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(54) Title: COATED MEMBRANE

(57) Abstract: The present invention is directed to a composite material which comprises a substrate and a continuous polymer coating applied to the substrate, the polymer containing a particulate solid and being imbibed into a face of the porous substrate; and the solid particles being distributed non-uniformly through depth of the polymer coating. The composite material may further take the form of a garment, a tape, a tent, a sleeping bag, or other forms where a lightweight, waterproof water-vapour-permeable material is desirable.

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## COATED MEMBRANE

### RELATED APPLICATIONS

The present application is a regular application based on co-pending  
5 United States Provisional Patent Application 60/135,226 filed May 21, 1999.

### FIELD OF THE INVENTION

The present invention relates to a composite material, especially a  
water-resistant water-vapour-permeable material which has improved abrasion  
10 resistance and other desirable properties.

### BACKGROUND OF THE INVENTION

Patent Specification WO98/06891 discloses a composite material for a  
garment which comprises in particular an expanded  
15 polytetrafluoroethylene(ePTFE) membrane having a fabric laminated to one  
side thereof and having a coating of a water-vapour-permeable hydrophilic  
polymer on the other side thereof. In order to protect the hydrophilic coating  
against abrasion forces, a plurality of discreet abrasion-resisting polymeric dots  
are provided over the surface of the coating. The composite material is  
20 particularly intended for use in the production of lightweight waterproof water-  
vapour-permeable (i.e. "breathable") garments. The provision of the pattern of  
abrasion-resisting dots on the internal hydrophilic coating avoids the need for a  
separate internal protective lining material, as is conventionally provided.

It is an object of the present invention to further improve the properties  
25 of such composite materials.

US Patent Specification 5,859,083 discloses the production of a water-  
vapour-permeable waterproof polyether ester membrane which contains 1-10%  
by weight of finely dispersed carbon particles, especially soot particles, having  
an average size of 5 to 40nm. The polymer is a heat meltable polymer and the  
30 incorporation of the carbon particles is in order to improve the UV stability of  
the membrane produced and to provide elevated IR reflectance. The  
membrane produced is a monolithic membrane rather than a coated material.

### DESCRIPTION OF THE INVENTION

According to the present invention it has now been surprisingly discovered that the incorporation of a particulate solid (particularly in low concentrations) in a polymer coating improves the abrasion-resisting properties of the polymer coating, even to the extent that the pattern of abrasion-resisting dots is no longer an absolute requirement. The prior art does not suggest that incorporation of such particulate solids would have this beneficial effect.

Thus, a first aspect of the present invention provides a composite material, which comprises:

- 10 - a substrate and
- a continuous coating of a polymer applied to the substrate, the polymer containing a particulate solid.

The composite material is preferably water-resistant and water-vapour-permeable.

15 The addition of particulate solid material results in an increase in tensile strength and abrasion resistance. Furthermore, tests of flexural rigidity show decrease in the material of the present invention.

Generally speaking, the substrate is in the form of a porous membrane, particularly a polyolefin (e.g. polyethylene or polypropylene), a polyurethane, a polyamide, a polyester, a polyacrylate, a polycarbonate, a copolyetherester, a 20 copolyetheramide, a polysulphone, a poly(ethersulphone), a polyetherketone or polytetrafluoroethylene; especially a porous expanded polytetrafluoroethylene (PTFE) membrane such as that taught in US Patent 3,953,566.

The polymer applied as a continuous coating to the substrate is 25 generally a water-vapour-permeable hydrophilic polymeric material which allows the passage of water vapour therethrough without being permeable to liquid water. Suitable polymers include hydrophilic polyurethanes, polyesters, polyethers, copolyetheresters, polyamides, copolyetheramides and polyethyleneimines, polyoxyethyleneamines, polyoxypropylene amines, 30 polyvinylamines and polyacrylics. Particularly preferred polyurethanes are disclosed in US patents 4,194,041 and 4,532,316. Copolyethers and copolyetheresters are described in US patents 4,725,481 and 4,493,870. Such polymers may also be available in non-water-vapour-permeable form. Generally, the coating has a thickness of 5 to 100 microns.

