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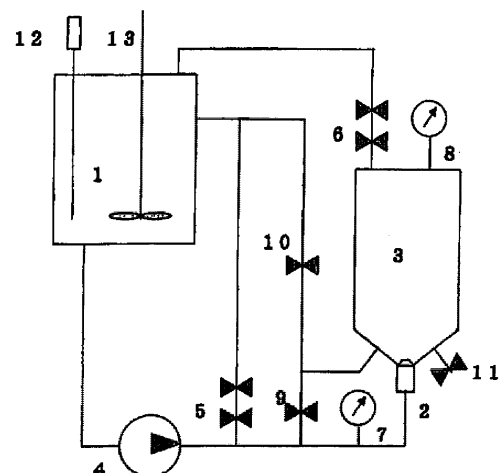
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(57) The present invention aims to provide soft and pleasant-to-touch tissue papers for household use with high strength.

Provided are a tissue paper for household use **characterized in that** it contains a pulp obtained by applying an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers and a tissue paper for household use consisting of two or more paper layers **characterized in that** at least one paper layer contains a pulp obtained by applying an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers.

*Figure 1*

**Description**

## TECHNICAL FIELD

**[0001]** The present invention relates to tissue papers for household use such as tissue papers including toilet tissue papers, facial tissues, etc., and paper towels and more specifically it relates to soft and pleasant-to-touch tissue papers for household use with high strength.

## BACKGROUND ART

**[0002]** Slushed pulp in a slurry state as prepared from chemical pulp obtained by cooking hardwood or softwood chips, dry pulp obtained by dewatering and drying this slushed pulp, or deinked recycled pulp obtained by deinking waste paper has been conventionally used for so-called tissue papers for household use such as toilet tissue papers, tissue papers including facial tissues, paper towels, etc., and these pulps are used as unbleached or bleached pulps or unbeaten or beaten pulps alone or in combination depending on the quality design.

**[0003]** Techniques for improving softness or hand feeling as an important quality of tissue papers have been previously studied, and various proposals have been made, including e.g., layered tissue papers in which the types or the proportions of the pulps layered and converted into paper are controlled and processes for preparing them (patent document 1, patent document 2); methods for improving hand feeling and softness by appropriately selecting paper machines such as Fourdrinier machines, paper machines having a short forming section, twin-wire machines, cylinder machines with a Yankee dryer, etc., or by adding auxiliary chemicals to slushed pulp to improve the lubricity of the slushed pulp per se, such as paper softeners, e.g., fatty acid ester-based softeners (patent document 3), quaternary ammonium salt-based cationic surfactants (patent document 4), urethane alcohols or salts or cationized products thereof (patent document 5), non-cationic surfactants (patent document 6, patent document 7), polyphosphates (patent document 8), polysiloxanes (patent document 9, patent document 10), etc., or by once concentrating and then mechanically kneading pulp to bend fibers (patent document 11, patent document 12).

**[0004]** The use of the auxiliary chemicals sometimes produced good softening effects, but had the disadvantage that their high foamability might disturb the paper-making operation per se and in some cases invite a decrease in paper strength and water absorbency. The mechanical processes for bending fibers were disadvantageous in energy consumption because of additional steps of concentrating raw materials.

**[0005]** In order to improve the wet strength of tissue papers, wet paper strength agents such as polyamides, polyamines and epoxy resins are mainly used, but they had negative effects on softness and hand feeling because they rigidify the tissue papers per se.

**[0006]** In order to improve surface smoothness, one or two calender sets consisting of a pair of an upper and a lower sufficiently polished chilled rolls and metal rolls have been conventionally used downstream of tissue paper making machines. However, this calender caused problems such as decreased thickness, increased rigidity and hard texture when the nip pressure was increased to improve smoothness.

References:**[0007]**

- Patent document 1: JPA No. Sho 54-46914.
- Patent document 2: JUA No. Hei 4-66992.
- Patent document 3: US Patent No. 3,296,065.
- Patent document 4: JPA No. Sho 48-22701.
- Patent document 5: JPA No. Sho 60-139897.
- Patent document 6: JPA No. Hei 2-99690.
- Patent document 7: JPA No. Hei 2-99691.
- Patent document 8: JPA No. Hei 2-36288.
- Patent document 9: JPA No. Hei 2-224626.
- Patent document 10: JPA No. Hei 3-900.
- Patent document 11: JPA No. Hei 5-23262.
- Patent document 12: JPA No. Hei 6-14848.

## DISCLOSURE OF THE INVENTION

### PROBLEMS TO BE SOLVED BY THE INVENTION

5 **[0008]** The present invention aims to provide soft and pleasant-to-touch tissue papers for household use with high strength.

### MEANS FOR SOLVING THE PROBLEMS

10 **[0009]** As a result of careful studies, we achieved the present invention on the basis of the finding that soft and pleasant-to-touch tissue papers for household use with high strength can be attained by including a pulp obtained by applying an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers.

### ADVANTAGES OF THE INVENTION

15 **[0010]** The present invention makes it possible to attain soft and pleasant-to-touch tissue papers for household use with high strength.

### BRIEF DESCRIPTION OF THE DRAWING

20 **[0011]** Figure 1 is a schematic diagram showing the cavitation jet treatment system used in the examples.

