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ADHESIVE COMPOSITIONS AND COMPOSITE MATERIALS

The present invention relates to adhesive compositions and to composite materials made from such adhesive compositions and solid foam materials. In further aspects it relates to method of making such composite materials, and articles made from them. The invention is primarily concerned with composite materials which are porous, resiliently compressable, and water resistant. Such materials may be particularly suitable for the manufacture of insoles and handgrips (e.g. for sports rackets).

The most widely used solid foam materials are polyurethane foams. As is well known, these can be produced with a wide range of rigidity (from very soft to rigid) and a wide range of density. A further variable is whether the material is open-cell (and hence porous) or closed cell.

Low density flexible polyurethane foams are materials of density 10-80 kg/m³, composed of lightly cross-linked open cells. Air can flow easily through them. They are soft, with little strength or resistance to abrasion. They are typically used as cushioning, in bedding or upholstery. In contrast, polyurethane foam materials conventionally used for shoe soling and the like are microcellular foams (i.e. denser than "high density foams"), with intermediate softness. Such materials have little if any porosity. They are generally self-skinning, which further reduces any



porosity they may have. Thus they typically have to be needled if they are required to be breathable.

5 In one aspect the present invention enables one to reinforce a low density flexible foam while preserving substantial porosity. Use is make of a water-resistant, water-transmissive glue. This may be based on a glue which is not substantially water-transmissive, typically a latex-type adhesive, in which a water-absorbent filler has been incorporated so that a film formed from the
10 adhesive is water absorbent.

It is known to incorporate fillers, including water-absorbent fillers, in adhesive compositions. However they are incorporated at low levels (e.g. $\frac{1}{4}$ - $1\frac{1}{2}$ w/w) and do not confer water-absorbance.

15 Thus in a first aspect the invention provides an adhesive composition comprising a water-resistant glue composition and a water-absorbent filler, the filler being incorporated in an amount sufficient to confer water absorbance on a film formed from the adhesive
20 composition.

Generally the glue composition is a latex e.g. a styrene-butadiene-rubber ("SBR") latex (preferably carboxylated) or a dispersion based on polyurethane or acrylonitrile-butadiene or acrylics or ethylene-vinyl
25 acetate (EVA) or copolymers or terpolymers based on any of these.

The glass transition temperature of the glue composition may be 10-15° (or lower if intended for low



temperature use, e.g. 0° or less).

The amount of filler is preferably 5-7% of the adhesive compositions (w/w). Suitable fillers are inorganic materials of small particle size (e.g. $< 5\mu\text{m}$, preferably $< 1\mu\text{m}$). Silica, particularly fumed silica, is currently preferred. Calcium carbonate is also usable.

The adhesive composition may be formed by mixing components A and B in approximately equal amounts by weight (e.g. 40-60% of A, 60-40% of B), where:

Component A is a latex of solid content 40-55% by weight (preferably a carboxylated SBR latex); and

Component B comprises water (86-90 parts) and filler (preferably silica such as Aerosil 200) (10-14 parts).

It may further include a bactericide (1-2 parts). (All parts are by weight.)

The compounded adhesive may also include a crosslinker which is reactive with carboxy and hydroxy groups, e.g. a polyfunctional aziridine such as trimethylolpropane-tris-(β -(N-aziridiny) propionate (available as XAMA-2 from EIT Inc), or CX-100 (Zeneca Resins). Use of 0.5-2% w/w of such a trifunctional linker can improve the water- and chemical-resistance and bond strength of the adhesive.

Alternative adhesive compositions which may be used are breathable adhesives or coatings. Their 'breathability' may be due to their molecular structure and is generally not dependent on fillers. Known examples



include water-based polyurethane products such as Witcoflex 120 and 130 (Baxenden Chemicals). These provide water-resistant, breathable, hydrophilic coatings. However they are relatively expensive. Furthermore they tend to be too soft for various applications such as insoles.

