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

(11) EP 3 051 021 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.08.2016 Bulletin 2016/31

(21) Application number: **16020011.9**

(22) Date of filing: **15.01.2016**

(51) Int Cl.:
D06M 15/263 *(2006.01)* ***D06M 15/643*** *(2006.01)*
D06M 15/693 *(2006.01)* ***D06M 23/16*** *(2006.01)*
A43C 9/00 *(2006.01)*

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

(30) Priority: **15.01.2015 GB 201500663**

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(54) WATERPROOF LACES AND METHOD

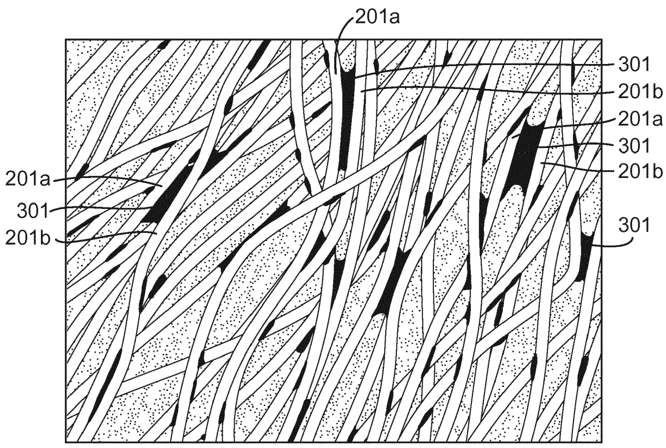
(57) The invention relates to treating cord of braided or woven fibres or fibre bundles, such as shoe laces, string, rope, fabric and textiles to make them waterproof. In particular the invention relates to waterproofing laces using small amounts of an elastic polymer within the lace structure.

A waterproof length of cord such as a shoe lace or rope is disclosed, the cord having a structure formed of a bundle or bundles of fibres, wherein gaps between the fibres in the structure define capillary channels capable of transporting water within the cord structure, the cord further including elastic polymer regions dispersed within the structure, wherein the regions of elastic polymer surround and include portions of neighbouring fibres of the cord structure thereby forming blockages in the capillary channels between the fibres and preventing water transport within the cord structure.

A method of waterproofing a length of cord is also disclosed comprising the steps of soaking the length of cord in a solution of curable pre-polymer and a solvent, causing the solvent to evaporate and causing the pre-polymer to polymerise within the length of cord to form polymer regions dispersed within the structure.

Solutions for use in the method of waterproofing lengths of cord are also disclosed.

Fig. 3



Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND

Field of the Invention

[0001] The invention relates to treating cord of braided or woven fibres or fibre bundles, such as shoe laces, string, rope, fabric and textiles to make them waterproof. In particular the invention relates to waterproofing laces using small amounts of an elastic polymer within the lace structure.

Description of Related Art

[0002] Cords such as shoe laces, boot laces and rope have many uses, including in sports such as running and mountain climbing where it is important that the cord material does not absorb water and become heavy or freeze. Manufacturers of high performance footwear often specify that components such as laces should be waterproof for this reason. However, waterproofing laces is difficult because of the stress they are subjected to during normal use.

[0003] Laces are typically made from bundles of fibres braided together to form the lace structure. In Figure 1, interwoven bundles 101 a, 101b of fibres 102a, 102b, 102c can be seen, as well as cross sections of individual fibres 103a, 103b, 103c. The lace structure includes a significant component of empty space between the fibres, forming capillary channels that can transport water through the material. A "packing factor" can be defined as follows:

$$\text{Packing factor} = \frac{\text{Lace density}}{\text{Fibre density}}$$

[0004] The lace density is the mass of a given length of lace divided by its volume. The fibre density is the mass of a given length of an individual fibre of the lace divided by its volume. The packing factor is a measure of the nominal cross sectional area of the lace occupied by the fibre. A low packing factor, around 0.5, indicates the presence of space in the lace and consequently can mean that it is more flexible. A high packing factor, close to 1, indicates less space and a more rigid lace.

[0005] Cord such as laces and rope can be made of organic material such as cotton, linen or hemp. More commonly synthetic fibres are used such a polyesters (e.g. PET, LCP), nylon, polypropylene, polyethylene, aramids and acrylics. Shoe and boot laces need to be hard wearing because they are subjected to many forces such as abrasion, stretching, folding and twisting, often simultaneously. This poses particular challenges for waterproofing these materials.

[0006] Conventional methods for waterproofing polyester laces use concentrated silicon or fluorocarbon solutions (as described in KR2008010777A) or using PTFE paste (such as US5638589A). These methods rely on filling all the capillaries between the filaments with the chemical compound. However, the above-mentioned methods of waterproofing have numerous problems. For example, the use of relatively concentrated processing solutions (up to 40%) or PTFE paste, respectively, makes these technologies expensive and can be harmful to the environment. Furthermore, laces waterproofed with these techniques increase the packing factor of the lace from 0.5 to around 1, because they waterproof by filling all of the free space in the lace and totally blocking all of the capillaries. This means that they are often too rigid for normal use and can quickly lose their waterproof abilities when they are twisted, bent and stretched during normal use because the waterproofing material can crack and introduce capillaries again.

[0007] Furthermore, typical synthetic fibers cannot be treated with aqueous solutions because such solutions do not wet the fibers sufficiently.

[0008] It is therefore an object of the present invention to overcome the problems existing in the prior art.

SUMMARY OF THE INVENTION

[0009] In an embodiment, there is provided a waterproof length of cord such as a shoe lace or rope, the cord having a structure formed of a bundle or bundles of fibres, wherein gaps between the fibres in the structure define capillary channels capable of transporting water within the cord structure, the cord further including elastic polymer regions uniformly dispersed within the whole structure, wherein the regions of elastic polymer surround and include portions of neighbouring fibres of the cord structure thereby forming blockages in the capillary channels between the fibres and preventing water transport within the cord structure, wherein the increase of the packing factor due to the treatment is between 0.0001 and 0.2. The elastic polymer regions may include bridges of elastic polymer, bridging two or more fibres within the lace structure. The elastic polymer regions within the lace structure may be dispersed within the lace structure such that the ratio of the weight of the elastic polymer to the weight of the lace structure is preferably between 1:5 and

1:10,000.

