(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number
WO 01/12000 A1

(51) International Patent Classification[7]: A41D 31/00, D04H 13/00, D06N 7/00

(21) International Application Number: PCT/US00/21963

(22) International Filing Date: 11 August 2000 (11.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/374,590 13 August 1999 (13.08.1999) US

(71) Applicant: GORE ENTERPRISE HOLDINGS, INC. [US/US]; 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714-9206 (US).

(72) Inventors: TRAPP, Benjamin, M.; 14 Belfort Loop, Newark, DE 19702 (US). HANNON, Greg, E.; 26 Bristol Lane, Newark, DE 19711 (US).

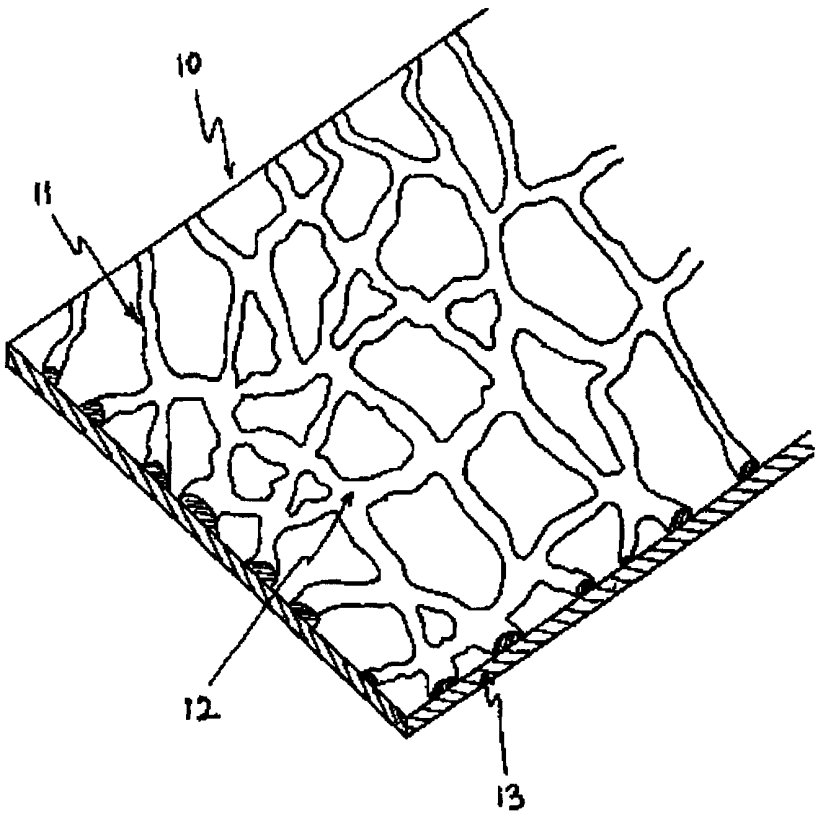
(74) Agents: CAMPBELL, John, S. et al.; W. L. Gore & Associates, 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714-9206 (US).

(81) Designated States *(national)*: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

[Continued on next page]

(54) Title: WATER VAPOR PERMEABLE COMPOSITE MATERIAL



(57) Abstract: The invention is a layered composite material made of a water resistant, water-vapor-permeable flexible substrate (13) in which one side of the substrate is provided with an abrasion resisting layer (11) made up of a plurality of abrasion resisting ribbons. The ribbons prevent abrasion of the flexible substrate. The material is useful in garment applications.

WO 01/12000 A1

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.

TITLE OF THE INVENTION
WATER VAPOR PERMEABLE COMPOSITE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a flexible water-resistant, water-vapor-permeable layered composite material, particularly for use in garments, which exhibits a combination of good breathability (i.e. water vapor transmission) and good durability.

BACKGROUND OF THE INVENTION

Water-resistant materials which resist liquid water penetration are well known to persons skilled in the art of making rainwear. It is of benefit to have the material also be water-vapor-permeable so that perspiration from the wearer's body can escape from within the garment by passage through the material, thus preventing build-up of liquid water within the garment and consequent clammy feeling. In order to be considered water-vapor-permeable, a flexible material should generally have a water-vapor-permeability of at least 1,000, preferably greater than 1500 and more preferably greater then 3000 $g/m^2/day$. However, values in excess of 100,000 $g/m^2/day$ are possible with certain materials.

Water-vapor-permeable materials which can be used in garments and which are resistant to liquid water penetration are known from U.S. patents 3,953,566 and 4,194,041 (W.L. Gore & Associates Inc.). U.S. Patent No. 3,953,566 describes the production of an expanded porous polytetrafluoroethylene (PTFE) membrane. The expanded porous PTFE has a micro-structure characterized by nodes interconnected by fibrils. Such membranes may be susceptible to abrasion and to clogging of the pores by body oils. U.S. Patent No. 4,194,041 discloses a material which comprises a porous membrane (particularly expanded PTFE) provided on one surface thereof with a continuous layer of a film or coating which is water-vapor-permeable. Certain polyurethanes can transport water-vapor molecules through the film or coating by absorbing individual molecules on one side of the film and desorbing or evaporating them on the opposite side. The film does not allow passage of gases or liquids through it. Thus, the film or coating is selective in passing water molecules (hence the designation "hydrophilic"), but retard passage of surface active agents and organic oils (such as may be found in perspiration). This film protects the membrane from body oil penetration. The film or coating is commonly referred to as hydrophilic film or coating. The membrane and film or coating together form a laminate or

substrate, which is referred to hereinafter as a water-resistant, water vapor permeable composite. If desired, the water-resistance may be enhanced by impregnating the expanded PTFE with a hydrophobic impregnant (such as a perfluoro compound or, for example, a perfluoroalkyl acrylate or methacrylate) polymer. Such impregnants are usually also oleophobic. The impregnants can coat the nodes and fibrils of the porous PTFE as described in 5,375,441.

Such water resistant, water vapor permeable composite is susceptible to abrasion and may be abraded or delaminated when subjected to abrasive forces. To protect against such abrasion, the composite is often laminated to an inner fabric liner which protects the polyurethane film side of the material against abrasion in use. The preformed liner is generally laminated to the polyurethane film face by means of a layer of adhesive. However, the liner adds to the cost, weight and bulk of the material. Moreover, the adhesive, if not water vapor permeable, cuts down the water vapor transmission rate (MVTR). But, if this liner is not used, the soft hydrophilic polyurethane is exposed directly to abrasive forces.

Henn U.S. Patent No. 5,026,591 describes the use of polyurethane film or coating as the adhesive. Henn teaches coating a scaffold material, such as expanded PTFE or microporous polypropylene, with a continuous coating of a hot melt hydrophilic polyurethane or polyurethane acrylate and embedding directly into the coating a protective material (a polyamide non-woven, a polycotton woven blend etc.) which protects the polyurethane from abrasion..