In a second aspect the invention provides a composite material formed from a low density flexible plastics foam material and an adhesive composition. The plastics foam material is preferably a polyurethane foam. (Other possibilities included polyethylene.) Its density is preferably 10-60 kg/m³, more preferably 20-60, still more preferably 30-50 and most preferably 40-45 kg/m³. It is desirably a flexible, fully open, sponge-like material. It is generally 3-12 mm thick. For use in producing insoles for normal use, thicknesses in the range 4-6mm are preferred. Insoles for sports shoes may be up to 10mm or more. Material for handgrips may be 3mm thick. (Thinner foam is not readily available.)

The adhesive is preferably a filler - containing adhesive as described above or, less preferably, a breathable adhesive.

In one type of embodiment, the adhesive composition is primarily present in a fabric layer which is adhered thereby to a major surface of the foam material. Preferably the foam material is in the form of a sheet, and said fabric layers are adhered to both major surfaces. This gives a product which is reversible and

washable. Preferably the fabric was soaked in the adhesive composition and the setting thereof both adhered the fabric to the foam material and provided the fabric with a protective coat. The fabric is preferably of a water-absorbent material, e.g. based on cotton (e.g. pure cotton or cotton-polyester or other known blend).

The fabric may be woven (cloth) or nonwoven. Suitable nonwovens include highly porous materials, composed of fibres of synthetic polymer materials.

In a second type of embodiment, the plastics foam material was saturated with the adhesive composition which was subsequently cured to produce a reinforced foam material. This type of embodiment generally does not have the cloth surface layer(s). The plastics foam is preferably of thickness 4 or 5 - 12mm.

A preferred method of producing the first type of embodiment comprises the following steps: (a) fabric is soaked with the adhesive composition (suitably by immersion); (b) the soaked fabric is applied to the foam material and the assembly is oriented so that the fabric is on the underside; and then (c) heat is applied to the fabric, preferably using a jet of hot gas or infra red irradiation. The orientation of the assembly reduces the penetration of the adhesive composition into the foam material.

The following table compares the properties of various materials for forming insoles. "Present invention" refers to preferred embodiments of the present

invention of the type consisting of polyurethane foam with cloth bonded to both faces. The adhesive used is based on a carboxy SBR latex containing silica. The cloth was saturated with the latex composition which thus provided surface protection for the cloth as well as bonding it to the foam.



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	Present Invention	Self-skinning Polyurethane Foam	Cloth Laminated on Rubber	Leather, Optionally Foam Backed
Resilient Compressibility	High (6/10mm Compressible to 2/2.5-3mm)	Moderate (3mm compressible to 1.5-2mm)	Moderate	Moderate
Water Absorbance (W/W)	400-500%	300%	300%	300%
Air Flow Efficiency	High	Poor unless perforated after formation	Reasonable	Reasonable
Durability	High	High	Moderate/Low	High
Reversibility	Yes	No	No	Yes (not if foam-backed)
Washability	Washable with detergent	Rinsable	Rinsable	Washable
Cost	Low	Low	Low	High

Some embodiments of the invention will now be described with reference to the accompanying drawings in which:

5 Fig. 1 is a schematic sectional view of a composite material which is a first embodiment of the invention; and

 Fig. 2 is a like view of a second embodiment.

10 The composite material 10 shown in Fig. 1 has a core of flexible, fully open-celled polyurethane sponge 12, of thickness 6mm. The raw material had a density of 40 kg/m³. Each of the major faces carries a layer 14 of woven cotton cloth. Prior to application, the cloth was soaked
15 with an adhesive composition (to be described later). This has soaked a small way into the foam material 12 (shown as surface layer 16). Additionally, it provides surface coating layers 18 on the outer faces of the cloth.

20 The adhesive composition was a carboxylated SBR latex having a glass transition temperature of 10° and a solids content of 50% w/w. It contained 6% by weight of a silica filler, namely Aerosil 200^(TM). It also contained a bactericide.

