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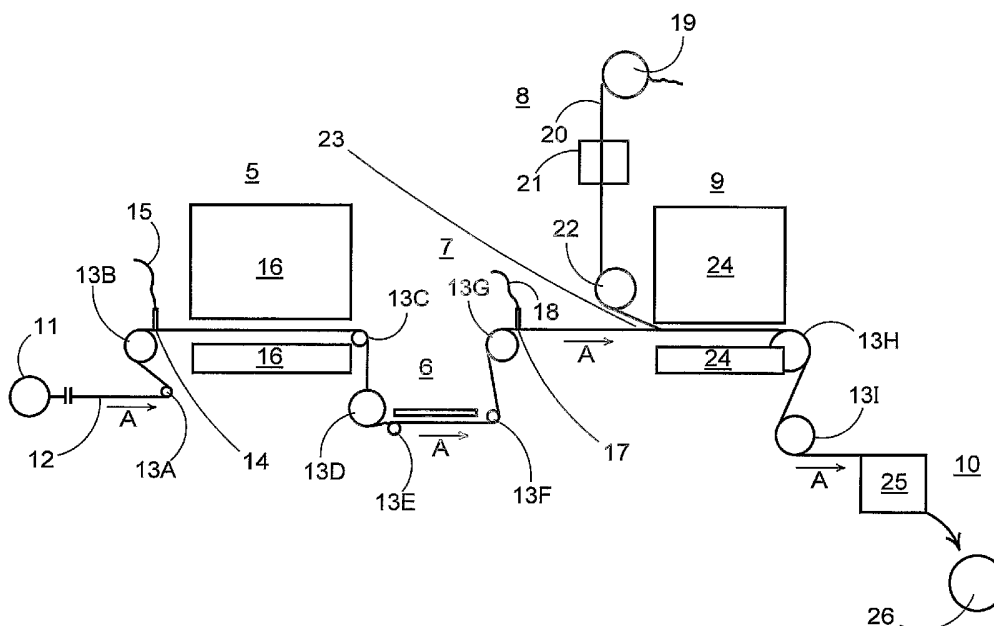
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(54) Title: FOAM MEMBRANES AND LAMINATES



(57) Abstract: A method of continuous in-line lamination of a foamed layer upon a moving carrier substrate, wherein a carrier substrate comprising a continuous sheet of carrier material (12) is directed to a liquid foam application station (7) in which an aqueous polymeric open-cell foam composition is applied as a liquid foam in a continuous manner upon a surface of the moving carrier substrate and the liquid foam layer thereby formed being allowed or caused to solidify, thereby forming a laminate comprising a solidified foamed layer adjacent to the carrier substrate.



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FOAM MEMBRANES AND LAMINATES

The present invention relates to foam membranes and laminates incorporating them and, in particular, foam membranes and such laminates particularly suited for used in laminated
5 performance fabrics and leathers, or alternatively in woundcare products such as wound dressings useful in the food packing industry.

A variety of processes are known for making laminated fabrics including a foam layer, particularly for fabrics exhibiting water-resistance with breathability (the ability to pass
10 moisture vapour) and which have acceptable drape, feel and elasticity. Conventionally, in making laminated fabrics, in-line lamination techniques using pre-formed sheets of material have been used to apply one or more further layers to substrates to produce a range of different fabrics. For example, in one technique a freestanding film is laminated to a heat-reactivated foam layer. However, heat reactivation increases the overall manufacturing costs due to
15 additional energy input.

In US Patent 4,539,255 a continuous layer of adhesive is used to bond a polyamino acid-modified polyurethane film to a textile fabric. However, a continuous adhesive layer not only impairs fabric breathability but also poses a solvent vapour exhaust problem. The
20 breathability problem is partially addressed in EP 0 296 361 (which is concerned with elastic fabrics) by using adhesive in a discontinuous layer to bond together two laminae. However, adhesive application in spot locations is troublesome and fails adequately to address the problem of organic solvent vapour exhaust.

In its broad sense, the invention provides in one aspect a method of continuous in-line lamination of a foamed layer upon a moving carrier substrate, wherein a carrier substrate comprising a continuous sheet of carrier material is directed to a liquid foam application station in which an aqueous polymeric foam composition is applied as a liquid foam in a continuous manner upon a surface of the moving carrier substrate and the liquid foam layer
30 thereby formed being allowed or caused to solidify, thereby forming a laminate comprising a solidified open-cell foamed layer adjacent to the carrier substrate.

The method optionally includes a step in which the substrate material not desired as part of the desired single or multiple layer end product and the remaining layer or layers are separated e.g. by mechanical splitting one from the other when the supplementary layer has formed a laminate with solid foam layer.

5

The textile fabric sheet, where used as a supplementary layer, may be made of a fabric for use in apparel, although textile fabrics for other purposes may be used e.g. medical drapes. In particular, any such textile fabric sheet as a supplementary layer may be made of a fabric for use in such apparel as garments, footwear, headwear or handwear. The fabric may be
10 filamentous or non-filamentous and when the former may be woven or non-woven.

The textile fabric sheet, where used as a supplementary layer, is preferably one made of material which resists water permeation (e.g. a material which is hydrophobic) such as one which has been rendered hydrophobic by oleophobic treatment of the fabric or e.g. the fibres
15 of which it may be made with a hydrophobicity-conferring agent such as a fluorocarbon resin, for example Scotchguard from 3M or Teflon from DUPONT.

In a particular embodiment of the invention, the supplementary layer e.g. textile fabric sheet is made of water-vapour-permeable material suitable for imparting breathability thereto in an
20 article of apparel. Such textile fabrics are often termed "performance fabrics". In any event, such textile fabric sheet may comprise a woven textile fabric (e.g. a textile fabric sheet which comprises synthetic textile fibres, such as polyester fibres) or the supplementary layer could comprise a leather fabric, for example a leather split for use in footwear.