Non-woven fabrics, comprised of a random array of fibers, have also been used to afford protection to the hydrophilic polyurethane layer. Dailey U.S. Patent 5,036,551 teaches the use of such layer used to create elastomeric composite fabrics. A problem with using such non-woven fabrics is that these are typically very weak against abrasion forces primarily due to their structure. Typically non-woven fabrics consist of a random array of fibers weakly held together by physical entanglements, binders or heat bonding. In its laminated form, only a part of the fibers are bonded to the substrate. As a result, when the non-woven fabric of the laminate is abraded, the loosley bonded fibers are easily detached and create defects such as holes, pills, etc.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide good abrasion resistance to water-resistant, water-vapor-permeable composites described above, without the need for a laminated protective liner.

According to the present invention there is provided a layered composite comprising

(a) a flexible substrate selected from the class consisting of polymeric membranes and polymeric films, having a first and second side; and

(b) a porous web of polymeric ribbons arranged with a number of crossover points over the surface of at least one side of the substrate, said ribbons substantially adhered to said surface substantially along their length, and said ribbons being coalesced at least at crossover points; said composite being water-resistant and water-vapor-permeable.

The composite should have a resistance to abrasion of at least 15,000 rub cycles without leakage as determined by the Martindale abrasion resistance test. According to a further aspect of the present invention, the composite material is embodied in articles of clothing such as hats, gloves, shoes, jackets, coats, trousers or the like.

According to a still further aspect of the present invention, there is provided product and a process of producing a composite lining material for a garment or the like comprising securing a fabric to a first side of the flexible, water-resistant, water-vapor-permeable substrate, and applying in a random fashion by meltblowing or spunbonding abrasion-resisting polymeric strands to a second side of said substrate in order to form a discontinuous pattern over the surface of said second side, followed by heating to melt and coalesce the filaments to form ribbons.

Thus, the present invention provides an abrasion-resisting layer over the flexible substrate material so as to provide a protective surface layer which protects the water-vapor-permeable flexible substrate from abrasion forces in a particularly lightweight, convenient and economical manner. It has been surprisingly found that the application of the porous web, comprising a web of polymeric ribbons is in itself sufficient to provide abrasion resistance and durability, without the need to apply a conventional inner liner. The polymeric ribbons constitute the surface layer of the composite material and is preferably the layer which is innermost when the material is used to form a garment; that is to say it is the surface layer which is closest to the skin of the wearer. It has been surprisingly found that the web pattern of the ribbons, while providing the necessary moisture vapor permeability, is sufficient to resist abrading of the material during flexing thereof, both against itself and against any other materials which may be present (for example other garments worn by the wearer). Alternatively, this abrasion resisting layer could also be used as the exterior layer of a garment.

DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic drawing depicting a product of the invention.

Fig 2 is an SEM of an inventive product taken at 50x depicting a porous web on a substrate before application of heat.

Fig. 3 is an SEM of an inventive product taken at 50x depicting a porous web of ribbons on a substrate prepared by heating a web like those shown in Fig. 2 above their softening point for 15 second.

Fig 4 is an SEM of an inventive product taken at 300x depicting a porous web on a substrate before application of heat.

Fig. 5 is an SEM of an inventive product taken at 300x depicting a porous web of ribbons on a substrate prepared by heating a web like those shown in Fig. 4 above their softening point for 15 seconds.

Fig. 6 is an SEM of an inventive product taken at 50x depicting a porous web of ribbons on a substrate after heating above the softening point of the web material for 5 seconds.

Fig. 7a and 7b are SEMs of the heat treated product of Example 1 taken at 50X and 300X respectively.

DEFINITIONS

"Porous Web" means a network of filaments or a network of ribbons in which the network of filaments or ribbons cross over one another and are spaced so as to leave open spaces.

"Planar" means flat or lying in one plane.

"Continuous" means essentially unbroken.

"Flexible" means bendable without breaking.

"Water Resistant" means that the material in question passes the water resistance test described further below.

"Water Vapor Permeable" means that the material in question has a water vapor permeability of at least 1000 $g/m^2/day$

"Durable" or "Durability" means that the material in question is abrasion resistant.

"Garment" means any article that can be worn.

"Fabric" means a planar textile structure produced from fibers.

"Coalesced" means merged to the point that individual identity is lost.

"Microporous" means a structure not visible to the naked eye.

"Ribbon" means a narrow strip.

"Porous" means full of passages or channels.

By "Substantially Adhere" is meant that two materials are attached, i.e., stuck together.

By "membrane" is meant a material that is microporous.

DETAILED DESCRIPTION OF THE INVENTION

The composite material comprises a liquid water-resistant, water-vapor-permeable flexible substrate selected from the class consisting of polymeric films and polymeric membranes, having adhered to at least one side of the substrate, an abrasion-resisting layer made up of a plurality of ribbons of an abrasion-resisting polymeric material such as an abrasion-resisting polyurethane. In one embodiment a protective fabric may be adhered to the other side.

Any flexible polymeric film or membrane suitable for use in fabrics may be used as the substrate. Preferably it will be a microporous membrane, such as a membrane of a high molecular weight polyethylene or polypropylene or polyurethane.

A preferred substrate is composed of an expanded polytetrafluoro-ethylene (ePTFE) membrane as disclosed in aforementioned US Patent No. 3,953,566 which has a porous microstructure, i.e., microporous, characterized by nodes interconnected by fibrils. The membrane is resistant to passage of liquid water therethrough but is water-vapor-permeable. The membrane preferably has a weight between 1 and 100 grams per square meter. The water-vapor permeability of the flexible composite material of the present invention will usually be at least 1,000 or 5,000 to 12,000 g/m^2/day or up to 30,000 or 50,000 g/m^2/day for certain substrates.

In a substrate containing ePTFE, the ePTFE can be impregnated with a hydrophobic impregnant (such as a perfluoro compound or, for example, perfluoroalkyl acrylate or methacrylate polymer.)

In a preferred substrate, the substrate is a composite of the material previously described, especially ePTFE, that has on it a continuous, nonporous layer of the hydrophilic film or coating of a water-resistant, water vapor permeable material described previously, such as a water-vapor-permeable monolithic polyurethane of the type disclosed in aforementioned US

Patent No. 4,194,041 The continuous water vapor permeable polymer layer is a hydrophilic polymer in the sense that it transports water molecules and will be referred to herein as a hydrophilic polymer. The hydrophilic layer selectively transports water by diffusion, but does not support pressure driven liquid or airflow. Therefore, moisture, i.e., water vapor, is transported but the continuous layer of the polymer precludes the passage of such things as air-borne particles, microorganisms, oils, or other contaminants. This characteristic imparts to the fabric good contamination control. Furthermore the water vapor transmitting characteristics of the material allow for comfort characteristics to the wearer.

The continuous water vapor permeable polymer layer is typically of a thickness of between 5 μm to 38 μm, preferably between about 10 μm to 20 μm.