[0010] The elastic polymer may be a silicone such as polydimethylsiloxane. In this instance the ratio of the weight of the elastic polymer to the weight of the lace structure is preferably between 1:1,000 and 1:10,000, or more preferably around 1:2,000. The errors associated with measuring the weight of laces is large and therefore the weight ratios are approximate and include a large error margin. Alternatively, the elastic polymer may be polymerised from an acrylate where each molecule has between 10 and 15 carbon atoms in its side chain. The acrylate may be lauryl acrylate with 12 carbon atoms in its side chain. In this instance the ratio of the weight of the elastic polymer to the weight of the lace structure is preferably between 1:10 and 1:10,000, or more preferably between 1:100 and 1:1,000.

[0011] The lace structure itself may be made of a material selected from the list of polyester, polypropylene, nylon, polyethylene, aramids or acrylics, or mixtures of these.

[0012] In a further embodiment of the invention, a method of waterproofing a length of cord such as a shoe lace or rope is provided, the cord having a structure formed of a bundle or bundles of fibres, wherein gaps between the fibres in the structure define capillary channels capable of transporting water within the cord structure, the method comprising the steps of soaking the length of cord in a solution, wherein the solution comprises a curable pre-polymer and a solvent, the method further comprising the steps of causing the solvent to evaporate, and causing the pre-polymer to polymerise within the length of cord to form polymer regions dispersed within the structure, wherein the regions of elastic polymer surround and include portions of neighbouring fibres of the cord structure thereby forming blockages in the capillary channels between the cord fibres and preventing water transport within the cord structure, where the ratio of pre-polymer to solvent is between 1 part pre-polymer to 5 parts solvent and 1 part pre-polymer to 10,000 parts solvent and the pre-polymer may form elastic bridges of polymer upon polymerisation within the cord structure.

[0013] The pre-polymer may be cured by heating the cord, so that the final polymerisation of the pre-polymer takes place within the cord structure. The polymer may be a silicone, derived from vinyl-terminated polydimethylsiloxane as a pre-polymer. In this instance, the ratio of pre-polymer to solvent may be between 1 part pre-polymer to 1,000 parts solvent and 1 part pre-polymer to 10,000 parts solvent, or more preferably the ratio of pre-polymer to solvent may be 1 part pre-polymer to 2,000 parts solvent. The polymerisation of the silicone may be catalysed using a platinum based catalyst. Alternatively, the pre-polymer may be an acrylate where each molecule has between 10 and 15 carbon atoms in its side chain, for example lauryl acrylate with 12 carbon atoms in its side chain. In this instance, the ratio of pre-polymer to solvent may be between 1 part pre-polymer to 10 parts solvent and 1 part pre-polymer to 10,000 parts solvent, or more preferably the ratio of pre-polymer to solvent may between 1 part pre-polymer to 100 parts solvent and 1 part pre-polymer to 1,000 parts solvent. The polymerisation of the acrylate may be initiated using AIBN or other radical initiator. The solvent may be selected from the list of pentane, hexane, heptane, isooctane or petroleum ether.

[0014] The solvent may be evaporated and the pre-polymer cured at a temperature of around 110 degrees Centigrade. The solvent may be selected from list of pentane, hexane, heptane, isooctane, dichloromethane, 1,2-dichloroethane, ethyl acetate, isopropyl alcohol or petroleum ether.

[0015] In an embodiment there is provided a waterproofing treatment solution for use in waterproofing lengths of cord, comprising a pre-polymer, a curing agent and a solvent, wherein the pre-polymer is vinyl-terminated polydimethylsiloxane and the ratio of pre-polymer to solvent is between 1 part pre-polymer to 5 parts solvent and 1 part pre-polymer to 10,000 parts solvent. The ratio of pre-polymer to solvent may be between 1 part pre-polymer to 1,000 parts solvent and 1 part pre-polymer to 10,000 parts solvent, or more preferably the ratio of pre-polymer to solvent may be 1 part pre-polymer to 2,000 parts solvent.

[0016] In an embodiment there is provided a waterproofing treatment solution for use in waterproofing lengths of cord, comprising a pre-polymer, a curing agent and a solvent, wherein the pre-polymer is lauryl acrylate and the ratio of pre-polymer to solvent is between 1 part pre-polymer to 10 parts solvent and 1 part pre-polymer to 10,000 parts solvent. The ratio of pre-polymer to solvent may be between 1 part pre-polymer to 100 parts solvent and 1 part pre-polymer to 1,000 parts solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

Figure 1 is a micrograph showing the structure of a cord at the level of individual fibres.

Figure 2 is a schematic representation of the fibres in an untreated lace.

Figure 3 is a schematic representation of the fibres in a treated lace showing regions of the second polymer incorporated in accordance with an embodiment of the invention.

Figure 4 is a schematic representation showing in detail two fibres in a lace joined by a polymer bridge in a resting state.

Figure 5 is a schematic representation showing in detail two fibres in a lace joined by a polymer bridge in an extended state.

Figure 6 is a micrograph showing the structure of a fabric at the level of individual fibres.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0018] The terminology "cord", "lace" and "rope" are used interchangeably within the description and claims because the structure of each is generally the same and therefore embodiments of the invention apply equally to each. The distinction between lace, rope and cord are in terms of scale and generally a lace has a diameter of 5mm to 10mm and a rope 10mm to 50mm, whereas a cord can be of any diameter. The term cord is used in the claims as a general term, which includes lace and rope. The length of the cord, lace or ropes is not significant; laces tend to be short lengths of between 100mm and 1000mm, but are typically manufactured in much longer lengths and cut to size. Embodiments of the invention can be used to waterproof any length of cord, rope or lace.

[0019] Shoe and boot laces are generally not formed of one single solid fibre, but are made from bundles of fine fibres or filaments braided or twisted together. Figure 2 shows in detail the structure of a polyester lace, including individual fibres 201 a, 201 b, 201 c in a bundle. The fibres are generally aligned. This multi-fibre composite construction imparts flexibility and strength to the lace. The composite nature of laces means that the lace structure includes a significant volume of free space, which provides numerous channels which act as capillaries. The capillaries, which can be seen in Figure 2 as reference 202a, 202b, 202c provide passageways for water to be transported within the lace structure under capillary action. While the individual filaments of the lace are relatively hydrophobic, untreated polyester laces absorb water mainly due to capillary forces.

[0020] The "packing factor", given as:

$$\text{Packing factor} = \frac{\text{Lace density}}{\text{Fibre density}}$$

[0021] The packing factor quantifies the free space in a lace. The absolute packing factor depends on the fibre material, fibre diameter, filament count in bundles and the braid, stitch or weave. For a polyester lace, polyester has a density of 1.4 g/ cm^3; a typical lace density for a 12 strand solid braid structure is 0.6 g/ cm^3, giving a packing factor of 0.4. This packing factor indicates the presence of free space in the lace structure, which is space that can absorb water. Conversely, a single polyester filament would have a packing factor of 1.0 because there is no free space within the filament. A low packing factor (i.e. significantly below unity, for example 0.7 or less) is characteristic of flexibility in laces, whereas a high packing factor indicates high filament density and less flexibility.