25 In the manufacture of the composite material 10, cloth was cut to provide pieces for covering the top and bottom faces of the foam. The cloth pieces were soaked in the adhesive composition. One piece of cloth was

removed and laid on the upper surface of the foam composition, which was immediately inverted. Hot air was then directed at the exposed surface of the cloth 14 until the adhesive was cured. Cloth 14 was then applied
5 to the upper surface of the foam material in the same way.

Fig. 2 shows a cheaper form of composite material. It consists of a piece of polyurethane foam 22 having the same characteristics as the foam material 12 of the first embodiment, except that it is 10mm thick. The material
10 was immersed in the same adhesive composition as described above, and squeezed so that it became saturated. It was then removed and dried using hot air. The result is a sheet of foam that is still substantially porous, but which is much stronger and more resistant to
15 abrasion than the untreated foam. It is also somewhat more rigid.

The composite materials as shown in Fig. 1 and 2 may be cut to provide insoles to other shaped objects. (Alternatively, the foam could be cut before the
20 treatment steps but this is not generally convenient). An insole (or a hand grip) is desirably porous, to allow absorption of sweat. It is clearly important that adhesive used in its production should not be water soluble. The adhesive composition used herein leads to
25 an adhesive bond which is highly resistant to water but which is still water absorbent, due to the high content of an appropriate filler.



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CLAIMS

1. An adhesive composition comprising a water-resistant glue composition and a water-absorbent filler, the filler being incorporated in an amount sufficient to
5 confer water absorbance on a film formed from the adhesive composition.
2. An adhesive composition according to claim 1 wherein the glue composition is a latex.
3. An adhesive composition according to claim 2
10 wherein the latex is a carboxylated SBR latex.
4. An adhesive composition according to any preceding claim wherein the amount of filler is 5-7% of the adhesive composition (w/w).
5. An adhesive composition according to any
15 preceding claim wherein the filler is silica or calcium carbonate.
6. An adhesive composition according to claim 5 wherein the filler is fumed silica.
7. An adhesive composition according to any
20 preceding claim which includes a polyfunctional crosslinker which is reactive with carboxy and hydroxy groups.
8. An adhesive composition according to any preceding claim which includes a bactericide.
- 25 9. A composite material formed from a low density flexible plastics foam material and an adhesive composition, wherein the adhesive composition is such that a film produced by the drying or curing thereof is

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water-resistant and water-absorbent.

10. A composite material according to claim 9 wherein the adhesive composition is according to any of claims 1-8.

5 11. A composite material according to claim 9 wherein the adhesive composition is a breathable hydrophilic water-resistant adhesive, optionally containing a bactericide.

12. A composite material according to claim 9, 10
10 or 11 wherein the plastics foam material is a polyurethane foam.

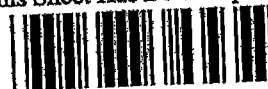
13. A composite material according to claim 9, 10, 11 or 12 wherein the density of the foam material is 10-60 kg/m³.

15 14. A composite material according to claim 9, 10, 11 or 12 wherein the density of the foam material is 30-50 kg/m³.

15. A composite material according to claim 9, 10, 11 or 12 wherein the density of the foam material is 40-
20 45 kg/m³.

16. A composite material according to any of claims 9 to 15 which includes at least one fabric layer, and wherein the adhesive composition is mainly present in the or each fabric layer which is adhered thereby to a
25 respective major surface of the foam material.

17. A composite material according to claim 16 wherein the foam material is in the form of a sheet having a said fabric layer adhered to both of its major





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surfaces.

18. A composite material according to any of claims
9 to 15 wherein the plastics foam material was saturated
with the adhesive composition which was subsequently
5 cured to produce a reinforced foam material.

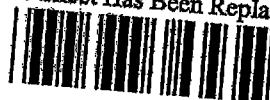
19. A method of producing a composite material
according to claim 16 or claim 17 which comprises the
following steps: (a) fabric is soaked with the adhesive
composition; (b) the soaked fabric is applied to a major
10 surface of the foam material and the assembly is oriented
so that the fabric is on the underside; and then (c) heat
is applied to the fabric.

