the paper with additives or reagents that promote the formation of inter-fiber bonds during production itself by addition into the substance.

[0018] To increase the wet strength according to the second technique, poly(ethylene imines), polyamide epichlorohydrin resins and urea or melamine formaldehyde condensates are for example used as wet-strength agents. The use of such synthetic resins results in permanent wet strength. On the other hand, however, enhanced wet strength can also be achieved by addition of water-soluble starches or starch derivatives. This effect is nevertheless only temporary and decreases as soon as the starch derivative dissolves. Apart from the aforementioned additives, modified soluble cellulose derivatives are used as wet-strength agents. In this way, for example, the addition of carboxymethyl cellulose is usual as an additive besides the aforementioned polyamide epichlorohydrin resins.

[0019] To bond cellulose fibers together according to the second technique, thereby increasing the strength, US-5 873 979 teaches the reaction of the cellulose's hydroxy functions with a C2-C9 dicarboxylic acid.

[0020] The techniques for increasing the strength of paper in the wet state as taught in the applications: WO 97/36051, WO 97/36053, WO 97/36037, WO 97/36054 and WO 97/36052 primarily make use of the second technique by incorporating wet strength increasing additives to the pulp. However, WO 97/36052 modifies this technique insofar as the short chain polysaccharide portion of pulps, typically referred to as hemicelluloses, is oxidized to generate aldehyde groups, which are capable of reacting with a water-soluble polymer used as additive.

[0021] Specifically WO 97/36052 describes a paper product exhibiting initial wet strength and comprising

(a) cellulosic fibers having free aldehyde groups originating from cellulosic fibers that include a polysaccharide (preferably galactose and/or mannose) in which the OH groups of least a part of the recurrent units are OH groups in this position, in combination with

(b) a water-soluble polymer having functional groups that can react with the aldehyde groups.

[0022] Since cellulose exhibits OH groups in trans position, the hemicellulose portion of pulps that have a high proportion of hemicellulose is to be oxidized and the oxidation product used as a "binder". Hemicelluloses are derived from (poly)saccharides with OH groups in cis position (e.g. galactose, mannose) that can be rapidly oxidized into aldehyde groups and which can then form (hemi)acetal bonds in accordance with the teaching of this document, such bonds holding the paper product together.

[0023] In example 1 of this document various pulps are oxidized with ozone in one step under slightly alkaline or slightly acidic conditions. Handsheets having a basis weight of 18 lb/3000 ft² (29,3 g/m²) or 26 lb/3000 ft² (42,3 g/m²) are prepared from the ozonated pulps and measured with respect to their initial wet strength, dry strength and wet strength after 30 min. Sulfite pulp is oxidized at a low consistency (0.9 to 1.3 wt.% of fibers) at an initial pH value of 7.88 and leads to an initial wet strength of 30 g/inch (0.00181 N/15mm) measured with a handsheet of 29.3 g/m². For handsheets with about 80 g/m² the wet strength value thus should be in the order of 0.003 N/15 mm. The highest value measured (for a chemi-thermo mechanical pulp) is 450 g/inch, which corresponds to 0.027 N/15 mm.

[0024] WO 97/36052 does not teach that paper made from these ozonated pulp displays wet and dry strength properties being sufficient for practical use. It rather emphasizes that the addition of a water-soluble polyhydroxy polymer, such as guar gum, is necessary to achieve a product having desirable properties. This document further does not disclose any washing steps prior to or after the ozonation.

[0025] EP 0 685 593 A2 is concerned with a surface modification of cellulose fiber, leading to paper products having a combination of good strength in both wet and dry applications. The modification involves the steps of:

(a) oxidizing cellulose fiber with an oxidizing agent to form aldehyde cellulose; and

(b) sulfonating the oxidized cellulose with a sulfonation agent to form sulfonated cellulose.

[0026] The oxidizing agent may be selected from various chemical compounds including ozone, whereby periodate is preferred and also used in the examples. This document does not teach that the use of ozone per se improves wet strength of papers.

[0027] WO 00/50462 further discloses that the dry strength or wet strength of paper can be improved by generating C6-aldehyde functions within the cellulosic chain.

[0028] The majority of prior art techniques for improving the wet strength of pulp or paper made therefrom is disadvantageous insofar as it requires the use of additives, such as wet strength agents or other low or high molecular additives, being capable of crosslinking modified or unmodified cellulose.

[0029] Techniques for modifying the pulp *per se* are often cumbersome, since they require multi-step procedures of different chemicals or chemicals which are not readily available.

[0030] The technical object of the present application is therefore to provide a process (use) for improving the wet strength of cellulosic fibers material, in particular pulp, and paper or nonwoven made therefrom, which does not require the use of further additives, such as wet strength agents or water-soluble polyhydroxy polymers.

[0031] It is a further object of the present invention to provide this process on the basis of a simple and efficient chemical treatment system.

[0032] It is a further object of the present invention to provide a cellulosic material, in particular pulp, and paper or nonwoven made therefrom, in particular tissue paper, which have an excellent wet strength and further a suitable balance of other relevant properties.

[0033] Further advantages may become apparent from the following specification.

SUMMARY OF THE INVENTION

[0034] The present inventors have found that ozone, which is traditionally employed as bleaching and delignification chemical in the pulp industry, can be used under specific conditions to increase the wet strength of pulp as well as paper or nonwoven, in particular tissue paper, made therefrom.

[0035] The present invention thus relates to the use of a treatment sequence comprising an ozonation under acidic conditions followed by an acidic wash for enhancing the wet strength of a cellulosic fibrous material, as well as the corresponding process.

[0036] Preferably the ozone treatment and the acidic wash are followed by a second ozonation step under acidic conditions.

[0037] The present invention further concerns a fibrous cellulosic material obtainable by this treatment sequence which preferably has a breaking length of at least 100 m.

[0038] In the context of the present invention the phrase "wet strength of a cellulosic material", or the corresponding parameters, such as the breaking length refer to measurements with paper test sheets under conditions which are explained in the section "test methods".

[0039] The present invention thus allows increasing the wet strength of a cellulosic fibrous material (e.g. pulp), paper or nonwoven without the use of additives, such as wet strength agents. This use of ozone is very simple and efficient, and leads to highly pure products. The use of ozone as the only treatment chemical in particular avoids the introduction of so-called "non-process elements" (NPE) into the treatment system, for instance metal oxides such as MgO, which are frequently used in the oxidative treatment of pulps.

[0040] The inventive use of ozone thus leads to a high quality cellulosic material (e.g. pulp), paper or nonwoven having wet strength.

DETAILED DESCRIPTION OF THE INVENTION

Use of ozone to enhance wet strength and corresponding process

[0041] According to the use or process according to the invention a fibrous cellulosic material is ozonated under acidic conditions followed by an acidic wash of the ozonated material.

[0042] "Cellulosic" means that the fibrous material contains as main component cellulose.