25 In the case of so-called performance fabrics, the textile fabric sheet may comprise microfibre fabric made, for example, of a polyester such as a hydrophobic lightwoven polyester microfibre textile. Such microfibre fabrics are widely used and commercially available, for example from Toray UK.

30 Preferably, the fabric is Corona treated to provide additional adherence characteristics without affecting handle. The preferred Corona power rating is between 75 and 600W/m². Corona treatment is preferably carried out at a power rating of from 150 to 300 W/m² (e.g. a rating of 200 to 250 W/m² such as about 255 W/m²).

This method aspect of the invention is particularly advantageous in its application to hydrophobic fabrics such as hydrophobic woven fibrous textile fabrics or other textile non-leather fabrics as hereinbefore referred to in the context of the invention. Although such fabrics intuitively provide a poor substrate for adherence and ordinarily would be expected to provide a poor key between the foam and textile fabric layers, in practise the textile fabric used in preferred embodiments of the invention will have a structure characterised by voids which admit the liquid foam to some extent. So admitted foam when solid forms a foam anchor in the body of the textile fabric.

A particularly significant embodiment of the invention, therefore, provides a textile fabric sheet which, prior to its presentation to a liquid foam layer, has a structure which includes interstitial voids communicating to at least one face of said textile sheet and interstitially admissible to said liquid foam, the liquid foam and the textile fabric sheet being brought into interfacial contact such that liquid foam penetrates into the interstices of the textile fabric, formation of a composite sheet in which said foam forms a solid layer married to said textile fabric sheet producing solid foam forming a continuum between said foam layer and the interstices of said textile fabric to anchor the solid foam layer in the interstitial spaces of said textile fabric.

Of course, non-hydrophobic fabrics structured with interstitial voids which admit foam also provide for firm anchorage of the foam within the textile fabric body. Care is required in practice, however, to avoid so-called "strike through", and this applies in particular to non-hydrophobic fabrics. Strike through, a manifestation which occurs when the foam runs through the fabric layer, is particularly undesirable as it results in a stiffer, sometimes unacceptably stiff, laminate, which may also show visual defects. Practical solutions for strike through avoidance are described hereinafter in more detail.

A laminate of foam and polymer film may be applied to leather splits as a supplementary layer (e.g. foam to leather) to give performance advantages dependent upon the laminate chosen. For example, the foam membranes of the present invention can be used in comfort footwear, non-polish footwear and hydrolysis-resistant footwear.

Application of a textile fabric supplementary layer to the foam can best be effected using in-line lamination of such layer to the foam layer whilst still in liquid form.

Liquid foam can be formed as a moving liquid layer upon the carrier substrate using coating techniques well-known in art. For example, the liquid foam layer may be formed using knife-over-roll coating techniques (KOR techniques) or curtain coating.

In practice, the liquid foam is preferably derived from a liquid foam precursor composition comprising the preferred polymer(s), a foaming agent together optionally with one or more of a rheology modifier, a foam stabilizer, a foam booster, a foam-refining surfactant component, a cross-linking agent, and in embodiments adapted for use as woundcare dressings in the food packing industry: a metallic component.

In a preferred embodiment the open-cell, water-based foam membrane comprises a polymer material, a foaming agent and a rheology modifier. The foaming agent may, for example, be ammonium stearate. The rheology modifier may, for example, be a polyacrylic acid or a hydrophobically-modified alkali-swelling emulsion. In practice, the liquid foam precursor rheology should preferably be carefully monitored, evaluated and controlled, by choice of a rheology modifier, to provide a desired bubble size on foaming.

A finer bubble size is preferred for more robust end use applications, for example in foam membranes for lamination to leather splits or where the foam is to be applied to a thick resin layer forming a layer of the carrier substrate material. Approximately 50% of the bubbles may, in practice, be less than 30 microns in diameter, on foaming, in the case of many embodiments of the method of the invention. Bubble size may have significant influence on the preferred properties of strength, feel and breathability of the end product foam layer or composite layers.

In addition, the rheology of the liquid form precursor should ideally be carefully controlled to prevent "strike-through" and maintain "handle" (i.e. the drape and feel of the end product).

A starting viscosity of 60Ps (as measured on a Brookfield RV viscometer) is, for example, suitable to initiate the required foaming behaviour and indeed starting viscosity of the liquid

foam precursor composition may be conveniently be 50 to 150Ps, 60 to 110Ps being, however, more preferred. A particularly preferred starting viscosity is 100Ps.

The rheology modifier, if necessary, should in practice be carefully selected to be shear thinning in nature. The foam composition needs to shear thin on mechanical foaming and on application to the substrate in order to achieve and maintain its desired fine bubble size.

The foam stabiliser is conveniently sodium lauryl sulphate. Conveniently, the foam booster will be, for example, a cocoamide betaine.

The foam-refining surfactant components if used may typically be amine oxides or a sulpho succinate or blends thereof.

The choice of polymer material as the principal polymeric component of the aqueous foam composition is dependent upon the end use. Suitable polymer materials for the foam composition include polyurethanes, polyethylene vinyl acetate, polyethylene vinyl chloride, (meth) acrylic resin or a mixture of two or more thereof. A polyurethane blended with a (meth) acrylic polymer is usually preferred to give the desirable physical and permeation properties for laminated fabric embodiments of the invention. The principal polymer material of foam membranes for lamination to leather splits (e.g. for use in footwear) is most suitably a polyurethane or a copolymer comprising a high polyurethane content.

The liquid foam precursor composition is normally formulated to give a solids content (by weight) in water (or other aqueous medium) of 35% to 55%, preferably about 45%, with the polymer material accounting for 40% to 50% by weight (e.g. approximately 40% by weight) of the liquid foam. Other components of the liquid foam precursor composition are typically included in total to less than 5% by weight, and more typically between 1 and 3% by weight. The percentages by weight are given based on the total weight of the liquid foam composition precursor.