According to the present invention, a particulate solid is incorporated into the water-vapour-permeable polymer, generally before the polymer coating is applied onto the substrate. A preferred particulate solid is carbon particles. Other particulate solids include inorganic particulate materials, pigments, metal  
5 oxides, metal salts or metal particles. Further particulate solids include particles of titanium dioxide, zinc oxide, iron oxide, aluminium oxide, silica, talc, mica, tin or silver.

The primary particle size of the particulate solid has been found to be of particular significance in the present invention. The primary particle size is  
10 generally less than 50,000nm, particularly less than 5,000nm, especially less than 500nm, more especially less than 200nm and most especially less than 50nm. The particle size of the primary particle may be determined as set out herein. The primary particle size is the particle size of the smallest discrete  
15 aggregates (typically 1 to 100, 1 to 20 or 1 to 5 microns median particle size). Aggregates are groups of primary particles in the form in which the particulate solid is present when dispersed in a liquid, such as a liquid prepolymer. An applied force is required to break the aggregate down into its primary particles. An agglomerate is the largest form the particulate solid exhibits and is the solid  
20 form prior to dispersion in a liquid.

The amount of particulate solid in the polymer is adjusted to achieve a balance of desired properties and processability in the final material but is typically less than 5% by weight, preferably less than 2% by weight. High solid  
25 contents tend to undesirably increase the viscosity of the polymer coating liquid. It is surprisingly found that the beneficial properties of the invention are evident at such low amounts of particulate solids. As mentioned above, the abrasion resistance of the material according to the present invention is improved by the inclusion of the particulate solid. Surprisingly, the "handle" of the material (i.e. its softness and flexibility) remains substantially unchanged,  
30 despite the fact that the presence of particulate solids might have been expected to make the material more rigid. When the particulate solid is carbon, it is found that the material exhibits electrical conductivity at surprisingly low carbon contents (around 1% by weight). This is valuable in providing a material having antistatic properties. Also, the carbon-loaded material is black

and discolouration due to exposure to the UV component of sunlight or in the presence of nitrogen oxides is avoided. Discolouration can also be due to sweat from the wearer of a garment. Furthermore, the carbon-loaded material avoids any problem of colour pick up when in contact with other items of clothing of poor colour fastness. The carbon-loaded material also shows good heat conductivity.

Without wishing to be limited by any theoretical mode of action, it is believed that at least some of the finer carbon particles pass with the coating material into the porous structure of the membrane substrate. Larger particles are unable to pass into the pores and remain on the surface of the membrane. The particle size distribution may therefore be significant. This may account for the unexpected properties of the material of the present invention.

Thus, a second aspect of the invention provides a composite material, which comprises:

- a porous substrate; and
- a continuous polymer coating applied to the substrate, the polymer containing a particulate solid and being imbibed into a face of the porous substrate; and the solid particles being distributed non-uniformly through the depth of the polymer coating.

The polymer may be a polymer as described above in water-vapour-permeable or non-water-vapour-permeable form.

The polymer coating is imbibed into the porous structure of the substrate. This means that some or all of the polymer is present within the substrate pores. Generally, some of the polymer is present within the pores and the remainder forms a layer above the face of the substrate.

The process of imbibing the polymer into the porous structure gives rise to non-uniformity in the distribution of solid particles through the depth of the polymer coating, possibly by a filtration mechanism. Thus, there may be a greater overall concentration (by wt.) of particles towards the surface of the polymer coating. Alternatively, the overall concentration (by wt.) may be the uniform, but the distribution by particle size may vary throughout the coating depth. In particular, larger particles and aggregates may be concentrated in the coating layer above the substrate, whilst primary particles and smaller

aggregates may predominate in the polymer present within the pores. This non-uniformity may explain the fact that the material surprisingly exhibits desirable properties at lower concentrations of particulate solids than might have been expected.

