

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 August 2003 (21.08.2003)

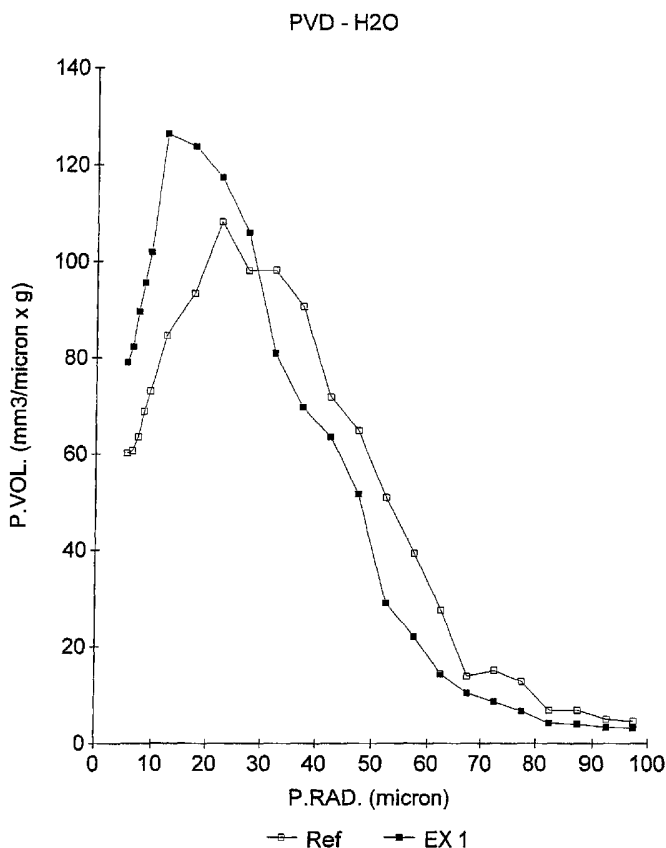
PCT

(10) International Publication Number
WO 03/069038 A1

- (51) International Patent Classification⁷: D04H 1/46, D06M 11/00, 13/00, D01F 11/08
- (74) Agent: STRÖM & GULLIKSSON IP AB; Sjöporten 4, S-417 64 Göteborg (SE).
- (21) International Application Number: PCT/SE03/00220
- (81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 11 February 2003 (11.02.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 0200476-0 15 February 2002 (15.02.2002) SE
- (84) Designated States (regional): ARIPO utility model (GH), ARIPO patent (GH), ARIPO utility model (GM), ARIPO patent (GM), ARIPO utility model (KE), ARIPO patent (KE), ARIPO utility model (LS), ARIPO patent (LS), ARIPO utility model (MW), ARIPO patent (MW), ARIPO utility model (MZ), ARIPO patent (MZ), ARIPO utility model (SD), ARIPO patent (SD), ARIPO utility
- (71) Applicant: SCA HYGIENE PRODUCTS AB [SE/SE]; S-405 03 Göteborg (SE).
- (72) Inventors: FINGAL, Lars; Uddevallaplatsen 12, S-416 70 Göteborg (SE). STRANDQVIST, Mikael; Dälavägen 87, S-437 36 Lindome (SE).

[Continued on next page]

(54) Title: HYDROENTANGLED MICROFIBRE MATERIAL AND METHOD FOR ITS MANUFACTURE



(57) Abstract: The invention relates to a method for manufacturing a microfibre material and to a microfibre material manufactured by means of hydraulic entanglement. The method comprises to form a fibre web containing microfibres and, thereafter, to subject the fibre web to hydraulic entanglement. At least a majority of the microfibres are provided in the form of microfibres having been stretched to orientation and having shell surfaces substantially completely covered by a hydrophilic lubricating layer. The method further comprises to disperse the microfibres in a foamed aqueous medium before the forming by means of the hydrophilic lubricating layer in interaction with the foamed aqueous medium in order to form a substantially homogenous fibre dispersion, wherein the microfibres in a straightened condition have a fibre thickness smaller than 0.5 denier and a fibre length larger than 5 mm both in the fibre dispersion and in the microfibre material. In the microfibre material a majority of the microfibres are stretched to orientation, exhibit a cross-sectional shape which substantially can be described by an arc or several successive arcs, and are uniformly distributed in a x, y-plane of the microfibre material.

WO 03/069038 A1



model (SL), ARIPO patent (SL), ARIPO utility model (SZ), ARIPO patent (SZ), ARIPO utility model (TZ), ARIPO patent (TZ), ARIPO utility model (UG), ARIPO patent (UG), ARIPO utility model (ZM), ARIPO patent (ZM), ARIPO utility model (ZW), ARIPO patent (ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Hydroentangled microfibre material and method for its manufacture

Technical field

The present invention relates to a method for manufacturing a microfibre material, which method includes to form a fibre web containing microfibrils and, thereafter, to
5 subject the fibre web to hydraulic entanglement in order to obtain the microfibre material.

The invention also relates to a microfibre material manufactured by means of hydraulic entanglement which material includes microfibrils which in a straightened
10 condition have a fibre thickness smaller than 0.5 denier and a fibre length larger than 5 mm.

Primarily, the microfibre material according to the invention is intended for use as a
15 wiping material, but it can also be used e.g. in absorbent articles for hygiene applications.

Background of the invention

Within the field of wiping materials utilised in industries, medical care and by
20 domestic users, so-called microfibre materials have come to be used.

These microfibre materials consist of textile materials or other fibre materials which contain very thin fibres or filaments. The thin fibres form a material structure having very small pores, which create capillary forces which are considerably stronger than
25 in conventional wiping materials when absorbing liquid. This is particularly valuable in applications which require a good dry wiping ability or where liquids with a low surface tension are to be absorbed.

Microfibre materials function particularly well when cleaning different surfaces with organic solvents, or when removing oils and fats e.g. from window panes or other surfaces.

5 The differences in material properties between microfibre materials and conventional fibre materials containing coarser fibres can be very large. This is particularly the case when the absorption properties are concerned, but also for other physical properties such as wear resistance, wet strength and softness/smoothness.

10 In order to provide the properties required by a microfibre material, the thin fibres or filaments should have a thickness no greater than 1 denier, and preferably below 0.5 denier. Calculated on a circular cross-section, and of course depending on the polymer density, one (1) denier corresponds to a fibre diameter of the magnitude 10-11 μm , whereas 0.5 denier corresponds to approximately 7-8 μm .

15 One type of microfibre material which is commonly occurring today comprises so-called meltblown filaments, i.e. thin, discontinuous filaments of varying dimensions. For instance, U.S. Patent No. 4,906,513 discloses a nonwoven wiper having improved absorbency characteristics. The wiper has a laminate construction with a relatively high basis weight middle layer consisting of thermoplastic microfibres, manufactured by means of a meltblown process, and additional fibres. On one side, the laminate has a lightweight layer of generally continuous thermoplastic filaments having a larger diameter and, on the other side, a microfibre layer. The disclosed wipers are claimed to be strong, fabric-like, and to be useful for industrial use, food service and other applications. According to US 4,906,513, the layers with continuous filaments provide strength and low linting, whereas the combination of different layers provides improved wiping properties. Preferably, the laminate is bonded by means of applying heat and pressure, and the individual components are treated with a surfactant in order to improve the wettability. A preferred combination is claimed to be a layer of microfibres of meltblown polypropylene and additional

20

25

30

fibres which can be pulp fibres, and which layer on one side has a filament layer of spunbonded polypropylene and on the other side a microfibre layer which can be filaments of meltblown polypropylene.