[0043] Cellulose is defined here, in accordance with the common understanding in the art, as the long-chain fibrous portion insoluble in 10% (wt.%) NaOH (R_{10} portion) and which is also known in older literature as α -cellulose (to determine the R_{10} value see ASTM Method D1695, Annual Book of ASTM standards, Section 15, Vol. 15.04, American Society for Testing and Materials, Philadelphia 1983 and "Cellulose Chemistry and its Applications", edited by T.P. Nevell and S.H. Zeronian, Ellis Harwood Pub., West Sussex, England 1985, p.16 et seq.).

[0044] The cellulose portion (R_{10} value) is preferably at least 50%, particularly at least 80%, relative to the total weight of the oven-dried fibrous material (Hereinafter, the term "oven-dried" refers to the determination of the dry content of fibrous material/pulp samples corresponding to DIN EN 20638). Greater preference is given to values of at least 83%, particularly of at least 86%.

[0045] Cellulose is present in the cells, particularly of lignified plants, in a proportion of up to 50% of the mass, whereas hemicelluloses and lignin account for the remaining 50% of the mass of lignified plant, depending on the particular variety in varyingly large proportions (see Dietrich Fengel and Gerd Wegener, Chemistry, Wood, Ultrastructure, Reactions, Walter de Gruyter (1984)).

[0046] Measurements have indicated that the weight content of mono- and oligosaccharides other than glucose of the fibrous material to be used is preferably less than 20%, more preferably less than 16%, in particular less than 13% by weight. It is assumed that these values also apply to the content of all hemicelluloses which may include minor proportions of glucose-derived mono- and oligosaccharides. It is also possible to perform the invention with non-wood derived fibrous cellulosic material, such as cotton linters, which contain essentially no hemicelluloses.

[0047] The fibrous cellulosic material is preferably selected from wood based-pulps or other non-wood derived fiber sources. If non-wood derived cellulosic material, such as cotton linters is used as a raw material, no further pulping steps are usually needed. Due to the morphological structure, the cellulose already exists in an open state. The pulp may be a primary fibrous materials (raw pulps) or a secondary fibrous materials, whereby a secondary fibrous material is defined as a fibrous raw material recovered from a recycling process.

[0048] In the production of paper, chemical pulp and mechanical pulp are differentiated.

[0049] According to DIN 6730, chemical pulp is a fibrous material obtained from plant raw materials from which most non-cellulose components have been removed by chemical pulping without substantial mechanical post-treatment. In case of chemical pulping processes such as the sulfite or sulfate (Kraft) process, primarily the lignin components and the hemi-cellulose components are dissolved from the wood to varying degrees depending on the field of application of the chemical pulp. The result is a fibrous material consisting primarily of cellulose.

[0050] Mechanical pulp is the general term for fibrous materials made of wood entirely or almost entirely by mechanical means, optionally at increased temperatures. Mechanical pulp is subdivided into the purely mechanical pulps (groundwood pulp and refiner mechanical pulp) as well as mechanical pulps subjected to chemical pretreatment: chemo-mechanical pulp (CMP), such as chemo-thermomechanical pulp (CTMP). Synthetic cellulose-containing fibers can also be used.

[0051] Chemical and mechanical pulp are also known by the general designation pulp.

[0052] According to the invention preference is given to the use of pulp from plant material, particularly wood-forming plants, more particularly softwood-forming plants. Fibers of softwood (usually originating from conifers, such as spruce or pine), hardwood (usually originating from deciduous trees) or from cotton linters can be used for example. Fibers from esparto (alfa) grass, bagasse (cereal straw, rice straw, bamboo, hemp), kemp fibers, flax and other woody and cellulosic fiber sources can also be used as raw materials. The corresponding fiber source is chosen in accordance with the desired properties of the end product in a manner known in the art. For example, the fibers present in softwood which are shorter than those of hardwood lend the final product a higher stability on account of the higher diameter/length ratio. If the softness of the product is to be promoted, which is important e.g. for tissue paper, eucalyptus wood is particularly suitable as a fiber source.

[0053] With regard to the softness of the products, the use of chemical raw pulps is preferred. The chemical raw pulps suitable according to the invention include, inter alia, sulfite pulps, kraft pulps (sulfate process), soda pulps (cooking with sodium hydroxide), pulps from high-pressure cooking with organic solvents (e.g. Organosolv, Organocell, Acetosolv, Alcell) and pulps from modified processes (e.g. ASAM, Stora or Sivola process). Among the kraft pulps, it is possible to use those which were obtained in continuous cooking systems (MCC (modified continuous cooking), EMCC (extended modified continuous cooking) and ITC (isothermal cooking)). The products of discontinuous kraft processes (e.g. RDH (rapid displacement heating), Superbatch and Enerbatch) are also suitable as a starting product. The sulfite processes include the acidic sulfite/(bi)sulfite processes, (bi)sulfite process, "neutral sulfite semi-chemical pulping" (NSSC) process and alkaline sulfite processes such as processes in which in addition to aqueous alkali, sulfite and/or anthraquinone in combination with organic solvents such as methanol were used for cooking, e.g. the so-called ASAM process (alkali sulfite anthraquinone methanol). The major difference between the acidic and neutral or alkaline sulfite processes is the higher degree of delignification in acidic cooking processes (lower kappa numbers). The NSSC process provides semi-chemical pulps which are advantageously defibered in downstream mechanical fibrillation before they are used according to the invention for the purpose of oxidation. The sulfite and kraft pulps considerably differ in terms of their fibrous material properties. The individual fiber strengths of sulfite pulps are usually much lower than those of kraft pulps. The mean pore width of the swollen fibers is also greater in sulfite pulps and the density of the cell wall is lower compared to sulfate pulps, which simultaneously means that the cell-wall volume is greater in sulfite pulps. For this reason, there are also obvious differences regarding water absorption and swelling behavior of the cellulosic fibrous materials, which must also be taken into consideration when selecting the raw material for oxidation.

[0054] According to the invention it is preferred to use among chemical pulps, in particular pulp derived from processes using sulfate ("Kraft pulp"), sulfite or (bi)sulfite ("sulfite pulp" or "bisulfite pulp"), preferably under acidic conditions.

[0055] The cellulosic material to be ozonated preferably has a residual lignin content (kappa number as determined according to DIN 54357, August 1978) of not more than 50, 40, 30 or 20 with increasing preference. Typically the pulps to be ozonated have kappa values above 10, in particular above 13.

[0056] The ozonation treatment of the invention does not only lead to an increase in wet strength, but is typically accompanied by a decrease of the kappa number, which is preferably in the order of at least 10, in particular at least 15.

[0057] Depending on the cellulosic material used, the final kappa number lies below 15, 10, 5, 3, or 1.5 with increasing

preference.