### EXPLANATION OF THE REFERENCE NUMERALS

25 **[0012]**

- 1: sample tank
- 2: nozzle
- 3: cavitation jet cell
- 30 4: plunger pump
- 5: upstream pressure regulating valve
- 6: downstream pressure regulating valve
- 7: upstream pressure meter
- 8: downstream pressure meter
- 35 9: water feed valve
- 10: circulating valve
- 11: drain valve
- 12: temperature sensor
- 13: mixer.

### THE MOST PREFERRED EMBODIMENTS OF THE INVENTION

**[0013]** The tissue papers for household use of the present invention are characterized in that they contain a pulp obtained by applying an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers. The application of an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers will be hereinafter referred to as cavitation treatment.

**[0014]** Pulps that can be used as targets for the cavitation treatment of the present invention are not specifically limited, but include chemical pulps obtained by cooking a lignocelluloses material with an alkaline cooking liquor (such as bleached kraft pulp (NBKP) or unbleached kraft pulp (NUKP) of softwoods, bleached kraft pulp of hardwoods (LBKP)), mechanical pulps (such as groundwood pulp (GP), refiner groundwood pulp (RGP), thermomechanical pulp (TMP), chemithermomechanical pulp (CTMP), etc.), deinked pulp (DIP), etc. Chemical pulps that can be used include kraft pulp, polysulfide pulp, soda pulp, alkaline sulfite pulp, sodium carbonate pulp, and oxygen-soda pulp, etc.

**[0015]** The chemical pulps may also include those obtained by adding a cyclic keto compound (e.g., anthraquinone, 1,4-dihydro-9,10-diketooanthracene, etc.) to the cooking liquor. Among the chemical pulps, kraft pulp is preferred for the present invention, which may be obtained by the so-called modified alkaline cooking process comprising adding the cooking liquor in portions and concurrent cooking and countercurrent cooking within a digester. These chemical pulps can be used as unbleached or bleached pulps or unbeaten or beaten pulps alone or in combination, as appropriate.

**[0016]** The cavitation treatment is more specifically defined as a process for promoting external fibrillation of pulp by

applying an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers while suppressing internal fibrillation to adjust freeness. The cavitation treatment is preferably a cavitation jet treatment as described in WO2005/012632.

**[0017]** It should be noted that pulp fibers can also be externally fibrillated by combining the cavitation treatment with mechanical beating. The pulp suspension may contain inorganic fine particles from fillers or pigments contained in waste paper or broke in addition to pulp fibers. The cavitation treatment affords a bulkier and stronger pulp as compared with those conventionally obtained by beating with a mechanical force using a refiner or the like at the same freeness because external fibrillation of pulp fibers is promoted while internal fibrillation is suppressed. Tissue papers for household use containing a pulp having external fibrils obtained by this cavitation treatment are softer and stronger.

**[0018]** The Canadian Standard Freeness of the pulp prepared by the cavitation treatment is preferably 50-650 ml in the case of chemical pulps and 50-400 ml in the case of mechanical pulps or recycled (deinked) pulp. In the case of mixtures of these pulps, the total Canadian Standard Freeness is preferably 100-550 ml.

**[0019]** Next, the cavitation treatment is explained in detail. When cavitation bubbles collapse, a high impact force reaching several Giga Pascal is produced in a local region on the order of several micrometers and the temperature microscopically rises to several thousand degrees Celsius due to adiabatic compression during the collapse of bubbles, as described in a book of Katoh (New Edition Cavitation: Basics and Recent Advance, Written and Edited by Yoji Katoh, Published by Makishoten, 1999). As a result, the temperature rises when cavitation occurs. For these reasons, cavitation has harmful influences on fluid machinery such as damage, oscillation and performance loss and it has been a technical challenge to control cavitation. Recently, rapid advances in studies on cavitation made it possible to precisely control the region in which cavitation occurs and even the impact force by using hydrodynamic parameters of cavitation jet as operation factors. This led to expectations that the strong energy of bubbles could be effectively utilized by controlling the impact force induced by collapse of bubbles. Thus, it became possible to precisely control cavitation by operation/adjustment based on hydrodynamic parameters. This shows that the stability of technical effects can be maintained, and the present invention is characterized in that bubbles generated by controlled cavitation are actively introduced into a pulp suspension to effectively utilize their energy rather than the conventional uncontrollably harmful cavitation spontaneously occurring in fluid machinery.

**[0020]** Means for generating cavitation in the present invention include, but not limited to, a liquid jet, an ultrasonic transducer, a combination of an ultrasonic transducer and a horn amplifier, and laser irradiation. It is preferable to use a liquid jet, which is more effective for pulp fibers because it efficiently generates cavitation bubbles and forms cavitation bubble clouds having a stronger impact force of collapse. The cavitation generated by the means described above is clearly different from the conventional uncontrollably harmful cavitation spontaneously occurring in fluid machinery.

**[0021]** As noted above, the cavitation treatment is preferably a cavitation jet treatment using a liquid jet as described in WO2005/012632 and as will be explained in detail below.

**[0022]** The liquid jet refers to a jet of a liquid or a fluid containing solid particles or a gas dispersed or mixed in a liquid, including a liquid jet containing a slurry of pulp or inorganic particles and bubbles. The gas here may include bubbles generated by cavitation.