5 In a still further preferred embodiment of the present invention, a discontinuous pattern of abrasion-resisting polymeric material may be provided on the coating, much in the manner disclosed in our patent specification WO98/06891. However, the discontinuous pattern may be any suitable pattern, such as a pattern of dots or lines, or a grid pattern. The pattern needs  
10 to be chosen so as to exhibit good handlability and to prevent the overall material becoming unduly stiff. For this reason patterns of dots are preferred. The dots may in principal be of any cross-section, such as squares, rectangles polygons etc. Shapes having sharp corners are not preferred. Preferably, the dots are roughly hemispherical, part-spherical or truncated hemispherical in  
15 shape. Each dot preferably has a maximum cross-sectional dimension less than 5,000 microns, for example in the range 100-1000 microns, preferably 200-800 and particularly 400-600 microns. The dots may be spaced apart centre-to-centre by 200-2000 microns, particularly 300-1500 microns, especially 400-900 microns. Each dot generally has a height in the range 10-  
20 200 microns, preferably 70-140 microns and particularly 80-100 microns. The percentage coverage of the surface by the discontinuous pattern is from 20-80%, preferably 30-70%.

The material of the present invention is particularly useful for those applications where a lightweight waterproof water-vapour-permeable material is  
25 needed, particularly garments, tents, sleeping bags etc. Generally, the material will have a water-resistance of greater than 0.1kg/cm and a water-vapour-permeability in excess of 1500g/m<sup>2</sup>/day. Furthermore, the carbon-loaded material will be useful where electrical conductivity and antistatic properties are desirable.

30 The material may be laminated to a face fabric by any conventional means. The face fabric can be any known woven, non-woven or knitted fabric of a material such as nylon or polyester, or a perforated monolithic film (e.g. of polyurethane, polyester, polyolefin etc). The face fabric constitutes the outer surface of a garment formed from the material and provides the required visual

or aesthetic appearance. If a discontinuous abrasion-resisting pattern is present on one face, then the face fabric is preferably laminated to the other face.

The material of the present invention is also particularly valuable in the production of a seam sealing tape which provides improved waterproofness in seam sealed garments. As is well known, when a garment is formed from a waterproof water-vapour-permeable material using conventional stitched seams, it is necessary to apply a tape over the seams in order to prevent water entry through the stitching holes. Conventionally, seam sealing tape is formed of porous membrane having a coating of water-vapour-permeable hydrophilic polymer on one side thereof. A hot melt adhesive is then coated over the water-vapour-permeable polymer. The seam sealing tape is applied by melting the adhesive under a high temperature stream of air and simultaneously applying under pressure over the seam. This construction is disadvantageous in that the surface of the seam sealing tape (i.e. porous membrane) is different to that of the interior surface of the garment itself (water-vapour-permeable polymer). However, this does not matter where a conventional internal lining is used. Surprisingly, it has been found that the material of the present invention may be coated with adhesive on the free membrane face of the substrate, which is then applied against the seam. Thus, the visible surface of the seam sealing tape is the same as that of the inside of the garment itself, which is visually more satisfying. Moreover, the seam sealing tape of the present invention has been found to withstand higher water entry pressures, particularly at points where two or more layers of seam sealing tape overlap.

### **Definitions**

By "liquid water resistant" is meant that the material is waterproof at a water pressure of 13.8 kN/M<sup>2</sup>.

By "air-impermeable" is meant that no airflow is observed for at least two minutes as determined by the Gurley test for air flow measured by a Gurley densometer (ASTM D726-58) manufactured by W. & L.E. Gurley & Sons.

By "water vapour permeable" is meant an MVTR of at least 1000g/m<sup>2</sup> per 24 hr.

Embodiments of the present invention will now be described by way of example only with reference to the following examples.