The continuous, water vapor-permeable polymers most useful herein, although not limited to, are those of either the polyurethane family or the copolyether ester family. Suitable copolyether ester hydrophilic compositions may be found in the teachings of U.S. Pat. No. 4,493,870 to Vrouenraets and U.S. Pat. No. 4,725,481 to Ostapachenko. Suitable polyurethanes may be found by way of example in the teachings of U.S. Pat. No. 4,194,041 to Gore and in PCT publication 90/00180 to Sakhpara. Typically these materials comprise a composition having a high concentration of oxyethylene units to impart hydrophilicity, typically greater than 45% by weight of the base polymer, preferably greater than 60%, most preferably greater than 70%. The most preferred polyurethanes useful herein are those where the polyol is a poly(oxyethylene) glycol, and the isocyanate is a diisocyanate.

In another embodiment, the substrate can be the continuous, nonporous hydrophilic material itself.

Another preferred substrate will have a continuous, water vapor permeable polymer coating described in the previous paragraph on an ePTFE substrate with the hydrophobic impregnant described in US Patent No. 5,375,441.

When the substrate comprises an ePTFE membrane that has the continuous layer of hydrophilic polyurethane film or coating described above, the abrasion-resistant ribbons are preferably adhered to the continuous layer of hydrophilic polyurethane. This does away with the need for an inner protective liner when the composite is used in garment constructions.

A fabric may be laminated to one side of the substrate by any conventional means. The fabric can be one of a number of known fabrics such

as a woven, non-woven or knitted fabric of a material such as nylon or polyester. In use, the fabric may constitute the outer surface of a garment formed from the composite material and provides the required visual or aesthetic appearance and the necessary mechanical properties.

Referring now to Fig. 1, the schematic drawing of the invention, the abrasion-resistant composite 10 formed in the present invention is seen to be a porous web of polymeric ribbons 11 randomly arranged with a number of crossover points 12 over the surface of one side of substrate 13. The ribbons are substantially adhered to the substrate, and are substantially coalesced at least at cross over points. The porous web is substantially planar.

A porous web of strands is first laid down on the substrate in any one of several ways. When a relatively high melt viscosity thermoplastic polymer is used, processes such as meltblowing and spunbonding are advantageous. In these processes, strands from the polymer melt are attenuated using controlled air streams and then deposited in a random pattern on the substrate. Polymer selection is dependent upon the rheology of the melt and will effect both the economics of the processes and the window or ease of processability. For meltblowing, polymers with a low melt viscosity at relatively low temperatures can also be used. Thermoplastic polymers which are common to both processes are as follows: polyamides, polyesters, polypropylenes, polyethylenes, polyurethanes, and the like.

If the melt or ambient viscosity is low enough, the polymer may lend itself to other production methods which will adequately deposit strands on the substrate. For example, in the form of a regular structure, e.g., a grid; or random. These processes are those typically associated with the printing or hot melt adhesive field. They include, but are not limited to, meltblowing, screen or gravure printing, starved die extrusion, etc. In many cases, the class of polymer used in these processes will not have adequate physical properties for the intended application. In these cases, it may be beneficial to use a post curing reactive polymer to build physical properties of the polymer following application. Polymers which lend themselves to these applications include polyurethanes, polyesters, silicones, acrylics, and polyvinylchlorides.

Selection of the appropriate polymer for a given abrasion resistance will be dictated by the end use requirements and the production methods available. In general, polyurethanes are known to be excellent in resisting abrasion which make them ideal materials for applications requiring a high level of abrasion resistance from the polymer layer. In addition, they can be formulated to yield a high degree of softness, making them excellent candidates where the handle of the finished composite is of concern. However, instances may arise where it

becomes beneficial to use an entirely different class of polymers. In these cases, the structure of the abrasion resisting layer of this invention will still work to provide a relative level of abrasion resistance. Additives may also be used to enhance other properties or to further increase the abrasion resistance, and may be used in conjunction with any of the aforementioned processes to provide a suitable or in some instances superior product. Examples of such materials include pigments, dyes, slip agents, UV inhibitors, oil repellants and the like. Finally, polymer selection will also be affected by the type of substrate the abrasion resistant layer is being applied to. In instances where the substrate is monolithic or presents a nonporous surface, it is usually best to select a polymer to provide chemical compatibility between the web layer and the substrate, allowing for a sufficient bond. In cases where the substrate is porous and allows for mechanical bonding, it may be beneficial to tailor the rheology and surface characteristics of the filaments to allow for sufficient wetting and/or pore penetration. Instances may also arise where the substrate will allow for both mechanical and chemical bonding.

The web polymer may itself be water-vapor-permeable. This, however, is generally not necessary provided that the percentage coverage of the substrate material surface is not too great to substantially affect the water-vapor-permeability thereof.

Due to the nature of meltblowing or spunbonding, the porous web forming polymer is usually laid down on the substrate in the form of strands, as shown in Figs. 2 and 4. A subsequent heating step is carried out at a temperature above the softening point of the polymer to cause the strands to flow and spread to form the planar coated ribbon structures shown in Figs. 3 and 5. The heating is most conveniently carried out in an oven. However, if the viscosity of the polymer is low, the ribbon structure may form on the substrate without any further application of heat.

The pattern of web ribbons in the form of polymeric ribbons coalesced at their junctions is discontinuous in the sense that it includes open areas on the surface of the substrate free of polymeric material. Generally, the percentage coverage of the surface of the flexible substrate by the polymeric ribbons is in the region 20-80%, particularly 30-70%, more especially 40-60% by area. It will be appreciated that the spacing between the ribbons should not be so great as to permit ready access to open areas whereby abrasion of these open areas may occur.

The ribbons need not exhibit a high degree of coalescing at the ribbon to ribbon intersections, but it has been found that to provide the maximum abrasion resistance and best adherence to substrate, coalescing is preferred.

It is understood that if the polyurethane of choice is limited in its hydrophilicity, the degree of coalescing and the percentage of surface area covered will be a large factor affecting the moisture permeability of the resulting composite material. The add-on weight will be 2-30 g/m^2, preferably 5-15 g/m^2.

Meltblowing is one method available to apply a polymeric, porous web. To form melt blown webs, a strand forming polymer is extruded from an extruder that can have one orifice or multiple orifices directly into convergent high velocity heated air streams to produce fine strands. The melt blown strands are deposited on the moving substrate in an entangled, random fashion and are then fused to form a coherent coalesced porous web of ribbons. Fig. 2 and Fig. 4 show strands deposited directly onto the substrate. It can be clearly seen that the degree of coalescing and the degree of adherence to the substrate can be furthered by subsequent heating (Fig. 3 and Fig. 5) above the softening point. It is also seen in Fig. 6 that an intermediate time of heating displays an intermediate degree of coalescing and adherence to the substrate. Heating times may be as little as a few seconds, e.g., 3 to 5 seconds or can be longer, e.g., 15 to 20 seconds or more.