In some embodiments of the invention, the solidified foam becomes cross-linked in that the lamination method overall includes a cross-linking step. For this purpose, the liquid foam

precursor composition may include, as indicated above, a cross-linking agent. The cross-linking agent may, for example, be a melamine formaldehyde cross-linking agent.

5 Formation of the solid foam layer from the liquid foam layer applied to the moving carrier substrate in practice may usually involve drying to drive off the water of the aqueous medium in which the solids of the foam composition are distributed. As noted above, there may also be cross-linking. Drying will in general be artificial drying at elevated temperature, for example in an oven, temperatures above 60°C (e.g. above 100°C) at which the materials of the composite sheet are thermally stable being suitable. Drying may be carried out as an
10 alternative by exposing the foam to a flowing stream of air (or other gas) and, of course, a combination of such flow and elevated temperatures may well be adopted.

Where cross-linking of the foam composition is required, processing of the liquid foam will normally need to provide cross-linking conditions. Thermally activated cross-linking agents
15 achieve cross-linking typically at moderately elevated temperatures. The required temperature in the case of melamine formaldehyde cross-linkers is in the region of 140°C and above and such temperatures are generally suitable for effecting drying of the foam layer mentioned above.

20 The thickness of the foam layer may, of course, vary quite widely. In general, the solid foam layer will have a thickness of 10 to 1000 microns. The foam membrane is most commonly less than 100 micron thick and is preferably 20 to 50 microns thick (particularly about 35 microns thick). Thickness of liquid foam as applied to the moving carrier substrate will need to be set having regard to the desired solid foam layer thickness. This can be determined by
25 simple experiment although it has been found in typical practice of the invention, the foam layer thickness changes little from liquid to solid form in the lamination method so that any particular liquid foam thickness tends to result in the equivalent solid foam thickness.

As already intimated, the carrier substrate material should be capable of withstanding drying
30 temperatures adopted to solidify the liquid foam (and to withstand cross-linker activation temperatures where cross-linking is practiced), but this has not been a substantial practical burden in terms of substrate material selection. The carrier substrate may be polymer-coated whilst moving in line before application thereto of the liquid foam composition.

Preferred embodiments of the invention incorporate a textile fabric sheet present as a layer disposed over the face of said foam layer remote from said carrier substrate, the method including the step of forming the layer of the liquid foam upon said substrate and, whilst said
5 foam layer remains fluid at least at its face remote from said carrier substrate, bringing said textile fabric sheet into interfacial contact with said remote face of said foam layer.

The carrier substrate will in general consist of a carrier layer or comprise a carrier layer for supporting the foam as a liquid layer formed in line directly thereon or upon a secondary
10 coating layer most preferably formed in line upon such carrier layer.

The carrier substrate may conveniently comprise a paper or a polymeric film material. Paper, where used, may be embossed. Such polymeric film may be made of a polyalkylalkene, for example polymethylpentene.

15 In preferred embodiments, the carrier substrate comprises a film which has a surface energy of 20 to 50 Dynes, for example 25 to 35 Dynes. Most preferably, such carrier substrate film has a surface energy of 28 to 30 Dynes. The carrier substrate film is, for reasons already indicated, usually composed of a heat-resistant polymer, polymethylpentene being an
20 example. The carrier film should have a matt surface, typically with a degree of gloss of 4.5 ± 0.5 Lange at 85FS. The carrier film should also confer surface wettability. The carrier film may be embossed or otherwise treated to impart a special finish or surface topography to the end product. For example, the carrier film may roughen an originally soft and blocky polymer layer so that it does not show any blocking behaviour.

25 In some embodiments, the carrier substrate may comprise a carrier film coated with a secondary resin layer, conveniently a peelable resin, and in the case of laminates in which a supplementary leather layer is interfaced to a foam layer, the face of the latter remote from the leather material will most preferably carry a resin film, e.g. a polyurethane and/or acrylic film,
30 the carrier substrate usually being stripped from the remainder of the laminated product once such can be accomplished without damage to the laminate. Such resin may be a hydrophilic resin such as a polyurethane elastomer having in particular a high polyethylene oxide content of, for example, between 50 and 70% by weight. In particularly preferred embodiments, the

resin is a linear urethane co-polymer, e.g. of MW about 100,000 derived from polyethylene oxide (PEO), diphenylmethane 4,4'-diisocyanate (MDI), and butanediol (BDO). The viscosity of the resin is conveniently 10Ps regardless of resin identity (viscosity preferably being measured on a Brookfield RV viscometer). The resin may be applied to the moving carrier substrate at a concentration of 15% solids in a solvent dispersion medium such as dimethylformamide (DMF). The resin may provide additional functionality to the foam membranes and may in particular impart improved waterproofness, durability and aesthetic control. The resin coating may, for example, incorporate a colourant such as a pigment (e.g. carbon black) particularly in the case of laminates including a leather split destined as "artificial" leather in view of the richly coloured appearance in the end product simulating conventional real leather finishes.

Preferably the in-line lamination processing to form the required laminate is carried out to form a solid layer of a foam which has a density of from 0.15 to 0.55 g/cc. It is particularly preferred for the liquid foam to have a density on application of from 0.15 to 0.35g/cc.

The invention will now be described, by way of non-limiting example only, reference being made to the accompanying drawing which illustrates schematically a production method and apparatus for making laminated fabrics according to several different preferred embodiments of the present invention.

The apparatus shown in the figure comprises a carrier substrate film supply station 11 provided with a replenishable roll (not shown) of polymethylpentene carrier film 12 which is heat resistant under prevailing thermal exposure conditions. Extending downstream of the carrier film supply station 11 is a film transport pathway defined by rollers 13A to 13I each of which is rotatably mounted and formed with a polished stainless steel surface. The transport pathway just referred to passes through resin coating station 5 and transport region 6 to foam formation and foam layer application station 7, lamination station 9 and carrier finishing (or carrier film stripping and product take-up) station 10. The direction of transport of the carrier film is represented by arrow A shown at various points on the transport pathway.