5 Furthermore, U.S. Patent No. 4,775,579 discloses an elastic nonwoven material which contains staple fibres intimately intertwined with an elastic web or scrim. According to US 4,775,579, pulp fibres and staple fibres can be hydraulically entangled with an elastic nonwoven web in order to form an absorbent, elastic
10 nonwoven material, wherein the staple fibres preferably are between $\frac{1}{4}$ inch and 2 inches long and have a fibre diameter of no greater than 6 denier, and preferably no greater than 1 or 1.5 denier. However, US 4,775,579 does not describe any specific examples with staple fibres, which are thinner than 1.5 denier, which is the reason why material properties possibly resembling the microfibre material according to the present invention originate entirely from the use of meltblown filaments.

15 EP-A-0 926 288 discloses a nonwoven fabric comprising meltblown fibers and pulp fibers which have been mechanically entangled. It is stated that a slurry is prepared containing pulp fibers and meltblown fibers. However it is not disclosed how the hydrophobic meltblown fibers, which normally stick together, are separated and
20 dispersed in the aqueous medium.

As a result of the functional principle of the meltblown process, the extruded and by means of air blowing formed plastic filaments will, in contrast to so-called staple fibres, not exhibit any proper "normal dimension", but will rather exhibit shapes,
25 lengths and thickness values within a relatively wide interval of distribution. Furthermore, filaments which have been formed in a meltblown process are non-stretched, and therefore lack the high degree of orientation and strength which can be given to staple fibres by means of a suitable stretching process before the cutting. By means of meltblown techniques, it has been possible to manufacture microfibre
30 materials having a sufficiently fine pore structure in order to obtain good absorption

properties, but not to achieve the high wear resistance and wet strength which is required for certain products, e.g. industrial wipes.

Accordingly, from a strength point of view, it would be an advantage to be able to
5 utilise stretched staple fibres when manufacturing microfibre materials.

U.S. Patent No. 4,902,564 discloses a method for manufacturing a highly absorbent nonwoven material, which substantially consists of papermaking pulp and synthetic staple length fibres. The method comprises to form a wetlaid web which contains
10 – 75 percent by weight of papermaking pulp and 25 – 50 percent by weight of synthetic fibres having a fibre length from about ¼ inch to about 1 inch, and to form a highly compacted web of entangled fibres by means of subjecting the fibres in the wetlaid web to hydraulic entanglement, and to dry the web in order to form said nonwoven material. Without any closer details, US 4,902,564 states that the fibre
15 thickness of the synthetic staple fibres can be within the interval from about 0.5 to about 3 denier. In the practical embodiments which are listed in the description, the synthetic staple fibres have the thickness 1.5 and 1.2 denier, i.e. fibres which are too coarse to enable the properties required in microfibre materials of the type discussed herein to be reached.

20

WO 93/06269 discloses how the water-dispersibility of polyester fibers and filaments is improved by treating the undrawn polyester filaments, when freshly extruded, with a small amount of kaustic, in a spin-finish.

25 Since, hitherto, it has been impossible to provide staple fibres which are thin enough for microfibre materials, instead so-called splitfibres have come to be used. Such splitfibres are staple fibres or filaments with internal weak points enabling a splitfibre to be split into a multitude of longitudinal, thinner fibres after the formation of a nonwoven web or sheet. The splitting can be accomplished e.g. by means of

supplying chemicals, or by means of supplying mechanical energy, for example via needling or hydraulic entanglement.

5 The use of splitfibres is known e.g. from U.S. Patent No. 4,476,186, which discloses an entangled nonwoven material comprising a first portion and a second portion. The first portion is constituted of bundles of ultrafine fibres of a dimension which does not exceed 0.5 denier, wherein the fibre bundles of the first portion are entangled (interweaved) with each other. The second portion comprises either ultrafine fibres or fibre bundles of ultrafine fibres or both, which branch outwards from the fibre
10 bundles of the first portion and are of a dimension smaller than the bundles of the first portion.

From US 4,476,186, it is evident that "bundle of ultrafine fibres" should be understood as a fibre bundle in which a plurality of fibres in staple or filament form
15 are arranged in parallel to each other. Furthermore, it is evident that the intended application, i.e. synthetic leather, requires a "grained" sheet having a non-uniform fibre distribution. In US 4,476,186, it stated that the utilised ultrafine fibres cannot be manufactured directly due to stability problems in the spinning process. Instead, splitfibres which can be modified to ultrafine fibres in a suitable stage of the
20 manufacturing process are utilised. Examples of such splitfibres are said to be such which have a chrysanthemum-shaped cross-section in which one component is radially interposed between another component, multilayered bicomponent type fibres, multilayered bicomponent fibres having a doughnut-shaped cross-section, mixed fibres obtained by means of mixing and spinning at least two components,
25 "islands-in-a-sea"-type splitfibres having a fibre structure with a plurality of ultrafine fibres in the fibre direction which are bonded together by other components. It is claimed that the split ultrafine fibres preferably are thinner than about 0.2 denier, and even more preferably thinner than about 0.05 denier.

The use of splitfibres as a raw material for microfibre materials, however, has a number of disadvantages, such as a complicated and expensive fibre manufacturing process and, as a result of the splitting process required after the forming process, an increased energy consumption. Furthermore, it has been found that the individual
5 microfibrils after splitting tend to remain in fibre bundles or flocs in the vicinity of the initial position of the splitfibre after the forming process. Such a non-uniform fibre distribution in the finished microfibre material impairs the strength properties, particularly when the wet strength, which often is a crucial property of a wiping material, is concerned. Furthermore, the non-uniform fibre formation of microfibre
10 materials based on splitfibres will result in a pore size distribution having a proportion of pores which are too large to enable a good dry wiping ability to be reached.

Summary of the invention

15 Accordingly, a first object of the present invention is to provide a method which eliminates the above-mentioned problems, and which makes it possible to manufacture a microfibre material having excellent absorption and strength properties, without the need of any complicated and expensive use of meltblown filaments or splitfibres.

20

In accordance with claim 1, this first object is achieved by means of a method which includes to form a fibre web containing microfibrils and, thereafter, to subject the fibre web to hydraulic entanglement in order to obtain the microfibre material. According to the invention, at least a majority of the microfibrils are provided in the
25 form of microfibrils having been stretched to orientation and having shell surfaces substantially completely covered by a hydrophilic lubricating layer, wherein the method includes to disperse the microfibrils in a foamed aqueous medium before the forming by means of the hydrophilic lubricating layer in interaction with the ^{foamed} aqueous medium in order to form a substantially homogenous fibre dispersion, and the
30 microfibrils in a straightened condition have a fibre thickness smaller than 0.5 denier

and a fibre length larger than 5 mm both in the fibre dispersion and in the microfibre material.

