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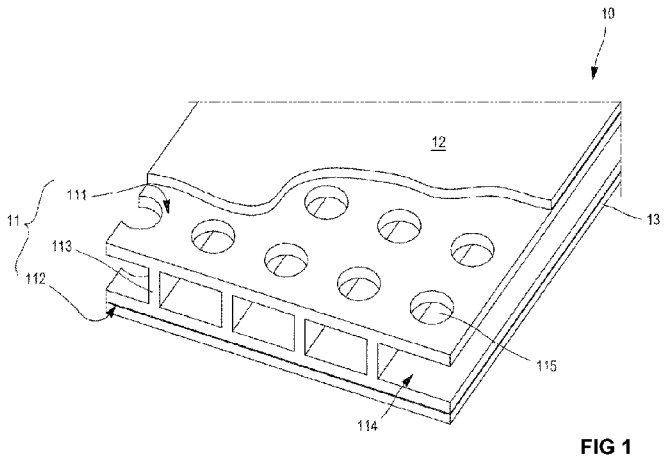



FIG 1

(57) **Abstract**: Membrane element (10, 50) for selective transport of one or more compounds, comprising a polymeric membrane layer (12, 13) and a support (11). The polymeric membrane layer (12, 3) is operable for selectively transporting the one or more compounds through the membrane layer and comprises a first polymer compound. The support (11) has a thickness of at least 200 μm and comprises a support layer (111, 112) enabling the one or more compounds to permeate through the support layer, wherein the support layer comprises a second polymer compound. The membrane layer (12, 13) is obtained by application of a solution of the first polymer compound on the support layer (111, 112) and forming the membrane layer through phase separation of the first polymer compound from the solution, wherein the membrane layer and the support layer share an interface. The first and second polymer compounds are such that the membrane layer is solvent bonded to the support layer through molecular interaction between the first and second polymer compounds at the interface when the membrane layer is formed.

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# SUPPORTED FILTRATION MEMBRANES AND METHODS OF MANUFACTURING

**[0001]** The present invention is related to improvements in polymeric membrane layers provided on a sheet-like, film-like or plate-like support, for use in solid-liquid, liquid-liquid or gas-liquid separation.

**[0002]** Polymeric membrane layers typically have a poor mechanical strength and need to be supported. The attachment of the membrane layer to its support is an issue of critical importance in applications in which the membrane must be able to withstand a pressure difference from both sides, and in applications in which the membrane is subjected to mechanical stress. This is the case in e.g. membrane filtration applications, in which backwashing and air bubbling (air scrub) is used for cleaning the membranes.

**[0003]** A number of solutions for bonding the membrane layer to its support have been proposed in the prior art. Most widespread is forming the membrane layer by applying a polymeric membrane solution on a non-woven fabric layer, followed by solidifying the membrane. In such cases, the membrane solution may penetrate between fibres of the fabric, such that bonding to the support is obtained by mechanical interlocking. Solutions of this kind are known from EP 0662341, EP 1462154 and JP 2009-045559. A drawback of using fabrics is that due to their rough surface, the membrane layer must be quite thick in order to obtain a covering without defects.

**[0004]** Another solution known from Japanese patent application publication No. 08-010587 (1996) is to bond the membrane on the support by welding. Weld seams are formed at distributed locations. A drawback of this solution is that, since the membrane is not porous at the weld seams, the proportion of welds to the total surface area must be limited in order to avoid a loss in separation performance. Furthermore, the membrane resistance to back pressure is very poor and fatigue cracks can readily form at the weld seams.

**[0005]** Yet another solution is known from WO 2013/113928, wherein a membrane forming solution is directly coated on a rigid, perforated support plate. The membrane solution penetrates the perforations to form undercuts which mechanically anchor the membrane layer on the support. In this case the perforations in the rigid support plate act both as anchor points and as passages for the filtrate.

**[0006]** WO 2006/071979 describes an air filtration membrane made of nanofibers obtained by electroblowing a polymer solution on a web formed of a scrim layer. The scrim layer is typically a woven supporting layer and comprises polymeric fibers. The polymer of these fibers is selected to be compatible with the polymer of the electroblown

nanofibers and at least partially miscible or swellable in the processing solvent for forming the nanofibers. Since the nanofibers are deposited on the scrim layer when still partially in solution, they solvent-bond to the fibers of the scrim layer when a vacuum pressure is applied underneat the web, which removes the solvent from the nanofibers.

**[0007]** The above nanofiber membranes are however not or poorly suitable for nanofiltration or ultrafiltration applications. Their permselectivity is very difficult to control and furthermore such membranes result to have poor mechanical strength. That is why nanofiber membranes are practically only used in air (solid-gas) filtration. Another disadvantage of the above nanofiber membranes is that they necessarily need be supported by a fibrous web, since otherwise the solvent cannot be removed. For the sake of clarity, membranes as described in the present invention relate to polymeric membranes obtained by phase separation, which is a distinct membrane forming process.

**[0008]** Along the edges, liquid-tight sealing must be ensured between the membrane layer and its support or backing. Sealing can be carried out by gluing or welding, such as described in JP 2009-045559 and JP 08-010587, or by clamping the membrane and support in a frame, such as described in WO 2011/026879. In all cases, edge sealing turns out to be an additional manufacturing step, which increases cost of the final membrane element.

**[0009]** An objective of aspects of the present invention is to provide an economical alternative for attaching a membrane, obtained through phase separation, to its support. An objective of aspects of the invention is to improve bonding between membrane and its support.

**[0010]** An objective of further aspects of the present invention is to provide an improved way of edge sealing the membranes.

**[0011]** According to first aspects of the invention, there are therefore provided membrane elements for selective transport of one or more compounds, as set out in the appended claims.

**[0012]** A membrane element for selective transport of one or more compounds comprises a polymeric membrane layer and a support. The polymeric membrane layer is operable for selectively transporting the one or more compounds through the membrane layer and comprises a first polymer compound. The support has a thickness of at least 200 µm and comprises a support layer provided with through-holes through the support layer. The through-holes have a diameter of at least 25 µm and enable the one or more compounds to permeate through the support layer. Advantageously, the through-holes form the only permeability for the one or more compounds through the support layer.

**[0013]** The membrane layer is obtained by application of a solution of the first polymer compound on the support layer and forming the membrane layer through phase separation of the first polymer compound from the solution. Advantageously, the solution, when applied, at least partially fills the through-holes, such that the membrane layer extends in the through-holes when it is formed. The membrane layer and the support layer comprise a common interface, which is advantageously porous.