Resin coating station 5 comprises a coating applicator head represented generally by reference numeral 14, flowable resin composition from a supply (not shown) being delivered thereto via

line 15. The resin coating station 5 further comprises an oven 16 which is electrically heated to a temperature of 60° to 90°C to evaporate solvent from the resin.

Foam layer formation station 7 comprises a KOR (knife-over-roller) foam application device
5 17 connected to a foam supply (not shown) by line 18. The foam supply will normally include a vessel in which the foam is produced mechanically in-situ immediately before application to the moving carrier substrate by injecting air into a suitable liquid foam precursor composition at the locus of an impeller mounted for rotation in the vessel.

10 Feeding to the transport path downstream of the foam layer formation station 7 but upstream of lamination station 9 is a textile fabric supply station 8 comprising a replenishable textile fabric supply roll 19 and a Corona treatment device 21, a lamination assembly (not shown in detail but including rotatable stainless steel surfaced roller 22 which redirects the Corona
15 treated face of the textile fabric web 20 to the surface of the still wet foam layer carried by carrier film 12) being provided to laminate the textile fabric web 20 to the foam layer. Oven 24 is provided to solidify the foam by evaporating water therefrom and is electrically heated to a temperature of up to 150°C.

Product finishing station 10 is fed with now formed and dried laminate from roller 13 I and
20 includes a stripper device (not shown) for stripping the carrier film from the laminate. The output from the stripper is to a laminate take-up station whose construction and make-up will be readily recognised by the skilled man as including an appropriate take-up roll but whose details have been omitted in the interests of simplicity.

25 In some embodiments of the method, the carrier film (whether resin coated or not) may be left intact, i.e. not removed from the remainder of the laminate. In these instances, the product finishing station may be omitted or adapted by exclusion of a carrier wind up roll.

The invention will now be exemplified by way of non limiting specific examples:-

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EXAMPLE 1 (In-line lamination of fabrics)

A polymer film/paper laminate carrier material namely Schoeller 165g TPX polymethylpentene (available from Felix Schoeller GmbH) is coated to a 60-300 micron wet

(10-50 micron dry) thickness with a polyurethane resin derived from MDI, BDO and a high content (60%) PEO and having a molecular weight of approximately 100,000. The polyurethane resin coating is applied as a 15wt% solids content in DMF dispersion having a viscosity of 10Ps. The polyurethane resin coating is dried by passing the resin coated film
5 into an oven with air flow assistance at a temperature of 60-90°C to produce a carrier substrate consisting of polyurethane coated polymethylpentene film. An aqueous polymer foam precursor dispersion (available as Dispersion 16 285D from Noveon, Inc.) is in situ mechanically foamed then immediately after foaming applied subsequently to the moving carrier substrate in an amount of 20-200 g/m² (20g for fabric – 200g for leather dry weight per
10 square metre). Whilst the foam layer is still wet, a Corona-treated hydrophobic lightwoven polyester microfibre having a weight of 50-150g/m² (available from Toray UK) is applied in line upon the still wet foam. The resulting laminate is dried and cured under cross-linking conditions in a further oven with air flow assistance at a temperature of 90-140°C. The carrier substrate and the remainder of the laminate are then stripped one from the other to produce a
15 3-layer laminate consisting of a textile fabric layer, a solidified foam layer having an open cell structure and a polyurethane film. The solid foam layer has a thickness of up to 1000 micron and a density of 0.4g/cm³. The open cells within the foam represented about 60% of the foam by volume.

20 EXAMPLE 2 (Split leather finishing treatment)

In a similar manner to the Example 1 procedure and also using production apparatus depicted in Figure 1, “Epsom” embossed paper carrier from Arjo Wiggins is resin-coated in-line with a highly pigmented polyester based urethane solution in DMF before drying and coating with a mechanically in-situ foamed 50/50 blend of Witcobond 279-34 from Baxenden Chemicals and
25 Hystretch V3 acrylic emulsion from Noveon Inc. The first resin layer of the moving carrier substrate is typically 20-30 microns thick and the foamed layer is 400 microns thick at a density of 0.4g/cc. The final product is removed from the carrier and wound or laminated in-line directly onto leather splits.

30 EXAMPLE 3 (Air flow control membrane for fabric systems)

In a procedure which is analogous to that described above with reference to Examples 1 and 2, and also using a production apparatus as depicted in Figure 1, an air flow control foamed membrane was produced for use in fabric systems. The carrier substrate was Schoeller 165g

TPX as in Example 1 which was not resin coated in any manner. Accordingly, in this embodiment, the moving carrier substrate initially consisted of two layers, namely a polymer film/paper laminate. The liquid foam precursor dispersion was polyurethane and/or acrylic based polymer, (although other polymer materials could be used providing an appropriate foam rheology, density and porosity). In this example, in-line lamination of a supplementary material layer is optional, as is carrier removal.

EXAMPLE 3A (Air flow control membrane for fabric systems)

The procedure of Example 3 was repeated. In addition, the foamed membrane was treated with a hydrophobicity-conferring coating sprayed on in-line before winding, namely a coating of Teflon from DuPont.

EXAMPLE 3B (Air flow control membrane for fabric systems)

The procedure of Example 3a was repeated except that the foamed material was subsequently spray coated off line.