The web forming polymer is preferably chosen to be compatible with the substrate surface so that the web readily adheres to the substrate surface as they are laid down or as later heated. Examples of classes of web forming polymers include polyurethanes, polyamides, polyesters, polyolefins, silicones, acrylics, polyvinyl chlorides, etc.

A thermoplastic polyurethane polymer is one of a number of polymers that are found satisfactory for the formation of ribbons in accordance with the present invention. It will be appreciated, however, that other polymeric materials can also be used provided their abrasion resistance is satisfactory for their purpose and they are able to be bonded to the substrate materials with which they are to be used.

An advantage of the composites of this invention over constructs that require an inner liner is that they provide good resistance to abrasion of the surface of the substrate membrane to which it is attached without covering the entire substrate. Another advantage is that the lay down of abrasion resistant filaments can be easily controlled to provide good flexibility of composite, i.e., good hand in fabric constructions, and good control of moisture vapor transmission.

A method for determining abrasion-resistance for present purposes is to measure the degree of abrasion until one or more leaks is formed in the material. The abrasion-resistance of the composite material including the abrasion-resisting layer according to the present invention has an abrasion

resistance which is greater (within experimental limits) than a flexible substrate without the abrasion-resisting layer. Depending on the nature of the abrasion-resisting layer, the abrasion resistance of the material according to the present invention may be at least 1.5 times, advantageously at least 4.0 times the abrasion resistance of the flexible substrate alone, In particular circumstances, the abrasion-resistance may be increased by up to 10 times or more. On the other hand, while the moisture vapor permeability of the substrate is decreased somewhat by the application of the web-forming polymer (which could itself have a degree of water vapor permeability), such decrease would be also expected from the lamination of an inner lining to a substrate as in previously proposed technology. Thus, the use of a web of ribbons according to the present invention has the capacity to markedly increase the abrasion resistance of the material, while at the same time not unduly decreasing the water-vapor-permeability.

Tests on the composite material of the invention to measure abrasion resistance and water-resistance or water-vapor permeability were carried out using the following methods.

In view of the difficulty in separating composites into their individual components, it is understood that when one component is said to have a certain property, such as a certain moisture vapor transmission rate, that property can be measured by testing the entire composite; for if the composite meets the test, the individual components inherently must meet the test.

TEST METHODS

MOISTURE VAPOR TRANSMISSION RATE

Moisture vapor transmission rate (MVTR), i.e. water-vapor-permeability, was measured by placing approximately 70 ml of a solution consisting of 35 parts by weight of potassium acetate and 15 parts by weight of distilled water into a 133 ml. polypropylene cup, having an inside diameter of 6.5 cm at its mouth. An expanded polytetrafluoroethylene (PTFE) membrane having a minimum MVTR of approximately 85,000g/m^2/24 hrs. as tested by the method described in US Patent No. 4,862,730 to Crosby and available from W. L. Gore & Associates, Inc. of Newark, Delaware, was heat sealed to the lip of the cup to create a taut, leakproof, microporous barrier containing the solution.

A similar expanded PTFE membrane was mounted to the surface of a water bath. The water bath assembly was controlled at 23°C plus or minus 0.2°C, utilizing a temperature controlled room and a water circulating bath. The sample to be tested was allowed to condition at a temperature of 23°C and a relative humidity of 50% prior to performing the test procedure. Three

samples were placed so that each sample to be tested was in contact with the expanded PTFE membrane mounted over the surface of the water bath, and was allowed to equilibrate for at least 15 minutes prior to the introduction of the cup assembly.

The cup assembly was weighed to the nearest 1/1000g and was inverted onto the center of the text sample.

Water transport was provided by the driving force between the water in the water bath and the saturated salt solution providing water flux by diffusion in that direction. The sample was tested for 20 minutes and the cup assembly was then removed, and weighed again to within 0.001g.

The MVTR of the sample was calculated from the weight gain of the cup assembly and was expressed in grams of water per square meter of sample surface area per 24 hours.

MARTINDALE ABRASION RESISTANCE TEST

Abrasion testing was carried out using a Martindale Abrasion machine and by rubbing samples with a standard wool tool SM25 which complied with draft ISO ST CD 12974-1 Table 1, clause 5.6.2 which is based on British Standard BS 5690, 1991.

The test procedure is as follows:

Circular specimens of sample material are abraded on a reference abradant of a cross-breed worsted spun plain-woven wool fabric under pressure of 12kPa with a cyclic planar motion in the form of a Lissajous figure, which is the resultant of two simple harmonic motions at right angles to each other. The resistance to abrasion corresponds to the number of rubs to the defined end point. The abrasion machine is of the type described by Martindale (J.Text.Inst. 1942:33,T151).

Each sample is removed from the machine after a predetermined number of rub cycles and tested for liquid water-resistance as described herein (under a hydrostatic pressure of 1 psi for 3 minutes) until a leak was detected which indicated breakdown of water-resistance. Samples were tested every 5,000 rub cycles up to a 20,000 rub cycles. They were then tested at every 10,000 rubs up to failure. At least two specimens were tested, and average value is reported.

For purposes of this invention, a sample has acceptable abrasion resistance if it passes 15,000 rub cycles.

WATER-RESISTANCE TEST

Samples of the materials were tested for water resistance by using a modified Suter test method, which is a low water entry pressure challenge. The test consists essentially of forcing water against one side of a test piece, and observing the other side of the test piece for indications of water penetration through it.

The sample to be tested is clamped and sealed between rubber gaskets in a fixture that holds the test piece inclined from the horizontal. The outer surface of the test piece faces upward and is open to the atmosphere and to close observation. Air is removed from inside the fixture and pressure is applied to the inside surface of the test piece, over an area of 7.62 cm (3.0 inches) diameter, as water is forced against it. The water pressure on the test piece was increased to 1 psi by a pump connected to a water reservoir, as indicated by an appropriate gauge and regulated by an in-line air valve.

The outer surface of the test piece is watched closely for the appearance of any water forced through the material. Water seen on the surface is interpreted as a leak. A sample achieves a passing grade when, after 3 minutes, no water is visible on the surface.

Without intending to limit the scope of the present invention, the following examples illustrate how the present invention may be made and used:

EXAMPLE 1

Expanded polytetrafluoroethylene, hereafter referred to as ePFTE, manufactured according to U.S. Patents 3,953,566 and 4,187,390 of 15-17 gm/m2 weight, was coated with a 12-15g/m2 layer of hydrophilic polyurethane as described in U.S. Patent 4,194,041 and then laminated to a polyester US101 (Milliken and Co., Spartansburg, SC) fabric on the ePTFE side using a dot pattern of polyurethane adhesive as described in U.S. Patent 4,532,316 to create a water vapor permeable, water resistant laminate.

A thermoplastic polyurethane was synthesized from 4,4'-diphenylmethane diisocyanate (MD1/1000 mol.ut. polycaprolactone diol/1,4-butane diol in the molar equivalents of 2:1:1.12 respectively using conventional polyurethane prepolymer type synthesis technique and then converted into pellets. The resulting polyurethane had a melt flow index of about 140 gm/10

min. (at 195°C, 5kg.) and was used to create the polymeric filaments through melt blowing.