**[0014]** The support layer comprises a second polymer compound. The first and second polymer compounds are such that the membrane layer is solvent bonded to the support layer through molecular interaction between the first and second polymer compounds at the interface when the membrane layer is formed. Advantageously, forming the membrane layer comprises removing a solvent from the solution at the interface.

**[0015]** According to second aspects of the invention, there are provided methods of manufacturing a membrane element operable for selective transport of one or more compounds, as set out in the appended claims.

**[0016]** A method of manufacturing a membrane element comprises: (i) preparing a membrane forming solution comprising a first polymer compound and a first solvent of the first polymer compound and (ii) providing a support having a thickness of at least 200 µm. The support comprises a support layer comprising a second polymer compound. The support layer is provided with through-holes through the support layer, advantageously having a diameter of at least 25 µm and enabling the one or more compounds to permeate through the support layer.

**[0017]** In a following step, the membrane forming solution is applied on the support layer to form a coating on the support layer. As a result, the support layer and the coating share a common interface, which is advantageously flat.

**[0018]** In a yet following step, a membrane layer is formed by phase separation of the first polymer compound from the membrane forming solution which removes the first solvent from the coating.

**[0019]** In methods of the invention, the second polymer compound is brought in a swollen or at least partially solvated state at the interface prior to or during application of the membrane forming solution on the support layer. The first polymer compound and the second polymer compound are selected, such that molecular interactions between the first polymer compound and the second polymer compound occur at the interface, in particular when the second polymer compound is in the swollen or at least partially solvated state. The molecular interactions are such that the membrane layer solvent bonds to the support layer when the membrane layer is formed. This bonding is advantageously assisted or brought about by removal of the first solvent from the interface by the phase separation.

**[0020]** In their efforts to continuously improve supported polymeric membranes and their method of manufacturing, and while directly coating a polymeric membrane forming solution on a polymeric support, the inventors found that, surprisingly, the membrane readily bonded to the polymeric support once the membrane layer was formed through phase separation. This bond resulted to be so strong, that not only can it make mechanical anchoring of the membrane layer to the support superfluous, but it also provides a strong sealing between membrane and support, so that, as a further advantage, no additional edge sealing is needed. Without wishing to be bound by any theory, it is believed that the bonding is due to the fact that a superficial layer of the polymeric support is softened or (at least partially) dissolved by action of the solvent used in the membrane solution. This makes the polymer chains of the support mobile. When furthermore the polymer of the membrane and the polymer of the support are compatible, sufficiently strong molecular interactions, such as but not limited to a (partial) interpenetration and entanglement between the chains of the two polymers, occur at the interface between membrane and support. Surprisingly, when phase separation is carried out to form (solidify) the membrane, these molecular interactions do not disappear, but are made permanent, resulting in strong bonds.

**[0021]** What was also found surprising, is that the interlinking of the membrane and the support did not negatively affect the membrane performance.

**[0022]** In a broader aspect of the invention, the solvent of the membrane solution, and the solvent used for solvating the support polymer does not need to be the same, as long as they are miscible.

**[0023]** It will hence be clear that aspects of the invention enable the creation of a strong bond between a membrane layer and its polymeric support during the process of forming the very own membrane layer. No special or additional manufacturing steps are required, so that the invention leads to more economical products and processes.

**[0024]** Aspects of the invention will now be described in more detail with reference to the appended drawings, wherein same reference numerals illustrate same features and wherein:

**[0025]** Figure 1 represents a perspective and partial cut-out view of a membrane element according to aspects of the invention;

**[0026]** Figure 2 represents a process for producing the membrane element of Fig. 1;

**[0027]** Figure 3 represents a modified process for producing the membrane element of Fig. 1, wherein a pre-treatment of the support is carried out before execution of the process of Fig. 2;

**[0028]** Figure 4 represents an alternative process for producing the membrane element of Fig. 1;

**[0029]** Figure 5 represents a front and partial cut-out view of a membrane element according to aspects of the invention;

**[0030]** Figure 6 represents a separation device implementing the membrane elements of Fig. 5;

**[0031]** Figures 7A and 7B represent SEM photographs of a PES/PVP membrane coated on a PC film; Figure 7B is an enlargement of Figure 7A;

**[0032]** Figures 8A and 8B represent SEM photographs of a PEI membrane coated on a PEI film; Figure 8B is an enlargement of Figure 8A;

**[0033]** Figure 9 is a partial cross section of the membrane element of Fig. 5;

**[0034]** Figures 10A and 10B represent SEM photographs of a comparative example of a Zirfon® membrane coated on a PC sheet; Figure 10B is an enlargement of Figure 10A.

**[0035]** A membrane as referred to in the present description refers to a layer or sheet of a solid, continuous and advantageously porous material having a structure allowing one or more compounds to be selectively transported through the membrane and hence enabling to separate the one or more compounds from a feed, which can be liquid or gaseous. Such membranes are referred to as semi-permeable membranes. A membrane hence features a determined permeability for the one or more compounds. The permselectivity can be determined by all kinds of separation mechanisms, such as but not limited to a characteristic pore size of the membrane (e.g. microporous or nanoporous filtration membranes), or by a characteristic attraction of specific charge types (e.g. an ion exchange membrane).

**[0036]** The membranes as referred to in the present description are advantageously configured for separation of compounds by microfiltration, ultrafiltration, nanofiltration, reverse osmosis, forward osmosis, pressure retarded osmosis, membrane bioreactors, pervaporation, membrane distillation, supported liquid membranes, pertraction, membrane absorbers, enzyme reactors, membrane contactors, or (reverse) electrodialysis. The membranes can be configured as ion exchange membranes. They can be configured as separator membranes, such as battery separator membranes e.g. allowing transport of monovalent ions (e.g. protons) through it while retaining other (multivalent) ions.

**[0037]** The membranes as referred to in the present description are membranes obtained by subjecting a polymer solution to a phase separation process. Phase separation, which is also referred to as phase inversion, is a well-known process wherein demixing between the polymer and the solvent is induced. As a result of demixing, the

polymer precipitates, thereby forming a membrane lattice with a desired structure (pore size, pore structure, etc.). Further process steps can be carried out in order to remove the solvent completely (e.g., washing in a possibly hot water bath) and to obtain a final pore structure (e.g., removing pore formers by washing in a bleach solution). Demixing can be induced based on several techniques. One possibility is thermally induced phase separation (TIPS), wherein demixing is induced by a temperature change at the interface of the polymer solution. Another possibility is to induce a chemical reaction in the polymer solution, causing demixing. This is referred to as reaction induced phase separation (RIPS). However, in the vast majority of cases, demixing is induced by phase diffusion. The polymer solution is contacted with another phase, being a liquid (liquid induced phase separation or LIPS), or a gas (vapour, referred to as vapour induced phase separation or VIPS), which is a non-solvent of the polymer but which is miscible with the solvent of the polymer solution. The liquid or vapour will diffuse through the polymer solution and cause a local change in the polymer solution composition, inducing demixing. As a result, the polymer precipitates from the solution. LIPS is also referred to as immersion precipitation. It will be convenient to note that any phase separation process can be applied to prepare the membranes as described herein.