EXAMPLE 4 (Wound dressing)

KB66 PUD based upon TMXDI from Cytec Industries and Terathane 2000MW polyol from Du Pont is available from Porvair and is supplied at 35-40% solids. This material is mechanically foamed and applied to a paper carrier (Super Bor Matt from Sappi) via conventional KOR coating techniques. The thickness of the finished membrane is 400 microns with a density of 0.25-0.3 g/cc. The material is dried and wound on to a reel with a matt finish polyethylene interleave (Hostophen available from Hoechst) to avoid blocking.

EXAMPLE 5 (Wound dressing)

CUR21 a PUD (polyurethane dispersion) available from Alberdink Boley was blended with Hystretch V29 (water based acrylonitrile latex) from Noveon in a 50/50 mix and made as above to a thickness of 300 micron.

The open-cell solid foam layers produced in examples 4 and 5 of the invention can provide superior breathability compared to the conventional closed cell foams and other wound dressing products that are presently available.

Examples 4 and 5 demonstrate production of laminated foam membranes for use as wound dressings for operatives in the food packing industry. The carrier substrate can be paper or TPX polymethylpentene film as in Example 1, the resin coating is used, being polyurethane based, the liquid foam precursor dispersion is based on polyurethane but also includes a
5 metallic component namely distaloy DH available from Hoganas, to ensure the end product wound dressing is 'metal-detectable' being an industry requirement in the relevant food preparation and packing trades. In line lamination is used based on PES (polyester) interleave and the carrier substrate is removed at product take up station 10.

Example 6

10 CUR21 castor oil based PUD and U400N polyether based PUD (both from Alberdinck Boley) are blended in a 50/50 mix with appropriate thickeners, pigments and stabilisers. Between 125phr and 300phr of stainless steel powder (430L available from Osprey Metals) is added to make the compound metal detectable when converted in to a dry product. This material is
15 produced as per the procedure in Example 3. However, due to the mass of the metal the final density of the product is around 1g/cc. The material is manufactured at a thickness of 100-150 micron.

The open-cell solid foam in laminates produced according to the invention can provide
20 superior breathability compared to conventional closed cell foams presently available. In addition, the process provides a foam layer or a foam membrane laminate which can be used in a variety of applications to enhance functionality. A particular advantage is that embodiments of the methods of the present invention can allow hydrophobically treated fabrics to be laminated in line to the foam layer whereas in conventional lamination
25 techniques fabrics must be treated after lamination to give the required water-resistant/waterproof qualities.

The foam membrane laminates of the invention enjoy abrasion resistance as a result of the cushion effect of the foam layer. Laminated fabrics of the present invention have several
30 further advantages over products made using conventional lamination techniques, particularly in relation to handling characteristics in that they are soft and drapable.

The invention expressly includes within its scope as a preferred embodiment thereof a method of producing a water-resistant laminated textile product which method comprises treating the filaments of a filamentous woven or non-woven textile fabric with a hydrophobicity-imparting agent before and/or after their formation into a fabric, bringing said fabric into interfacial
5 contact with a layer of a liquid aqueous polymer foam composition having an open-cell structure, said foam layer being supported upon a substrate comprising a separable carrier and said fabric being a sheet forming a part of said substrate exposed to said foam and/or a sheet disposed in contact interfacially with the face of said foam layer remote from said substrate, the ingredients and form of said foam composition being selected so that said foam
10 composition is a liquid which is admitted to interstices within the filamentous structure of said fabric, evaporating water from said foam composition, and optionally crosslinking the polymer thereof, so that said foam solidifies as a continuum which extends from the foam layer to the depth of interstitial invasion of the fabric by said liquid foam composition to form a laminate comprising the solid foam layer and said fabric, and thereafter optionally separating
15 one from the other (i) the laminated foam layer: fabric combination comprising any desired substrate component layers and (ii) said carrier so far as not desired as part thereof and any further substrate component layer not so desired. The features set out above may naturally be in any of the preferred forms of the invention described earlier herein either with or without reference to the figure or the Examples.

20 A particular embodiment of the invention is a multiple layer sheet-foam textile product comprising a textile fabric layer married directly to and interfacially in direct contact with a solid polymer foam layer having an open-cell structure, said textile fabric layer and solid polymer foam layer having no continuous or discontinuous layer of another material disposed
25 there between but one or more layers differently disposed optionally being present. The features set out above may naturally be in any of the preferred forms of the invention described earlier herein either with or without reference to the figure of the Examples.

CLAIMS

1. A method of continuous in-line lamination of a foamed layer upon a moving carrier substrate, wherein a carrier substrate comprising a continuous sheet of carrier material is directed to a liquid foam application station in which an aqueous polymeric foam composition is applied as a liquid foam in a continuous manner upon a surface of the moving carrier substrate and the liquid foam layer thereby formed being allowed or caused to solidify, thereby forming a laminate comprising a solidified open-cell foamed layer adjacent to the carrier substrate.
2. A method as claimed in claim 1 wherein said carrier material includes a surface layer for supporting the foam initially as a liquid layer.
3. A method as claimed in claim 2 wherein said carrier material comprises or is treated to become a two layer laminate comprising a primary carrier layer and a secondary coating layer before contacting said liquid foam.
4. A method as claimed in any preceding claim wherein said carrier substrate comprises paper based material and/or polymeric carrier film, such as a polyalkylalkene film, preferably polymethylpentene film.
5. A method as claimed in claim 3 or 4 wherein said secondary coating layer has a hydrophilic surface which is exposed to and becomes in interfacial contact with said foam layer.
6. A method as claimed in any one of claims 3 to 5 wherein said secondary coating layer is a polymeric layer.
7. A method as claimed in claim 6 wherein the polymeric layer is formed in-situ upon the moving carrier substrate and applied as a polymeric resin coating upon said primary supporting layer of the carrier material.