20. A method according to claim 19 wherein heat is
applied to the fabric using a jet of hot gas.

15 21. An insole comprising a composite material
according to any of claims 9 to 18.

22. A handgrip for a racket comprising a composite
material according to any of claims 9 to 18.

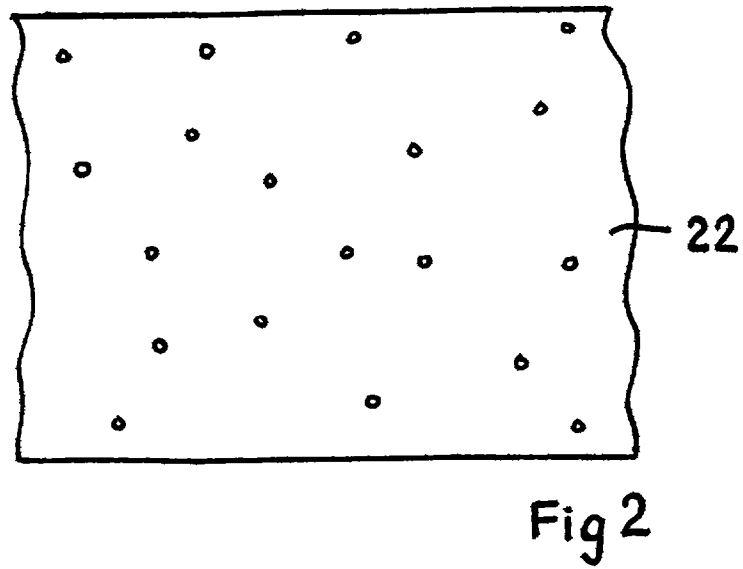
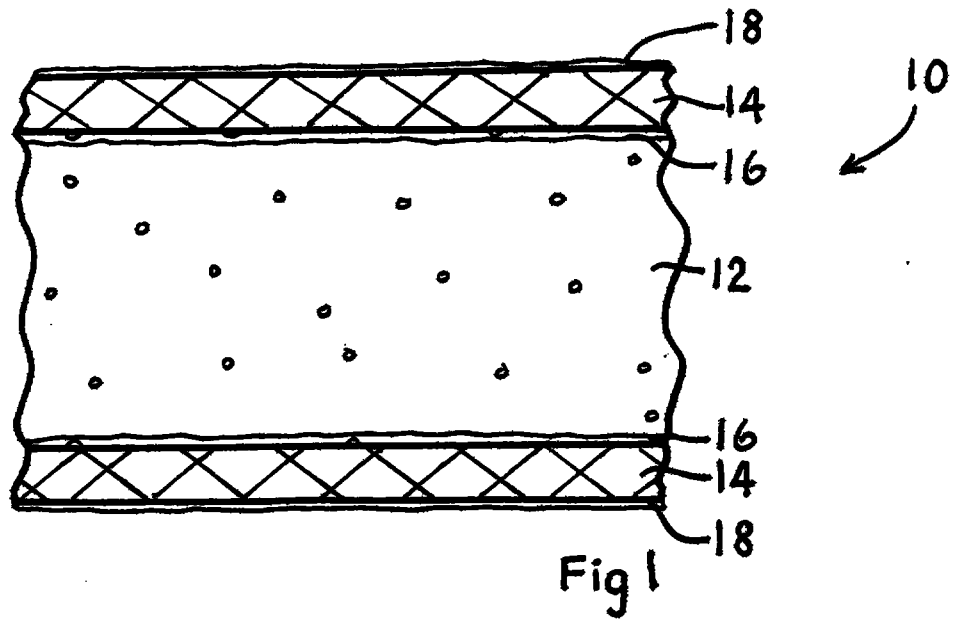
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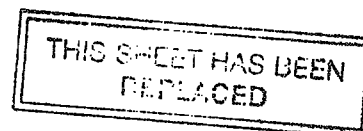


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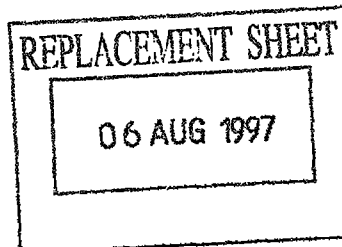