[0022] A measure of waterproofness for laces is how much of the material's weight in water is absorbed. A typical lace will absorb over 200% of its own weight in water when fully immersed in water or even when just one end is submerged in water, the lace acting as a wick. Conventional waterproofing treatments that fill all of the capillaries with a second material. This is characterised by a packing factor that dramatically increases after treatment, sometimes by over 100%, i.e. the packing factor can increase from a value of 0.3 to around 1.0, an increase of over 300%, where the majority of free space within the lace structure is occupied by a waterproofing material. Laces treated in this way can initially show waterproof qualities, where for example water absorption is around 15% of the weight of the dry lace. However, after mechanical working this can rise to 125% weight of water absorbed in relation to the dry weight of the laces as the waterproofing system breaks down. Conventional waterproofing techniques give very inconsistent results, as some treated laces will be waterproof to a degree after mechanical treatment, but some fail immediately, depending on many variables, including lace structure, fibre type and treatment conditions including the humidity of air. Some treatment methods treat only the surface of the lace, by coating the outer structure of the lace in a waterproofing material, i.e. the overall packing factor remains low because there is free space within the lace structure, but the packing factor at the surface is at or close to unity. Again, the waterproofing of laces produced with this technique will fail with continued use, because the rigid outer surface cracks with continued use, allowing the ingress of water.

[0023] By contrast, a variety of laces treated in accordance with an embodiment of the invention consistently absorb below 2% water by weight after treatment, typically around 1% and remain at 1% absorption of water by weight after prolonged mechanical working. Importantly, the treatment of laces using embodiments of the present invention produces a very low change in the packing factor; changes of 0.1 % are typical. Also, the lace is uniformly treated, not just the surface, so the change in packing factor is consistent throughout the lace structure.

[0024] Treatment of filaments or cords may be achieved in several ways - one is that a new chemical bond is established between the two materials. However, with polyester, this is hard to accomplish because polyester is unreactive. The approach of an embodiment of the invention is to include a second polymer structure interspersed as regions within the primary lace structure. The resulting lace has a more uniform structure as there is no need to find active sites for chemical bonding. The process is faster and the lace has improved mechanical properties.

[0025] An embodiment of the invention provides a lace with regions of a second material added to the lace to block the capillaries. Blocking the channels within the lace structure creates an overall waterproof structure by preventing water transport within the structure. Capillary blocking is achieved by forming bridges between the fibres in the lace structure, as shown in Figure 3. Bridges 301 can be seen bridging fibres 201 a, 201 b.

[0026] The selection of the material of which the bridges are formed is important because the bridging material must stretch and move as the fibres of the lace move during use. To ensure that the bridges remain intact during normal mechanical loading of the lace, the bridging material should be elastic; an elastic polymer is most suited to this application because it can stretch as the lace fibres move in relation to each other when the lace is pulled, twisted or folded. However, not all elastic polymers are suitable for this application. Selection of the second bridging polymer material is dependent on a number of factors. For example, the bridging polymer must be capable of being dispersed within the lace structure at the required concentration. This is achieved by transporting the polymer to the required locations using the capillary channels themselves. As this transport takes place in the liquid phase, the polymer should be soluble in a solvent that does not harm the fibres of the lace structure. Furthermore, the polymer should not clog the channels before it is in place, which necessitates the use of a pre-polymer. Furthermore, when the polymer is in place it should remain there firmly during subsequent use of the lace, which requires transporting the polymer there as a pre-polymer, or curable monomer, and curing it in-situ and evaporating the solvent to form the elastic bridges.

[0027] Another requirement is that, if the lace fibres are non-polar, for example laces made of polyester, the pre-polymer should be non-polar too, so that it is not repelled by the lace structure but incorporates well. Furthermore, the selection of solvent is important because it should be able to wet the lace fibres adequately. An aqueous solution would not be suitable in treating polyester because water cannot wet the hydrophobic polyester filaments and the pre-polymer would not be deposited on the polyester filaments. A further demand of the solvent is that the pre-polymer needs to be soluble in it.

[0028] Another requirement of the bridging polymer is that the pre-polymer is capable of being cured within the lace structure, preferably by heating. UV treatment is unsuitable because the light cannot reach the polymer within the structure.

[0029] Another requirement is that the pre-polymer is capable of being cured within a commercially realistic time frame, i.e. hours rather than days.

[0030] The location and distribution of the bridges within the lace structure is also important. It has been found that the bridges can be widely dispersed within the lace structure and still prevent water transport. This has the advantage that a greatly reduced quantity of the bridging material can be used in comparison to conventional waterproofing techniques. A further advantage is that the physical properties of the lace are not affected, i.e. the lace is not noticeably any more stiff after treatment than before and the lace is not sticky or waxy to the touch. The dispersion of the bridges can be quantified by the change in packing factor before and after treatment, or the change in weight of the lace before or after treatment if the overall volume of the lace does not change appreciably.

[0031] The bridging polymer is incorporated into the lace by dissolving a small amount of curable pre-polymer in a solvent, soaking the lace in this pre-polymer and curing agent solution, then drying and curing the polymer. The concentration of the pre-polymer in the solvent determines the distribution of bridging polymer within the lace structure.

[0032] Pre-polymers that meet the above requirements include elastic monomers. Of particular suitability are acrylates with long alkyl chains. This is counterintuitive because acrylates with long alkyl chains are not conventionally used for waterproofing textiles. In the case of acrylates, ideally the side-chain should be hydrophobic and the best performance is obtained if the number of carbon atoms is in the range of 10-15, with lauryl (C12, linear chain) being preferable. The chain does not have to be linear or cyclic, as branched isomers are suitable, as long as they are hydrophobic and therefore water repellent.

[0033] It is also found that some silicones are suitable as a bridging polymer. This is also counterintuitive because silicone pre-polymers are not conventionally used for waterproofing laces.

[0034] Suitable pre-polymers for the invention are oligomerized acrylates with a long hydrocarbon tail (like lauryl-) and a mixture of vinyl-terminated polydimethylsiloxane and poly(dimethylsiloxane-co-methylhydrosiloxane).