8. A method as claimed in any one of claims 2 to 7 wherein said secondary coating layer essentially consists of hydrophilic material, such as hydrophilic resin, preferably hydrophilic polyurethane.
- 5 9. A method as claimed in claim 8 wherein said polyurethane has a polyethylene oxide content of 50% to 70% by weight.
10. A method as claimed in claim 9 wherein said polyurethane is derived from polyethylene oxide, diphenylmethane 4,4'-diisocyanate and butanediol.
- 10 11. A method as claimed in any preceding claim including the step of mechanically foaming a liquid precursor to the liquid foam to be applied to the moving carrier substrate by agitation whilst injecting a gaseous phase, such as air or nitrogen, into the precursor.
- 15 12. A method as claimed in any preceding claim wherein the foam layer solidifies to form a solid layer of foam which has a density of from 0.15 to 0.45 g/cc.
13. A method as claimed in any preceding claim wherein said liquid foam is applied in such a thickness that said solid foam layer has a thickness of from 10 to 1000 microns and/or the application density of the liquid foam is 0.25 to 0.30 g/cc, and/or the liquid foam is applied to the carrier substrate in a dry weight of 15 to 300 g/m², preferably 30 to 250g/m².
- 20 14. A method as claimed in any preceding claim wherein the liquid foam is produced from a foam precursor composition comprising a polymer and a foaming agent together optionally with one or more of a rheology modifier, a foam stabilizer, a foam booster, a foam-refining surfactant component, a cross-linking agent, and a metallic component.
- 25 15. A method as claimed in any one of claims 11 to 14 wherein the liquid foam is produced from the precursor by agitating said precursor liquid in a container
- 30

agitated by an impeller, the gaseous phase being injected into the liquid precursor at the locus of the impeller.

- 5 16. A method as claimed in claim 14 or 15 wherein the rheology modifier is a hydrophobically-modified alkali-swellaable emulsion.
17. A method as claimed in any one of claims 14 to 16 wherein the foam stabilizer is sodium lauryl sulphate and/or the foaming agent is ammonium stearate.
- 10 18. A method as claimed in any one of claims 14 to 17 wherein the foam booster is a cocoamide betaine.
19. A method as claimed in any one of claims 14 to 18 wherein the foam-refining surfactant component is a surfactant blend.
- 15 20. A method as claimed in any preceding claim wherein the polymeric foam composition comprises polyurethane, a (meth)acrylic polymer, an ethylene copolymer or a mixture of two or more thereof.
- 20 21. A method as claimed in claim 20 wherein the polymeric foam composition comprises a blend of a polyurethane with a (meth)acrylic polymer.
22. A method as claimed in claim 20 or 21 wherein the ethylene copolymer is a copolymer of ethylene with vinyl acetate or vinyl chloride comonomer.
- 25 23. A method as claimed in any preceding claim wherein the liquid foam has a solids content of from 35% to 55% by weight of the liquid foam.
24. A method as claimed in any preceding claim wherein the polymer content of the liquid foam is from 40% to 50% by weight of the liquid foam.
- 30 25. A method as claimed in claim 24 wherein the additive content of the liquid foam is from 1% to 3% by weight of the liquid foam.

26. A method as claimed in any preceding claim wherein the liquid foam is a foam made by mechanical foaming.
- 5 27. A method as claimed in any preceding claim wherein about 50% of the void cells in the liquid foam have a diameter of less than 30 microns.
28. A method as claimed in any preceding claim wherein the liquid foam is applied to said moving carrier substrate at a viscosity of 50 to 150 Ps, preferably 60 to 110
10 Ps.
29. A method as claimed in any preceding claim wherein the solid foam is or becomes cross-linked.
- 15 30. A method as claimed in claim 29 wherein the liquid foam includes a cross-linking agent and said continuous in-line lamination is carried out at least in part under cross-linking conditions.
31. A method as claimed in claim 30 wherein said cross-linking agent is a melamine
20 formaldehyde.
32. A method as claimed in any preceding claim wherein said lamination includes drying of the liquid foam at elevated temperature such as at a temperature of 90° - 150°C, preferably 115° - 140°C, more preferably 115° to 130°C.
- 25 33. A method as claimed in any preceding claim wherein the lamination includes an additional step of applying a layer of supplementary material in line to the polymeric foam composition whilst in liquid form upon the carrier substrate, which supplementary material comprises a fabric material, a leather material or a
30 polymeric interleave material.
34. A method as claimed in claim 33 wherein the supplementary material comprises a textile fabric sheet made of a fabric useful in apparel.

35. A method as claimed in claim 34 wherein the textile fabric sheet is made of a fabric useful in garments, footwear, headwear or handwear.
- 5 36. A method as claimed in claim 34 or 35 wherein said textile fabric sheet is made of material which resists water permeation, such as hydrophobic material, or said textile fabric sheet is treated in-line or subsequently off-line with a hydrophobicity-conferring coating, so as to become resistant to water permeation.
- 10 37. A method as claimed in any one of claims 34 to 36 wherein said textile fabric comprises water-vapour-permeable material capable of imparting breathability thereto in an article or apparel.
- 15 38. A method as claimed in claim 33 wherein said layer of supplementary material comprises a layer of leather.
39. A method as claimed in claim 38 wherein said layer of leather comprises a leather split.
- 20 40. A method as claimed in any one of claims 34 to 37 wherein said textile fabric sheet comprises one or more of: synthetic textile fibres, non woven textile fibres, polyester fibres, and microfibre fabric.
- 25 41. A method as claimed in claim 40 wherein said textile fabric sheet comprises a hydrophobic lightwoven polyester microfibre textile.
- 30 42. A method as claimed in any one of claims 34 to 37 or 41 wherein said textile fabric sheet is subjected to corona treatment so that it has a corona-treated face, said corona-treated face being presented interfacially to said liquid foam layer for infiltration of said textile fabric sheet by said liquid foam layer before solidification of said foam layer.