A 60 inches wide meltblowing die with 0.014 inches diameter orifices arranged in a single row with a spacing of 30 holes per inch was used. The polyurethane in pellet form was fed into a three inch single screw extruder along with 2.5% of a color concentrate (Clariant Remafin Black CEA 8020A). The extruder temperature profile was maintained at 460°F and the extruder fed the melt into a gear pump set at 18 rpm to provide a steady flow of the melt to the die orifices at a throughput of 126 lbsw./hr. The die nose piece was set back by 0.030 inches and the air gap was set at 0.030 inches. The air temperature was maintained at 520°F at an air volume of 950 cfm and the die temperature was set to 460°F. A water spray was used to quench the melt blown polyurethane.

Above conditions were used to melt blow polyurethane strands on to the hydrophilic polyurethane side of the laminate, moving over a collector at 45 meters/min and located 9 inches from the die. Under these conditions, about 14 gm/m2 of strands was deposited on the laminate.

Later four 8" x 12" samples were cut from the above composite and placed into a forced air tenter oven to enhance the coalesced ribbon structure, two for 15 seconds and two for 30 seconds at 320°F. The samples were then allowed to cool at room temperature. SEMs of the product heated at 30 °C are seen in Figures 7a and 7b.

Martindale abrasion and MVTR measurements were then performed on the composites and the results averaged and presented in Table 1.

EXAMPLE 2

The same procedure set forth in Example 1 was followed, except the strands were collected on the laminate moving at 25 meters/min., resulting in a filament laydown of 24 gm/m2. The resulting composite sample was placed into the forced air tenter oven at a temperature of 320° F for a dwell time of 30 sec.

Martindale abrasion and MVTR measurements were then performed on the composites and the results are averaged and presented in Table 1.

EXAMPLE 3

A water resistant, water vapor permeable laminate similar to that used in Example 1 was used. A different thermoplastic polyurethane Morthane® PS455-203 (Morton Polyurethanes, Chicago, IL) with melt flow index of the polymer of 22gm/10 min. @ 177°C, 2.16 kg.) was used.

A 60 inches wide meltblowing die with 0.014 inches diameter orifices arranged in a single row with a spacing of 30 holes per inch was used. Morthane PS455-203, in pellet form, was fed into a 3 inch single screw extruder along with 1.25% of a color concentrate (Clariant Remafin Black CEA 8202A). The extruder temperature profile was maintained at 460°F and the extruder fed the melt into a gear pump set at 24 rpm to provide a steady flow of the melt at a throughput of 168 lbs./hr to the die maintained at 470°F. The die nose piece was set back by 0.060 inches and the air gap was set at 0.060 inches. The air temperature was maintained at 520°F at an air volume of 950 cfm. A water spray was used to quench the melt blown filaments.

Above conditions were used to melt blow Morthane PS455-203 strands on to the hydrophilic polyurethane side of the laminate moving over a collector at 80 meters/min. and located 5.5 inches from the die. Under those conditions, about 10 gm/m2 of Morthane PS455-203 was deposited on the laminate.

Later 8" x 12" samples were cut form the above composite and placed into a forced air tenter oven to enhance the coalesced ribbon structure for 15 seconds at 320°F. The samples were then allowed to cool at room temperature.

Martindale abrasion and MVTR measurements were then performed on the composite and the results are presented in Table 1.

TABLE 1

Sample I.D.	Filament Polymer	Martindale Abrasion Test (rubs to 1st leakage) (Mean)	Moisture Vapor Transmission Rate (g/m^2/day)
Laminate	NONE	10,000	16,496
Example #1 Composite	Polyurethane 14 gsm	175,000	4915
Example #2 Composite	Polyurethane 24 gsm	>210,000	2652
Example #3 Composite	Morthane® 9 gsm	45,000	8489

As can be seen from Table 1, the water-vapor-permeability (MVTR) of the composite material of the present invention is less than that of the starting laminate but is at a level which is acceptable

Also seen from Table 1 is the significant improvement in abrasion as measured by the Martindale Abrasion Tester per the test method quoted as compared to that of the starting laminate.

The composite material of the present invention has generally been found to possess durability close to that of materials using a conventional inner lining without significantly compromising the comfort.

The thermoplastic polyurethane polymer used is one of a number of polymers that could be found satisfactory for the present invention. It will be appreciated, however, that other polymeric materials can also be used provided their abrasion resistance is satisfactory for their purpose and they are compatible with the substrate materials with which they are to be used.

CLAIMS:

1. A layered composite comprising

(a) a flexible substrate selected from the class consisting of polymeric membranes and polymeric films having a first and second side; and

(b) a porous web of polymeric ribbons arranged with a number of crossover points over the surface of at least one side of the substrate, said ribbons substantially adhered to said surface substantially along their length, and said ribbons being coalesced at least at crossover points;

said composite being water-resistant and water-vapor-permeable.

2. The composite of claim 1 wherein the composite has a resistance to abrasion of at least 15,000 cycles without leakage on the polymeric ribbon side as measured by the Martindale abrasion resistance test.

3. A layered composite comprising

(a) a flexible substrate comprising expanded polytetrafluoroethylene having a first and second side; and

(b) a porous web of polymeric ribbons arranged with a number of crossover points over the surface of at least one side of the substrate, said ribbons substantially adhered to said surface substantially along their length, and said ribbons being coalesced at least at crossover points;

said composite being water-resistant and water-vapor-permeable.

4. The composite of claim 3 wherein the composite has a resistance to abrasion of at least 15,000 cycles without leakage as measured on the polymeric ribbon side by the Martindale abrasion resistance test.

5. A layered composite comprising

(a) a flexible substrate comprising expanded polytetrafluoroethylene impregnated with a hydrophobic impregnant and having a first and second side; and

(c) a porous web of polymeric ribbons with a number of crossover points over the surface of at least one side of the substrate, said ribbons substantially adhered to said surface substantially along their length, and said ribbons being coalesced at least at crossover points;

said composite being water-resistant and water-vapor-permeable.

6. The composite of claim 5 wherein the composite has a resistance to abrasion of at least 15,000 cycles without leakage as measured on the polymeric ribbon side by the Martindale abrasion resistance test.

7. A layered composite comprising

(a) a flexible substrate comprising expanded polytetrafluoroethylene impregnated with a hydrophobic impregnant and coated with a continuous hydrophillic polymeric layer, having a first and second side; and

(b) a porous web of polymeric ribbons arranged with a number of crossover points over the surface of at least one side of the substrate, said ribbons substantially adhered to said surface substantially along their length, and said ribbons being coalesced at least at crossover points;

said composite being water-resistant and water-vapor-permeable.

8. The composite of claim 7 wherein the composite has a resistance to abrasion of at least 15,000 cycles without leakage as measured on the polymeric ribbon side by the Martindale abrasion resistance test.