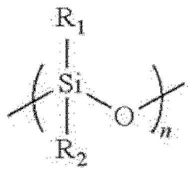
[0035] For siloxanes, a two-part pre-polymer of vinyl-terminated polydimethylsiloxane with poly(dimethylsiloxane-co-methylhydrosiloxane) and platinum catalyst are used without further pre-polymerisation - they are dissolved in hexane and this solution is used for treating laces. Final polymerisation takes place within the lace at a higher temperature which also evaporates the solvent. Conventionally, synthesis of polysiloxanes is carried out without dissolving pre-polymers in any solvent, so it is counterintuitive to dilute the pre-polymer for treating purposes. In the case of polydimethylsiloxanes for use in embodiments of the invention, it is not possible to determine a range of carbon atoms because the material is already polymeric and hydrophobic by nature. The molecular weight can be varied, but usable compounds are restricted by commercial availability.

[0036] Alternatively the vinyl terminated PDMS can be self-polymerised. However, two components are preferable because they generate a network of chains, which allows more control over the properties of the resulting material. The combination of the hydro- and vinyl-terminated PDMS is preferable because the hydrogen atoms of the former join the double bond of the latter, leaving no by-products. The properties can be altered by adjusting the number of the hydro-groups in the polymer chain relative to the dimethyl. In this way the number of crosslinks, and thus the properties, can be altered. The process is preferably performed with a Pt catalyst, but there are alternatives, like tin catalysts or peroxide activation. Further alternatives include using the hydro-PDMS with some Si-OH functional PDMS as well, which are conventionally used on fabric for water repellent coatings.

[0037] A common material for making laces is polyester. An embodiment of the present invention closes the capillaries between polyester filaments in the lace structure by forming numerous local links or bridges between the filaments. The pre-polymer is heavily diluted in a solvent and the lace is soaked in solvent/ pre-polymer solution. The pre-polymer used to form the bridges has a non-polar nature which enables it to interact strongly with polyester filaments while repelling water. As the solvent is evaporated, regions of pre-polymer condense out and begin to polymerise around neighbouring polyester fibres forming a strong covalent bond within the bridge structure and therefore create the crosslink or bridge between the filaments and closing the capillary. The polymer bridges are elastic, so the lace remains soft and holds knots.

[0038] Figure 4 shows in detail a polymer bridge 402 spanning two individual lace fibres 401 a, 401 b. The bridge can be envisaged as a droplet of pre-polymer that condenses out of the solvent as the solvent evaporates, forming a film 402a around each fibre and joining the fibres where the fibres touch, 402b. Figure 5 shows how the bridge can extend as the fibres move away from each other a distance d, which can be up to 10 times their original separation.

[0039] Long chain acrylates ($RO(C{=}O)CR'{=}CH_2$) and polysiloxane



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prepolymers both have a non-polar nature which enables them to interact strongly with the also non-polar polyester filaments. With the final polymerization step, neighbouring prepolymer fragments react with each other, forming a strong covalent bond and therefore creating a crosslink between the filaments and locally closing the capillary.

Therefore any elastic pre-polymer, which has a non-polar nature could be fit for this purpose. It is found that rather dissimilar compounds, such as lauryl acrylate ($C_{12}H_{25}O(C{=}O)CR'{=}CH_2$) and polysiloxanes are suitable for waterproofing laces.

[0040] Laces made from synthetic polymers which have large non-polar regions that can strongly interact with the pre-polymer, are suitable, for example polyester laces with highly hydrophobic properties. Other lace materials can be treated such as polypropylene, nylon, polyethylene, aramids or acrylics, or mixtures of these. Mass increase of the lace, when immersed in water, is less than 2%, which is not diminished during wear. Also, the appearance of the laces does not change during processing and a waterproof lace is visually indistinguishable from a lace that has not been processed. An embodiment of a method according to the invention includes the preparation of pre-polymer solutions, treating textiles with pre-polymers and conducting the final polymerization inside the fabric, creating numerous local bridges between the filaments.

[0041] During the drying and heating phase, capillaries tend to dry last in locations where they are the narrowest and this is where the important part of the final polymer is formed. Some of the second polymer will condense as a film along the filaments only but this is not functional in capillary blocking. Therefore, the drying/fixing phase is important. The pre-polymer is like a film, without another filament nearby, and does not form in isolation away from the lace filaments themselves. For polyester, no chemical bonding takes place between the second polymer and the polyester filament because polyester is inactive chemically.

[0042] The individual filaments are rarely quite parallel. The structure strongly depends on the type of filament used - multifilament and spun polyester look rather different. The filament can also be either round (cross section-wise) or square or something else.

[0043] The elastic polymer regions within the lace structure can be highly dispersed within the lace structure. As an example, the ratio of the weight of the elastic polymer to the weight of the lace structure can be 1:5 but could be as low as 1:10,000. This can be evaluated visually by studying a micrograph of a portion of treated lace and estimating the proportion of elastic polymer in relation to the lace structure. Alternatively, the weights of treated and untreated laces could be compared. This change in weight is a good indicator of the change in packing factor, because the volume of the lace does not change appreciably after being treated. Therefore, a ratio of weight of polymer to weight of untreated lace of 1:5 indicates a change in packing factor of 20%; whereas a ratio of weight of polymer to weight of untreated lace of 1:10,000 means a change in packing factor of 0.01 %. In an embodiment, the ratio of the packing factor of the untreated cord to the packing factor of the treated cord can be between 0.0001 and 0.2. A typical ratio of the weight of the polymer to weight of the untreated lace is between 1:1000 and 1:2000, i.e. treatment of the lace typically causes a change in packing factor of between 0.1-0.2%, or a change in weight of the lace of between 0.1 % and 0.2%.

[0044] The concentration of pre-polymer in solvent ranges depends on the particular lace material and structure. Solubility issues start to limit the maximum concentration of the solution. The ideal concentration of pre-polymer in solution has a lower range and an upper range for a particular lace and bridging polymer. For example, polydimethylsiloxanes (PDMS) can be used at lower concentrations than polyacrylates. If the concentration is too low the lace will not be waterproof but if too high then the physical properties of the lace such as stiffness will be affected. Thus, the concentrations are selected between these extremes so that the procedure is general enough for a wide variety of laces.

[0045] Suitable solvents for treating polyester laces include low boiling point alkanes like pentane, hexane, heptane, isooctane, dichloromethane, 1,2-dichloroethane, ethyl acetate, isopropyl alcohol or petroleum ether. Hexane is preferable.