[0058] It is also preferred that before and/or after ozonation, preferably after ozonation, the chemical pulp should undergo additional surface treatment (beating) which has a favorable effect on the strength properties of the obtained paper or nonwoven. This may be preferably brought about within the pulp refinement system of a paper/tissue paper machine. In another preferred embodiment, such surface treatment (beating) occurs as part of pulp production, i.e. while it is still at the pulp plant. A refiner is particularly suitable for this purpose. Fibrillation of the surface occurs during mechanical treatment of the pulp/water suspension. This treatment affects the static and dynamic strength properties. Fibrillability of the fiber crucially depends on the fiber's swelling capability. In this way, it is known that due to a low polyuronic acid content, kraft pulps produced according to the sulfate process are less readily beatable. Effects of beating in accordance with e.g. the specific edge load, total energy expenditure etc. are discussed in detail by the following authors: Lothar Götsching, *Stofftechnologie - Mechanische Faserbehandlung; Wochenblatt für Papierfabrikation* 23/24, (1998), 1194; M.L. Wild, *Festigkeitsentwicklung von Holz- und Deinkstoff aus Zeitungsdruckpapier mit niedriger spezieller Kantenbelastung; Wochenblatt für Papierfabrikation* 23/24, (1998), 1218.

[0059] Fibrillation of the fibers during beating occurs either by the fibers themselves or by the refiner knives. During beating, the fibers are subjected to a variety of physical loads. Axial and tangential shearing and compressive forces acting upon the fiber play a particular role as regards fiber reforming. This leads to a change in fiber morphology. In this way, the outer primary wall is the first to be separated. The associated change in fiber morphology can be described as follows:

- a) tearing open and removing the fibrous material's outer wall layer designated as the primary wall;
- b) exposing the fibrils and fibrillation out of the wall layers designated as S1 and S2;
- c) partially shortening the total fiber unit or producing accepts by shearing off fibrils.

[0060] The influences of the cutting angle of the ribs and grooves attached to the beating unit in relation to the change in characteristic of the fibrous material are described in PTS Research Report: G. Bär, *Faserstoffoptimierung durch modifizierten Mahlprozess* PTS-FB 19/98, 1st edition, (1998).

[0061] Depending on the refiner's operating mode, the fibers are shortened (cut) or are fibrillated, which includes the separation of the outer layers of the fiber wall, this latter process substantially increasing the surface and bonding capacity of the fibers. The refiner operating mode that accompanies fibrillation is therefore preferred (to simplify matters, this process step will also be designated as beating in the following). Beating is particularly used in the case of chemical pulps.

[0062] The "acid wash" used in the inventive treatment sequence has been found to increase the efficiency of the ozone treatment and the wet strength properties of the cellulosic material obtained.

[0063] According to a preferred embodiment of the invention, the (first) ozone treatment is preceded by a further acidic wash ("pre-wash") which also has a beneficial effect on the strength properties of the pulp obtained after ozonation.

[0064] Further it was found that the use of at least two separate ozonation steps further increases the strength properties of the pulp obtained. Therefore it is advantageous if ozonation and acidic wash are followed by a second ozonation step under acidic conditions.

[0065] If more than one ozonation step is employed, it is also preferred that each ozonation is followed by an acidic wash. In this case, too, it has proven beneficial to employ an acidic wash as first step of the entire treatment, i.e. prior to the first ozonation step.

[0066] Moreover, it is preferred to maintain acidic conditions after the last ozonation step of the treatment sequence. Similarly it is advantageous to use at no point in time an alkaline wash. According to a more preferred embodiment, the entire treatment sequence is performed under acidic conditions.

[0067] It is also possible to perform more than one acid wash prior to and/or after the ozonation step(s).

[0068] "Washing" means in the context of the present invention that the cellulosic material is contacted with an acid aqueous medium, accompanied or followed by removing this medium at least partially from the cellulosic material. The medium can be removed by filtration, at ambient pressure or by means of applying a vacuum to the filtrate. To remove the medium as far as possible without mechanically damaging the fibers, it can further be preferred to press the pulp with devices typically used for this purpose (e.g. screw press or (double) wire press). It is further possible to combine washing and pressing steps in a washing press.

[0069] Each washing step can take from a few seconds to several minutes or even hours. Typical treatment times range from 1 sec to 10 hours, preferably from 10 sec to 1 hour.

[0070] In one embodiment of the washing step, the acidic washing medium is in motion with respect to the fibers. Preferably a filtration device is used for this purpose. Usually shorter contact times, e.g. from 1 sec to 5 min, more preferably from 10 sec to 1 min, provide a sufficient washing effect. It is believed that the washing effect is primarily based on replacing the aqueous medium (film) surrounding the fibers by the fresh washing medium (being acidic in

line with the invention). This washing mechanism is referred to as "W_R" (R=replacement) in the following. It can be performed with filtration devices known in the art, for instance with a Buchner funnel on a lab scale or a trommel screen (rotary screen) on an industrial scale.

[0071] In an alternative embodiment, fibers and washing medium are left to stand for a longer period of time or are both stirred. It is desirable to select contact times allowing for the formation of an equilibrium at the fiber surfaces, e. g. from 5 min to 10 hour, preferably 10 min to 1h, more preferably from 15 minutes to 30 min. With longer treatment times, it is believed that the aqueous medium (film) surrounding the fibers is primarily diluted by the fresh (acidic) washing medium. This washing mechanism will be referred to "W_D" (D=dilution) in the following. Preferably a washing press as known in the art is used for this step.

[0072] It is also possible to combine both techniques (W_R and W_D) in one washing step.

[0073] It should be noted that in both cases (W_R and W_D) the combination of both effects or any other mechanism may also contribute to the observed washing effect being beneficial for the desired wet strength increase in the following ozonation step. It should also be understood that the above explanations are given without being bound to theory.

[0074] The "dilution wash" step ("W_D") is preferably conducted prior to at least one "W_R" step. In the "W_D" step, the fibrous material is left for a longer period of time, for instance 5 min to 10 hours, preferably 10 min to 1h, more preferably from 15 min to 30 min in contact with an aqueous acidic medium, e.g. acidified water, before removing the medium, preferably by pressing. It is possible to perform this washing/acidification step ("W_D") within a wide concentration range for the acid and consistency range for the cellulosic material. It is preferred to adjust the consistency of the fibrous material to values from 0,01 to 10 weight %, preferably 0,1 to 5 weight %, based on the oven-dried material.

[0075] It is preferred to perform an acid wash, be it of "W_R" and/or "W_D" type, with an aqueous medium, in particular acidified water, having a pH below 7, more preferably at most 6, in particular at most 5. The lower pH limit is preferably at least 2, more preferably at least 3.

[0076] According to the invention it is possible to use commercial pulps and subject the same to an ozonation under acidic conditions.

[0077] In preferred embodiments, typically moist pulp as obtained from a pulping process is employed. "Pulping process" means here the afore-mentioned chemical and/or mechanical digestion of ligno-cellulosic material, preferably wood, most preferably the chemical digestion of wood, in particular Kraft or (bi)sulfite processes. Under these circumstances an "acid wash" prior to the first ozonation step can substantially remove the "carry-over" from the cooking liquor which has been found to contribute to strength properties of the pulp after ozonation.

[0078] It is further preferred that prior to the ozone treatment, the cellulosic material has not been subjected to any bleaching or other oxidizing steps.

[0079] It is thus also preferred to use ozone as the only oxidant in the post-pulping process.

[0080] Further it is possible to use ozone as the only oxidant during the entire processing from the raw material, in particular wood, to the final fibrous cellulosic material, in particular pulp.