**[0023]** Flow rates and pressures are especially important for cavitation because it occurs when a liquid is accelerated and a local pressure decreases below the vapor pressure of the liquid. Therefore, the cavitation number  $\sigma$ , which is a basic dimensionless number expressing a cavitation state, is defined as follows (New Edition Cavitation: Basics and Recent Advance, Written and Edited by Yoji Katoh, Published by Makishoten, 1999).

$$\sigma = \frac{P_{\infty} - P_v}{\frac{1}{2} \rho U_{\infty}^2}$$

where  $P_{\infty}$ : local pressure (absolute pressure),  $U_{\infty}$ : characteristic flow velocity,  $P_v$ : vapor pressure of fluid (absolute pressure),  $\rho$ : density.

**[0024]** If the cavitation number here is high, it means that the flow site is in a state where cavitation occurs hard. Especially when cavitation is generated through a nozzle or an orifice tube as in the case of a cavitation jet, the cavitation number  $\sigma$  can be rewritten by equation (2) below where  $p_1$ : nozzle upstream pressure (absolute pressure),  $p_2$ : nozzle downstream pressure (absolute pressure),  $P_v$ : vapor pressure of fluid (absolute pressure), and the cavitation number  $\sigma$  can be approximated as follows in the case of a cavitation jet because the pressure difference between  $p_1$ ,  $p_2$  and  $P_v$  is significant so that  $p_1 \gg p_2 \gg P_v$  (H. Soyama, J. Soc. Mat. Sci. Japan, 47 (4), 381 1998).

$$\sigma = \frac{p_2 - p_v}{p_1 - p_2} \approx \frac{p_2}{p_1}$$

**[0025]** In this manner, the cavitation number  $\sigma$  is expressed by two values, i.e., the pressures upstream and downstream of the nozzle. It should be noted that all of the pressures measured in the examples herein are gauge pressures, and the cavitation number  $\sigma$  in the present invention is expressed by equation (3) below:

$$\sigma = p_4/p_3$$

where  $p_3$ : nozzle upstream pressure (gauge pressure),  $p_4$ : nozzle downstream pressure (gauge pressure).

**[0026]** Cavitation conditions in the present invention are as follow: the cavitation number  $\sigma$  defined above is desirably 0.001 or more and 0.5 or less, preferably 0.003 or more and 0.2 or less, especially 0.01 or more and 0.1 or less. If the cavitation number  $\sigma$  is less than 0.001, little benefit is attained because the pressure difference against the surroundings is small when cavitation bubbles collapse, but if it is greater than 0.5, the pressure difference in the flow is too small to generate cavitation.

**[0027]** When a jetting liquid is emitted through a nozzle or an orifice tube to generate cavitation, the pressure of the jetting liquid (nozzle upstream pressure) is desirably 0.01 MPa (gauge pressure) or more and 60 MPa (gauge pressure) or less, preferably 0.7 MPa (gauge pressure) or more and 30 MPa (gauge pressure) or less, especially 2 MPa (gauge pressure) or more and 15 MPa (gauge pressure) or less. If the nozzle upstream pressure is less than 0.01 MPa (gauge pressure), little benefit is attained because a pressure difference is less likely occur against the nozzle downstream pressure. If the nozzle upstream pressure is greater than 60 MPa (gauge pressure), special pumps and pressure vessels are required and energy consumption increases, leading to cost disadvantages, but also pulp fibers are excessively damaged so that they become unsuitable for use as raw materials for papermaking. On the other hand, the pressure in the vessel (nozzle downstream pressure) is preferably 0.05 MPa (gauge pressure) or more and 2.6 MPa (gauge pressure) or less expressed in static pressure. A pressure is also applied on the downstream side to increase the pressure in the region where cavitation bubbles collapse by pressurizing the vessel containing a target liquid (pulp suspension), resulting in an increase in the pressure difference between bubbles and the surroundings, whereby bubbles more vigorously collapse to produce a stronger impact force. However, cavitation per se hardly occurs if the pressure in the vessel excessively increases. The ratio between the pressure in the vessel and the pressure of the jetting liquid ((gauge pressure)/(gauge pressure)) is preferably in the range of 0.001-0.5.

**[0028]** The jet flow rate of the jetting liquid is desirably in the range of 1 m/sec or more and 200 m/sec or less, preferably in the range of 20 m/sec or more and 100 m/sec or less. If the jet flow rate is less than 1 m/sec, little benefit is attained because the pressure drop is too small to generate cavitation. If it is greater than 200 m/sec, however, cost disadvantages occur because high pressure is required and therefore, a special equipment is required.

**[0029]** The cavitation treatment in the present invention takes place at a site that can be selected from, but not limited to, the inside of any vessel such as a tank or the inside of a pipe. The treatment can be performed in one pass, but a greater effect can be obtained by repeating a necessary number of cycles. The treatment can be performed in parallel or in series using multiple generating means.

**[0030]** A jet for generating cavitation may be injected into a vessel open to the atmosphere such as a pulper, but preferably within a pressure vessel to control cavitation.

**[0031]** In the method for generating cavitation by a liquid jet in the present invention, liquids that can be jetted to a pulp suspension include, but not limited to, e.g., distilled water, tap water, industrial water, recycled water recovered from papermaking processes, pulp drain water, white water, pulp suspensions, alcohols, etc. Preferably, a pulp suspension per se is jetted to provide a greater benefit because not only cavitation is generated around the jet but also a hydrodynamic shear force is obtained when the jet is emitted from an orifice at a high pressure. When a pulp suspension is used as a jet liquid, the total amount to be treated can be circulated.