[0046] In particular, for PDMS based treatment, the most diluted that works is 1 part PDMS to 10,000 parts hexane as solvent. The most concentrated is 1:5 but increased stiffness is observed. An ideal range is around 1:1,000 to 1:10,000. For lauryl acrylate, at 1 part pre-polymer to 10 parts solvent the laces are slightly oily to the touch. At the other end of the concentration range, 1: 1000 works well but can be up to 1:10,000. Below this concentration, the result depends on the particular lace material. For example, spun polyester requires higher concentrations than regular textured/multifilament polyester, differences are also observed depending on the structure of the lace for example between flat laces (empty braided tube) and round laces (filled braided tube), and also lace thickness.

<u>Example 1: PDMS treatment of polyester lace: Use of polysiloxanes as pre-polymers.</u>

Step 1: Preparation of Solution 1, concentrated 1:10 polysiloxane stock solution:

[0047] To a tightly sealable Erlenmeyer flask 375-440 (preferably 425) parts by weight of vinyl-terminated polydimethylsiloxane pre-polymer,

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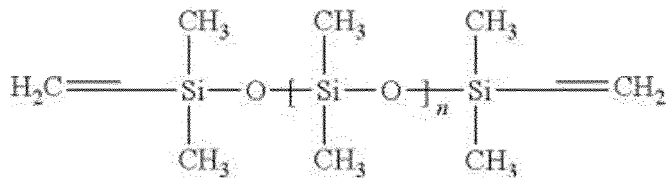
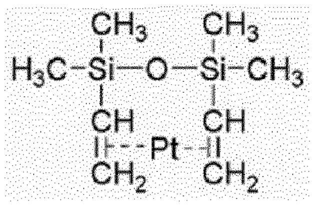
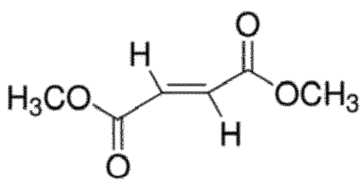


is added to 1 part by weight of catalyst 0.005-0.1 M (preferably 0.05M) platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution



and 2 to 12 parts (preferably 4 parts) by weight of polymerization inhibitor 0.005-0.1 M (preferably 0.05M) dimethylfumarate

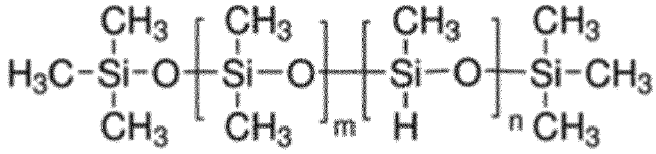


in solution in ethyl acetate.

[0048] Previously weighed components are dissolved in 500 to 5,000 parts (preferably 5,000 parts) by volume of n-hexane at room temperature.

60-125 (preferrably 75) parts by volume of poly(dimethylsiloxane-*co*-methylhydrosiloxane)

[0049]



which contains 3-4% of methylhydrosiloxane fragments, is added to the solution and agitated until the poly(dimethylsiloxane-co-methylhydrosiloxane) is completely dissolved.

Step2: Preparation of Processing Solution

[0050] Into a suitable stainless steel or glass container 1 part of Solution 1 is mixed with 0-999 parts (199 parts is optimal considering both the economical aspect and quality of the final product) of n-hexane or petroleum ether (bp 40-65 °C) and stirred.
This step is separately described because it is found that a more concentrated solution is more stable over time. Therefore Solution 1 can be prepared in advance and the final Processing Solution is prepared when it is required. Alternatively, the final Processing Solution can be prepared in Step 1 by dissolving components mentioned in Step 1 in 1,000,000 parts solvent, and omitting Step 2.

Step 3: Lace Treatment

[0051] Into the Processing Solution is submerged appropriate quantity of polyester lace (4 meters of lace per 1 litre of solution) and the solution with the lace stirred or otherwise agitated for 5 minutes at between 10 and 40 deg C (preferably room temperature) for 2 to 10 minutes (preferably 5 minutes), depending on quantity of the lace.

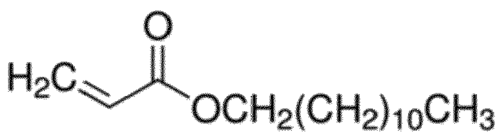
Step 4: Lace Drying and Curing

[0052] The lace is taken out of the solution, slightly drained, centrifuged at low rpm's (500-1000) for 0.5-2 minutes (again, depending on lace quantity) and put into drying cabinet at 80-130 °C, (preferably 100-110 °C) for 3 to 24 hours, depending on lace quantity and the solvent used.
[0053] Costs and environmental impact can be reduced by reclaiming the solvent. The solvent can be reclaimed by ventilating the drying cabinet, collecting the outflow from the drying cabinet and condensing the solvent from the vapour phase.

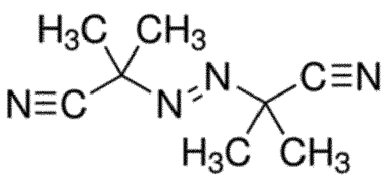
<u>Example 2: Using long-chained oligoacrylates as prepolymers</u>

Step 1: Preparation of Solution 2, 1% oligomerized lauryl acrylate solution To 10 to 1000 parts (preferably 100 parts) by weight of lauryl acrylate

[0054]



is mixed 1 part of the polymerization initiator AIBN



in a suitable glass container. Components are stirred for 15 seconds by shaking the flask lightly. The solution is put into a preheated drying closet (110 °C) and kept there for 5-120 minutes depending on the solvent used. The flask is taken out of the drying closet and allowed to cool. The resulting solution contains partially polymerized lauryl acrylate.

[0055] The solution is then dissolved in 900-99900 parts (9900-99900 parts preferably) of suitable solvent (dichloromethane, 1,2-dichloroethane, ethyl acetate, isopropyl alcohol or hexane). The mixture is stirred intensively using a magnetic stirrer for 15 minutes or until most of the oligomerized lauryl acrylate is dissolved (some of the acrylate may remain insoluble).

Step 3: Treatment of laces

[0056] Into Solution 2 an appropriate quantity (4 meters per 1 litre of solution) of polyester lace is submerged and stirred or agitated for 15-45 minutes. After that, the lace is taken from the solution, hung from a thin metal rod and put into a preheated drying closet (110 °C) for 24-72 h. In this drying step, the lace should have minimal contact with the walls of the drying closet. Also self contact (overlapping) of the lace should be minimized.

[0057] The pre-cursors vinyl-terminated polydimethylsiloxane pre-polymer, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane, dimethylfumarate and poly(dimethylsiloxane-co-methylhydrosiloxane), lauryl acrylate, AIBN and solvents are all available commercially from suppliers such as Sigma Aldrich.

[0058] From above it can be seen that the ranges of usable solution concentration are large. The exact concentration within these ranges is not critical to the success of the waterproofing treatment.