[0081] The advantage of using ozone as the only oxidant in the post-pulping process, or even during the entire pulp production, is the possibility of decreasing the amount of so-called "non-process elements" (NPE), such as metal oxides (e.g. MgO, which is often used with other oxidants, such as hydrogen peroxide). The term "NPE" further covers metal impurities being present in the raw material which are often difficult to remove during the pulping process. If so-called NPEs are introduced or present in the process, they tend to enrich in recycled process streams and therefore should be reduced as far as possible.

[0082] Consequently, the inventive process (use of ozone) can lead to very pure fibrous cellulosic materials, in particular pulps.

[0083] Having regard to the purity and the wet-strength properties of a desirable cellulosic material, in particular pulp, it is preferred to adjust the TOC value of the filtrate obtained from the acid wash(es) to TOC values (total organic carbon, DIN ISO 8245 (1991)) from 10-10000 mg/ml, preferably 10-500 mg/ml by using corresponding amounts of washing medium. Ozone is less consumed due to side reactions, when the TOC level is reduced as much as possible. The less ozone is consumed by dissolved organic compounds, the more efficient the ozonation is.

[0084] For the same reason it is further desirable to adjust the CSB values ("Chemischer Sauerstoffbedarf") of the said filtrate(s) within the range of from 10 to 10000 mg/ml, in particular 10 to 600 mg/ml. The conductivity of the filtrate is preferably from 50 to 5000 µS, in particular 500 to 1600µS.

[0085] Furthermore, it is preferred to work countercurrent, i.e. to wash the completely ozonated fibrous material with clean(er) water and to use preferably the resulting wash water (filtrate), if necessary after acidification, for "an acid wash" in the sense of the present invention. Finally, the wash water (filtrate) from the "acid wash" after the first ozonation step is preferably used for washing the pulp following the pulping process. It is possible in the cases described above to use fresh water in addition to the wash water that is led in countercurrent.

[0086] In addition, the use of ozone is favorable, since the increase of wet strength is achieved under simple process conditions. The inventors have also found that the use of ozone under acidic conditions, rather than alkaline conditions, can lead to an improved wet strength.

[0087] "Acidic conditions" means in this context that at least part of the ozonation step(s) is performed at a pH below 7. It is further preferred that the initial pH is also below 7. More particularly, the pH of the entire ozonation step(s) should be below 7.

[0088] It is preferred to use in the ozonation step(s) a pH of at most 6, in particular at most 5. As regards the lower pH limit, values of at least 2, more preferably at least 3 are most suitable.

[0089] It is preferred to use anorganic (for instance sulfuric acid) or organic acids for adjusting an acid pH value. Preferably, the anorganic acid is a carboxylic acid having 1 to 4 carbon atoms or dicarboxylic acid having 2 to 4 carbon atoms, in particular, formic acid, acetic acid or oxalic acid.

[0090] The same acids can also be employed for adjusting the aqueous washing medium (to be used in one of the washing steps after and/or prior to the ozonation) to a suitable acidic pH.

[0091] Preferably, ozone is applied in a concentration as high as possible. For practical reasons, a concentration of about 0.01 to 20% wt.-% ozone based on the ozone/O₂-mixture prepared by the ozone generator is typically used. It is further possible to apply condensed ozone as a liquid phase.

[0092] The amount of ozone to be consumed by the fibers is adjusted according to the desired increase in wet strength, whereby typically pulps having high kappa values require higher amounts of ozone to develop a sufficient wet strength. The weight ratio ozone based on the oven-dried fibrous material can suitably be from 0,1 to 20 wt.-%, preferably from 0,5 to 5 wt.-%. If multi-step ozonation processes are performed, the ozone consumption of each step is preferably smaller, more preferably at least 30% smaller than that of the preceding step.

[0093] It is possible to use ozone at low consistency of the fibrous material (typically less than 3%, based on the dry weight of the fibers), medium consistency (from 3 to less than 30%, typically around 10%) and high consistency (at least 30%) whereby the %-values refer to the weight proportion of the fibrous material (oven-dried) with respect to the weight of the aqueous reaction medium. Preferably, the consistency of the fibrous material is at least 30%, or even at least 35%. A consistency of about 35 to 45% has shown to give good results. Working at high consistency requires dewatering the cellulosic material before it is contacted with ozone. This can be done by pressing a moist fibrous material, as it is typically obtained from the pulping process, or by adjusting the moisture content of a dry material. Dewatering can be achieved with any pressing equipment, i.e. with a screw press or a (double)wire press. It is also possible to combine the acid pre-treatment (explained below) and the pressing step by using a washing press.

[0094] If the ozone treatment is performed at high consistencies, a pseudo two-phase system, consisting only of fibers and gas is generated. Thus, there are less or no problems regarding the miscibility of the reaction gas with a liquid phase. The cell walls and luminae of the fibers are saturated with water and only a thin water film surrounds the fibers. In order to expose the surface of the fibers as much as possible, a fluffing step (explained below) further can be advantageous, though not necessary.

[0095] Typically, the oxidant is dried before it reaches the ozone generator. In order to increase the affinity of the ozone towards the fibers material, the oxidant/ozone mixture obtained from the ozone generator is preferably rewetted before being introduced in the fibrous material. Wetting of the ozone or ozone/oxygen gas mixture can be achieved by leading the gas through water in any kind of equipment used for gas-washing applications.

[0096] Temperatures of 0 to 120°C, or even lower can be used for the ozonation step(s), whereby a more favorable temperature range is from 10 to 40°C, in particular, 20 to 30°C. It can become necessary to cool the reaction mixture, since the reaction with ozone is exothermal, in order to keep the temperature in the reaction vessel within the above-stated ranges.

[0097] The reaction can be performed in any kind of vessel or reactor or closed system, which is inert towards ozone.

[0098] It is preferred, though not necessary, to fluff the cellulosic material before the at least one ozonation step. More preferably each ozonation step is preceded by fluffing (in the following designated by letter "F"), Fluffing typically leads to a wadding-like material having no multifiber aggregates and a high surface, which can be exposed to the ozone and increases its effectiveness.

[0099] The fibrous material can be fluffed per hand by disintegrating fiber assemblies. It is preferred to use a hammer mill or a refiner, for instance a disk refiner. However, in contrast to the beating treatment described above, fluffing, as a rule, does not open and remove the outer wall layer of the fibrous material, nor shortens or fibrillates the fibers. Therefore, this fluffing treatment should also not alter the water retention behavior of the fibrous material to a major extent. To achieve this, the hammer mill or the refiner can be provided with more coarse units acting upon the cellulosic material, for instance with larger ribs and grooves. "Fluffing" is a process known in the art and commercially available devices offered for this purpose can be used in the invention. Another example of a suitable "fluffer" is disclosed in EP 0 492 040 A1.

[0100] It is further preferred to stir or mix the fibrous material when being in contact with ozone, in order to increase the efficiency of the reaction. It is also possible to use downflow tubes or towers in which fluffed or separated pulp fibers are treated with ozone. Any technique to improve the penetration and permeability of the fibrous material towards the ozone gas is in the scope of the process conditions.