**[0038]** The membrane comprises or consists of an advantageously thermoplastic polymer compound, which will be referred to hereinafter as the first polymer compound. The first polymer compound is the principal or primary polymeric compound used for preparing the membrane forming solution, e.g. the polymer compound present in largest amount in the membrane forming solution. The first polymer compound can be polysulfone (PSU), polyethersulfone (PESU), a grafted variant of them, or a copolymer of either one of the polymers. The first polymer compound can be polyvinylidene fluoride (PVDF), polyvinylidene chloride (PVDC), a grafted variant of them, or a copolymer of either one of the polymers. The first polymer compound can be polyvinyl chloride (PVC), chlorinated polyvinyl chloride (CPVC), a grafted variant of them, or a copolymer of either one of the polymers. The first polymer compound can be a polymer of the polyaryletherketone (PAEK) family, such as polyether ether ketone (PEEK), a grafted variant of any of these polymers, such as sulfonated polyether ether ketone (PEEK-WC), or a copolymer of any one of these polymers. The first polymer compound can be polychlorotrifluoroethene (PCTFE), polyether imide (PEI), polyimide (PI), polyamide imide (PAI), polyacrylonitrile (PAN), polyurethane (PUR), in particular a thermoplastic polyurethane, a grafted variant of any of these polymers, or a copolymer of any one of these polymers. The first polymer compound can be polyphenylene sulphide (PPS), cellulose acetate (CA), cellulose triacetate (CTA), a grafted variant of any of these polymers, or a copolymer of any of these polymers. The

copolymers as indicated above can be suitable copolymers of the indicated polymer with any one of polyvinyl chloride, polymethyl methacrylate (PMMA), polycarbonate (PC), cyanoacrylate, cellulose triacetate, polyphenylene sulphide, polystyrene (PS), polyvinyl alcohol (PVA), polyvinyl acetate (PVAc), and polyamides such as polycaprolactam (nylon 6) and nylon-6,6. The first polymer compound can be a suitable blend of two or more of the above listed polymers.

**[0039]** The amount of first polymer compound in the (dry) (final) membrane is advantageously at least 5% by weight, advantageously at least 10% by weight, advantageously at least 25% by weight, advantageously at least 35% by weight, advantageously at least 50% by weight. The first polymer compound can be an organic binder forming a matrix or lattice of the membrane, in which a possibly hydrophilic filler material is optionally dispersed. The filler material may be organic and is advantageously one or a combination of: hydroxypropylcellulose (HPC), carboxymethylcellulose (CMC), polyvinyl pyrrolidone (PVP), cross-linked polyvinyl pyrrolidone (PVPP), polyvinyl alcohol, polyvinyl acetate, polyethylene oxide (PEO), polyethylene glycol (PEG), and glycerol. Such filler materials can be provided as pore formers and can be removed in a post treatment step, such as by washing in a bleach solution (e.g. for PVP). Other filler materials, which remain in the final membrane layer are listed below. The filler material can be an amine, such as but not limited to one or a combination of: monoethanolamine (MEA), diethanolamine (DEA), polyethylenimine (PEI), aminopropyl-trimethoxysilane and polyethylenimine-trimethoxysilane. The filler material can be an amide or amine containing polymer, such as but not limited to one or a combination of: polyamide (PA), polyurethane (PUR), polyvinylamine (PVAm) and melamine. The filler material may be inorganic, such as one or a combination of $TiO_2$, $HfO_2$, $Al_2O_3$, $ZrO_2$, $Zr_3(PO_4)_4$, $Y_2O_3$, $SiO_2$, carbon, possibly on Pt, Ru or Rh support, $BaSO_4$, $BaTiO_3$, perovskite oxide powder materials, zeolites, metal-organic frameworks (MOF) and silicon carbides. Functionalized variants of the filler materials (such as aminated, sulfonated, acrylated) can be used. Combinations of the above organic and inorganic materials can be used as well as filler material.

**[0040]** A membrane element as used in the present invention, comprises a membrane and a support to which the membrane is bonded.

**[0041]** The support, which can be a reinforcing support for the membrane, is advantageously shaped as a (flat) plate, board, panel, (polymeric) film, (continuous) web or the like. The support advantageously comprises or consists of an extruded or otherwise made continuous polymeric film or sheet forming a surface layer configured for forming an interface with the membrane. An advantage of using continuous polymeric films is that the interface (or contact) area between support and membrane will be large resulting in a large

area for molecular interactions and hence strong bonds. Such films also are stronger and more rigid than fabrics of a same thickness. The support advantageously comprises or consists of a layer bonded to the membrane, the layer having one or more of the following properties: it is dense, it is solid, it is impermeable – at least for liquids. The term dense may refer to a material being free from pores which are interconnected from one surface to the opposite surface, advantageously a material being free from porosity at all. In determining the quality of being dense, the through-holes, as defined below, shall be disregarded.

**[0042]** Supports according to aspects of the invention have a permeability for the one or more compounds which the membrane is configured to selectively transport or separate. The permeability is advantageously obtained by through-holes (e.g. perforations) provided in at least the (impermeable) surface layer. The dimensions of the through-holes are not particularly limited and suitable dimensions depend on the application. The through-holes advantageously have a size smaller than or equal to 2 mm, advantageously smaller than or equal to 1.5 mm, advantageously smaller than or equal to 1.2 mm, advantageously smaller than or equal to 1.0 mm. When the holes are too large, smooth coating may be problematic. The through-holes have a size of at least 25 µm, advantageously at least 50 µm, advantageously at least 100 µm. When holes are too small, a reduced flow rate results. In addition, too small holes can be closed under attack by the solvent. The size of the through-holes refers to a dimension along a straight line passing from side to side of the through-hole, through its centre, i.e. diameter.

**[0043]** The through-holes (perforations) advantageously have monodisperse shape and/or size (diameter). By way of example, considering all the through-holes in the surface layer of the support, a mean diameter and a standard deviation of the diameter can be determined. Advantageously, the standard deviation of the diameter has a value smaller than or equal to 25% of the mean diameter, advantageously smaller than or equal to 20% of the mean diameter, advantageously smaller than or equal to 15 % of the mean diameter, advantageously smaller than or equal to 10% of the mean diameter.