[0059] The above description is directed towards the treatment of a shoe or boot lace. However, the invention could work with string, rope, cord, thread or yarn or any composite line made by braiding, twisting or plaiting these components together. The invention works by blocking capillary channels between bundles of fibres and therefore wherever there are bundles of fibres, for example in fabrics and textiles, this treatment method could be applied. Fabrics are not subject to the same extreme use cycles as laces, therefore other waterproofing treatments are effective, such as applying a waterproof coating to the exterior of the fabric. However, the present treatment method can be used on fabrics. Figure 6 shows a detailed view of a conventional fabric, where bundles 601 a, 601 b of interwoven fibres 602a, 602b, 602c can be seen.

[0060] An embodiment of the invention includes treating textiles with prepolymers (such as long-chain polyacrylates and polysiloxanes) and conducting the final polymerization inside the fabric, which closes the capillaries by forming numerous local crosslinks or bridges between the filaments. These local bridges are resistant to twisting and bending while maintaining the flexibility of the lace structure. Also, the consumption of chemicals is significantly lower compared to technologies which presume the filling of all the capillaries.

[0061] The invention can be used to treat natural fibres such as cotton or hemp. As these materials are typically far more hydrophilic than synthetic polymers, the approach needs to be adjusted. The solvent system has to be changed, due to the more hydrophilic nature of the fibre surface. For example, alcohols with a hydrophobic chain could be used. Also, pretreatment is needed, as natural fibres tend to store moisture. The pre-polymer itself has to be altered, as there is the option of binding the pre-polymer to the fibres by means of covalent bonding depending on conditions. For example, as cellulose contains -OH groups, esterification with carboxylic acids, their salts, acid anhydrides, etc could be used, all with a hydrophobic tail to facilitate the waterproofing.

[0062] Definitions:

POLYESTER (PET): A manufactured fibre in which the fibre-forming substance (polyester) is characterized by a long chain polymer having 85% by weight of an ester of a substituted aromatic carboxylic acid. The most frequently used acid is terephthalic acid in the presence of ethylene glycol.

NYLON (PA): A manufactured fibre in which the fibre-forming substance (polyamide) is characterized by recurring amide groups as an integral part of the polymer chain. The two principal types of nylon fibre used in rope production are type 66 and type 6. The number six in the type designation is indicative of the number of carbon atoms contained in the reactants for the polymerization reaction.

POLYETHYLENE: An olefinic polymer produced from by the polymerization of ethylene gas, and used in the production of manufactured fiber. Polyethylene is similar to polypropylene in its properties but has a higher specific gravity and a lower melting point.

POLYMER: A long chain molecule from which man-made fibres are derived; produced by linking together molecular units called monomers.

PRE-POLYMER: refers to a monomer or system of monomers that have been reacted to an intermediate molecular mass state. This material is capable of further polymerisation by reactive groups to a fully cured high molecular weight state. As such, mixtures of reactive polymers with un-reacted monomers may also be referred to as pre-polymers. The term "pre-polymer" and "monomer" may be interchanged.

POLYMERIZATION: A chemical reaction resulting in the formation of a new compound whose molecular weight is a multiple of the reactants; involving a successive addition of a large number of relatively small molecules (monomers) to form the polymer. The term "curing" also refers to polymerization.

POLYPROPYLENE (PP): An olefinic polymer produced by the polymerization of propylene gas, and used in the production of manufactured fibre. Polypropylene may be extruded into a number of fibre forms for use as ropes or cords.

Claims

1. A waterproof length of cord such as a shoe lace or rope, the cord having a structure formed of a bundle or bundles of fibres, wherein gaps between the fibres in the structure define capillary channels capable of transporting water within the cord structure,
characterised in that the cord further includes elastic polymer regions uniformly dispersed within the structure, wherein the regions of elastic polymer surround and include portions of neighbouring fibres of the cord structure thereby forming blockages in the capillary channels between the fibres and preventing water transport within the cord structure, wherein the inclusion of the elastic polymer regions increases the packing factor of the bundle of fibres by between 0.0001 and 0.2.

2. A waterproof length of cord in accordance with claim 1, wherein the ratio of the weight of the elastic polymer to the weight of the untreated lace structure is between 1:5 and 1:10,000.

3. A waterproof length of cord in accordance with claim 1 or 2, wherein the elastic polymer is a silicone.

4. A waterproof length of cord in accordance with claim 3, wherein the elastic polymer regions within the lace structure are dispersed within the lace structure such that the ratio of the weight of the elastic polymer to the weight of the lace structure is between 1:1,000 and 1:10,000.

5. A waterproof length of cord in accordance with claim 1 or 2, wherein the elastic polymer is polymerised from an acrylate where each molecule has between 10 and 15 carbon atoms in its side chain.

6. A waterproof length of cord in accordance with claim 5, wherein the elastic polymer regions within the lace structure are dispersed within the lace structure such that the ratio of the weight of the elastic polymer to the weight of the lace structure is between 1:10 and 1:10,000.

7. A waterproof length of cord in accordance with any preceding claim, wherein the lace structure is made of a material selected from the list of polyester, polypropylene, nylon, polyethylene, aramids or acrylics, or mixtures of these.

8. A method of waterproofing a length of cord such as a shoe lace or rope, having a structure formed of a bundle or bundles of fibres, wherein gaps between the fibres in the structure define capillary channels capable of transporting water within the cord structure, comprising the steps of soaking the length of cord in a solution, wherein the solution comprises a curable pre-polymer and a solvent, the method further comprising the steps of causing the solvent to evaporate, and
causing the pre-polymer to polymerise within the length of cord to form polymer regions dispersed within the structure, wherein the regions of elastic polymer surround and include portions of neighbouring fibres of the cord structure thereby forming blockages in the capillary channels between the cord fibres and preventing water transport within the cord structure, **characterised in that** the ratio of pre-polymer to solvent is between 1 part pre-polymer to 5 parts solvent and 1 part pre-polymer to 10,000 parts solvent and the pre-polymer is elastic and forms elastic bridges of polymer upon polymerisation within the cord structure.

9. A method of waterproofing a length of cord in accordance with claim 8, wherein the pre-polymer is cured by heating the cord such that the final polymerisation of the pre-polymer takes place within the cord structure.

10. A method of waterproofing a length of cord in accordance with claims 8 to 9, wherein the solvent is selected from list of pentane, hexane, heptane, isooctane, dichloromethane, 1,2-dichloroethane, ethyl acetate, isopropyl alcohol or petroleum ether.