[0101] According to the invention any cellulosic material is preferably subjected to the following treatment sequences

comprising one ozonation step:

F-Z-W or W-F-Z-W,

or two ozonation steps:

F-Z-W-Z, Z-W-F-Z, F-Z-W-F-Z,

F-Z-W-Z-W, Z-W-F-Z-W, F-Z-W-F-Z-W,

W-F-Z-W-Z, W-Z-W-F-Z, W-F-Z-W-F-Z,

W-F-Z-W-Z-W, W-Z-W-F-Z-W, or W-F-Z-W-F-Z-W,

wherein "W" means acidic wash, "F" means fluffing and "Z" ozone treatment.

[0102] From the above preferred embodiments it is seen that during the inventive treatment, alkaline conditions are preferably avoided.

[0103] Without being bound by theory, it is believed that the following effects contribute to the wet strength increase, observed for the inventive use of ozone. It would appear that the ozonation of cellulosic fibrous material primarily leads to the formation of carbonyl functional groups (ketone groups) resulting from the attack at C2 and/or C3 hydrogen atoms of the anhydroglyucose unit of the cellulose chain, whereas aldehyde and carboxy functions are generated to a lesser extent. C. Chirat and V. de la Chapelle demonstrate in a recent publication ("Heat and Light induced Brightness Reversion of bleached Pulps", Journal of Pulp and Paper Science, vol. 25, No 6, June 1999, 201-205) that during ozonation at low consistency (3.5 % at room temperature) the aldehyde and carboxy level remains almost constant (aldehyde below 20 meq/100g and carboxy below 60 meq/100g cellulose), whereas the ketone level constantly increases. It is believed that at least similar ketone levels (above 80 meq/g, in particular above 100 meq/g cellulose, as measured according to C. Chirat) can also be reached with the present invention.

[0104] Presumably, it is the formation of ketone groups which enhances the formation of inter-fiber bonds in a wet stage, possibly by hydrogen bonds or even via (semi)ketal formation. The formation of these bonds could thus contribute to the strength of a cellulosic web in a wet state.

Cellulosic Material Having Wet Strength

[0105] If the present specification makes reference to the strength properties (dry, wet) of pulp, we do not mean the mechanical strength of the individual fibers, but rather the strength of paper test sheets made from the pulp. More specifically, these test sheets have a basis weight of about 80 g/m², are formed and conditioned in line with the procedure described in the section "test methods", and are subjected to the measurements explained therein.

[0106] A fibrous cellulosic material, in particular pulp treated in line with the present invention, shows excellent wet strength properties and preferably has a breaking length (wet) of at least 100 m, more preferably at least 200 m, in particular at least 300 m; for instance 600 m. These values were measured, in line with the section "test methods", on test sheets having a basis weight of about 80g/m² prepared from unbeaten cellulosic material (beating degree of about 12 to 14 °SR, DIN-ISO 5267/1). Higher beating degrees can further increase the wet strength. To achieve this, a beating degree of at least 15, and preferably from 18 to 25 °SR can be used.

[0107] The above wet strength parameter can be reached without adding effective amounts of wet strength enhancing additives, which increase the initial, temporary or permanent wet strength of modified or unmodified fibrous cellulosic material. For instance, it is possible to attain these wet strength properties without adding a water-soluble polymer having functional groups capable of reacting with aldehyde groups (e.g. guar gum) as disclosed in WO 97/36052.

[0108] The inventive use of ozone does not have a major impact on the dry-breaking length of the cellulosic fibrous material obtained, or paper or nonwoven made therefrom. The dry-breaking length of the cellulosic material (as measured with a 80g/m² test sheet under the condition described in the section "test methods") preferably is at least 2500 m, more preferably at least 3000 m, in particular at least 4000 m.

[0109] Further, the ozone treatment does not appear to lead to a major change in terms of tearing resistance of the cellulosic fibrous material, or paper or nonwoven made therefrom. The tearing resistance of the cellulosic material (as measured with a 80g/m² test sheet under the condition described in the section "test methods") thus is preferably at least 300 m, in particular at least 500 m, more preferably at least 1000 m, in particular at least 1500 m.

[0110] The kappa number of the inventive cellulosic material (measured according to DIN 54 357) is preferably less than 15, 10, 5, 3, 1.5 with increasing preference.

[0111] Further, it was observed that the ozone treatment of the present invention, as a side effect, can contribute to the brightness of the fibrous material (e.g. pulp) obtained, which is typically at least 80% ISO and may reach values as high as at least 85% ISO, in particular at least 90% ISO.

Paper or Nonwoven

[0112] The present invention also relates to paper or nonwoven comprising the ozone-treated cellulosic fibrous material according to the invention, preferably in the amount of at least 50 % by weight, in particular at least 80 % by weight, relative to the dry weight of the finished product.

[0113] The paper can be a packaging paper, a graphic paper or tissue paper. Preferably, the paper is a tissue paper.

[0114] In the following, depending on the context, the term "paper" or "nonwoven" does not only refer to the raw material as obtained from the paper/nonwoven machine, but also covers the corresponding further processed products, since often there is often no strict borderline to distinguish the same. Further, it should be understood that the term "paper" or "nonwoven", in particular "tissue paper", as used in the claims, extends to the corresponding products which make use of raw paper, in particular raw tissue paper or raw nonwoven.

[0115] The German terms "Vlies" and "Vliesstoffe" are applied to a wide range of products which in terms of their properties are located between the groups, paper, paperboard, and cardboard on the one hand and the textile products on the other, and are currently summarized under the term "nonwovens" (see ISO 9092 - EN 29092). The invention allows the application of known processes for producing nonwovens, such as what are called air-laid and spun-laid techniques, as well as wet-laid techniques.

[0116] Nonwovens may also be called textile-like composite materials, which represent flexible porous fabrics that are not produced by the classic methods of weaving warp and weft or by looping, but by intertwining and/or by cohesive and/or adhesive bonding of fibers which may for example be present in the form of endless fibers or prefabricated fibers of a finite length, as synthetic fibers produced *in situ* or in the form of staple fibers. The nonwovens according to the invention may thus consist of mixtures of synthetic fibers in the form of staple fibers and the fibrous material according to the invention.

[0117] "Papers" are also planar materials, albeit essentially composed of fibers of a plant origin and formed by drainage of a fibrous-material suspension on a wire or between two continuously revolving wires and by subsequent compression and drainage or drying of the thus produced fibrous mat (cf. DIN 6730, May 1996). The standard restricts the range of mass per unit area (basis weight) for paper to a maximum of 225 g/m².

[0118] Depending on the type of paper, the production process comprise also a sizing and/or smoothing step, along with the typical process steps of sheet formation, pressing, and drying described above.