**[0044]** The through-holes can be such that the surface layer of the support advantageously exhibits an open area (porosity due to the through-holes) of at least 2%, advantageously at least 5%, advantageously at least 10%, advantageously at least 15%, advantageously at least 20%, advantageously at least 25%, advantageously at least 30%, advantageously at least 35%. The open area can be 80% or smaller and is advantageously at most 70%, advantageously at most 60%, advantageously at most 55%, advantageously at most 50%. The open area refers to the area of the through-holes per unit total area of the outer surface (including the through-holes), expressed in percentage values. In defining the total area of the outer surface, any edge region of the membrane element where the

membrane layer is sealed fluid-tightly, is disregarded. The open area should advantageously be not too low to provide for sufficient flux through the support outer layers on the one hand, but neither too high in order not to compromise the stiffness of the support structure on the other. It will be convenient to note that the complement of the open area (i.e. 100% – open area) refers to the interfacial surface between membrane and support, which is the area that is available for bonding. Hence also in this regard, the open area should not be too high.

**[0045]** There is no restriction on the cross-sectional shape of the through-holes, i.e. they may be circular, square, polygonal, star-shaped or slit-shaped holes, or holes of any other suitable shape. Circular or polygonal perforations are preferred, and the perforations advantageously have substantially cylindrical or prismatic shape with axes advantageously perpendicular to the outer surface(s). The through-holes advantageously are not interconnected between one another within the surface layer.

**[0046]** When one disregards the through-holes, the film is advantageously non-porous, or advantageously comprises a dense layer (being non-porous). The film advantageously does not have an open or interconnected porosity other than the perforations. Open or interconnected porosity refers to a porosity providing liquid (water) permeability at 1 bar differential pressure.

**[0047]** The support can comprise an integrated permeate channel. That is, the support can be structured so as to comprise opposite outer surface layers which are spaced apart and secured to each other by spacing members extending between the outer surface layers throughout the support. The spacing members hence define a permeate collection layer interposed between the outer surface layers, referred to as an integrated permeate channel. In this case, the permeability of the outer surface layers allows access to the integrated permeate channel. Such a structure can e.g. be obtained by multi-walled or multi-skinned boards or panels.

**[0048]** The support has a thickness of at least 200 µm, which refers to the total thickness of the support structure.

**[0049]** The support (i.e. at least the outer surface layer arranged for forming an interface with the membrane) advantageously does not comprise any fabric, such as a non-woven or woven sheet made of mono- or multifilaments. These filaments are very prone to attack by the solvent which may lead to early disintegration of the fabric support.

**[0050]** According to aspects of the invention, the membranes are bonded to the support by molecular interaction, such as molecular interpenetration, molecular entanglement, molecular interdiffusion, or molecular adhesion between polymer chains of the membrane and polymer chains of the support. Such molecular interactions are advantageously physical interactions between molecules, rather than chemical ones.

**[0051]** In order to obtain membrane bonding to the support according to aspects of the invention, it will be appreciated that the membrane and the support need to share an interface in which the first polymer compound (of the membrane) can interact at the molecular level with an advantageously thermoplastic polymer compound of the support, which will be referred to hereinafter as the second polymer compound. Hence, both the first polymer compound and the second polymer compound need to be present at the interface.

**[0052]** The second polymer compound can be polysulfone (PSU), polyethersulfone (PESU), a grafted variant of them, or a copolymer of either one of the polymers. The second polymer compound can be polyvinylidene fluoride (PVDF), polyvinylidene chloride (PVDC), a grafted variant of them, or a copolymer of either one of the polymers. The second polymer compound can be polyvinyl chloride (PVC), chlorinated polyvinyl chloride, a grafted variant of them, or a copolymer of either one of the polymers. The second polymer compound can be a polymer of the polyaryletherketone (PAEK) family, such as polyether ether ketone (PEEK), a grafted variant of any of these polymers, such as sulfonated polyether ether ketone (PEEK-WC), or a copolymer of any one of these polymers. The second polymer compound can be polychlorotrifluoroethene (PCTFE), polyether imide (PEI), polyimide (PI), polyamide imide, polyacrylonitrile (PAN), polyurethane, in particular a thermoplastic polyurethane, a grafted variant of any of these polymers, or a copolymer of any one of these polymers. The second polymer compound can be polyphenylene sulphide (PPS), cellulose acetate, cellulose triacetate (CTA), a grafted variant of any of these polymers, or a copolymer of any of these polymers. The second polymer compound can be: polycarbonate (PC), poly(methyl methacrylate) (PMMA), polyamide (e.g., nylon), polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), polychlorotrifluoroethylene (PCTFE), polybutyrene terephthalate (PBT) and polyphenylene sulphide (PPS), a grafted variant of any of these polymers (such as aminated sulfonated, or acrylated), or a copolymer of any of these polymers. The second polymer compound can be polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), possibly modified by copolymerization such as PET-G (Glycol-modified), or amorphous PET (PET-A). The second polymer compound can be a suitable blend of two or more of the above listed polymers. It will be convenient to note that the support can be formed as a multi-layer structure wherein the layers can be made of different materials, such as PET-GAG (a multilayer PET-G foil with PET-A core), or including non-polymers such as metals. Alternatively, the support can be formed of a structure formed of different compounds and having a gradient of one or more compounds across the structure. At least an outer surface of the support forming an interface with the membrane, and possibly the entire support, comprises or consists of the second polymer compound. Hence, at the outer surface of the

support forming an interface with the membrane, the second polymer compound is present in a sufficient amount to cause sufficiently strong interactions with the first polymer compound.

**[0053]** The amount of second polymer compound in an outer surface layer of the support forming an interface with the membrane is advantageously at least 5% by weight, advantageously at least 10% by weight, advantageously at least 25% by weight, advantageously at least 35% by weight, advantageously at least 50% by weight. The outer surface layer, and possibly the entire support, can consist of the second polymer compound. An outer surface layer can be defined as a material outermost layer or skin of the support configured to contact the membrane and having a thickness of 10 µm, advantageously 25 µm, advantageously 50 µm, advantageously 100 µm.

**[0054]** In order to obtain sufficiently strong interactions yielding suitable bonding between membrane and support, the first polymer compound and the second polymer compound must be compatible. In general, compatibility refers to the first and the second polymers being able to forming a miscible, homogeneous blend being usually caused by sufficiently strong interactions between the polymers. In general, miscibility refers to the ability of the first and the second polymer to forming a blend that is a single phase structure. The concepts of compatible and miscible polymers are defined by *"W.J. Work, K. Horie, M. Hess and F.T. Stepto in International Union of Pure and Applied Chemistry – Definitions of terms related to Polymer Blends, Composites and Multiphase Polymeric Materials - Pure & Applied Chemistry, Vol. 76, No. 11, page1987 (miscible) and page 1993 (compatible) "*.