5 Furthermore, a second object of the present invention is to provide a microfibre material having a very high wet strength and a pore size distribution enabling a good dry wiping ability, without any need of adding meltblown filaments or splitfibres.

10 In accordance with claim 9, this second object is achieved by means of the microfibre material including microfibrils which in a straightened condition have a fibre thickness smaller than 0.5 denier and a fibre length larger than 5 mm, wherein according to the invention at least a majority of the microfibrils have been stretched to orientation, exhibit a cross-sectional shape which substantially can be described by an arc or several successive arcs, and are uniformly distributed in a x,y-plane of the microfibre material.

15

Further objects of the present invention will become evident from the following description, while the features enabling these further objects to be achieved are listed in the appended, dependent claims

20 **Brief description of figures**

In the following, the invention will be described in greater detail, *inter alia*, with reference to the attached figures, in which:

25 Fig. 1 in the form of a diagram shows results from a determination of pore volume distribution in water for a hydroentangled fibre material containing conventional staple fibres (Ref), and for a microfibre material according to the invention (EX 1); and

30 Fig. 2 shows corresponding results from a determination of pore volume distribution in hexadecane.

Examples

In order to illustrate the very positive results which can be achieved by means of the present invention, the following Table 1 shows results from physical testing of a hydroentangled fibre material containing conventional staple fibres (Ref), and
5 corresponding test results for a hydroentangled microfibre material according to the invention (EX 1).

Both nonwoven materials were foamformed in a hydrodynamic sheet-former,
10 hydroentangled, pressed, and dried, using laboratory equipment intended for the purpose. The skilled person who has read the present description can achieve the results with knowledge about the foamforming and entangling techniques disclosed in U.S. Patent No. 5,720,851.

15 The fibre raw materials in the comparative example (Ref) were 60 weight-% bleached, chemical softwood fluff pulp with the product designation Vigor Fluff from the producer Korsnäs AB, Sweden, and 40 weight-% of a commercially available polyester staple fibre with the designation EPM 133 and the normal fibre dimension 1.3 denier x 20 mm from Kuraray Ltd, Japan. Foamformed and
20 hydroentangled wiping materials with similar fibre recipes are commercially available.

The fibre raw materials for the microfibre material according to the invention (EX 1) were 60 weight-% Vigor Fluff and 40 weight-% of a recently developed polyester
25 staple fibre with the designation EPM 043 and the normal fibre dimension 0.4 denier x 15 mm, from Kuraray Ltd, Japan.

Both materials were foamformed in the hydrodynamic sheet-former at a foam surfactant concentration of 0.05 %, wherein it should be mentioned that suitable
30 foam surfactants can be found via the above-mentioned document US 5,720,851.

Thereafter, both materials were entangled by means of 3 passages x 120 bar per material side on top of a conventional, relatively close wetforming wire, using an entangling nozzle with an aperture pattern adapted to the fibre recipe in the Comparative example (Ref). Accordingly, the entanglement parameters were left unchanged for the microfibre material in the example according to the invention (EX 1).

Both materials were pressed lightly in a conventional laboratory pressing device at 1 m/min and 2.5 bar pressure. Finally, both materials were dried for 5 minutes at 140 °C in a laboratory through-air dryer, and were conditioned at 23 °C and 55 % relative humidity for 4 hours.

The obtained results are evident from the following Table 1.

Table 1

	Ref (Comparative example)	EX 1 (Invention)
Fibre recipe	60 weight-% Vigor fluff 40 weight-% PET EPM 133 (1.3 den x 20 mm)	60 weight-% Vigor fluff 40 weight-% PET EPM 043 (0.4 den x 15 mm)
Grammage setting	80 g/m ²	80 g/m ²
Specific entangling power	302 kWh/ton	288 kWh/ton
Entangling pressure, max	120 bar	120 bar
Grammage	84.6 g/m ²	88.8 g/m ²
Bulk	5.1 cm ³ /g	5.3 cm ³ /g
Tensile strength MD, dry	4590 N/m	3939 N/m
Tensile strength CD, dry	1362 N/m	1433 N/m
MD/CD-ratio	3.4	2.7
Stretch at break $\sqrt{MD*CD}$	62 %	47 %

Work to rupture index $\sqrt{\text{MD} \cdot \text{CD}}$	11.2 J/g	7.6 J/g
Tensile index, dry $\sqrt{\text{MD} \cdot \text{CD}}$	29.6 Nm/g	26.8 Nm/g
Tensile index, water $\sqrt{\text{MD} \cdot \text{CD}}$	14.8 Nm/g	24.4 Nm/g
Tensile index, surfactant solution $\sqrt{\text{MD} \cdot \text{CD}}$	5.9 Nm/g	19.2 Nm/g
Relative strength, water	50 %	91 %
Relative strength, surfactant solution	20 %	72 %

As is evident from Table 1 above, the foamformed and hydroentangled microfibre material according to the invention (EX 1) obtained considerably higher wet strength in water and in surfactant solution than the foamformed and hydroentangled fibre material with conventional staple fibres (Ref). A commercially available fatty alcohol ethoxylate (Lutensol AO 7) from BASF GmbH, Ludwigshafen, Germany was utilised for the wet strength testing in surfactant solution.

The improvement of the wet strengths, which can be obtained by means of the invention (EX 1), is particularly valuable since the strength in water and in aqueous, lubricating and hydrogen bond-dissolving hydrophilic liquids (e.g. the surfactant solution utilised for the material testing) often is the weakest point of hydroentangled wiping materials. This is particularly the case when fibre recipes containing pulp fibres are concerned.

The fact is that the microfibre material (EX 1) exhibits considerably better strength values than those of previously known microfibre materials based on non-stretched meltblown filaments.

In the form of a diagram, the attached Fig. 1 shows results from determination of pore volume distribution in water (H₂O) for the foamformed and hydroentangled fibre material in the comparative example (Ref), and corresponding measurement results for the microfibre material in the example according to the invention (EX 1).

5

The determination of the pore size distribution (pore volume distribution) was performed within the pore radius range 5 – 250 µm and by means of using a so-called PVD-apparatus (Pore Volume Distribution), which functions by a principle which is well known to the skilled person. For reasons of clarity, Figs. 1 and 2 only illustrate

10

the results, which were obtained within the pore radius range 5 – 100 µm.

When determining the pore volume distribution, a material specimen having a determined weight is placed in a pressure chamber, and is wetted completely. Thereafter, the pressure is increased so that the liquid gradually is pressed out of the material pores. The weight of the expelled liquid is measured at each pressure increase by means of a pair of scales connected to the test chamber by means of a communicating vessel. A computer records the signals from the pair of scales and the pressure in the test chamber at each pressure increase. Thereafter, the pore volume distribution can be calculated and plotted for evaluation by means of the LaPlace equation, which is well known to the skilled person, and knowledge about the physical properties of the testing liquid.

15

20

As is evident from Fig. 1, the microfibre material according to the invention (EX 1) exhibits a more narrow pore volume distribution in water than the fibre material in the comparative example (Ref). Furthermore, the microfibre material according to the invention (EX 1) exhibits a much larger volume of pores having a pore radius smaller than 30 µm than the fibre material in the comparative example (Ref).