[0119] Based on the underlying compatibility of the production processes (wet laying), "tissue" production is counted among the paper making techniques. The production of tissue is distinguished from paper production by its extremely low basis weight of normally less than 40 g/m² and its much higher tensile energy absorption index. (In processing inventive fibrous material to tissue paper, one generally selects a basis weight of 10 to 40 g/m² per ply. The total basis weight of multiple-ply tissue products is preferably equal to a maximum of 65 g/m².) The tensile energy absorption index is arrived at from the tensile energy absorption in which the tensile energy absorption is related to the test sample volume before inspection (length, width, thickness of sample between the clamps before tensile load). Paper and tissue paper also differ in general with regard to the modulus of elasticity that characterizes the stress-strain properties of these planar products as a material parameter.

[0120] A tissue's high tensile energy absorption index results from the outer or inner creping. The former is produced by compression of the paper web adhering to a dry cylinder as a result of the action of a crepe doctor or in the latter instance as a result of a difference in speed between two wires ("fabrics"). This causes the still moist, plastically deformable paper web to be internally broken up by compression and shearing, thereby rendering it more stretchable under load than an uncreped paper. Most of the functional properties typical of tissue and tissue products result from the high tensile energy absorption index (see DIN EN 12625-4 and DIN EN 12625-5).

[0121] One example of papers and paper products is represented by hygiene papers, particularly tissue papers and hygiene products (tissue products) made therefrom and which are e.g. used in personal grooming and hygiene, the household sector, industry, the institutional field in a wide variety of cleaning processes. They are used to absorb fluids, for decorative purposes, for packaging or even as supporting material, as is common, for example, in medical practices or in hospitals.

[0122] Hygiene paper primarily includes all kinds of dry-creped tissue paper, as well as wet-creped paper and cellulose or pulp wadding.

[0123] The one-ply intermediate products originating from the papermaking machine and made of lightweight paper usually dry-creped on a yankee cylinder by means of a crepe doctor are generally described as "tissue paper" or more accurately raw tissue paper. The one-ply raw tissue may be built up of one or a plurality of layers respectively.

[0124] All one-ply or multi-ply final products made of raw tissue and tailored to the end user's needs, *i.e.* fabricated with a wide variety of requirements in mind, are known as "tissue products".

[0125] Typical properties of tissue paper include the ready ability to absorb tensile stress energy, their drapability, good textile-like flexibility, properties which are frequently referred to as bulk softness, a high surface softness, a high specific volume with a perceptible thickness, as high a liquid absorbency as possible and, depending on the application,

a suitable wet and dry strength as well as an interesting visual appearance of the outer product surface. These properties allow tissue paper to be used for example as cleaning wipes (paper wipe, windscreen cleaning wipe, kitchen paper), sanitary products (e.g. toilet paper), paper handkerchiefs, household towels, towels, cosmetic wipes (facials), as serviettes/napkins, bed linen or garment.

[0126] If tissue paper is to be made out of the fibrous material according to the invention, the process essentially comprises

a) forming that includes the headbox and the wire portion,

b) the drying portion (TAD (through air drying) or conventional drying on the yankee cylinder) that also usually includes the crepe process essential for tissues,

c) as a rule, the monitoring and winding area.

[0127] Paper can be formed by placing the fibers, in an oriented or random manner, on one or between two continuously revolving wires of a paper making machine while simultaneously removing the main quantity of water of dilution until dry-solids contents of usually between 12 and 35 % are obtained.

[0128] Drying the formed primary fibrous web occurs in one or more steps by mechanical and thermal means until a final dry-solids content of usually about 93 to 97 %. In the case of tissue making, this stage is followed by the crepe process which crucially influences the properties of the finished tissue product in conventional processes. The conventional dry crepe process involves creping on a usually 4.5 to 6 m diameter drying cylinder, the so-called yankee cylinder, by means of a crepe doctor with the aforementioned final dry-solids content of the raw tissue paper (wet creping can be used if lower demands are made of the tissue quality). The creped, finally dry raw tissue paper (raw tissue) is then available for further processing into the paper product or tissue paper product according to the invention.

[0129] Instead of the conventional tissue making process described above, the invention gives preference to the use of a modified technique in which an improvement in specific volume is achieved by a special kind of drying within process section b and in this way an improvement in the bulk softness of the thus made tissue paper is achieved. This process, which exists in a variety of subtypes, is termed the TAD (through air drying) technique. It is characterized by the fact that the "primary" fibrous web (like a nonwoven) that leaves the sheet making stage is pre-dried to a dry-solids content of about 80% before final contact drying on the yankee cylinder by blowing hot air through the fibrous web. The fibrous web is supported by an air-permeable wire or belt and during its transport is guided over the surface of an air-permeable rotating cylinder drum. Structuring the supporting wire or belt makes it possible to produce any pattern of compressed zones broken up by deformation in the moist state, resulting in increased mean specific volumes and consequently leading to an increase in bulk softness without decisively decreasing the strength of the fibrous web.

[0130] Another possible influence on the softness and strength of the raw tissue lies in the production of a layering in which the primary fibrous web to be formed is built up by a specially constructed headbox in the form of physically different layers of fibrous material, these layers being jointly supplied as a pulp strand to the sheet making stage.

[0131] When processing the raw fibrous web or raw tissue paper into the final product, the following procedural steps are normally used individually or in combination: cutting to size (longitudinally and/or cross cutting), producing a plurality of plies, producing mechanical ply adhesion, volumetric and structural embossing, chemical ply adhesion, folding, imprinting, perforating, application of lotions, smoothing, stacking, rolling up.

[0132] To produce multi-ply tissue paper products, such as handkerchiefs, toilet paper, towels or kitchen paper, an intermediate step preferably occurs with so-called doubling in which the raw tissue in the finished product's desired number of plies is usually gathered on a common multiply master roll.

[0133] The processing step from the raw tissue that has already been optionally wound up in several plies to the finished tissue product occurs in processing machines which include operations such as repeated smoothing of the tissue, edge embossing, to an extent combined with full area and/or local application of adhesive to produce ply adhesion of the individual plies (raw tissue) to be combined together, as well as longitudinal cut, folding, cross cut, placement and bringing together a plurality of individual tissues and their packaging as well as bringing them together to form larger surrounding packaging or bundles. The individual paper ply webs can also be pre-embossed and then combined in a roll gap according to the foot-to-foot or nested methods.

EXAMPLES

Test methods

[0134] The following test methods were used to evaluate the ozonated fibrous materials according to the invention as compared to fibrous materials which correspond, but which have not been modified by ozonation.

1) Producing the test sheets

[0135] The test sheets (having a basis weight of approx. 80 g/m²) were made in accordance with the Rapid Köthen method (DIN 54 358-1, February 1981; see also ISO 5269-2: 1980). Before being tested in terms of physical properties e.g. by means of the tensile test, the thus obtained test sheets were always conditioned for a duration of at least 12 hours in a standard climate at a temperature of (23±1) °C and a relative humidity of (50±2) % in accordance with DIN EN 20187, Paper, Cardboard and Pulp, a standard climate for pretreatment and testing and a method of monitoring the climate and pretreatment of samples, November 1993 (see ISO 187 : 1990).