ADHESIVE COMPOSITION AND COMPOSITE MATERIALSABSTRACT

A water-resistant adhesive (preferably a carboxylated SBR latex) is rendered water-absorbent by
5 incorporation of a large amount (e.g. 5-7% w/w) of a water-absorbent filler (e.g. fumed silica). It is then suitable for treating a low density flexible open-cell foam (e.g. polyurethane foam of density 10-60, preferably 40-45, kg/m³) to make it suitable for forming insoles and
10 racket handgrips. The treatment may involve the application of pieces of fabric (14) soaked in the adhesive (16,18) to the top and bottom faces of a sheet of the foam (12).

(Fig. 1) soluble. The adhesive composition
15 used herein leads to an adhesive bond which is highly resistant to water but which is still water absorbent, due to the high content of an appropriate filler.

	Present Invention	Self-skinning Polyurethane Foam	Cloth Laminated on Rubber	Leather, Optionally Foam Backed
Resilient Compressibility	High (6/10mm Compressible to 2/2.5-3mm)	Moderate (3mm compressible to 1.5-2mm)	Moderate	Moderate
Water Absorbance (W/W)	400-500%	300%	300%	300%
Air Flow Efficiency	High	Poor unless perforated after formation	Reasonable	Reasonable
Durability	High	High	Moderate/Low	High
Reversibility	Yes	No	No	Yes (not if foam-backed)
Washability	Washable with detergent	Rinsable	Rinsable	Washable
Cost	Low	Low	Low	High



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ADHESIVE COMPOSITION AND COMPOSITE MATERIALS

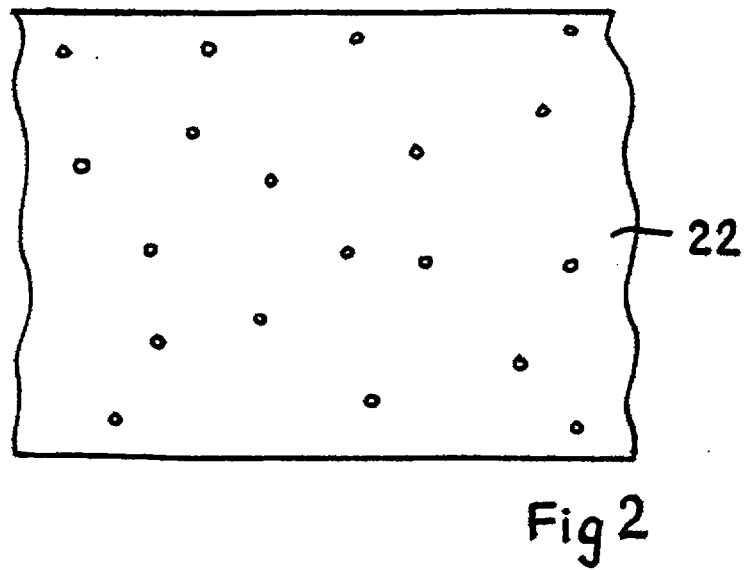
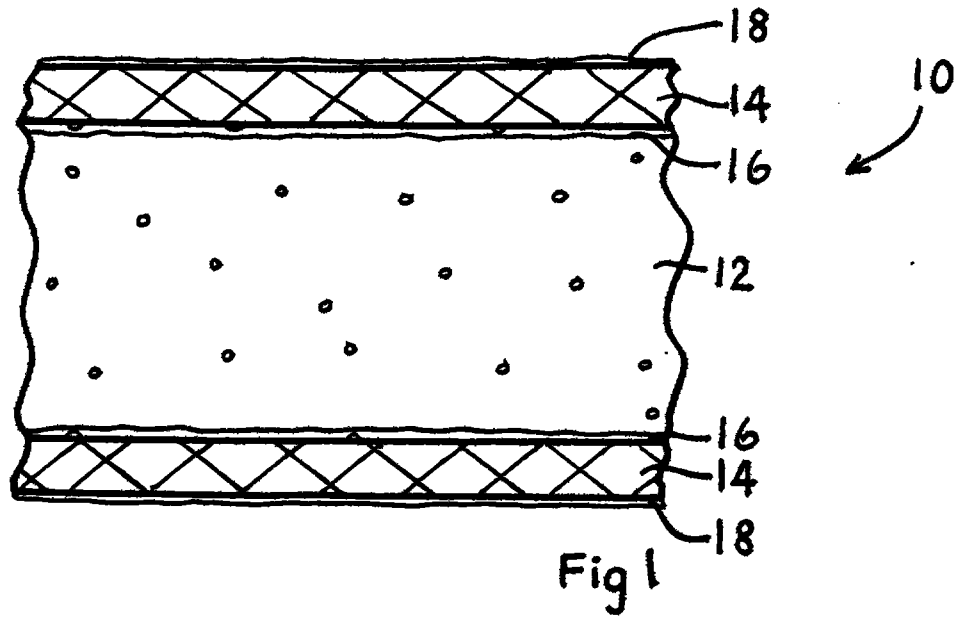
ABSTRACT