25

The appended fig. 2 shows corresponding results as Fig. 1, but for PVD-measurement in hexadecane. Amongst other things, it is evident from Fig. 2 that the

30

microfibre material according to the invention (EX 1) exhibited a considerably larger volume of pores having a pore radius smaller than 20 μm than the fibre material in the comparative example (Ref).

5 As a matter of fact, the microfibre material according to the invention (EX 1) exhibits a pore size distribution of the type, which is particularly advantageous for achieving a good dry wiping ability both with water and non-polar liquids with a low viscosity. Previously, a pore size distribution of this type has been possible to achieve by means of utilising non-oriented meltblown filaments which, however, give comparatively
10 low material strengths, but it has hardly been possible to achieve by means of using splitfibres which, furthermore, are expensive and require separate splitting steps. The pore size distribution according to the invention (EX 1) makes it possible to achieve a better dry wiping ability than what normally can be achieved with splitfibres (not shown in the drawings). The reason for this is that, even if the
15 splitfibres which consist of a plurality of potential microfibrils bonded together can be comparatively uniformly distributed in the fibre web during the forming, the splitting of the splitfibres into the desired microfibrils after the forming process often becomes incomplete. The result is that splitfibre-based microfibre materials, in addition to portions with the desired microfibre structure, also will exhibit undesired,
20 incompletely split splitfibres or completely or partially aggregated bundles of microfibrils. Such portions with incompletely split splitfibres or aggregated microfibre bundles means that the maximum strength- and stretch-providing potential of the microfibrils will not be utilised. Furthermore, the more sparse portions between the incompletely split portions will create pores in the material
25 structure which are larger than desired to obtain a good dry wiping ability, particularly when absorption of liquids with a low surface tension, such as many organic solvents, are concerned.

As is evident from Fig. 1, the microfibre material according to the invention (EX 1)
30 exhibits a pore size distribution with a very small volume of pores with a pore radius

larger than 70 μm . The reason for this is, amongst other things, that a majority of the added microfibrils are uniformly distributed in a x,y-plane of the material structure.

5 The low volume of pores which are larger than 70 μm is also a result of the fact that there are no incompletely split fibres or fibre bundles present in the microfibre material according to the invention, *inter alia*, since all microfibrils in their fibre manufacturing process have been coated with a hydrophilic lubricating agent or finish (also called spin finish), something which makes a uniform formation of the microfibrils possible in foamforming. Furthermore, the hydrophilic lubricant is
10 capable of facilitating the movements of the microfibrils in relation to each other during the entanglement, something which improves the uniformity of the entanglement result and contributes to the more narrow pore size distribution which is desired for dry wiping ability.

15 When utilising splitfibrils according to prior art, however, it is true that the "parent fibres" can be provided with a finish, which facilitates a uniform formation in the forming process. Such a finish, however, will only be active at the external surfaces of the splitfibre, whereas the boundary surfaces between the individual microfibrils after the splitting will exhibit residues of the connecting material or "adhesive"
20 which has kept the splitfibre together. It is easy to understand that such adhesive residues, for example in an entangling process which both is intended to split the splitfibrils into individual microfibrils and to entangle or interweave these into a continuous microfibre material, are more likely to obstruct than facilitate the mobility of the individual microfibrils in relation to each other. The comparatively poor fibre
25 mobility in the entangling process results in a more non-uniform entanglement result, and in a comparatively wide pore size distribution which makes it difficult to achieve a good dry wiping ability.

The following Table 2 summarizes further results from the PVD-measurements in water on the two nonwoven materials (Ref and EX 1). In Table 2, the so-called cumulative pore volume distributions of the two materials are compared.

Table 2

PVD WATER	Ref (Comparative example)		EX 1 (Invention)	
	Pore radius (μm)	Cumulative volume (mm^3/mg)	% of total pore volume	Cumulative volume (mm^3/mg)
5	0	0	0	0
10	0.32	6	0.45	9
20	1.22	24	1.70	35
30	2.24	44	2.81	58
40	3.19	63	3.57	74
50	3.87	76	4.14	85
60	4.32	85	4.40	91
70	4.53	89	4.52	93
80	4.67	92	4.60	95
90	4.73	93	4.64	96
100	4.78	94	4.67	96
150	4.88	96	4.75	98
200	4.94	98	4.8	99
250	5.06	100	4.85	100

Amongst other things, it is evident from Table 2 above that the cumulative pore
5 volume distribution in water rises considerably faster with the pore radius for the
microfibre material according to the invention (EX 1) than for the fibre material in
the comparative example (Ref).

The following Table 3 shows corresponding results as Table 2, but obtained from
10 measurements in hexadecane. In such a non-polar solvent, the pore structure of the

material will change relatively little in comparison to the pore structure, which is present in dry state.

Table 3

5

PVD HEXADECANE	Ref (Comparative example)		EX 1 (Invention)	
	Pore radius (μm)	Cumulative volume (mm^3/mg)	% of total pore volume	Cumulative volume (mm^3/mg)
5	0	0	0	0
10	0.17	3	0.25	5
20	0.94	19	1.31	28
30	1.64	34	1.92	41
40	2.06	42	2.45	52
50	2.68	55	3.02	64
60	3.25	67	3.58	76
70	3.70	76	3.88	83
80	4.01	82	4.06	87
90	4.28	88	4.20	90
100	4.44	91	4.31	92
150	4.75	97	4.58	98
200	4.82	99	4.64	99
250	4.87	100	4.69	100

As is evident from Table 3 above, the cumulative pore volume rises considerably faster also in hexadecane for the microfibre material according to the invention (EX 1) than for the fibre material in the comparative example (Ref).

Detailed description of preferred embodiment

In the following, a preferred embodiment and a number of alternative embodiments of a method for manufacturing a microfibre material according to the invention will
5 be described in greater detail.

The method includes to form a fibre web containing microfibres and, thereafter, to subject the fibre web to hydraulic entanglement in order to obtain the microfibre material. Suitable pressing and drying steps, of a type which is known *per se*, follow
10 after the hydraulic entanglement.

In the method according to the invention, at least a majority of the microfibres are provided in the form of microfibres having been stretched to orientation and having shell surfaces substantially completely covered by a hydrophilic lubricating layer.
15 The use of stretched microfibres enables the microfibre material according to the invention to obtain a considerably higher strength than what is possible e.g. with non-stretched meltblown filaments. In the preferred embodiment, the hydrophilic lubricating layer is constituted of a spin finish of a type, which is adapted for wetforming. Suitable chemicals for use as a spin finish on staple fibres are well
20 known to the skilled person.

According to the invention, the method further comprises to disperse the microfibres in a foamed aqueous medium before the forming by means of the hydrophilic lubricating layer in interaction with the foamed aqueous medium in order to form a
25 substantially homogenous fibre dispersion. According to a theory, however the invention not being bound to this theory, it is believed that since a foamed aqueous medium is used the hydrophilic lubricating layer will not be washed away from the fibers as easily that it would have been in case the fibers would have been dispersed in water. It is thus believed that the foam contributes in maintaining the lubricating
30 layer on the fiber surface for a longer time period.