**[0032]** When a pulp suspension is treated by cavitation generated by a liquid jet, the solids content of the suspension is preferably 5 % by weight or less, more preferably 3 % by weight or less, still more preferably 0.1-1.5 % by weight in terms of the bubble generating efficiency..

**[0033]** The pH of the pulp suspension is preferably pH 1-13, more preferably pH 3-12, still more preferably pH 4-11. If the pH is less than 1, problems such as corrosion of equipments occur, which are disadvantageous in terms of materials and maintenance or the like. If the pH exceeds 13, however, alkaline discoloration of pulp fibers occurs to unfavorably lower brightness. Alkaline conditions are more desirable because pulp fibers are highly swollen and more OH active

radicals are produced.

**[0034]** According to the present invention, the flow rate of the jetting liquid increases by increasing the jetting pressure of the liquid to generate stronger cavitation. Moreover, the vessel containing a target liquid is pressurized to increase the pressure in the region where cavitation bubbles collapse, resulting in an increase in the pressure difference between bubbles and the surroundings, whereby bubbles vigorously collapse to produce a stronger impact force. Here, the jetting liquid refers to a liquid emitted from an orifice at a high pressure, and the target liquid refers to a liquid exposed to a jet within a vessel or a pipe. Cavitation is influenced by the amount of gas in the liquid, and if the gas is excessive, bubbles collide with each other and join together to create a cushioning effect so that the impact force of collapse is absorbed by other bubbles and the impact force decreases. Thus, the process temperature must be the melting point or more and the boiling point or less in view of the influence of dissolved gas and vapor pressure. When the liquid medium is water, significant effects can be obtained at a temperature of preferably 0-80°C, more preferably 10°C - 60°C. Considering that the impact force is normally maximal at the midpoint between the melting point and the boiling point, temperatures around 50°C are most preferred in the case of aqueous solutions, though significant effects can be obtained even at lower temperatures within the range defined above because there is no influence of vapor pressure. Temperatures exceeding 80°C are unsuitable because the pressure resistance of the pressure vessel for generating cavitation considerably decreases so that the vessel may be liable to damages.

**[0035]** According to the present invention, the energy required for generating cavitation can be reduced by adding a material that lowers the surface tension of a liquid, such as a surfactant. Materials that are added include, but not limited to, known or novel surfactants, e.g., nonionic surfactants, anionic surfactants, cationic surfactants and ampholytic surfactants such as fatty acid salts, higher alkyl sulfates, alkyl benzene sulfonates, higher alcohols, alkyl phenols, alkylene oxide adducts of fatty acids or the like, or organic solvents, etc. These may be added as single components or mixtures of two or more components. They may be added in any amount necessary for lowering the surface tension of the jetting liquid and/or target liquid. They may be added at any site in a process preceding the site where cavitation is generated, and when the liquid is circulated, they may be added even after the site where cavitation is generated.

**[0036]** According to the present invention, the proportion of the cavitation-treated pulp to the total amount of pulp is not specifically limited, but stronger and softer tissue papers for household use can be obtained as the proportion increases. From this point of view, the proportion is preferably 5 % by weight or more, more preferably 30 to 100 % by weight, still more preferably 60 to 100 % by weight based on the bone dry weight of the total pulp. If the proportion is less than 5 % by weight, the softness and hand feeling remain unchanged and the strength cannot be improved.

**[0037]** The tissue papers for household use consist of a single layer or multiple layers, and the single layer or multiple layers may be prepared from a single cavitation-treated pulp or a mixture of two or more cavitation-treated pulps or a mixture of a cavitation-treated pulp and a conventional slushed pulp, dry pulp or deinked pulp (DIP).

**[0038]** When two plies of a tissue paper for household use consisting of multiple layers are layered, hand feeling is further improved if a layer containing a cavitation-treated pulp faces outward so that the layer containing a cavitation-treated pulp contacts hands. Hand feeling is further improved by drying the layer containing a cavitation-treated pulp against a Yankee dryer and placing this face on the outside of two plies of a tissue paper for household use.

**[0039]** In addition to the cavitation-treated pulp, chemical pulps (bleached kraft pulp (NBKP) or unbleached kraft pulp (NUKP) of softwoods, bleached kraft pulp (LBKP) or unbleached kraft pulp (LUKP) of hardwoods, etc.), mechanical pulps (groundwood pulp (GP), refiner groundwood pulp (RGP), thermomechanical pulp (TMP), chemithermomechanical pulp (CTMP), etc.), and deinked pulp (DIP) may be used as a mixture at any ratio.

**[0040]** The cavitation-treated pulp shows improved external fibrillation, and sometimes has scale-like external fibrils, as explained below.

**[0041]** According to a book of Isogai et al. (Akira Isogai: "Materials Chemistry of Cellulose", The University of Tokyo Press, p. 68, 2001), beating of pulp refers to a process in which a mechanical shear stress is applied to hydrated pulp fibers to form gaps between microfibrils within the pulp fibers (internal fibrillation) and to raise fibrils on the outer sides of the pulp fibers (external fibrillation), thereby increasing the specific surface area to improve swelling of the pulp fibers with water, and at the same time, partially cutting the fibers and generating fine fibers flaked off the outer peripheral faces of the fibers.