11. A method of waterproofing a length of cord in accordance with claims 8 to 10, wherein the polymer is a silicone.

12. A method of waterproofing a length of cord in accordance with claim 11, wherein the ratio of pre-polymer to solvent is between 1 part pre-polymer to 1,000 parts solvent and 1 part pre-polymer to 10,000 parts solvent.

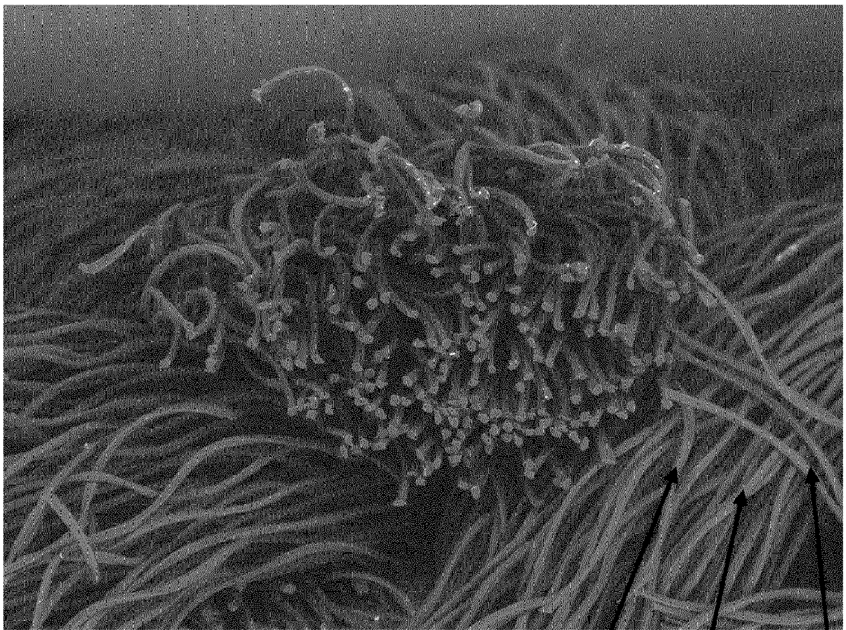
13. A method of waterproofing a length of cord in accordance with claims 8 to 12, wherein the pre-polymer is an acrylate where each molecule has between 10 and 15 carbon atoms in its side chain.

14. A method of waterproofing a length of cord in accordance with claim 13, wherein the ratio of pre-polymer to solvent is between 1 part pre-polymer to 10 parts solvent and 1 part pre-polymer to 10,000 parts solvent.

15. A method of waterproofing a length of cord in accordance with claims 8 to 14, wherein the polymerisation of the acrylate is initiated using AIBN.