In the method according to the invention, when seen in a straightened condition, the microfibrils have a fibre thickness smaller than 0.5 denier and a fibre length larger than 5 mm both in the fibre dispersion and in the microfibre material. Depending on the intended application, the microfibrils which are utilised in the present invention
5 can include different polymers, e.g. polyester, polyamide, polypropylene, polyethylene, cellulose, etc.

As a result of the microfibrils in the method according to the invention being separate microfibrils already prior to the forming and all microfibrils being coated by a
10 hydrophilic lubricating layer, a considerably more uniform microfibre distribution is obtained in the finished nonwoven material than what is possible with microfibrils included in a splitfibre which are not to be separated from each other until after the forming. Amongst other things, the more uniform microfibre distribution according to the invention makes it possible to achieve very high wet strengths and a narrow
15 pore volume distribution which provides good dry wiping properties and very strong capillary forces.

Since the microfibrils are dispersed in a foamed aqueous medium the microfibrils are guided in a controlled way by the gas bubbles in the foam, which makes it possible to
20 obtain a very uniform fibre formation also with considerably longer microfibrils than what would be possible if the aqueous medium primarily would have been water. Preferably the microfibrils have a fibre length between 10 and 25 mm.

In one embodiment of the method according to the invention, also a proportion of
25 pulp fibres are dispersed in the foamed aqueous medium together with the microfibrils. The pulp fibres can be e.g. unbleached or bleached softwood fibres in applications where a high bulk and total absorption are needed, and unbleached or bleached hardwood fibres in applications where a particularly dense pore structure and high dry wiping ability are needed. When adding pulp fibres, counted on a total

quantity of dry fibres, advantageously 10 – 100 weight-% of the microfibrils and 0-90 weight - % of the pulp fibres are dispersed in the foamed aqueous medium.

5 Embodiments involving addition of pulp fibres are advantageous, *inter alia*, for economic reasons, since pulp fibres are a considerable less expensive raw material than microfibrils. In some cases, however, the admixture of pulp fibres also can provide improved absorption properties, particularly when absorption of polar solvents such as water is concerned.

10 According to the invention, particularly advantageously the hydrophilic lubricating layer is applied as a spin finish before short-cutting said microfibrils. However, it is also conceivable with embodiments where the lubricating layer is applied in another suitable way, for example by means of the short-cut microfibrils being impregnated with a suitable chemical agent, after the fibre cutting but before the dispersing step.

15 As a result of their higher flexibility, lower fibre-fibre friction, and larger number of fibre ends, the microfibrils which are utilised in the method according to the invention, are easier to entangle than the previously utilised coarser and stiffer splitfibrils, and consume no entangling power for splitting the splitfibrils into
20 individual microfibrils. Therefore, in a particularly advantageous embodiment of the method according to the invention, less than 300 kWh/ton entangling power is consumed in the hydraulic entanglement.

25 In another advantageous embodiment, as a result of the microfibrils in the method according to the invention being so easy to entangle, a hydraulic pressure no greater than 120 bar can be utilised in the hydraulic entanglement. This embodiment is of course advantageous both for process-technical and economic reasons.

30 In a particularly advantageous embodiment, the microfibre material is subjected to a corona or plasma treatment after the hydraulic entanglement in order to modify a

possible residue of the hydrophilic lubricating layer to provide an increased fibre-fibre friction. The modification of the hydrophilic lubricating layer preferably takes place after the drying of the microfibre material, and particularly advantageously includes an oxidation with the oxygen in the air, but also other chemical reactions
5 may occur. The basic technique for plasma and corona treatment of hydroentangled nonwoven materials is disclosed in the European Patent No. 0 833 877 B1.

In the following, a preferred embodiment and a number of alternative embodiments of a microfibre material according to the invention will be described in greater detail,
10 wherein reference is made the attached tables and figures.

The microfibre material according to the invention has been manufactured by means of hydraulic entanglement and includes microfibres, which in a straightened condition have a fibre thickness smaller than 0.5 denier, i.e. 0.56 dtex, and a fibre
15 length larger than 5 mm. Naturally, these fibre dimensions are referring to average dimensions, and it should be evident to the skilled person that a certain variation around the average values will occur.

In the microfibre material according to the invention, at least a majority of the
20 microfibres are stretched to orientation. This makes it possible to give the microfibre material according to the invention a higher strength than what is possible e.g. by means of non-stretched meltblown filaments.

According to the invention, the microfibres of the material also exhibit a cross-
25 sectional shape which can be described by an arc or several successive arcs, wherein the microfibres are uniformly distributed in a x,y-plane of the microfibre material.

Accordingly, the microfibres in the material according the invention advantageously exhibit a circular, elliptical or ribbon-shaped cross-section, which provides a high
30 fibre-fibre mobility during the entanglement and makes it possible to accomplish a

well-defined pore volume distribution. Furthermore, according to the invention, the microfibrils are uniformly distributed in a x,y-plane of the microfibril material. Thereby, "uniformly distributed" should be understood as a uniform formation at least after the forming step, and a formation which is as uniform as possible after a possible aperturing process or the like in connection with the hydraulic entanglement.

The uniform distribution in the x,y-plane according to the invention differs greatly from previously known microfibril materials in which comparatively coarse splitfibrils first have been formed into a web and thereafter, in connection with the entanglement or another subsequent process step, have been split into microfibrils. In the previously known materials which are based on splitfibrils, after splitting the individual microfibrils will still remain in the vicinity of the position a splitfibril had in the material after the forming step, and produce "islands" or "flocs" in the finished material with a raised concentration of microfibrils surrounded by regions with a lower content of microfibrils. Such a non-uniform microfibril distribution in the x,y-plane will give a wider pore volume distribution and a dry wiping ability which is inferior compared to the one which can be achieved in the microfibril material according to the invention.

Preferably, the microfibril material according to the invention is characterised in that substantially all shell surfaces of the majority of the microfibrils exhibit an equivalent micro-surface roughness. This should be understood as if the shell surfaces of the fibres exhibit substantially the same surface properties along the entire fibre length and around the entire fibre circumference, and that these surface properties have been adapted both for enabling a uniform fibre formation in the forming step and a high fibre-fibre mobility in the entangling step. This feature distinguishes the microfibril material according to the invention from nonwoven materials based on splitfibrils in which the microfibrils formed in the splitting process both will exhibit portions which have been facing the exterior of the splitfibril, and portions which before the splitting have been facing inwards towards the interior of the splitfibril and which

have surface properties which are disadvantageous for the fibre-fibre mobility and the uniformity of the formation.

5 In another advantageous embodiment, the microfibre material according to the invention is characterised in that substantially all neighbouring microfibrils, out of the above-mentioned majority of the microfibrils, exhibit different extensions in said x,y-plane. This is an advantage, *inter alia*, from a material durability point of view, and is made possible since the microfibrils are separate and can be distributed in a comparatively anisotropic way in the forming step (i.e. without being oriented in any
10 particular sheet direction). This differs from splitfibre-based materials in which, as mentioned above, the microfibrils after the splitting tend to remain close to the initial positions of the splitfibrils, and in which neighbouring microfibrils easily form bundles along their entire length or portions of their length.