**[0042]** The beating process of pulp increases the bonding area between fibers formed during papermaking, thereby causing changes in various mechanical properties, optical properties and liquid absorption. However, when pulp fibers are observed at the molecular level, the molecular weight of cellulose decreases only slightly and the crystallinity is almost unchanged during the beating process. This is attributed to the fact that amorphous and hydrophilic hemicellulose moieties serve as a cushion to absorb mechanical energy.

**[0043]** According to a book of Shimaji et al. (Ken Shimaji et al.: "Wood Tissue", Morikita Publishing, p. 55, 1976), external fibrils seen in wood pulp beaten by conventional methods refer to filamentous structures having a width of about 0.4 - 1  $\mu\text{m}$  observable by light microscopy, while microfibrils are elemental structural units present in cell walls as an assembly of cellulose molecules having a width of about 9 - 37 nm. In the pulps having scale-like external fibrils used in the present invention, the characteristic scale-like external fibrils refer to flakes or hairs on the surface of a fiber having

a width of 3  $\mu\text{m}$  or more, preferably similar to the width of the pulp fiber and consisting of a wide layer formed of an assembly of the microfibrils aligned side by side, i.e., the microfibrils on the surface of the fiber wall are flaked while retaining a layer structure. They are also characterized by a thickness ranging from 90 nm to 2  $\mu\text{m}$ . When a fiber is observed by electron microscopy, it is desirably observed in the dry state eliminating hydrogen bonding, but it is difficult to observe external fibrils with high precision because such fibrils would be attracted to the surface of the fiber by capillarity so that they would be difficult to discern if the fiber was simply dried.

**[0044]** The scale-like external fibrils in the present invention are characterized in that they are stained by a high molecular dye having a molecular weight of 10,000 or more. Thus, the external fibrils refer to an assembly of microfibrils to which a high molecular dye having a molecular weight of 10,000 or more can be adsorbed. Dyes having a molecular weight of 10,000 or more include orange dyes such as CI Constitution nos. 40000 to 40006 including Direct Orange 15 (old Color Index (CI) no. 621, or CI Constitution no. 40002/3) as described in a literature of Simon et al. (F.L. Simons, Tappi Journal, 33 (7), 312 (1950)) and a literature of Xiaochun et al. (Y. Xiaochun et al., Tappi Journal, 78 (6), 175 (1995)), but they are not specifically limited so far as they can stain cellulose-based fibers.

**[0045]** According to the literature of Xiaochun et al., the dyes having a molecular weight of 10,000 or more described above are molecules having a hydrodynamic size of 5 nm or more as measured by light scattering and cannot permeate into pores of less than 5 nm present on the surfaces of pulp fibers. However, the dyes having a molecular weight of 10,000 or more described above can readily access and selectively stain fibrillated regions by adsorbing to them because fibrils consisting of an assembly of microfibrils on the surfaces of pulp fibers are exposed outside the pulp fibers.

**[0046]** In order to optically highlight fibrillated regions, they can be observed with enhanced contrast by staining the entire fiber using a low molecular dye such as Direct Blue 1 (old Color Index (CI) no. 518, or CI Constitution no. 24410) or Direct Blue 4, Direct Blue 15, Direct Blue 22, Direct Blue 151 or the like as described in the literatures above. The low molecular dye is adsorbed to the entire fiber, but displaced by a high molecular dye having a higher bonding force. As a result, the fibrillated regions to which the high molecular dye (orange dye) can be adsorbed can be stained in orange while fiber pore regions to which the high molecular dye cannot be adsorbed can be stained with the low molecular dye (blue dye), whereby the fibrillated regions can be highlighted. Suitable low-molecular dyes contain 51 % or more of molecules having a molecular weight of less than 10,000, preferably less than 2000, more preferably 300-1500.

**[0047]** In a single unit of the pulps having scale-like external fibrils of the present invention, the area ratio of the externally fibrillated part expressed by equation 4 below is preferably 20 % or more and the peripheral length index of the externally fibrillated part expressed by equation 5 below is 1.5 or more. In the pulps of the present invention, these values increase because the scale-like external fibrils have a greater surface area as compared with conventional fibrils.

**[0048]** Area ratio of externally fibrillated part (%) =  $\frac{\text{area of externally fibrillated part}}{\text{area of externally fibrillated part} + \text{total surface area of pulp fiber}} \times 100$  (equation 4).

**[0049]** Peripheral length index of externally fibrillated part =  $\frac{\text{peripheral length of externally fibrillated part} + \text{entire peripheral length of fiber}}{\text{entire peripheral length of pulp fiber}}$  (equation 5)

## MECHANISM

**[0050]** The reason why tissue papers containing cavitation-treated pulp show good hand feeling and strength is assumed as follows.

**[0051]** Generally, tissue papers having a high bulk (low density) and a smooth surface show improved hand feeling. As noted above, cavitation-treated pulp has been specifically promoted in external fibrillation. Thus, external fibrillation has been promoted while retaining fiber rigidity as described in WO2006/085598, so that the strength increases at a similar bulk or the bulk increases when the pulp is prepared at a similar strength as compared with conventional mechanical treatments such as double disc refiners.