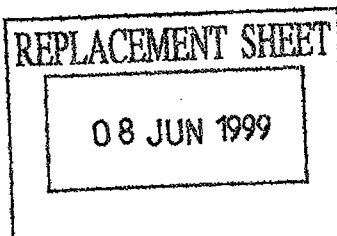
A water-resistant adhesive (preferably a carboxylated SBR latex) is rendered water-absorbent by
5 incorporation of a large amount (e.g. 5-7% w/w) of a water-absorbent filler (e.g. fumed silica). It is then suitable for treating a low density flexible open-cell foam (e.g. polyurethane foam of density 10-60, preferably 40-45, kg/m³) to make it suitable for forming insoles and
10 racket handgrips. The treatment may involve the application of pieces of fabric (14) soaked in the adhesive (16,18) to the top and bottom faces of a sheet of the foam (12).

(Fig. 1) soluble. The adhesive composition
15 used herein leads to an adhesive bond which is highly resistant to water but which is still water absorbent, due to the high content of an appropriate filler.

FIG. 1

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ADHESIVE COMPOSITIONS AND COMPOSITE MATERIALS

The present invention relates to adhesive compositions and to composite materials made from such adhesive compositions and solid foam materials. In further aspects it relates to method of making such composite materials, and articles made from them. The invention is primarily concerned with composite materials which are porous, resiliently compressable, and water resistant. Such materials may be particularly suitable for the manufacture of insoles and handgrips (e.g. for sports rackets).

The most widely used solid foam materials are polyurethane foams. As is well known, these can be produced with a wide range of rigidity (from very soft to rigid) and a wide range of density. A further variable is whether the material is open-cell (and hence porous) or closed cell.

Low density flexible polyurethane foams are materials of density 10-80 kg/m³, composed of lightly cross-linked open cells. Air can flow easily through them. They are soft, with little strength or resistance to abrasion. They are typically used as cushioning, in bedding or upholstery. In contrast, polyurethane foam materials conventionally used for shoe soling and the like are microcellular foams (i.e. denser than "high density foams"), with intermediate softness. Such materials have little if any porosity. They are generally self-skinning, which further reduces any

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porosity they may have. Thus they typically have to be needed if they are required to be breathable.

In one aspect the present invention enables one to reinforce a low density flexible foam while preserving substantial porosity. Use is made of a water-resistant, water-transmissive glue. This may be based on a glue which is not substantially water-transmissive, typically a latex-type adhesive, in which a water-absorbent filler has been incorporated so that a film formed from the adhesive is water absorbent.

It is known to incorporate fillers, including water-absorbent fillers, in adhesive compositions. However they are incorporated at low levels (e.g. $\frac{1}{2}$ - 1% w/w) and do not confer water-absorbance.