15 In a preferred embodiment of the invention, the microfibre material exhibits a fibre formation created by foamforming. In a further preferred embodiment the majority of the microfibrils have a fibre length between 10 and 25 mm. Normally, by means of a visual inspection or a microscope, a skilled person is capable of determining if a material is foamformed.

20 In one advantageous embodiment of the invention, the microfibre material includes a proportion of pulp fibres together with the microfibrils. Counted on a total quantity of dry fibres, the microfibre material advantageously includes 10 - 100 weight-% of the microfibrils and 0 - 90 weight-% pulp fibres,.

25 Advantageously, the microfibre material according to the invention is characterised in that certain shell surfaces of the microfibrils exhibit a residue of a hydrophilic lubricating agent.

In a particularly preferred embodiment, certain shell surfaces of the microfibrils exhibit an oxidised residue of a hydrophilic lubricating agent, wherein the oxidation particularly advantageously has been accomplished by means of plasma or corona treatment in the presence of oxygen.

5

In the preferred embodiment, the microfibre material according to the invention exhibits a tensile index $\sqrt{MD*CD}$ which is higher than 20 Nm/g both in dry state and in water, and preferably also a tensile index $\sqrt{MD*CD}$ which is higher than 15 Nm/g in a lubricating, hydrogen bond-dissolving surfactant solution, such as a water
10 solution of fatty alcohol-ethoxylate or a solution with corresponding properties.

Furthermore, the microfibre material according to the invention preferably exhibits a pore volume distribution, measured by PVD within the pore radius interval 5 – 250 μm , having a volume maximum at a pore radius smaller than 20 μm . This is the case
15 either when measuring in water or hexadecane, but most preferably in both cases. When this embodiment and the ones described in the following description are concerned, particular reference is made to the results shown in tables 2 and 3, and in Figs. 1 and 2.

20 In one advantageous embodiment, the microfibre material exhibits a pore volume distribution, measured by PVD in water, having a cumulative pore volume which is at least 30 % of the total pore volume of the microfibre material for pore radii between 5 and 20 μm and at least 90 % of the total pore volume for pore radii between 5 and 60 μm . This embodiment provides properties which are particularly
25 advantageous for absorption of aqueous liquids.

For absorption of non-polar liquids, such as many organic solvents, the microfibre material particularly advantageously exhibits a pore size distribution, measured by PVD in hexadecane, having a cumulative pore volume which is at least 25 % of the

total pore volume of the microfibre material for pore radii between 5 and 20 μm and at least 70 % of the total pore volume for pore radii between 5 and 60 μm .

Particularly advantageously, the microfibre material exhibits a pore size distribution, measured by PVD in water, in which less than 20 % of the total pore volume of the microfibre material is located in pores having a pore radius exceeding 40 μm , and particularly advantageously also a pore size distribution, measured by PVD in hexadecane, in which less than 20 % of the total pore volume of the microfibre material is located in pores having a pore radius exceeding 70 μm . This ensures sufficiently strong capillary forces when the microfibre material according to the invention is utilised as a wiping material.

In a particularly preferred embodiment, the microfibre material exhibits a pore volume distribution, measured by PVD, in which less than 2.5 % of the total pore volume of the microfibre material, both when measured in water and in hexadecane, is located in pores having a pore radius which exceeds 150 μm . This embodiment ensures that the microfibre material according to the invention, when utilised as a wiping material, does not absorb any large amount of liquid in pores which have capillary forces which are too weak to retain the liquid safely. Therefore, the particularly preferred embodiment provides good dry wiping characteristics both when absorbing aqueous liquids and non-polar liquids with low surface tension.

A major advantage of the present invention is that hydroentangled microfibre materials with high strength can be manufactured at a low energy consumption, since the microfibres which are utilised according to the invention can be very uniformly distributed in the sheet in the forming process and have good entangling properties, and since no splitting energy is required in order to make the fibres thinner, something which is required when using conventional splitfibres.

In the foregoing, the present invention has been described by means of examples and a number of different embodiments. However, the invention should not be regarded as being limited exclusively to these examples and embodiments, but its scope is defined in the following claims.

5

Accordingly, it is also conceivable that the microfibre material according to the invention is utilised for other purposes than as a wiping material, for example that the microfibre material is utilised as a part in an absorbent article for hygiene purposes.

Claims

- 5 1. A method for manufacturing a microfibre material,
including to form a fibre web containing microfibrils and, thereafter, to subject said
fibre web to hydraulic entanglement in order to obtain said microfibre material,
c h a r a c t e r i s e d i n that at least a majority of said microfibrils are provided in
the form of microfibrils having been stretched to orientation and having shell surfaces
10 substantially completely covered by a hydrophilic lubricating layer, and that the
method includes to disperse said microfibrils in a foamed aqueous medium before
said forming by means of said hydrophilic lubricating layer in interaction with said
foamed aqueous medium in order to form a substantially homogenous fibre
dispersion, wherein said microfibrils in a straightened condition have a fibre
15 thickness smaller than 0.5 denier and a fibre length larger than 5 mm both in said
fibre dispersion and in said microfibre material.
2. A method according to claim 1,
c h a r a c t e r i s e d i n that said microfibrils are provided with a fibre length which
20 is between 10 and 25 mm.
3. A method according to any one of the preceding claims,
c h a r a c t e r i s e d i n that also a proportion of pulp fibres is dispersed in said
foamed aqueous medium together with said microfibrils.
- 25 4. A method according to any one of the preceding claims,
c h a r a c t e r i s e d i n that, counted on a total quantity of dry fibres, 10 - 100
weight-% of said microfibrils and 0 - 90 weight-% of pulp fibres are dispersed in said
foamed aqueous medium.

5. A method according to any one of the preceding claims,
c h a r a c t e r i s e d i n that said hydrophilic lubricating layer is applied as a spin
finish before short-cutting said microfibres.
- 5 6. A method according to any one of the preceding claims,
c h a r a c t e r i s e d i n that less than 300 kWh/ton of entangling power is
consumed in said hydraulic entanglement.
7. A method according to any one of the preceding claims,
10 c h a r a c t e r i s e d i n that a hydraulic pressure no greater than 120 bar is used in
said hydraulic entanglement.
8. A method according to any one of the preceding claims,
c h a r a c t e r i s e d i n that the microfibre material is subjected to a corona or
15 plasma treatment after said hydraulic entanglement in order to modify a possible
residue of said hydrophilic lubricating layer to provide an increased fibre-fibre
friction.
9. A microfibre material manufactured by means of hydraulic entanglement,
20 said microfibre material including microfibres which in a straightened condition have
a fibre thickness smaller than 0.5 denier and a fibre length larger than 5 mm,
c h a r a c t e r i s e d i n that at least a majority of said microfibres have been
stretched to orientation, exhibit a cross-sectional shape which substantially can be
described by an arc or several successive arcs, and are uniformly distributed in a x-y-
25 plane of said microfibre material.
10. A microfibre material according to claim 9,
c h a r a c t e r i s e d i n that substantially all shell surfaces of said majority of
microfibres exhibit an equivalent micro-surface roughness.