**[0052]** Moreover, papers prepared from cavitation-treated pulp tend to be smoother because smooth surfaces such as metal rolls are readily transferred.

**[0053]** For these reasons, tissue papers containing cavitation-treated pulp are assumed to tend to show good hand feeling and strength at the same time.

## EXAMPLES

**[0054]** The following examples and comparative examples further illustrate the present invention without, however, limiting the invention thereto. Unless otherwise specified, % in the examples and comparative examples refers to % by weight. The pulps prepared in the following examples and comparative examples were converted into papers in a twin-wire triple layer paper machine with a Yankee dryer. The web was dry-creped by driving the dryer and the winder reel at different speeds. Unless otherwise specified, two plies of this raw tissue paper were layered in such a manner that the face having contacted the Yankee dryer (YD face) might form the outside (i.e., the side contacting users' hands) and the face dried against the Yankee dryer was soft-calendered. The pulps used in all of the examples and comparative

examples were bleached hardwood pulps prepared by the kraft process from hardwood chips produced in Japan and bleached to a Hunter brightness of 84 %.

**[0055]** The evaluation methods used in the examples and comparative examples are as follows.

<Hand feeling>

**[0056]** Feel against hands and skin was evaluated by ten panelists. The results were expressed as follows. ◎: very good, ○: good, △: fair, X: poor.

<Determination method of (longitudinal) tensile strength>

**[0057]** Tensile strength: Samples of 15 mm in MD and CD directions were cut and the tensile strength of a single ply in each direction was measured to calculate the total tensile strength by the equation below.

**[0058]** Tensile strength (g) = (tensile strength in MD x tensile strength in CD)<sup>1/2</sup>.

<Determination method of bulk>

**[0059]** Bulk was expressed as the thickness (mm) of 10 plies of each sample.

<Determination of basis weight>

**[0060]** Basis weight was determined according to JIS P 8124: 1998 (ISO 536: 1995).

<Preparation of cavitation-treated pulp>

**[0061]** Cavitation treatment was performed in the cavitation jet treatment system shown in Figure 1. In Figure 1, a pulp suspension (consistency 1.1 %) not shown is contained in a sample tank 1, and a temperature sensor 12 and a mixer 13 are inserted into the sample tank 1. The pulp suspension in the sample tank 1 is introduced as a jetting liquid into a cavitation jet cell 3 via a given line provided with a plunger pump 4. A nozzle 2 is provided at the bottom of the cavitation jet cell 3, and more specifically, the pulp suspension in the sample tank 1 is injected from the nozzle 2 into the jet cell 3. On a line extending from the periphery of the sample tank 1 to the jet cell 3 are provided a water feed valve 9 and a circulating valve 10, through which the pulp suspension in the sample tank 1 is supplied as a target liquid into the jet cell 3. On another line extending from the periphery of the sample tank 1 to the nozzle 2 is provided an upstream pressure regulating valve 5. On another line extending from the top of the jet cell 3 to the sample tank 1 is provided a downstream pressure regulating valve 6 so that the jetting pressure of the pulp suspension into the nozzle 2 can be controlled by adjusting each valve 5, 6. An upstream pressure meter 7 is provided at the inlet of the nozzle 2, and a downstream pressure meter 8 is provided at the top of the jet cell 3. A drain valve 11 is provided at the bottom of the jet cell 3.

#### EXAMPLE 1

**[0062]** The raw material for the top and bottom layers of triple layers was prepared as follows. A pulp sheet of a bleached hardwood kraft pulp was disintegrated in a low-consistency pulper and adjusted to a desired consistency, and then treated in one pass by using the cavitation jet treatment system (nozzle diameter 1.5 mm) shown in Figure 1 at a jetting liquid pressure (nozzle upstream pressure) of 8 MPa (gauge pressure, jet flow rate 80 m/sec.) and a pressure in the target vessel (nozzle downstream pressure) of 0.4 MPa (gauge pressure). A pulp suspension having a consistency of 3 % by weight was used as a jetting liquid to treat the pulp suspension (consistency 3 % by weight) in the vessel by cavitation, thus giving raw material A having a Canadian Standard Freeness of 435 mL. A facial tissue was prepared from raw material A and raw material B for the middle layer (prepared by disintegrating a pulp sheet of a bleached hardwood kraft pulp in a low-consistency pulper and having a Canadian Standard Freeness of 500 mL). The basis weight of the resulting facial tissue was adjusted to 16.6 g/m<sup>2</sup>.

#### COMPARATIVE EXAMPLE 1

**[0063]** The raw material for the top and bottom layers was prepared by beating in a double disc refiner instead of the cavitation treatment to give raw material C having a Canadian Standard Freeness of 470 mL. A facial tissue was prepared from raw material C and raw material B for the middle layer. The basis weight of the resulting facial tissue was adjusted to 16.6 g/m<sup>2</sup>.



Table 1

	Example 1	Comparative example 1
Hand feeling	Δ	Δ
Bulk (mm/10 plies)	0.88	0.91
Tensile strength (g)	263	214

**[0064]** As shown in Table 1, Example 1 and Comparative example 1 were comparable in hand feeling, but the tensile strength of Example 1 was higher by about 20 % than that of Comparative example 1. Example 1 remarkably increased in strength over Comparative example 1 despite of a slight decrease in bulk.