9. A layered composite comprising

(a) a flexible substrate comprising expanded polytetrafluoroethylene and a continuous hydrophilic polymeric layer, having a first and second side; and

(b) a porous web of polymeric ribbons arranged with a number of crossover points over the surface of at least one side of the substrate, said ribbons substantially adhered to said surface substantially along their length, and said ribbons being coalesced at least at crossover points;

said composite being water-resistant and water-vapor-permeable.

10. The composite of claim 9 wherein the composite has a resistance to abrasion of at least 15,000 cycles without leakage as measured on the polymeric ribbon side by the Martindale abrasion resistance test.

11. A layered composite of claim 1 wherein the flexible substrate of part (a) comprises two layers of ePTFE with a continuous layer of a hydrophillic polymeric layer in between them.

12. The composite of claim 11 wherein the composite has a resistance to abrasion of at least 15,000 cycles without leakage as measured on the polymeric ribbon side by the Martindale abrasion resistance test.

13. The composite of claims 7, 9 or 11 wherein the hydrophilic polymeric layer is a polyurethane.

14. The composite of claims 8, 10 or 12 wherein the hydrophilic polymeric layer is a polyurethane.

15. The composite of claims 1, 3, 5, 7, 9, or 11 wherein the add-on weight of the polymeric ribbons is between 2 and 30 g/m^2.

16. The composite of claims 1, 3, 5, 7, 9, or 11 wherein the ribbons of element (b) are comprised of thermoplastic polyurethane.

17. The composite of claim 1, 3, 5, 7, 9 or 11 wherein the ribbons of element (b) are comprised of a reactive polyurethane.

18. The composite of claim 1, 3, 5, 7, 9 or 11 wherein the ribbons of element (b) are comprised of an acrylic polymer.

19. A composite material as claimed in claim 1, 3, 5, 7, 9, or 11 in which the percentage coverage of the surface by the ribbons is 15 to 80%.

20. A composite material as claimed in claim 1,3, 5, 7, 9, or 11 in which the polymer forming ribbons of element (b) is water-vapor-permeable.

21. A composite material as claimed in claim 1, 3, 5, 7, 9, or 11 in which the polymeric ribbons of element (b) contain at least one additive.

22. An article of clothing formed from a composite as claimed in claim 1, 3, 5, 7, 9, or 11.

23. A layered composite comprising

(a) a flexible substrate selected from the class consisting of polymeric membranes and polymeric films having a first and second side; and

(b) a porous web of polymeric ribbons of a thermoplastic polyurethane comprising diphenylmethane diisocyanate, polycaprolactone diol and butane diol arranged with a number of crossover points over the surface of at least one side of the substrate, said ribbons substantially adhered to said surface substantially along their length, and said ribbons being coalesced at

least at crossover points;

said composite being water-resistant and water-vapor-permeable.

24. A process of producing a composite material for a garment comprising providing a flexible, water-resistant, water-vapor-permeable substrate comprising a polymeric film or membrane; applying an array of strands to the substrate; and forming a porous web of polymeric ribbons with a number of crossover points over at least one surface of said substrate; said ribbons substantially adhered to the substrate substantially along their length, and said ribbons being coalesced at least at crossover points.

25. A process as in claim 24 which is followed by a further heating step.

26. The process of claim 24, wherein said array of strands are applied to the substrate by melt blowing.

27. The process of claim 24, wherein said array of strands are applied to the substrate by screen printing.

Fig. 1. Schematic of invention.

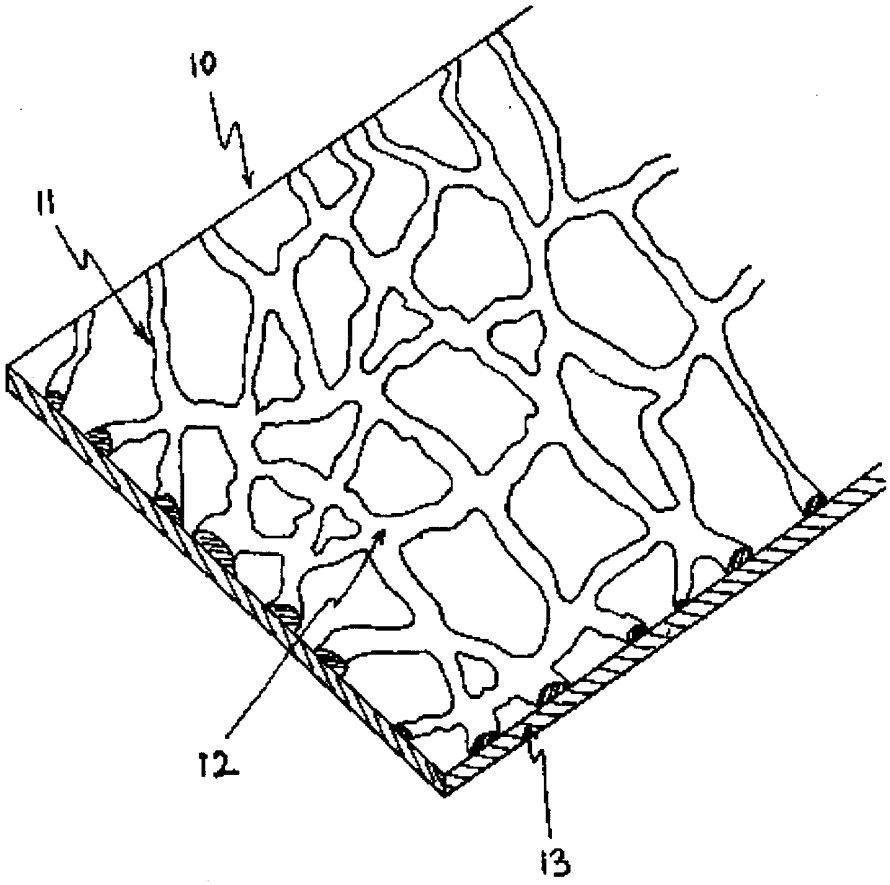


Fig. 2. Polymer applied directly to the hydrophillic PU side of laminate, prior to any heat treating. 50x