Fig. 1

101b



101a

102a 102b 102c

Fig. 2

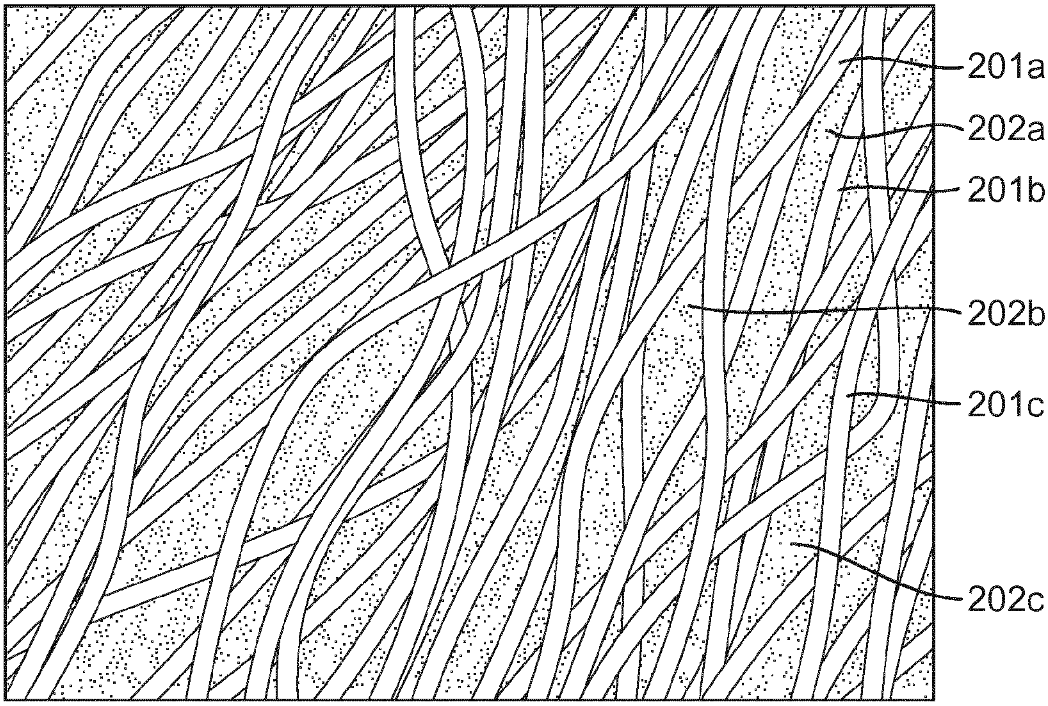

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Fig. 3

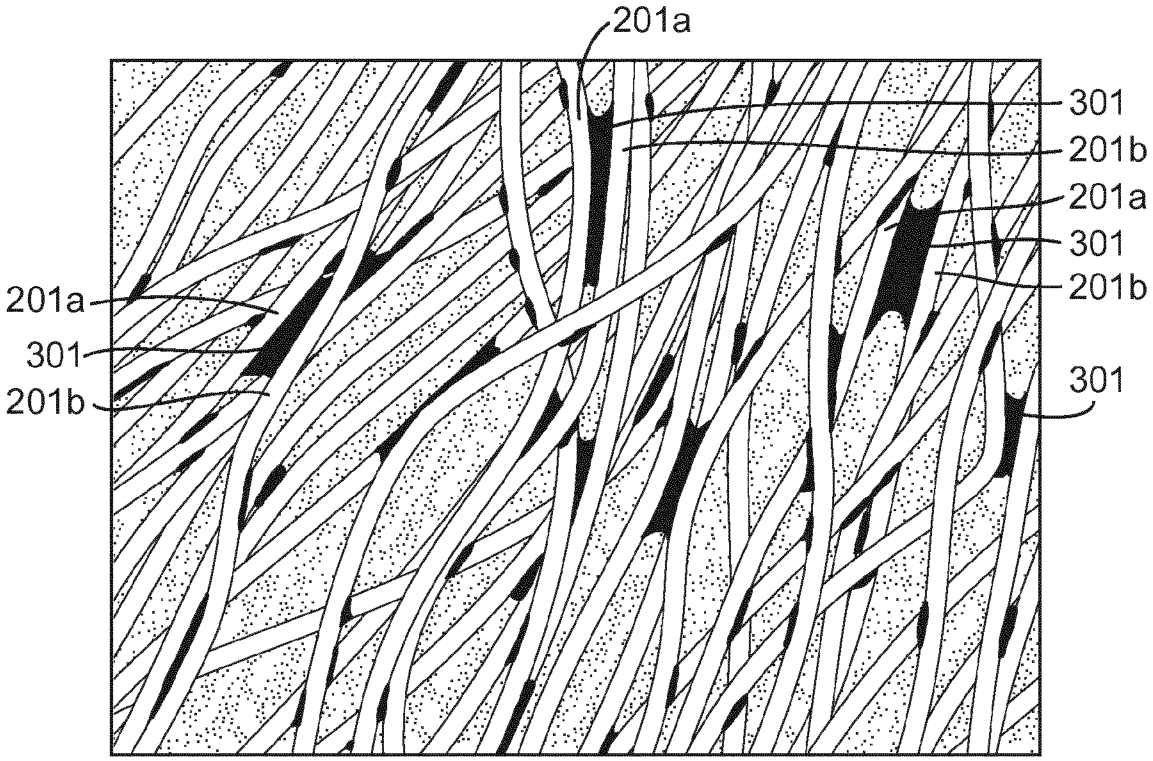
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Fig. 4

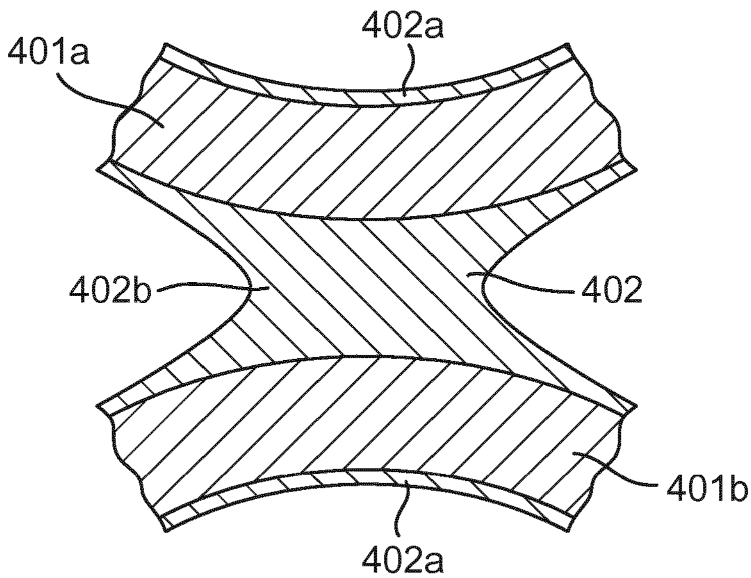


Fig. 5

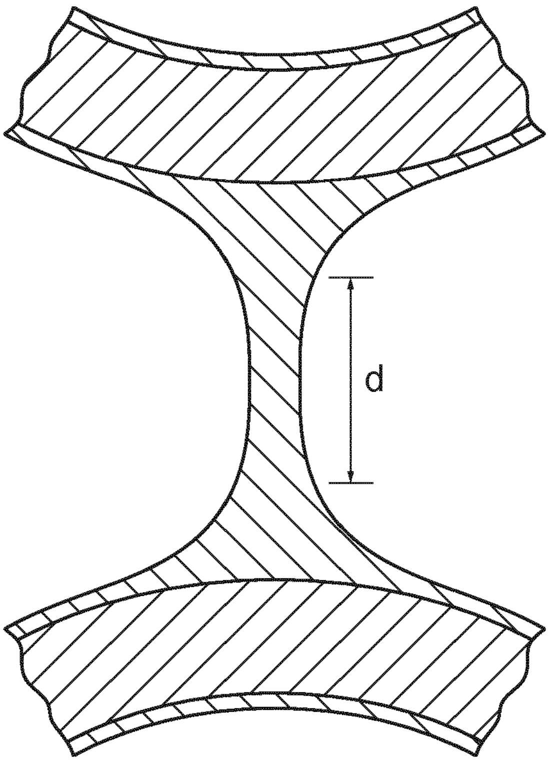
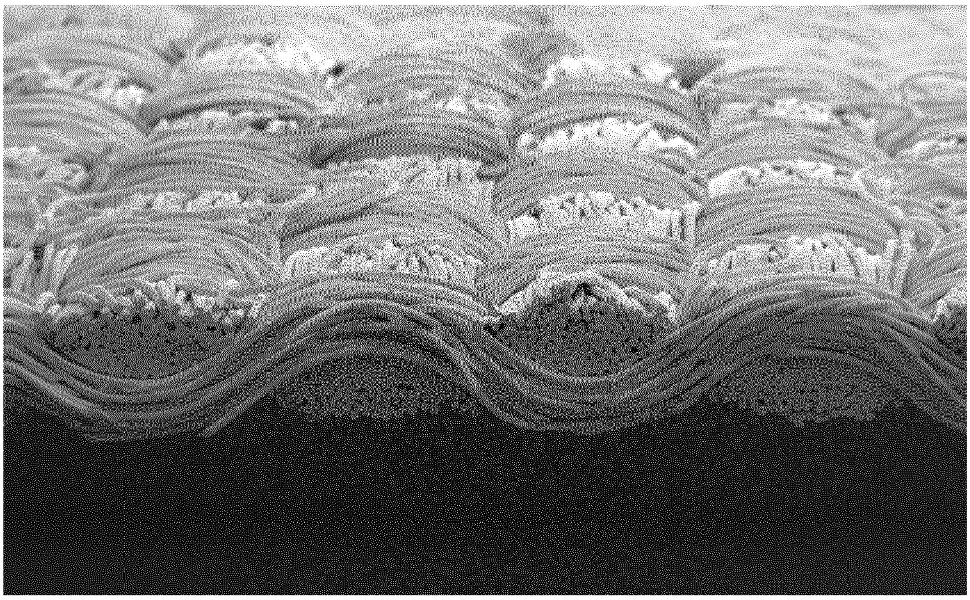


Fig. 6



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EUROPEAN SEARCH REPORT

Application Number
EP 16 02 0011

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	29 June 2016	Rella, Giulia

CATEGORY OF CITED DOCUMENTS

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