#### EXAMPLE 2

**[0065]** The raw material for the top and bottom layers was prepared by the same treatment as in Example 1 to give raw material D having a Canadian Standard Freeness of 420 mL. A facial tissue was prepared from raw material D and raw material B for the middle layer by adding 0.1 % (based on the bone dry weight of the pulp) of a wet paper strength agent. The basis weight of the resulting facial tissue was adjusted to 13.0 g/m<sup>2</sup>.

#### COMPARATIVE EXAMPLE 2

**[0066]** The raw material for the top and bottom layers was prepared by the same treatment as in Comparative Example 1 to give raw material E having a Canadian Standard Freeness of 410 mL. A facial tissue was prepared from raw material D and raw material B for the middle layer by adding 0.1 % (based on the bone dry weight of the pulp) of a wet paper strength agent. The basis weight of the resulting facial tissue was adjusted to 13.0 g/m<sup>2</sup>.

Table 2

	Example 2	Comparative example 2
Hand feeling	⊙	○
Bulk (mm/10 plies)	0.78	0.73
Tensile strength (g)	155	160

**[0067]** As shown in Table 2, Example 2 showed better hand feeling than that of Comparative example 2 and a nearly comparable tensile strength. Moreover, Example 2 improved in bulk by about 7 % over Comparative example 2.

#### EXAMPLE 3

**[0068]** The raw material for the top and bottom layers was prepared by the same treatment as in Example 1 except that 2 pass treatment was performed by using the cavitation jet treatment system (nozzle diameter 1.5 mm) at a jetting liquid pressure (nozzle upstream pressure) of 8 MPa (gauge pressure, jet flow rate 80 m/sec.) and a pressure in the target vessel (nozzle downstream pressure) of 0.4 MPa (gauge pressure) to give raw material F having a Canadian Standard Freeness of 390 mL. A facial tissue was prepared from raw material F and raw material B for the middle layer by adding 0.1 % (based on the bone dry weight of the pulp) of a wet paper strength agent. The basis weight of the resulting facial tissue was adjusted to 15.1 g/m<sup>2</sup>.

#### COMPARATIVE EXAMPLE 3

**[0069]** The raw material for the top and bottom layers was prepared by the same treatment as in Comparative Example 1 to give raw material G having a Canadian Standard Freeness of 470 mL. A facial tissue was prepared from raw material G and raw material B for the middle layer by adding 0.1 % (based on the bone dry weight of the pulp) of a wet paper strength agent. The basis weight of the resulting facial tissue was adjusted to 15.1 g/m<sup>2</sup>.

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Table 3

	Example 3	Comparative example 3
Hand feeling	⊙	○
Bulk (mm/10 plies)	0.85	0.87
Tensile strength (g)	205	174

**[0070]** As shown in Table 3, Example 3 showed better hand feeling and a tensile strength higher by about 20 % as compared with Comparative example 3. Example 3 remarkably increased in strength over Comparative example 3 despite of a slight decrease in bulk.

### EXAMPLE 4

**[0071]** The raw material for the top and bottom layers was prepared by the same treatment as in Example 1 except that a bleached hardwood kraft pulp sheet tending to favor strength but compromise hand feeling (a pulp sheet having a moisture content of about 50 % by weight (based on the bone dry weight of the pulp)) was used to give raw material H having a Canadian Standard Freeness of 440 mL. A facial tissue was prepared from raw material H and raw material B for the middle layer by adding 0.1 % (based on the bone dry weight of the pulp) of a wet paper strength agent. The basis weight of the resulting facial tissue was adjusted to 15.1 g/m<sup>2</sup>.

### COMPARATIVE EXAMPLE 4

**[0072]** The raw material for the top and bottom layers was prepared by the same treatment as in Comparative Example 1 except that a bleached hardwood kraft pulp sheet tending to favor hand feeling (a pulp sheet having a moisture content of about 10 % by weight (based on the bone dry weight of the pulp)) was used to give raw material I having a Canadian Standard Freeness of 480 mL. A facial tissue was prepared from raw material I and raw material B for the middle layer by adding 0.1 % (based on the bone dry weight of the pulp) of a wet paper strength agent. The basis weight of the resulting facial tissue was adjusted to 15.1 g/m<sup>2</sup>.

Table 4

	Example 4	Comparative example 4
Hand feeling	○	○
Bulk (mm/10 plies)	0.79	0.84
Tensile strength (g)	247	177

**[0073]** As shown in Table 4, Example 4 using a bleached hardwood kraft pulp tending to compromise hand feeling was comparable in hand feeling as compared with even Comparative example 4 using a bleached hardwood kraft pulp sheet tending to favor hand feeling. Moreover, Example 4 improved in tensile strength by about 40 % over Comparative example 4.

### Claims

1. A tissue paper for household use, containing a pulp obtained by applying an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers.
2. A tissue paper for household use, consisting of two or more paper layers, at least one paper layer of which contains a pulp obtained by applying an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers.
3. The tissue paper for household use of claim 1 or 2, wherein the pulp obtained by applying an impact force produced during the collapse of bubbles generated by cavitation to pulp fibers has scale-like external fibrils.
4. The tissue paper for household use of any one of claims 1 to 3, wherein the pulp obtained by applying an impact

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force produced during the collapse of bubbles generated by cavitation to pulp fibers is contained at 30 to 100 % by weight based on the bone dry weight of the total pulp.