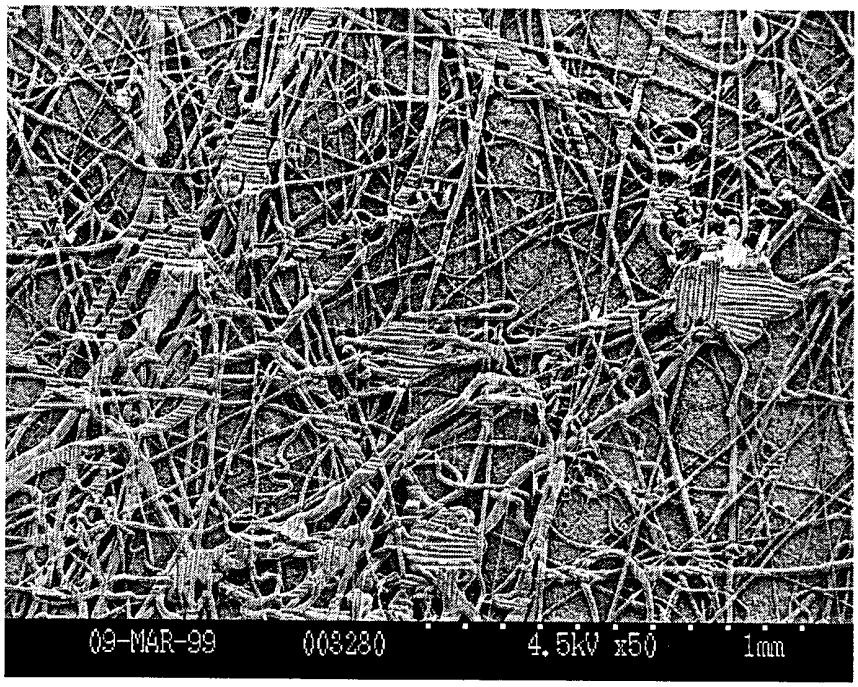


Fig 3. Ribbons adhered directly to the hydrophillic PU side of laminate.
After 15 seconds of heat treating at 160C. 50x

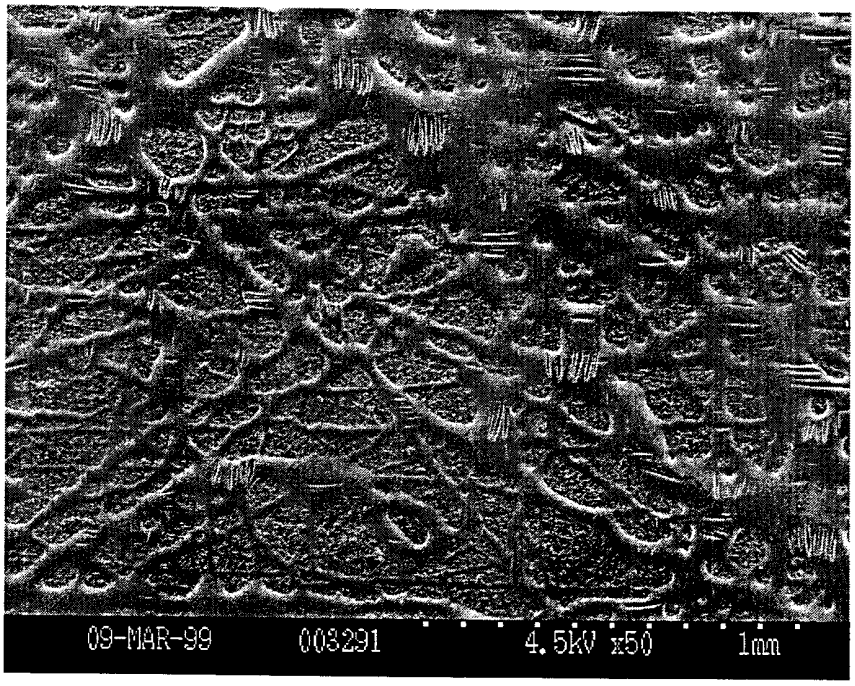


Fig 4. Polymer applied directly to the hydrophillic PU side of laminate.
Prior to any heat treating. 300x



Fig 5. Ribbons adhered directly to the hydrophillic PU side of laminate.
After 15 seconds of heat treating at 160C. 300x

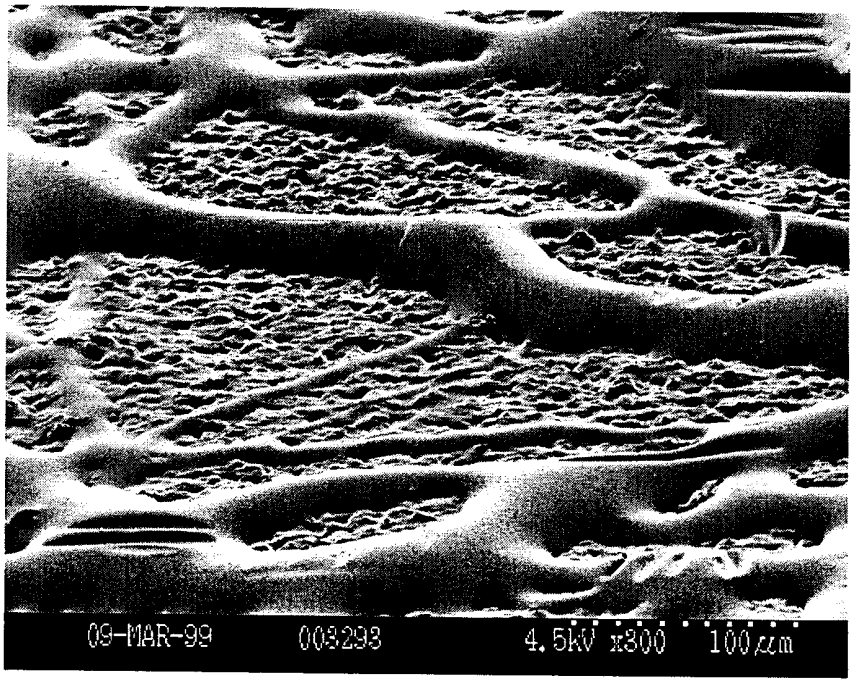


Fig 6. Ribbons adhered directly to the hydrophillic PU side of laminate.
After 5 sec of heat-treating. 50x

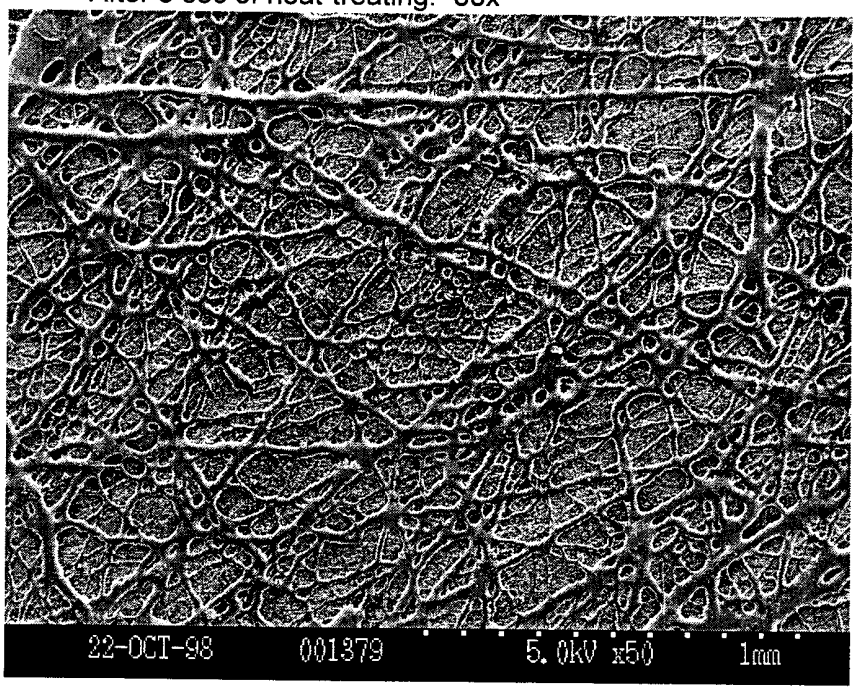


Fig. 7a. An SEM of product of Example #1 after application of heat at 50x.