**[0055]** In order to be compatible, the first and second polymers advantageously exhibit good solubility. The Hildebrand solubility parameter is most often used to characterize solubility between materials. It is derived from the cohesive energy density of the material which in turn is derived from the heat of vaporization. The Hildebrand solubility parameter provides a numerical estimate of the degree of interaction between materials and can be a good indication of solubility particularly for polymers. It can provide simple predictions of phase equilibrium based on a single parameter and is readily reported in literature.

**[0056]** Materials with similar Hildebrand solubility parameters will be able to interact with each other, resulting in solvatation, miscibility or swelling, in particular when characterized by similar polar interactions, more specifically similar hydrogen bonding capabilities. As far as hydrogen bonding capability is concerned, distinction can be made between weak hydrogen bonding materials comprising hydrocarbon-, halogenated hydrocarbon- and/or nitrohydrocarbon- radicals; moderate hydrogen bonding materials

comprising ketone-, ester-, ether- and/or glycol-radicals; and strong hydrogen bonding materials comprising alcohol-, amine-, acid-, amide- and/or aldehyde-radicals. Solubility/ miscibility of materials is greatest for similar Hildebrand solubility parameter and similar hydrogen bonding properties. The Hansen hydrogen bonding solubility parameter can be used for interpreting similarities in hydrogen bonding properties, such as when the absolute value of the difference in Hansen hydrogen bonding solubility parameter is less than or equal to 3 $MPa^{1/2}$.

**[0057]** When it is described that Hildebrand solubility parameters are similar, this refers to the absolute value of the difference between the Hildebrand solubility parameters of the corresponding materials being lower than or equal to 4 $MPa^{1/2}$, advantageously lower than or equal to 3 $MPa^{1/2}$, advantageously lower than or equal to 2.5 $MPa^{1/2}$. The Hildebrand solubility parameter of a mixture can be determined by averaging the Hildebrand values of the individual components by volume.

**[0058]** Polymer compounds which can advantageously be used in the present invention (i.e., the first and the second polymer compounds) have a Hildebrand solubility parameter of at least 10 $MPa^{1/2}$, advantageously at least 14 $MPa^{1/2}$, advantageously at least 16 $MPa^{1/2}$, and advantageously smaller than or equal to 35 $MPa^{1/2}$, advantageously smaller than or equal to 32 $MPa^{1/2}$, advantageously smaller than or equal to 30 $MPa^{1/2}$. Hildebrand solubility parameters for most polymers are available from literature, such as the CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters by Allan F. M. Barton, CRC Press. The Hildebrand solubility parameter is advantageously determined based on contact angle measurement.

**[0059]** In order to be compatible, the first and second polymer compounds advantageously exhibit good wettability. In adhesive bonding, wettability is generally used to determine the suitability of a plastic (polymeric) surface to bonding. The material of the membrane will wet the material of the support when its surface energy is equal to or lower than the support material's surface energy. If the surface energy of the membrane material is higher than the surface energy of the support material, the membrane material beads up into small spheres, resulting in poor interactions.

**[0060]** Wettability is related to the surface energy of the membrane material (at the surface interface) on the one hand, and to the surface energy of the support material (at the surface interface) on the other. The surface energy of the membrane material can be assessed based on the surface energy of its principal constituent, or mixture of constituents, viz. the first polymer compound. The surface energy of the support material can be assessed based on the surface energy of its principal constituent, or mixture of constituents, viz. the second polymer compound. For good wetting, the surface energy of the first polymer

compound is advantageously equal to or lower than the surface energy of the second polymer compound.

**[0061]** The surface energy can be determined through contact angle measurements. A standard test method for polymer films using water contact angle measurements is ASTM D5946.

**[0062]** It will be convenient to note that the first and second polymer compounds can be identical compounds (e.g. identical chemical species).

**[0063]** Without wishing to be bound by any theory, according to aspects of the invention, the strong molecular interactions between the first polymer compound and the second polymer compound are assisted by one or more solvents of the polymer compounds. The solvents are used, on the one hand, to form the membrane forming solution wherein the first polymer compound is dissolved, and, on the other hand, to at least partially solvate the second polymer compound. Different solvents can be used for distinctively solvating the first and the second polymer compounds, or even a mixture of solvents. In such case, it will be advantageous that the different solvents be miscible in a proportion of at least 90/10 or higher (e.g. 70/30, 50/50, 30/70 or 90/10) by weight, wherein the first numbers of the fractions (e.g. '90' in '90/30') refer to the solvent of the first polymer compound. The solvents are advantageously miscible in all proportions. As a result, the first polymer compound is solvated and the second polymer compound at the surface of the support is softened (swells) or (at least partially) solvated, hence allowing for molecular mobility, which causes interactions between molecules of the polymers leading to bonding of the membrane to the support.

**[0064]** It follows from the above discussion, that the bonding between membrane and support obtained in the present invention can be described as "solvent bonding".

**[0065]** The solvent or mixture of solvents firstly needs to be able to dissolve the first polymer compound in order to obtain the membrane forming solution for preparing a membrane through phase separation. Those skilled in the art are knowledgeable in selecting appropriate polymers and solvents for forming suitable membrane forming solutions. To this end, the first polymer compound and the solvent advantageously have similar Hildebrand solubility parameters. Advantageously, the first polymer compound and the solvent have similar polar interactions, more specifically similar hydrogen bonding properties.

**[0066]** The membrane forming solution can comprise suitable fillers as described above and other ingredients as known in the art, such as thickeners (viscosity increasing agents). In selecting the ingredients for the membrane forming solution, care is needed to ensure that the solution properly wets the support comprising the second polymer

compound. Good wetting may appear when the surface energy of the second polymer compound is advantageously higher than the surface energy of the solution comprising the first polymer compound and the solvent. As indicated above, the surface energy of the second polymer compound is also advantageously higher than the surface energy of the first polymer compound as such (i.e. not in solution).

**[0067]** In addition, the second polymer compound present at the outer surface (interface) of the support must be at least partially dissolved, or made to swell under the action of a solvent, which advantageously is a solvent present in the membrane forming solution. Good solubility appears when the Hildebrand solubility parameter of the solvent (used for swelling/ dissolving the second polymer compound) is similar to the Hildebrand solubility parameter of the second polymer compound Advantageously, the second polymer compound and the corresponding solvent have similar polar interactions, more specifically similar hydrogen bonding properties.

**[0068]** Advantageously, the Hildebrand solubility parameter of the membrane forming solution and the Hildebrand solubility parameter of the second polymer compound are similar.