Thus in a first aspect the invention provides a porous, resiliently compressible and water-resistant composite material formed from (i) a low density flexible plastics foam material; (ii) an adhesive composition comprising a water-resistant glue composition and a water-absorbent inorganic filler, the filler being incorporated in an amount sufficient to confer water absorbance on a film formed from the adhesive composition; and (iii) at least one fabric layer, and wherein the adhesive composition is mainly present in the or each fabric layer which is adhered thereby to a respective major surface of the foam material.

Generally the glue composition is a latex e.g. a styrene-butadiene-rubber ("SBR") latex (preferably carboxylated) or a dispersion based on polyurethane or acrylonitrile-butadiene or acrylics or ethylene-vinyl acetate (EVA) or copolymers or terpolymers based on any of these.

The glass transition temperature of the glue composition may be 10-15° (or lower if intended for low

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temperature use, e.g. 0° or less).

5 The amount of filler is preferably 5-7% of the adhesive compositions (w/w). Suitable fillers are inorganic materials of small particle size (e.g. < 5µm, preferably < 1µm.). Silica, particularly fumed silica, is currently preferred. Calcium carbonate is also usable.

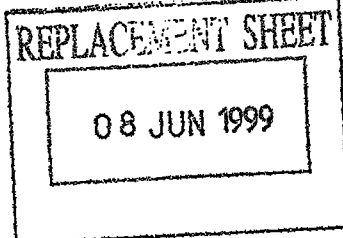
10 The adhesive composition may be formed by mixing components A and B in approximately equal amounts by weight (e.g. 40-60% of A, 60-40% of B), where:

Component A is a latex of solid content 40-55% by weight (preferably a carboxylated SBR latex); and

15 Component B comprises water (86-90 parts) and filler (preferably silica such as Aerosil 200) (10-14 parts). It may further include a bactericide (1-2 parts). (All parts are by weight.)

20 The compounded adhesive may also include a crosslinker which is reactive with carboxy and hydroxy groups, e.g. a polyfunctional aziridine such as trimethylolpropane-tris-(β-(N-aziridinyl) propionate (available as XAMA-2 from EIT Inc), or CX-100 (Zeneca Resins). Use of 0.5-2% w/w of such a trifunctional linker can improve the water- and chemical-resistance and bond strength of the adhesive.

25 ~~Alternative adhesive compositions which may be used are breathable adhesives or coatings. Their 'breathability' may be due to their molecular structure and is generally not dependent on fillers. Know examples~~

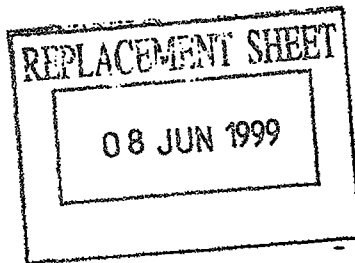


include water-based polyurethane products such as Witcoflex 120 and 130 (Baxenden Chemicals). These provide water-resistant, breathable, hydrophilic coatings. However they are relatively expensive. Furthermore they tend to be too soft for various applications such as insoles.

In a second aspect the invention provides a composite material formed from a low density flexible plastics foam material and an adhesive composition. The plastics foam material is preferably a polyurethane foam. (Other possibilities included polyethylene.) Its density is preferably 10-60 kg/m³, more preferably 20-60, still more preferably 30-50 and most preferably 40-45 kg/m³. It is desirably a flexible, fully open, sponge-like material. It is generally 3-12 mm thick. For use in producing insoles for normal use, thicknesses in the range 4-6mm are preferred. Insoles for sports shoes may be up to 10mm or more. Material for handgrips may be 3mm thick. (Thinner foam is not readily available.)

The adhesive is preferably a filler - containing adhesive as described above or, less preferably, a breathable adhesive.