2) Initial wet strength (width-related breaking strength (wet)) and breaking length (wet)

[0136] The wet strength according to DIN ISO 3781, Paper and Cardboard, tensile test, determination of the width-related breaking strength after immersion in water, October 1994 (identical to ISO 3781 : 1983), is herewith defined as initial wet strength of the fibrous material networks according to the invention, e.g. paper/tissue paper/nonwoven.

[0137] When experimentally checking the invention, the tensile test was accordingly performed by means of an electronic tensile test apparatus (Model 1122, Instron Corp., Canton, Mass., USA) with a constant rate of elongation of 10 mm/min using a Finch device. The width of the test strips was 15 mm. The strip length was about 180 mm. The free clamping length when using the Finch clamp was about 80 mm. The test strip was secured with both ends in a clamp of the test apparatus. The other end (loop) formed in this way was placed around a pin and treated at 20°C with distilled water until complete saturation. The soaking period of the samples before tensile testing was fixed at 30 s. Six test strips at a time were measured, the result being indicated as an arithmetic mean.

[0138] To ensure that the wet strength of the samples has fully developed, the samples to be tested were always artificially aged before conducting the tensile test. Aging was effected by heating the samples in an air-circulating drying cabinet to (125 ± 1) °C for a period of 10 min.

[0139] A similar approach applies to paper/tissue paper/nonwoven products, modified only to the extent that the test strips to be examined were taken from the finished product itself or from the product made thereof and that they do not originate from a laboratory test sheet.

[0140] As regards tissue paper and tissue products, DIN ISO 3781 is replaced by DIN EN 12625-5 Tissue Paper and Tissue Products - Part 5: determination of width-related wet load at break, January 1999. The strip width is then 50 mm, the free clamping length is shortened to about 50 mm, the depth of immersion of the loop formed by the test strip is at least 20 mm. The soaking duration (immersion time) is shortened to 15 s, the rate of elongation is set to a constant (50 ± 2) mm/min, the measurement of the breaking strength is performed on the sample immersed in distilled water.

[0141] Six test strips at a time were measured, the result being indicated as an arithmetic mean.

[0142] The breaking length (wet) was calculated from the width-related breaking strength in accordance with the following formula (see TAPPI 494-96, Comment 9):

$$RL = 102000 (T/R)$$

where

T is the initial wet strength in kN/m and

R is the basis weight in g/m²(in a standard climate)

3) Dry strength (width-related breaking strength (dry)) and breaking length (dry)

[0143] The dry strength was determined according to DIN EN ISO 1924-2, Paper and Cardboard, determination of properties under tensile load. Part 2: Method at a constant rate of elongation, April 1995, (ISO 1924-2 : 1994).

[0144] In the case of tissue paper and tissue products, the test is performed in accordance with DIN EN 12625 - 4, Tissue Paper and Tissue Products - Part 4: Determination of width-related breaking strength, elongation at break and tensile energy absorption, January 1999.

[0145] The breaking length (dry) was calculated from the width-related breaking strength in accordance with the following formula (see TAPPI 494-96, Comment 9):

$$RL = 102000 (T/R)$$

where

T is the tensile strength in kN/m and

R is the basis weight in g/m²(in a standard climate)

4) Relative wet strength

[0146] The relative wet strength (WS) was calculated as follows:

$$\text{rel. WS} = \text{BS}_{\text{wet}}/\text{BS}_{\text{dry}}$$

where BS_{wet} is the width-related breaking strength of the wet sample strip and BS_{dry} is the width-related breaking strength of the dry sample strip, and these values were ascertained in the manner described above.

5) Kappa number

[0147] The kappa number is determined according to DIN 54357 (August 1978; "Examination of pulp, determination of the kappa number")

6) Brightness

[0148] The degree of brightness (in percent) was determined according to ISO following scan S11 1975.

7) Air permeability

[0149] The air permeability was determined according to Bendtsen (Zellcheming-Merkblatt V26/75).

9) Tearing resistance (dry-tear strength) according to Elmendorff

[0150] The tearing resistance was determined according to Elmendorff using a test sheet according to the above item 1 following a process described in DIN 53128.

10) Bursting strength (kPa)

[0151] The bursting strength was determined according to "Zellcheming-Merkblatt V12/57".

11) Beating degree

[0152] The beating degree was measured by means of the freeness value (in °SR) according to DIN-ISO 5267/1; March 1999.

12) Dry content

[0153] The wording "oven-dried" refers to the determination of the dry content of fibrous material/pulp samples corresponding to DIN EN 20638.

[0154] In the examples, %-values always refer to the weight, if not indicated otherwise.

Example 1

[0155] Beech sulfite pulp stemming from an acid sulfite pulping process and having a brightness (% ISO) of 61.0 and a kappa number of 13.9 was subjected to the following treatment steps.

a) After thoroughly washing the pulp with water, it was treated over approximately 20 minutes with an acid aqueous solution, which was adjusted to pH 3 with sulfuric acid, at a consistency of 0.5 to 3% (typically 1 to 1.5%), based on the oven-dried material. The slurry obtained thereby was filtrated over a Buchner funnel and then further de-watered in a centrifuge to a consistency of about 40%.

b) The pulp obtained from the acid wash was disintegrated per hand into individual fibers.

c) A laboratory rotary evaporator was charged with about 30g disintegrated pulp having a pH of 3 and a consistency of 40%. This vessel was cooled in order to keep the temperature at approximately room temperature during the reaction. A re-wetted ozone/O₂-mixture was introduced in the rotating vessel by means of a glass frit being submerged into the pulp dispersion. The reaction was stopped after a consumption of 1.0 % ozone, based on the weight of the pulp sample. The consumption was measured by introducing small samples of the ozone/O₂-mixture into an aqueous KJ-solution having a predetermined content of KJ and calculating the ozone concentration in the mixture from a titrimetric measurement of J₂ formed. Based on the assumption that ozone immediately and completely reacts with pulp at suitable low flow rates, the reaction time could be calculated from the ozone concentration and the flow rate of the ozone/O₂ mixture.

d) After completion of the reaction, the pulp was washed again with a sulfuric acid solution (pH 3) over approximately 20 minutes at a consistency of 0.5 to 3% (typically 1 to 1.5%), based on the oven-dried material. The slurry obtained thereby was filtrated over a Büchner funnel and then further dewatered in a centrifuge to a consistency of about 40%.

[0156] Then handsheets were produced from the ozonated and washed pulp in the manner described above.

[0157] The breaking length (dry), breaking length (wet), air permeability and tearing resistance (dry) of the handsheets were determined in the manner explained above.

[0158] Further, the brightness and kappa number of the ozone-treated pulp was measured in accordance with the section "test methods."

[0159] The results obtained are shown in the following Table 1.

Table 1

Beech Sulfite Pulp		
Properties	untreated	after O ₃ -treatment
Pulp (unbeaten)		
Brightness, % ISO	61,0	94,5
Kappa number	13,9	1,0
Handsheet		
Breaking length (dry), m	2700	2900
Breaking length (wet),m,(rel. %)	70 (2,7)	117 (4,0)
Air permeability, ml/min	2800	2800
Tearing resistance(dry),mN·m/m	300	400
O ₃ -treatment carried out at room temperature, pH 3, 1.0 % O ₃ .		