**[0069]** Suitable solvents for carrying out aspects of the invention are advantageously aprotic solvents and are advantageously one or more of: dimethylformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetate (DMAc), N-methyl-2-pyrrolidone (NMP), and N-ethyl-2-pyrrolidone (NEP), since these allow for being easily removed from a membrane forming solution by phase separation. Additional suitable solvents are: tetrahydrofuran (THF), tetramethyl urea (TMU), N,N-dimethylpropylene urea (DMPU), trimethyl phosphate (TMP), triethyl phosphate (TEP), tri-n-butyl phosphate (TBP), tricresyl phosphate (TCP), acetone, aniline. Ketones, such as methyl ethyl ketone (MEK) can be suitable solvents as well. Chlorinated hydrocarbons, such as methylene chloride, dichloromethane, and trichloroethylene can be suitable solvents as well. Tamisolve® NxG solvent (Taminco bvba, Belgium) can be suitable as well. It will be convenient to note that those skilled in the art can select a suitable solvent for a predetermined combination of first and second polymer compounds based on readily available solubility data, such as Hildebrand and/or Hansen solubility parameters.

**[0070]** Other possibly suitable solvents, which can be used in combination with the above indicated solvents, in particular for softening or solvating polymer compounds of the support, are aromatic fluids, such as Solvesso™ (Exxon Mobil Corp.) solvents, and chloroform.

**[0071]** The amount of solvent (or mixture of solvents) in the membrane forming solution is advantageously at least 25% by weight, advantageously at least 35% by weight,

advantageously at least 45% by weight based on the total amount of solvents and polymers in solution.

**[0072]** The membrane forming solution 24 may comprise a filler material as described above and/or a pore former, such as dextran, PVP, PEG or polyol, as known in the art. When assessing compatibility, and solubility in particular, of the first and second polymer compounds, these organic materials may be taken into account, e.g. in determining the Hildebrand solubility parameter.

**[0073]** In the following a number of possible processes are described for producing or obtaining membrane elements according to aspects of the invention. It will be apparent that the processes can be readily adapted to work with other types of support as long as the polymer materials are the same.

**[0074]** Referring to Fig. 1, an example membrane element 10 comprises a support 11 and two membranes 12, 13 arranged at opposite sides of the support. An advantageous support for use in membrane filtration applications and contemplated by the invention, is formed as a planar and advantageously rigid support structure 11 having oppositely arranged support layers 111 and 112 defining the outer surfaces of the support and on which a membrane layer 12 and 13 respectively is formed. The outer support layers 111 and 112 are advantageously continuous polymeric films or sheets and can comprise through-holes 115 configured for evacuation of the compounds which have passed (are separated by) the membrane layer 12 or 13 (i.e. the filtrate or permeate).

**[0075]** An integrated permeate channel structure is interposed between outer support layers 111 and 112. To this end, outer support layers 111 and 112 are spaced apart by an installation of spacing members 113, which also connect the outer support layers to each other. This composition may be brought about integrally as one unit in a single formation step, or may arise by assembling the distinguishable parts as separate units into one.

**[0076]** Spacing members 113 are themselves spaced apart to permit the creation of the permeate channel, which is an open structure, allowing the filtrate to be collected and to be drained off. The spacing members 113 are advantageously distributed throughout the support structure 11 to provide securement of the outer support layers 111, 112 to each other at a multitude of points, which are advantageously regularly or uniformly distributed throughout the support. The spacing members 113 may be shaped as ridges extending – either continuously or intermittently – along one dimension of the support structure 11, as shown in Figure 1. They may extend along two dimensions, such as arranged as lines forming an S or zigzag shape. Equally suitable spacer member installations may comprise spacer members shaped as pillars, nubs, pleated sheets,

corrugated sheets, etc. Any installation of spacing members spacing apart the support outer surfaces at an advantageously predetermined distance and securing the outer surfaces to each other while providing a drainage compartment will be suitable for use within aspects of the present invention.

**[0077]** Support structures of the above kind may be made by extrusion, by laminating, by moulding or casting, by additive manufacturing or by any other available technique. In case the components of the support structure, viz. the outer support layers 111, 112 and the spacing members 113, are assembled by lamination, all or part of these components can be made out of extruded or otherwise made continuous polymeric sheets or films by extrusion, rolling and any other technique available to this end.

**[0078]** Suitable support structures 11 are e.g. double or multi-skinned (or multi-walled) polycarbonate sheet, such as Makrolon® multi UV sheets (Bayer, Germany). Other suitable examples are POLISNAKE® polycarbonate panels (Politec Polimeri Tecnici SA, Switzerland) described in EP 1543945, polypropylene KIBO X-panels and KIBO M-panels (KIBO Kunststoffe GmbH, Germany), and TRIPLEX 3 and TRIPLEX 5 composites (TRIPLEX Kunststoffe GmbH). Laminated panels, such as tri-laminates as described in US 2008/000827 or EP 1215037 with outer skins spaced apart by nubs, or tri-laminates made by lamination of two sheets to double side ribbed sheet, or such as bi-laminates (two laminated ribbed sheets), are suitable as well.

**[0079]** The outer support layers 111 and 112 are provided with through-holes 115, such as perforations, for conducting the filtrate into the permeate channels 114. Such perforations can be brought about by laser or by mechanical perforation techniques, e.g. punching such as advantageously hot needle punching, piercing, micro drilling, etc., to provide through-holes 115, advantageously arranged in a regular pattern, and advantageously uniformly distributed over the support outer layers 111, 112.

**[0080]** The membranes 12 and 13 are advantageously formed at opposite sides on top of the support 11 by possibly direct coating/casting followed by phase separation, which also causes *in-situ* bonding of the membrane to the support. In a possible example, a membrane forming solution 24, also referred to as dope, comprising the first polymer compound solvated in a solvent of the first polymer compound is applied on the support outer layers 111, 112 with the aid of a duplex type coating system as shown in Fig. 2. In this system, the support structures 11 are successively and advantageously vertically fed through the duplex type coating system 20, as indicated by the arrow. The duplex type coating system 20 comprises two coating apparatuses 21 and 22 arranged at opposite sides of the support 11. The coating apparatuses 21 and 22 are arranged in facing relationship and are spaced apart such that, when the support structure 11 is fed in between, each

coating apparatus 21, 22 faces a corresponding support outer layer 111, 112. The coating apparatuses 21, 22 can be of the type used for slot coating and can comprise a distribution chamber 201 into which membrane dope is fed by a metering pump (not shown). A slot 202 extends from the distribution chamber to an outlet. Substantially flat lips 203 and 204 extend at the upstream and downstream sides of the slot outlet, respectively.