43. A method as claimed in any one of claims 34 to 38 wherein the textile fabric sheet, prior to its presentation to said foam layer, has a structure which includes interstitial voids communicating to at least one face of said textile sheet and interstitially admissible to said liquid foam and wherein the liquid foam and the textile fabric sheet are brought into interfacial contact such that liquid foam penetrates into the interstices of the textile fabric, said formation of the composite sheet in which said foam forms a solid layer married to said textile fabric sheet producing solid foam forming a continuum between said foam layer and the interstices of said textile fabric to anchor the solid foam layer in the interstitial spaces of said textile fabric.
44. A method as claimed in any one of claims 34 to 38 or 42 wherein a said textile fabric sheet is present as a layer disposed over the face of said foam layer remote from said substrate, the method including the step of forming the layer of the liquid foam upon said substrate and, whilst said foam layer remains fluid at least at its face remote from said substrate, bringing said textile fabric sheet into interfacial contact with said remote face of said textile fabric sheet.
45. A method as claimed in any one of claims 2 to 10 wherein the substrate comprises a carrier coated with a resin film, the method comprising applying over said resin film a layer of a liquid water-based polymer open-cell foam and overlaying a textile fabric sheet onto said foam layer whilst at least the face of the foam layer for interfacially contacting said sheet remains a liquid foam face, the foam layer being subjected to artificial drying to form a solid layer married to said textile fabric sheet and the method including the optional step of separating one from the other the carrier of said substrate and said resin film when said foam layer has become solid.
46. A multiple layer sheet-foam textile product comprising a textile fabric layer married directly to and interfacially in direct contact with a solid polymer foam layer having an open-cell structure, said textile fabric layer and solid polymer foam layer having no continuous or discontinuous layer of another material disposed

there-between but one or more other layers differently disposed optionally being present.

47. A method of making an open-cell foam product in sheet or strip form for use as, or as part of, a wound dressing, which method comprises forming an open-cell solid foam layer from a liquid open-cell water-based polymer foam disposed as a layer upon a carrier substrate, and separating one from another the solid foam layer on the one hand and the carrier on the other hand, an interleave material optionally being present as a layer loosely adherent to the foam layer.

48. A fabric for use as, or as part of, a wound dressing comprising an open-cell polymer foam in sheet or strip form, the foam being free or substantially free of pyrogens, containing no organic solvent or derivatives thereof, the voids of the foam being air-filled.

49. Polymeric foamed material of open-cell structure in sheet or strip form in which the principal component of the foam comprises polymer of at least one of the following types; polyurethane, polyethylene vinyl acetate, polyethylene vinyl chloride and (meth) acrylic resin, the sheet or film material having a thickness of 10 to 1000 microns, and wherein at least about 50% of the foam bubbles have a diameter of less than 30 microns.

50. Material as claimed in claim 49 having a thickness of less than 100 microns.

51. Material as claimed in claim 50, in which the thickness is in the range 20 to 75 microns.

52. Material as claimed in any one of claims 49 to 51, in which the solidified foam is cross linked.

53. Material as claimed in claim 52, in which the cross linking agent present is or is derived from melamine formaldehyde.

54. Material as claimed in any one of claims 49 to 53, in which the principal polymeric component of the foam comprises (i) a polyurethane or (ii) a polyurethane copolymer comprising a high proportion of polyurethane, or (iii) polyurethane or a polyurethane copolymer blended with (meth) acrylic polymer.
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55. Material as claimed in any one of claims 49 to 54, in which the principal polymeric component is derived from aqueous polymer dispersion, suspension or solution, foaming agent and rheology modifier.
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56. Material as claimed in claim 55, in which the principal polymeric component is derived from aqueous foam precursor comprising polymer(s), foam stabiliser, foam booster, foam-refining surfactant and optionally (a) cross-linking agent and (b) metallic component.
- 15
57. A two layer laminate which consists of a layer of material as claimed in any one of claims 49 to 56 bonded directly to a secondary material or other continuous or discontinuous layer interposed between said layer of material and said secondary layer.
- 20
58. A laminate as claimed in claim 57, in which the secondary material comprises a resin film comprising polyurethane, polyurethane copolymer or acrylic film.
59. A laminate as claimed in claim 58, in which the resin is hydrophilic.
- 25
60. A laminate as claimed in any one of claims 57 to 59, in which the secondary material comprises an elastomer of polyurethane with a high proportion of polyethylene oxide.
61. A laminate as claimed in claim 60, in which the said proportion is in the range of
- 30
- 50% to 70% by weight.
62. A laminate as claimed in any one of claims 57 to 61, in which the secondary layer comprises a linear urethane copolymer.

63. A laminate as claimed in claim 62, in which the copolymer has a molecular weight of about 100,000 or greater.

5 64. A laminate as claimed in claim 62 or 63, in which the copolymer comprises polyethylene oxide.

65. A laminate as claimed in any one of claims 57 to 64, in which the secondary layer includes a colourant, such as a pigment, such as carbon black.

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66. A multi-layer laminate comprising a laminate as claimed in any one of claims 57 to 65 upon a carrier substrate from which the said two-layer laminate can be peeled.

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67. A multi-layer laminate as claimed in claim 66, in which the carrier substrate comprises paper which is optionally embossed.

68. A multi-layer laminate as claimed in claim 66 or 67, in which the carrier substrate comprises heat resistant polymeric film such as polyalkalkene and preferably polymethylpentene.

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69. A multi-layer laminate as claimed in claim 68, in which the polymeric film has a surface energy of 20 to 50 Dynes/cm², and a matt surface.