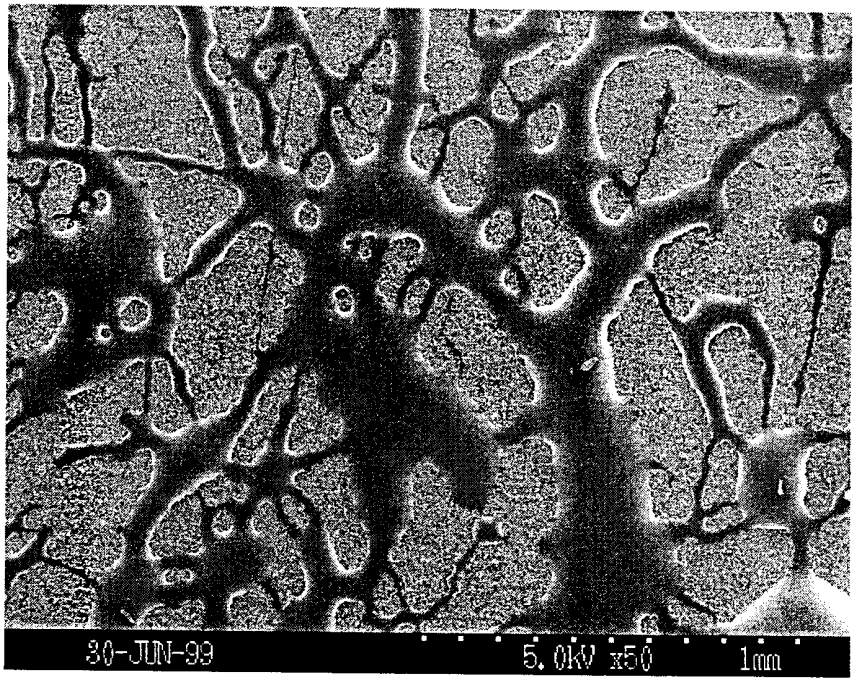
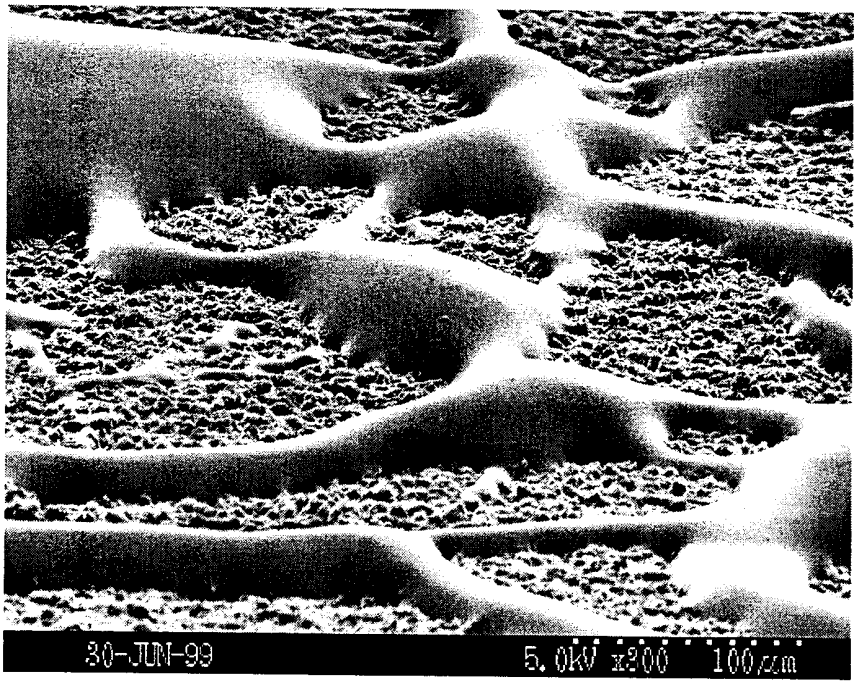


Figure 7b. An SEM of product of Example # after application of heat at 300x.



INTERNATIONAL SEARCH REPORT

Ir ational Application No
PCT/US 00/21963

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A41D31/00 D04H13/00 D06N7/00

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)
IPC 7 A41D D04H D06N

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 06891 A (GORE W L & ASS UK ;HALLEY DAVID GEORGE (GB); CLARKSON GEORGE (GB);) 19 February 1998 (1998-02-19) page 6, line 18 -page 7, paragraph 2; claims; figures page 8, line 2 - line 10 page 10, line 6 - last line ---	1-27
A	US 3 821 012 A (LATTARULO C ET AL) 28 June 1974 (1974-06-28) abstract; claims; figures column 1, line 60 -column 2, line 65 column 3, last paragraph -column 4, paragraph 1 column 8, line 16 - line 35 --- -/--	1-27

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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)

"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

"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

"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

"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 November 2000	06/12/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Pamies Olle, S

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Ir ational Application No
PCT/US 00/21963

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 690 977 A (LOFT JOHN T ET AL) 12 September 1972 (1972-09-12) abstract column 1, line 48 -column 2, line 25 column 3, line 51 -column 4, line 39 column 8, paragraph 2 column 9, paragraph 2	1,22,24, 25

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Ir ational Application No
PCT/US 00/21963

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9806891 A	19-02-1998	AU	715103 B	13-01-2000
		AU	3947697 A	06-03-1998
		CA	2236090 A	19-02-1998
		CN	1228821 A	15-09-1999
		EP	0918902 A	02-06-1999
		GB	2316341 A,B	25-02-1998
		HU	9903858 A	28-03-2000
		PL	331519 A	19-07-1999
US 3821012 A	28-06-1974	AU	7630274 A	27-03-1975
		BE	751643 A	08-12-1970
		CA	933050 A	04-09-1973
		CH	518402 A	31-01-1972
		DE	2028361 A	10-12-1970
		ES	380524 A	01-04-1973
		FR	2045940 A	05-03-1971
		GB	1325850 A	08-08-1973
		IE	35128 B	26-11-1975
		IL	34679 A	16-05-1974
		JP	54027031 B	07-09-1979
		LU	61084 A	10-08-1970
		NL	7008380 A	11-12-1970
		SE	369872 B	23-09-1974
US 3690977 A	12-09-1972	CA	964423 A	18-03-1975
		DE	2127414 A	16-12-1971
		GB	1303961 A	24-01-1973
		JP	55008625 B	05-03-1980
		US	3932682 A	13-01-1976