**[0081]** Premetered and possibly substantially identical quantities of the membrane forming solution (dope) are fed by the coating apparatuses 21 and 22 to the support outer layers 111 and 112, while the support structure 11 is transported through the coating system 20. The membrane forming solution is applied as an advantageously uniform coating layer on both support outer layers.

**[0082]** The support can be pre-heated to a temperature substantially equal or close to the temperature of the membrane forming solution upon coating, such as a temperature within 10°C, possibly within 5°C of the temperature of the membrane forming solution exiting the coating apparatus 21, 22.

**[0083]** When the solvent used in the membrane forming dope is also able to at least partially dissolve the polymer compound of the support (i.e. the second polymer compound), and furthermore the first and second polymer compounds are compatible, e.g. they have similar Hildebrand solubility parameters, interaction will occur between the first and the second polymer. Due to molecular mobility and the interaction between first and second polymers, advantageously, the polymer chains of the first polymer compound penetrate into and/or entangle with the polymer chains of the second polymer compound at the interface between membrane and support.

**[0084]** The membrane layers are subsequently formed by subjecting the coated support to a phase separation process as described above. It has been observed that the phase separation process enables to make the process of molecular interaction between the first polymer compound and the second polymer compound permanent and to consolidate it.

**[0085]** What is key in the present invention, is that the phase separation assists in solvent bonding. As a result, a bond interface, in which the first and second polymer compounds interact, is obtained which is an interface between a porous material (of or comprising the first polymer compound) and a dense material (of or comprising the second polymer compound). It will be convenient to note that it is possible that part of the the support film (comprising or consisting of the second polymer compound) can be dissolved by the solvent prior to phase separation. This superficial layer of the support film will be subjected to the same phase separation process as for the membrane forming dope, and can become porous. As a result, a bond interface is obtained which is an interface

between two porous materials. Hence, phase separation assists solvent bonding to create a very open or porous bond interface between the membrane layer and the support film which cannot be obtained with conventional solvent bonding techniques. The bond interface is at least porous towards the membrane layer side.

**[0086]** Phase separation can be initiated by immersing the coated support structures 11, as they exit the duplex coating system 20, in a liquid bath 23 containing a non-solvent of the first polymer compound. The non-solvent, which is not (or only slightly) able to dissolve the polymer compound of the membrane forming solution, is miscible with the solvent of the membrane forming solution (in all proportions) and causes immersion precipitation of the membrane. In addition, or alternatively, a concentrated vapour of a non-solvent, or of a liquid comprising the non-solvent can be provided just below the duplex coating system 20 to induce VIPS. Such a concentrated vapour may help in forming a desired skin porosity of the membranes.

**[0087]** By careful adjustment of the contact time between the membrane forming solution and the support before membrane formation (i.e. before solvent removal, i.e. before phase separation), a suitable degree of molecular interaction can take place at the interface between membrane solution and support surface layers 111, 112, while the softening of the second polymer compound can be limited to a superficial thickness of the surface layers 111, 112.

**[0088]** Suitable contact times between membrane forming solution and support (before phase separation) can differ between various combination of materials used, and generally depend on the degree of solubility of the second polymer compound in the solvent and on the degree of interaction between the first and the second compounds. Suitable contact times can be as low as 0.1 s, possibly at least 0.5 s, possibly at least 1 s. From an industrial process point of view, contact times are advantageously smaller than or equal to 10 s. The contact time can also be limited by the maximal time period in which the membrane dope can be in contact with ambient before membrane formation, which can influence characteristic pore size.

**[0089]** Since the phase separation process is carried out after softening/dissolving of the second polymer compound, it is advantageously obtained that also the softened/dissolved second polymer compound (of the support) is subjected to the phase separation process, in addition to the membrane forming solution. As a result, a porous interface layer in which the first and second polymer compounds interact on a molecular level is possibly formed. It is believed that the solvent bonding obtained by removing the solvent through phase separation improves the firmness of the bond and/or does not alter the structure of the membrane layer, even at the interface.

**[0090]** What is also possible and advantageous with the process of Fig. 2 is to manufacture membrane elements wherein the first and second polymer compounds are the same. By way of example, it is possible to produce a polypropylene (porous) membrane on a polypropylene support assisted by a solvent such as dioctyl phthalate (DOP), dibutyl phthalate (DBP), diallyl phthalate (DAP) and diphenyl ether (DPE). Another example is producing polysulfone membrane on a polysulfone support assisted by solvents such as NMP or NEP. Since the polymer compounds are the same, strong interactions will occur at the interface between membrane and support.

**[0091]** Still referring to Fig. 2, it is possible to mix in the membrane forming solution 24 a second solvent, which is miscible with the solvent of the first polymer compound and which is a better solvent of the second polymer compound. Advantageously, both solvents are removed simultaneously and by same means in the solvent removal step by phase separation. It is however also possible to remove the solvents consecutively by different processes (e.g. by liquid induced phase separation (LIPS) followed by thermal removal or washing).

**[0092]** By way of example, a solvent mixture can be applied in the manufacture of membrane elements comprising a polysulfone or PVDF membrane (PSU or PVDF forming the binding phase) on a polyester support. Both polysulfone and PVDF are soluble in DMSO. Polyester is soluble in an aromatic solvent (Solvesso™ 100, Exxon Mobil Corp.), which is furthermore miscible with DMSO. To obtain PSU and PVDF membrane bonding to the polyester support, a membrane forming solution is prepared in which a suitable quantity of polysulfone or PVDF is dissolved in a mixture of e.g. 70% DMSO and 30% Solvesso™ 100 (by weight). The membrane forming solution is coated on the polyester support. Upon coating, the Solvesso™ 100 present in the membrane forming solution softens/dissolves the polyester and interaction between the polymers is initiated. The coated support is subsequently immersed in a liquid bath containing a non-solvent of polysulfone or PVDF respectively (e.g. water) to obtain phase separation and remove the solvents.

**[0093]** Still referring to Fig. 2, it is also possible to use different membrane forming solutions in coating heads 21 and 22, so as to coat different membranes on the outer support layers 111 and 112. Hence, the membrane forming solution in coating head 21 can comprise a first membrane solvent and a first membrane polymer compound, whereas the membrane forming solution in coating head 22 can comprise a second membrane solvent different from or equal to the first membrane solvent and a second membrane polymer compound different from the first polymer compound. It will be convenient to note that both first and second membrane polymer compounds need be compatible with the polymer(s) of the corresponding support layers 111, 112 as described above. By way of

example, the membrane forming solution in coating head 21 may be a PSU solution in NEP or DMSO with a $ZrO_2$ filler, whereas the membrane forming solution in coating head 22 may be a PVDF solution in NEP or DMSO with a $SiO_2$ or $TiO_2$ filler. The support 11 may then be a PSU perforated film. By so doing a composite membrane is made having a $ZrO_2$/PSU membrane at one side and a $SiO_2$ (or $TiO_2$) /PVDF membrane at the other side on a PSU support.