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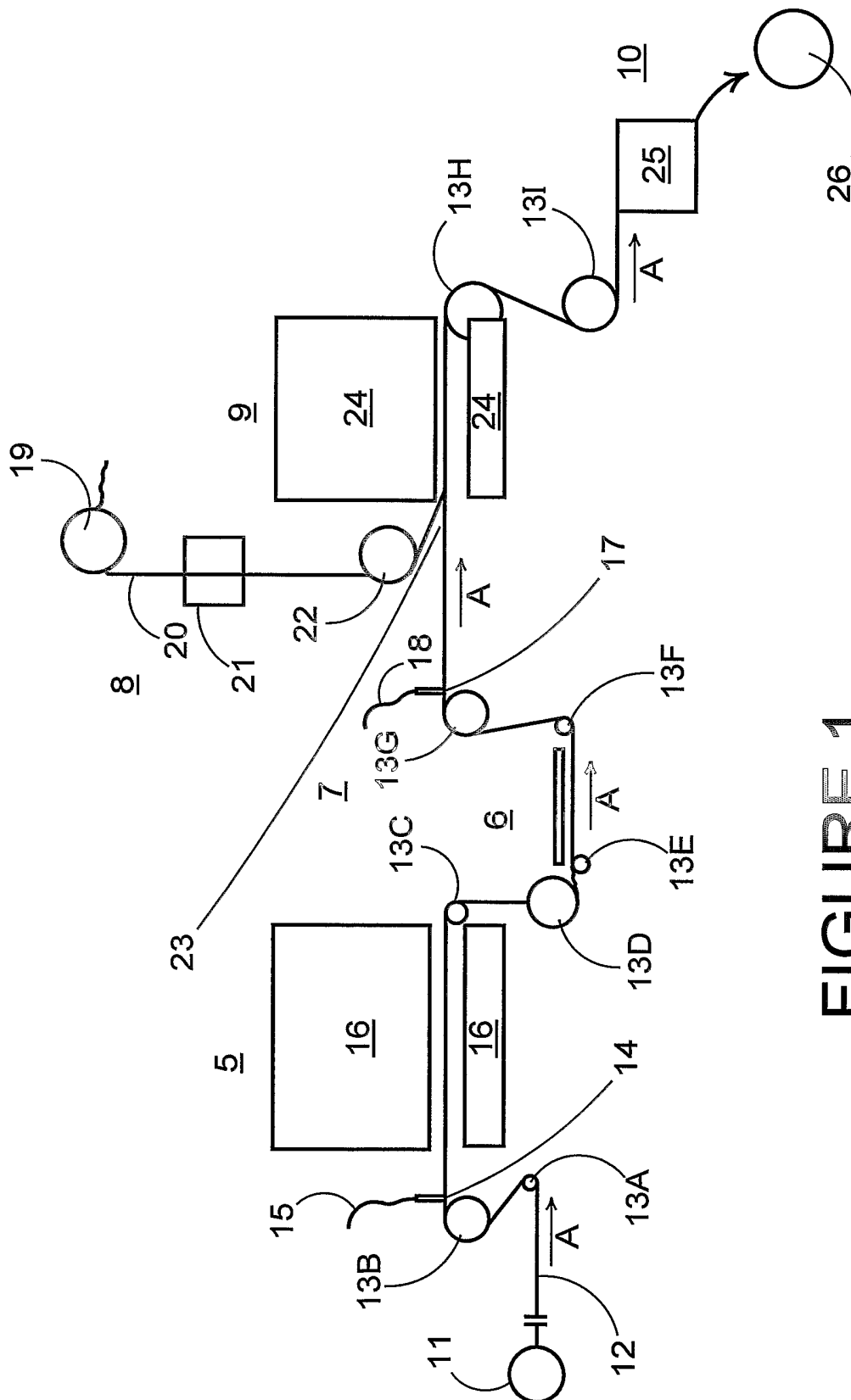
70. A multiple layer laminate comprising a laminate as claimed in any one of claims 57 to 69 and a supplementary layer in direct and intimate contact with a surface of the polymeric open cell foam layer.

71. A multiple layer laminate as claimed in claim 70, in which the supplementary layer comprises a textile fabric sheet or a leather sheet.

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72. A multiple layer laminate as claimed in claim 71, wherein the textile fabric sheet is hydrophobic, or has been rendered hydrophobic by oleophobic treatment of the said fabric or of its fibres, or by treatment with a hydrophobicity conferring agent.

73. A multiple later laminate as claimed in claim 71 or 72, wherein the textile fabric sheet is a water vapour permeable material for imparting breathability.
- 5 74. A multiple layer laminate as claimed in claim 73, in which the textile fabric sheet is a performance fabric.
75. A multiple layer laminate as claimed in claim 73 or 74 in which the textile fabric comprises a woven textile fabric comprising synthetic textile fibres.
- 10 76. A multiple layer laminate as claimed in claim 75, in which the fibres comprise polyester fibres.
- 15 77. A multiple layer laminate as claimed in any one of claims 70 to 76, wherein the supplementary layer is a flexible fabric sheet including interstitial voids.
Communicating to at least one face of said laminate and wherein solidified foam has penetrated into the interstices of the textile fabric.
- 20 78. A multiple layer laminate as claimed in any one of claims 70 to 77, in the form of a composite sheet or strip in which the foamed layer forms a solid layer married to the textile sheet whereby said solid foam forms a continuum between the foamed layer and the interslices of the textile fabric.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/000809

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B29C44/32 B32B5/20 B32B31/12		
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 D06N B29C B32B A61F		
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) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 279 762 A (KOATSU CLOTH CO LTD) 29 January 2003 (2003-01-29) abstract paragraphs '0009!', '0010! page 3, line 28 - line 31 paragraphs '0013!', '0022! - '0031! paragraph '0041! figures 2b,6a	1-78
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A	GB 1 171 932 A (CARL FREUDENBERG) 26 November 1969 (1969-11-26) page 1, line 37 - line 71 page 2, line 8 - line 96 page 3, line 29 - line 39	1-78
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> 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 3 June 2004		Date of mailing of the international search report 11/06/2004
Name and mailing address of the ISA 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		Authorized officer Lanaspeze, J

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In International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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