11. A microfibre material according to claim 9 or 10,
c h a r a c t e r i s e d i n that substantially all neighbouring microfibres, of said
majority of microfibres, exhibit different extensions in said x,y-plane.
- 5 12. A microfibre material according to any one of claims 9 to 11,
c h a r a c t e r i s e d i n that the microfibre material exhibits a formation created by
foamforming, and that said majority of microfibres have a fibre length between 10
and 25 mm.
- 10 13. A microfibre material according to any one of claims 9 to 12,
c h a r a c t e r i s e d i n that the microfibre material includes a proportion of pulp
fibres together with said microfibres.
14. A microfibre material according to any one of claims 9 to 13,
15 c h a r a c t e r i s e d i n that the microfibre material, counted on a total quantity of
dry fibres, includes 10 - 100 weight-% of said microfibres and 0 – 90 weight-% of
pulp fibres.
15. A microfibre material according to any one of claims 9 to 14,
20 c h a r a c t e r i s e d i n that certain shell surfaces of said microfibres exhibit a
residue of a hydrophilic lubricating agent.
16. A microfibre material according to any one of claims 9 to 15,
c h a r a c t e r i s e d i n that certain shell surfaces of said microfibres exhibit an
25 oxidised residue of a hydrophilic lubricating agent.
17. A microfibre material according to any one of claims 9 to 16,
c h a r a c t e r i s e d i n that the microfibre material exhibits a tensile index
 $\sqrt{MD*CD}$ which is larger than 20 Nm/g both in a dry state and in water.

18. A microfibre material according to any one of claims 9 to 17,
c h a r a c t e r i s e d i n that the microfibre material exhibits a tensile index
 $\sqrt{MD*CD}$ which is larger than 15 Nm/g in a lubricating, hydrogen bond-dissolving
surfactant solution.
- 5
19. A microfibre material according to any one of claims 9 to 18,
c h a r a c t e r i s e d i n that the microfibre material exhibits a pore size
distribution, measured by PVD in water within the pore radius interval 5 – 250 μm ,
having a volume maximum at a pore radius smaller than 15 μm .
- 10
20. A microfibre material according to any one of claims 9 to 19,
c h a r a c t e r i s e d i n that the microfibre material exhibits a pore size
distribution, measured by PVD in hexadecane within the pore radius interval 5 – 250
 μm , having a volume maximum at a pore radius smaller than 15 μm .
- 15
21. A microfibre material according to any one of claims 9 to 20,
c h a r a c t e r i s e d i n that the microfibre material exhibits a pore size
distribution, measured by PVD in water, having a cumulative pore volume which is
at least 30 % of the total pore volume of the microfibre material for pore radii
20 between 5 and 20 μm and at least 90 % of said total pore volume for pore radii
between 5 and 60 μm .
22. A microfibre material according to any one of claims 10 to 21,
c h a r a c t e r i s e d i n that the microfibre material exhibits a pore size
25 distribution, measured by PVD in hexadecane, having a cumulative pore volume
which is at least 25 % of the total pore volume of the microfibre material for pore
radii between 5 and 20 μm and at least 70 % of said total pore volume for pore radii
between 5 and 60 μm .
- 30
23. A microfibre material according to any one of claims 9 to 22,

c h a r a c t e r i s e d i n that the microfibre material exhibits a pore size distribution, measured by PVD in water, in which less than 20 % of the total pore volume of the microfibre material is located in pores having a pore radius exceeding 40 μm .

5

24. A microfibre material according to any one of claims 9 to 23,

c h a r a c t e r i s e d i n that the microfibre material exhibits a pore size distribution, measured by PVD in hexadecane, in which less than 20 % of the total pore volume of the microfibre material is located in pores having a pore radius exceeding 70 μm .

10

25. A microfibre material according to any one of claims 9 to 24,

c h a r a c t e r i s e d i n that the microfibre material exhibits a pore size distribution, measured by PVD, in which less than 2.5 % of the total pore volume of the micro fibre material, both when measured in water and in hexadecane, is located in pores having a pore radius exceeding 150 μm .