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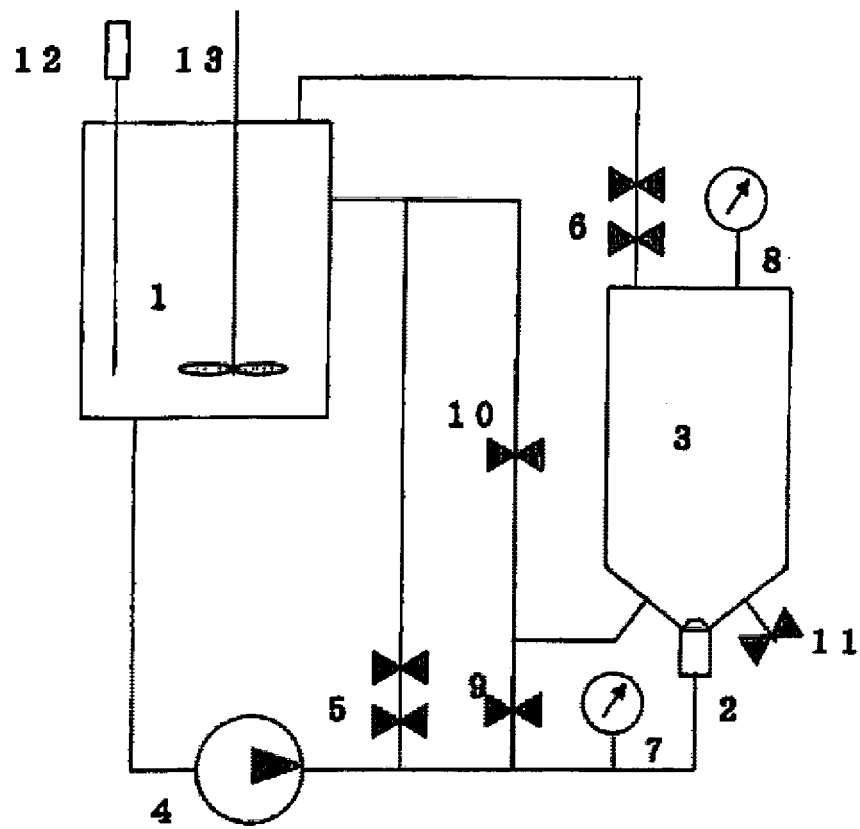
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*Figure 1*



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/055988

## A. CLASSIFICATION OF SUBJECT MATTER

D21D1/00(2006.01) i, A47K10/16(2006.01) i, D21H11/16(2006.01) i, D21H27/00(2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21D1/00, A47K10/16, D21H11/16, D21H27/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/123229 A1 (Nippon Paper Industries Co., Ltd.), 01 November, 2007 (01.11.07), Full text; Figs. 1 to 7 & EP 2014828 A1	1-4
X	JP 1-213491 A (I Zui I Purodakutsu Inc.), 28 August, 1989 (28.08.89), Full text; Figs. 1 to 2 (Family: none)	1-4
X	JP 49-55908 A (Wiggins Teape Research & Development Ltd.), 30 May, 1974 (30.05.74), Full text & DE 2333781 A & FR 2236986 A & GB 1397308 A	1-4

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
13 April, 2009 (13.04.09)Date of mailing of the international search report  
21 April, 2009 (21.04.09)Name and mailing address of the ISA/  
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/055988

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 49-13403 A (Wiggins Teape Research & Development Ltd.), 05 February, 1974 (05.02.74), Full text & DE 2254517 B & FR 2179149 A & GB 1329409 A	1-4
A	WO 2005/012632 A1 (Nippon Paper Industries Co., Ltd.), 10 February, 2005 (10.02.05), Full text; Figs. 1 to 15 & EP 1652999 A1	1-4

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## REFERENCES CITED IN THE DESCRIPTION

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### Patent documents cited in the description

- JP SHO5446914 A [0007]
- JP HEI466992 A [0007]
- US 3296065 A [0007]
- JP SHO4822701 A [0007]
- JP SHO60139897 A [0007]
- JP HEI299690 A [0007]
- JP HEI299691 A [0007]
- JP HEI236288 A [0007]
- JP HEI2224626 A [0007]
- JP HEI3900 A [0007]
- JP HEI523262 A [0007]
- JP HEI614848 A [0007]
- WO 2005012632 A [0016] [0021]
- WO 2006085598 A [0051]

### Non-patent literature cited in the description

- **Katoh.** New Edition Cavitation: Basics and Recent Advance. Makishoten, 1999 [0019]
- New Edition Cavitation: Basics and Recent Advance. Makishoten, 1999 [0023]
- **H. Soyama.** *J. Soc. Mat. Sci. Japan*, 1998, vol. 47 (4), 381 [0024]
- **Akira Isogai.** Materials Chemistry of Cellulose. The University of Tokyo Press, 2001, 68 [0041]
- **Ken Shimaji et al.** Wood Tissue. Morikita Publishing, 1976, 55 [0043]
- **F.L. Simons.** *Tappi Journal*, 1950, vol. 33 (7), 312 [0044]
- **Y. Xiaochun et al.** *Tappi Journal*, 1995, vol. 78 (6), 175 [0044]