#### **EXAMPLE 1(Production of Material)**

5 The following materials were produced:

- (1) A porous expanded PTFE membrane coated with a water-vapour-permeable hydrophilic coating was produced according to US Patent 4,194,041;
- (2) A face fabric (ripstop plain weave nylon 66 42warp/61 weft threads, weight 55g/m<sup>2</sup>) having laminated thereto the expanded PTFE membrane coated with a water-vapour-permeable hydrophilic polymer is produced according to US Patent 4,194,041; and
- (3) A material the same as (2) above but having a pattern of abrasion-resisting polymer dots on the hydrophilic coating is produced according to the teachings of patent specification W098/06891. The polymer contained 0.3% by wt. of carbon particles referred to below.

15 In each case, the water-vapour-permeable material was a polyurethane containing 0% (control), 0.3%, 0.65% and 1.5% by weight of a fine carbon (Black Pearls 2000 Carbon Black, Cabot Corporation, Billerica, USA) of typical mean particle size 13 nanometers. The carbon particles were intimately mixed into the polyurethane prepolymer mixture of material (1) using a paint mixer, and then a Ross mixer emulsifier or high speed disperser for about 20mins. The mixture was then coated onto the expanded PTFE membrane.

#### **EXAMPLE 2 (Properties)**

25 The three materials produced in Example 1 were tested for moisture vapour permeability (MVTR), resistance to washing, abrasion resistance and handle according to methodologies given herein. Controls without added carbon were also tested. The results are given in Tables 1 to 3. It can be seen that abrasion resistance (abrasion-to-leak) of the materials according to the present invention including particulate carbon are significantly improved over the control materials, whilst handle and resistance to washing (wash-to-leak) are maintained.



**EXAMPLE 3 (Electrical Conductivity)**

A membrane material (1) according to Example 1 was tested for electrical conductivity according to the methodology given herein. The results are set out in Table 4. It can be seen that at 1.3% carbon, the material was

5 conductive.

**TABLE 1 (Membrane)**

Sample	Particle % wt	MVTR (mean) g/m <sup>2</sup> /d	Wash to leak	Abrasion to leak (cycles)	Handle (mean)
Control	-	13406			
1	0.3	17274			
2	0.65	14196			
3	1.5	16635			

10

**TABLE 2 (fabric & membrane)**

Sample	Particle % wt	MVTR (mean) g/m <sup>2</sup> /d	Wash to leak hr	Abrasion to leak (cycles)	Handle (mean)
Control	-	13447	504-672	6000 (1155)	34.8 (1.30)
1	0.3	12851	672-864	26250 (9465)	
2	0.65	12127	504-672	32500 (8660)	30.2 (0.83)
3	1.5	13054	672-864	70,000 (34641)	31.6 (1.67)

15

Bracketted figures are standard deviations.

**TABLE 3 (fabric & membrane & dots)**

Sample	Particle % wt	MVTR (mean) g/m <sup>2</sup> /d	Wash to leak hr	Abrasion to leak cycles	Handle (mean)
Control	-	6344	504-672	87500 (1500)	46.8 (2.69)
1	0.3	7736	504-864	140,000 (23094)	47.9 (1.25)
2	0.65	7736	672-864	120,000 (23094)	45.0 (1.18)
3	1.5	6924	504-672	110,000 (47610)	42.3 (2.32)

5 Bracketted figures are standard deviations.

**TABLE 4 (Conductivity)**

Carbon black type	Percent carbon	Particle size (nm)	Form	Run	Decay time in sec. (amb)	Decay time in sec. (dry)
Cabot BP2K	0.70%	13	Pellet	17	0.01	0.01
Cabot BP2K	1.00%	13	Pellet	7	0.02	0.01
Cabot BP2K	1.30%	13	Pellet	21	0.01	0

Note: Decay time for a pass for antistatic properties is 0.5 sec and below. All with higher decay times will be an insulator material.

BP2K = Black Pearl (Cabot Corporation)

**EXAMPLE 4 (Seam Sealing)**

Seams formed in material A according to the invention (Example 1, material (3)) and the same material B but without carbon particles (comparison) were seam-sealed as described herein using various seam-seal tapes.