15

Fig. 1
PVD - H2O

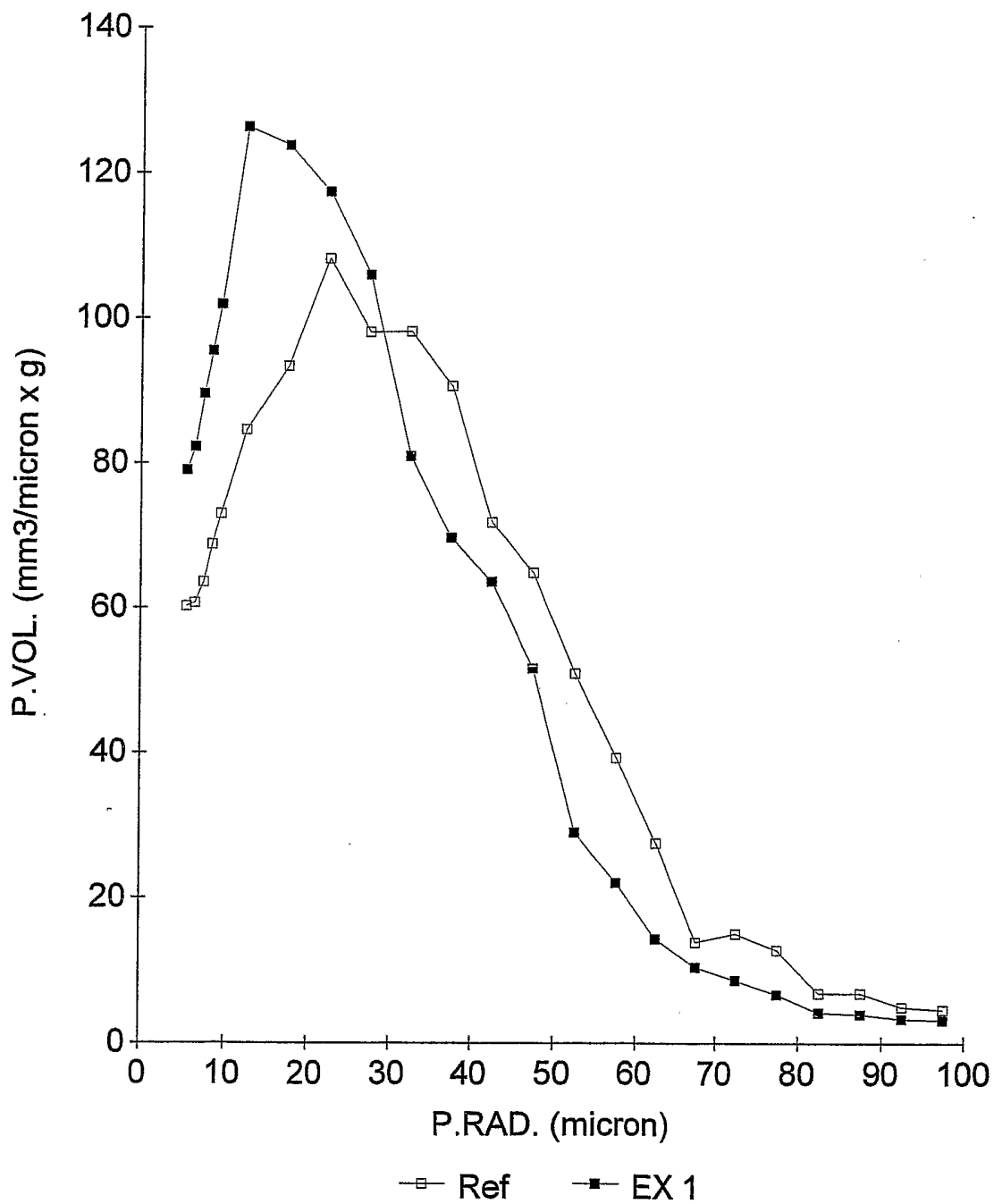
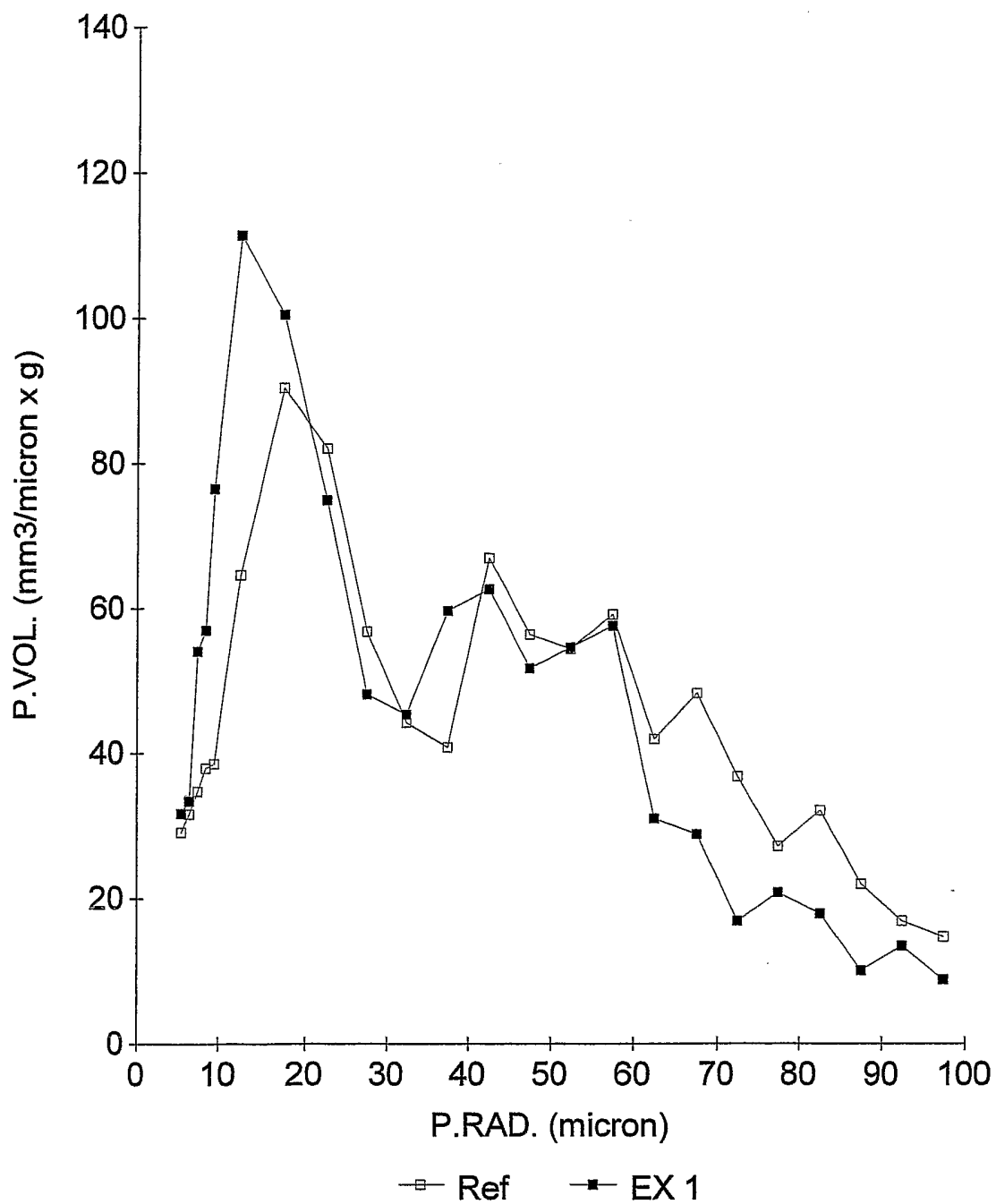


Fig. 2
PVD - HEXAD.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/00220

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D04H 1/46, D06M 11/00, D06M 13/00, D01F 11/08
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)

IPC7: D04H, D06M, D01F

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

SE,DK,FI,NO classes as above

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.
Y	EP 0926288 A1 (UNI-CHARM CORPORATION), 30 June 1999 (30.06.99), column 2, line 5 - line 15, abstract --	1-25
Y	WO 9306269 A1 (E.I. DU PONT DE NEMOURS AND COMPANY), 1 April 1993 (01.04.93), page 3, line 5 - page 4, line 30 --	1-25
A	EP 1022363 A1 (J.W. SUOMINEN OY), 26 July 2000 (26.07.00), abstract --	1,5,8

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"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 28 April 2003	Date of mailing of the international search report 16 -05- 2003
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Authorized officer Marie Karlsson/EÖ Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/00220

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1091028 A1 (FIBER INNOVATION TECHNOLOGY, INC.), 11 April 2001 (11.04.01), column 1, line 26 - line 41 --	1,9-10
A	US 3607588 A (JOHN W. SOEHNGEN), 21 Sept 1971 (21.09.71), figures 4 and 5 --	9
A	GB 1087087 A (MONSANTO COMPANY), 11 October 1967 (11.10.67), page 1, line 15 - line 24 -- -----	1-5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/00220

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
EP	0926288	A1	30/06/99	AU	9820398 A	15/07/99
				BR	9805841 A	14/12/99
				CN	1222597 A	14/07/99
				JP	11189959 A	13/07/99
				SG	71186 A	21/03/00
				US	2002006760 A	17/01/02
				AU	750350 B	18/07/02
WO	9306269	A1	01/04/93	US	6107394 A	22/08/00
EP	1022363	A1	26/07/00	FI	4085 U	31/08/99
				FI	107343 B	00/00/00
				FI	990109 A,V	21/07/00
EP	1091028	A1	11/04/01	US	2002013111 A	31/01/02
US	3607588	A	21/09/71	US	3738884 A	12/06/73
				US	3740302 A	19/06/73
				US	3749633 A	31/07/73
GB	1087087	A	11/10/67	BE	657547 A	23/06/65
				CH	444374 A	30/09/67
				DE	1469429 A	02/01/69
				DK	117014 B	09/03/70
				FR	1418620 A	19/11/65
				IL	22660 A	25/07/68
				LU	47634 A	22/06/65
				NL	127152 C	00/00/00
				NL	6414954 A	24/06/65
				SE	315865 B	13/10/69