In one type of embodiment, the adhesive composition is primarily present in a fabric layer which is adhered thereby to a major surface of the foam material. Preferably the foam material is in the form of a sheet, and said fabric layers are adhered to both major surfaces. This gives a product which is reversible and



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CLAIMS

1. A porous, resiliently compressible and water-resistant composite material formed from (i) a low density flexible plastics foam material; (ii) an adhesive composition comprising a water-resistant glue composition and a water-absorbent inorganic filler, the filler being incorporated in an amount sufficient to confer water absorbance on a film formed from the adhesive composition; and (iii) at least one fabric layer, and wherein the adhesive composition is mainly present in the or each fabric layer which is adhered thereby to a respective major surface of the foam material.

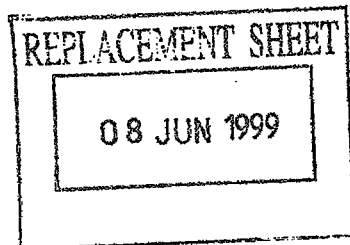
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2. A composite material according to claim 1 wherein the foam material is in the form of a sheet having a said fabric layer adhered to both of its major surfaces.

15
3. A composite material according to claim 1 or claim 2 wherein the adhesive composition includes a polyfunctional crosslinker which is reactive with carboxyl and hydroxyl groups.

20
4. A porous, resiliently compressible and water-resistant composite material formed from a low density flexible plastics foam material and an adhesive

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composition comprising a water-resistant glue composition
incorporating a polyfunctional aziridine crosslinker and
a water-absorbent inorganic filler, the filler being incorporated
in an amount sufficient to confer water absorbance on a
5 film formed from the adhesive composition.

5. A composite material according to claim 4 wherein
the plastics foam material was saturated with the
adhesive composition which was subsequently cured to
10 produce a reinforced foam material.

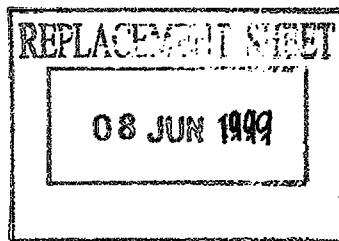
6. A composite material according to any preceding
claim wherein the glue composition is a latex.

15 7. A composition material according to claim 6 wherein
the latex is a carboxylated SBR latex.

8. A composite material according to any preceding
claim wherein the amount of filler is 5-7% of the
20 adhesive composition (w/w).

9. A composite material according to any preceding
claim wherein the filler is silica or calcium carbonate.

25 10. A composite material according to claim 9 wherein



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the filler is fumed silica.

5 11. A composition material according to any preceding claim wherein the adhesive composition includes a bactericide.

10 12. A composite material according to any preceding claim wherein the plastics foam material is a polyurethane foam.

13. A composite material according to any preceding claim wherein the density of the foam material is 10-60 kg/m³

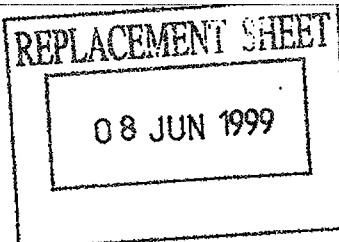
15 14. A composite material according to claim 13, wherein the density of the foam material is 30-50 kg/m³.

15. A composite material according to claim 14 wherein the density of the foam material is 40-45 kg/m³.

20

16. A method of producing a composite material according to any of claims 1-3 or any of claims 6 to 15 as appendant, directly or indirectly, on claim 1 which

25 comprises the following steps: (a) fabric is soaked with the adhesive composition; (b) the soaked fabric is



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applied to a major surface of the foam material and the assembly is oriented so that the fabric is on the underside; and then (c) heat is applied to the fabric.

17. A method according to claim 16 wherein heat is applied to the fabric using a jet of hot gas.

18. An insole comprising a composite material according to any of claims 1 to 15.

19. A handgrip comprising a composite material according to any of claims 1 to 15.

20. A method of producing or repairing a handgrip which comprises a composite material according to any of claims 1 to 15, said method comprising a step of applying a said adhesive composition to a substrate of low density flexible plastics foam material.

21. A method according to claim 20 wherein said adhesive composition comprises a polyurethane dispersion.

22. A method according to claim 20 or 21 wherein said adhesive composition comprises fumed silica.