Each material A, B comprised layers of nylon 66 face fabric, membrane, hydrophilic polymer and pattern of abrasion resisting dots in that order.

The following seam sealing tapes were used. As a first comparison, a conventional tape as described herein was used comprising layers of adhesive, hydrophilic polymer and membrane in that order. A second comparison tape comprised adhesive, membrane, hydrophilic polymer and a pattern of abrasion  
 5 resisting dots in that order. The tape of the invention was the same as the second comparison tape but included carbon particles in the hydrophilic polymer and in the abrasion-resisting polymer dots.

The resistance to washing of the various constructions and the water entry pressure of the sealed seams was determined and the results are shown  
 10 in Tables 5, 6 and 7. The seam seal tape of the present invention shows improved resistance to washing compared to the 1st comparison (conventional) tape and comparable performance to the 2nd comparison tape when applied to material B (Table 5). However, the seam seal tape of the invention performs better than both comparison tapes when applied to material A (invention)  
 15 (Table 6). Water entry pressure is better for the inventive tape applied to inventive material A than for comparison tape applied to comparison material B (Table 7).

**TABLE 5 (Seam Seal - Material B)**

20

<b>Tape</b>	<b>1st Comparison</b>	<b>2nd Comparison</b>	<b>Invention</b>
Hrs			
10	1	0	1
25	4	3	2
50	7	3	2
75	12	3	6
100	12	6	6

**TABLE 6 (Seam Seal - Material A)**

<b>Tape</b>	<b>1st Comparison</b>	<b>2nd Comparison</b>	<b>Invention</b>
Hrs			
10	1	1	0
25	2	3	0
50	4	3	0
75	9	4	0
100	10	4	4

The figures show the number of holes which formed after the stated time period, for material A (invention), and material B (comparison) sealed with two comparison tapes and a tape according to the invention.

**TABLE 7 (Seam Seal - Water entry pressure)**

<b>Water Entry Pressure (psi)</b>		
Material B/ 2nd Comparison tape	7.5	(0.76)
Material A / Invention Tape	11.0	(1.32)

## **METHODOLOGY**

Test methods for moisture vapour transmission rate (MVTR), wash to leak and abrasion to leak, are given in patent specification W098/06891.

Test methods for handle, electrical conductivity and water entry pressure are given below.

### **Handle**

The "hand" of the material was determined using a Thwing-Albert Handle-O-Meter (Thwing Albert, Philadelphia, USA), which measures the resistance that a penetrator blade encounters when forcing a specimen of material into a slot with parallel edges. The mean of five test specimens is reported.

**Conductivity**

The electrostatic (and conductivity) properties of the material were tested by measuring the intensity and polarity of an induced charge and the decay time required for complete dissipation of an induced charge, under both ambient and dry conditions. An electrostatic test chamber equipped with an electrometer or recording oscilloscope was used according to US Federal Test Method Standard No. 101C.

**Water entry pressure**

Water entry pressure provides a test method for water intrusion through membranes. A test sample is clamped between a pair of testing plates. The lower plate has the ability to pressurize a section of the sample with water. The sample is then pressurized in small increments, waiting 10 seconds after each pressure change until the appearance of the first bead of liquid on the uppermost surface of the sample indicates water entry. The water pressure at breakthrough or entry is recorded as the Water Entry Pressure. The test results are taken from the centre of test sample to avoid erroneous results that may occur from damaged edges.

**Seam Sealing**

Seam sealing was carried out using a hot air sealing machine (of type available from Rosslyn Precision Engineering, Dalkeith, UK) under nominal conditions of air temperature 500°C, seam seal tape speed 3.5m/min and quill pressure 25psi (1.75 kg/cm<sup>2</sup>).

**Primary particle size**

The particle size of primary particles of particulate solid in the nanometer range was determined by transmission electron microscopy according to method ASTM D-3849. The particle size data are typical arithmetic mean diameters of a suitable number of primary particles.