Example 2

[0160] Spruce sulfite pulp stemming from an acid sulfite pulping process and having a brightness (% ISO) of 67.1 and a kappa number of 18.1 was subjected to the same treatment steps (a) - (d) as in Example 1, before handsheets were produced therefrom in the manner described above.

[0161] The breaking length (dry), breaking length (wet), air permeability and tearing resistance (dry) of the handsheets were determined in the manner explained above.

[0162] Further, the brightness and kappa number of the ozone-treated pulp was measured in accordance with the section "test methods".

[0163] The results obtained are shown in the following Table 2.

EP 1 316 639 A1

Table 2

Spruce Sulfite Pulp (61A_00)		
Properties	untreated	after O ₃ -treatment
Pulp (unbeaten)		
Brightness, % ISO	67,1	92,1
Kappa number	18,1	1,0
Handsheet		
Breaking length (dry), m	3500	3200
Breaking length (wet),m, (rel. %)	89 (2,6)	224 (7,2)
Air permeability, ml/min	2200	2100
Tearing resistance(dry),mN·m/m	1300	1200
O ₃ -treatment carried out at room temperature, pH 3, 1.0 % O ₃ .		

Example 3

[0164] Spruce sulfite pulp stemming from an acid sulfite pulping process and having a brightness (% ISO) of 64.0 and a kappa number of 19.1 was subjected to the treatment steps a-d) as explained in Example 1.

e) The pulp obtained from the acid wash was disintegrated again under the same conditions given above under item (b).

f) The fluffed (disintegrated) pulp was finally subjected to a second ozonation step using the same condition as under (c) with the sole difference that the ozonation was stopped after an ozone consumption of 0.4 %, based on the weight of the oven-dried pulp sample (total consumption 1,4 % by weight).

g) After completion of the reaction, the pulp was washed again with a sulfuric acid solution (pH 3) as explained under item d) of Example 1, before handsheets were produced therefrom in the manner described above.

[0165] The breaking length (dry), breaking length (wet), air permeability and tearing resistance (dry) of the handsheets were determined in the manner explained above.

[0166] Further, the brightness and kappa number of the ozone-treated pulp was measured in accordance with the section "test methods".

[0167] The results obtained are shown in the following Table 3.

Table 3

Spruce Sulfite Pulp (02A_01)		
Properties	untreated	after O ₃ -treatment
Pulp (unbeaten)		
Beating degree, °SR	14	15
Brightness, % ISO	64,0	89,0
Kappa number	19,1	1,3
Fiber length 1.w., mm	2,61	2,54
Handsheet		
Breaking length (dry), m	4300	4200
Breaking length (wet),m, (rel. %)	98 (2,3)	314 (7,5)

Table 3 (continued)

Spruce Sulfite Pulp (02A_01)		
Properties	untreated	after O ₃ -treatment
Handsheet		
Air permeability, ml/min	1850	1650
Bursting strength, kPa	193	237
Tearing resistance(dry),mN·m/m	1400	1500
2-step O ₃ -treatment carried out at room temperatures, pH 3, 1,4 % O ₃ and intermediate acid washing.		

[0168] From the above Table 3, it is seen that a 2-step ozone treatment with an intermediate acid wash considerably improves the wet-strength properties of paper produced with the ozonated pulp.

Claims

1. Use of a treatment sequence comprising an ozonation of a fibrous cellulosic material under acidic conditions followed by an acidic wash of the ozonated material for enhancing the wet strength of said fibrous cellulosic material.
2. Use according to claim 1, wherein the ozone treatment is preceded by a further acidic wash.
3. Use according to claim 1, wherein the acidic wash is followed by a second ozonation step under acidic conditions.
4. Use according to claim 3, wherein the second ozonation is followed by a further acidic wash.
5. Use according to claim 3 or 4, wherein the first ozone treatment is preceded by a further acidic wash.
6. Use according to any of claims 1 to 5, wherein after the last ozonation step of the treatment sequence acidic conditions are maintained.
7. Use according to any of claims 1 to 5, wherein the treatment sequence comprises at no point in time an alkaline wash.
8. Use according to any of claims 1 to 7, wherein the entire treatment sequence is performed under acidic conditions.
9. Use according to any of claim 1 to 8, wherein the cellulosic material is selected from sulfite pulps, bisulfite pulps, Kraft pulps, cotton linters, or fibers from Esparto Grass, bagasse, hemp, flax and agricultural crops.
10. Use according to any of claims 1 to 9, wherein the initial kappa number of the cellulosic fibrous material to be treated is less than 50.
11. Use according to claim 10, wherein the initial kappa number is more than 13.
12. Use according to any of claims 1 to 11, wherein the final kappa number of the ozone-treated cellulosic material is less than 15, in particular less than 10.
13. Use according to any of claims 1 to 12, wherein the ozone treatment(s) lead(s) to a Kappa reduction of at least 10, in particular at least 15.
14. Use according to any of claims 1 to 13, wherein ozone is used as the only oxidant in the treatment of a cellulosic material (pulp) obtained by a pulping process.
15. Use according to any of claims 1 to 14, wherein prior to the ozone treatment no bleaching or other oxidizing step is employed.
16. Use according to any of claims 1 to 15, wherein the initial pH of the ozone treatment(s) is 5 or lower.

EP 1 316 639 A1

17. Use according to any of claims 1 to 16, wherein an anorganic acid, carboxylic acid having 1 to 4 carbon atoms or dicarboxylic acid having 2 to 4 carbon atoms is used for acidifying.

18. Use according to claim 17, wherein the anorganic acid is sulfuric acid.

19. Use according to any one of claims 1 to 18, wherein the consistency of the cellulosic fibrous material to be ozonated is at least 30% (per weight).

20. Use according to any one of claims 1 to 19, wherein the ozone is wetted before contact with the cellulosic fibrous material.

21. Use according to any of claims 1 to 20, wherein the cellulosic fibrous material is fluffed immediately before subjecting to the ozone treatment(s).

22. Process for the treatment of a fibrous cellulosic material comprising the steps of ozonating a fibrous cellulosic material under acidic conditions followed by an acidic wash of the ozonated material.

23. Process according to claim 22, wherein the process conditions are as laid down in any of claims 2 to 22.

24. Fibrous cellulosic material obtainable by a process comprising ozonation of the fibrous cellulosic material under acidic conditions followed by washing the material under acidic conditions.

25. Fibrous cellulosic material according to claim 24, wherein the ozone treatment is preceded by a further wash under acidic conditions.

26. Fibrous cellulosic material according to claim 24, wherein the process is performed as laid down in any of claims 3 to 22.

27. Cellulosic material according to any of claims 24 to 26, containing no effective amount of wet strength-enhancing additives.

28. Fibrous cellulosic material according to any of claims 24 to 27 having a wet breaking length of at least 100m.

29. Paper or nonwoven comprising the fibrous cellulosic material of any of claims 24 to 28.

30. Paper according to claim 29 being a tissue paper.



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Application Number
EP 02 02 6454

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