**Aggregate (particle size)**

The particle size of aggregated primary particles of particulate solid in the micron range were measured in the prepolymer used to form the water-

vapour-permeable polymer using a Coulter particle size analyser and employing standard methodology.

CLAIMS

1. A composite material, which comprises:
  - a substrate and
  - 5 - a continuous polymer coating applied to the substrate, the polymer containing a particulate solid and being imbibed into a face of the porous substrate;  
and the solid particles being distributed non-uniformly through the depth of the polymer coating.
- 10 2. A material according to the preceding claim wherein the substrate is a porous membrane.
3. A material according to claim 2 wherein the porous membrane is expanded polytetrafluoroethylene.
- 15 4. A material according to any preceding claim wherein the polymer is a water-vapour-permeable polyurethane, a polyester or a polyamide.
5. A material according to any preceding claim wherein the coating has a  
20 thickness of 5 to 100 microns.
6. A material according to any preceding claim wherein the particulate solid is carbon particles.
- 25 7. A material according to any of claims 1 to 5 wherein the particulate solid is an inorganic particulate material, a pigment, a metal oxide, a metal salt or metal particles.
8. A material according to any of claims 1 to 5 wherein the particulate solid  
30 comprises particles of titanium dioxide, zinc oxide, iron oxide, aluminium oxide, silica, talc, mica, tin or silver.
9. A material according to any preceding claim wherein the primary particle size of the particulate solid is less than 5,000nm.

15

10. A material according to claim 9 wherein the primary particle size is less than 500nm.

11. A material according to claim 10 wherein the primary particle size is less  
5 than 200nm.

12. A material according to claim 11 wherein the primary particle size is less than 50nm.

10 13. A material according to any preceding claim wherein the amount of particulate solid in the polymer is less than 10% by weight.

14. A material according to claim 13 wherein the amount of particulate solid in the polymer is less than 5% by weight.

15

15. A material according to claim 13 wherein the amount of particulate solid in the polymer is less than 2% by weight.

16. A material according to any preceding claim which comprises a  
20 discontinuous pattern of polymeric material formed on the coating.

17. A material according to claim 16 wherein the discontinuous pattern comprises a pattern of dots.

25 18. A material according to claim 16 wherein the discontinuous pattern comprises a grid pattern.

19. A material according to any preceding claim having a water-resistance of greater than 0.1kg/cm.

30

20. A material according to any preceding claim having a water-vapour-permeability in excess of 1500 g/m<sup>2</sup>/day.



21. A material according to any preceding claim which is laminated to a fabric.

22. A garment which comprises the material of any preceding claim.

5

23. A seam-sealing tape which comprises the material of any of claims 1 to 20 having a layer of adhesive applied thereto.

24. A tape according to claim 23 wherein the adhesive layer is applied to the substrate.

10

25. A process for the production of a water-resistant water-vapour-permeable material, which comprises;

15

- applying a continuous coating of a water-vapour-permeable polymer over a substrate;
- the polymer comprising solid particles being distributed non-uniformly through the depth of the polymer coating.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/13904

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A41D31/02 C08J9/36 D06N3/12 //C08L27/18

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 C08J 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)

EP0-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 33007 A (GORE & ASS) 7 December 1995 (1995-12-07) page 9, line 15-29 page 9, line 36 -page 10, line 7 page 13, line 27-38 example 4 claims ---	1-4, 6-8
X	GB 1 509 719 A (HAIRLOK LTD) 4 May 1978 (1978-05-04) page 2, line 22-31 claims ---	1, 7, 8
X	US 3 524 755 A (HOCHBERG JEROME) 18 August 1970 (1970-08-18) column 3, line 39-46 claims ---	1, 2, 4-6
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 3 821 012 A (LATTARULO C ET AL)  28 June 1974 (1974-06-28)  figure 1  column 2, line 53 -column 3, line 18  column 3, line 48-55  claims  -----</p>	1-8

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Information on patent family members

International Application No

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