**[0094]** In addition, by independently selecting the coating parameters of the coating heads 21 and 22 (e.g. feed rate and gap clearance between head lips 202, 203 and support 11), different thickness of membrane dope 24 can be coated at the two sides.

**[0095]** In case the time to soften or partially dissolve the second polymer compound of the support is larger than the maximum allowable contact time between membrane solution and support, a support pre-treatment step can be carried out as shown in Fig. 3. The process in Fig. 3 differs from the process of Fig. 2 in the presence of a support pre-treatment step 30. In pre-treatment step 30, the solvent is applied to the support 11, such as by spraying, before being coated in the coating system 20. To this end, spray nozzles 31 can be arranged to spray a suitable quantity of solvent on the surface layers of the support which will be coated with membrane forming dope 24 in the coating system 20. In pre-treatment step 30, the solvent is allowed a sufficient time to soften or partially dissolve the second polymer compound in a superficial layer of the support, before coating the membrane forming solution 24.

**[0096]** The contact time of the support with the solvent of the second polymer compound in the pre-treatment step 30 should be sufficient for swelling/softening or at least partially dissolving a superficial layer of the support. The contact time may not be too long in order not to compromise the geometrical and mechanical stability of the support.

**[0097]** The solvent for pre-treating the support in step 30 can be the same solvent as used in the membrane forming solution 24 (i.e. the solvent of the first polymer compound). Alternatively, it can be a different solvent (e.g. a solvent of the second polymer compound, but not a solvent of the first polymer compound), which is miscible with the solvent of the membrane forming solution. The latter alternative is useful in cases wherein the solvent of the membrane forming solution cannot suitably dissolve the second polymer compound. Due to the fact that the two solvents are miscible and the first and second polymer compounds are compatible, the occurrence of molecular interactions is not hampered. It is equally possible to use a mixture of the solvent of the first polymer compound and the solvent of the second polymer compound in the pre-treatment step 30 for application on the support. It is also possible to add surfactants and/or viscosity increasing compounds (thickeners) to the solvent for pre-treating the support in order to enhance

wettability and surface coverage. In these cases, an amount of solvent of the second polymer compound can be mixed in the membrane forming solution in order to enhance prompt miscibility or wettability when the membrane forming solution is applied on the pre-treated support.

**[0098]** It will be convenient to note that both the solvent of the first polymer compound and the solvent of the second polymer compound are advantageously removed by the very process of forming the membrane layer.

**[0099]** The process of Fig. 3 can be applied as an alternative to the process of manufacturing membrane elements comprising a polysulfone or PVDF membrane on a polyester support described above. In the present case, the polyester support can be pre-treated by spraying with either Solvesso™ 100 solvent or a mixture of Solvesso™ 100 and DMSO (e.g. in a respective amount 70/30 or 50/50 by weight). The pre-treated support is then coated with a membrane forming solution in the same way as described above.

**[0100]** What is surprising, is that the softening or solution of the polymer compound of the support does not prejudice the performance or characteristics of the membrane. In fact, at the through-holes 115, no support is present, and hence there is no difference in overall permeability of the membrane element (combination of membrane and support) compared to the prior art.

**[0101]** By careful adjustment of the dope viscosity and the dope feed rate and by correct selection of the size and incidence of the through-holes 115, one can obtain that the dope can or cannot enter the through-holes 115 of the support 11. In case the dope enters the through-holes 115, it can form mushroom-like plugs extending through the holes 115 to the back side of the outer layer, to form mechanical anchor points of the membrane 12, 13 to the surface layer 111, 112 respectively, as described in WO 2013/113928. It will be convenient to note that, for aspects of the present invention, it is not required to have mechanical anchors for attaching the membrane to the support, since the membrane is solvent-bonded to the support, such as through molecular entanglement and/or molecular interpenetration, even though a combination of mechanical anchoring and solvent-bonding can be present. Therefore, possibly, the membrane extends into, but does not form undercuts into the through-holes 115, such that there is no (substantial) mechanical anchoring in or at the through-holes 115. In addition, advantageously, no adhesive is used to bond the membrane layer to the support.

**[0102]** It is advantageous to use a high viscosity membrane forming solution (dope) in methods according to the present invention. Such a dope advantageously has a viscosity of at least 100 Pa.s, advantageously at least 200 Pa.s at 35°C. Viscosity can be measured with a HAAKE MARS rotational rheometer (Thermo Electron, Germany) using two

titanium discs of 35 mm diameter. In addition to enabling coating of the through-holes, such a high-viscosity dope also allows to obtain membranes with high cohesive strength, and hence high-resistant membranes. This is not possible with low-viscosity dopes as they are generally used in the prior art.

**[0103]** A high viscosity dope as indicated above hence enables to obtain membrane layers having a total porosity smaller than or equal to about 80% and advantageously falling in the range between about 50% and about 80%. The total porosity is calculated as (1 minus the relative density of the membrane material) multiplied by 100%.

**[0104]** It will be convenient to note that in the processes described in relation to Fig. 2 and Fig. 3, a double-sided coating is not required. The coating can be single-sided. It will also be clear that the kind of supports that can be used in the above described processes is not particularly limited and can include (continuous) webs and films.

**[0105]** The manufacturing of membrane layers on the above described supports by direct coating or casting is advantageous, since preferred paths are created in the porous structure of the membrane to the perforations. The flow rate is hence improved compared to bonding of preformed membrane layers on the same supports.

**[0106]** Membrane elements made according to an alternative process will now be described referring to Fig. 4. In this process, a pre-formed and possibly unsupported membrane 42 is used on the one hand, and a support 11 as the ones described above, on the other. The membrane 42 is formed beforehand by phase separation and is possibly unsupported (not reinforced with a fabric layer). In order to bond the membrane 42 to the support 11, either the membrane 42, or the support 11, or both are treated by application of a solvent on the contacting surface in corresponding steps 45 and 46. In Fig. 4, the case wherein both the back surface 421 of the membrane 42 and the top surface 411 of the support 11 are sprayed with a solvent (or respective solvents) by corresponding spray nozzles 43 and 44 is shown. By so doing, a softening and/or partial dissolution of the first polymer compound and the second polymer compound take place at the surfaces 411 and 421.

**[0107]** Thereafter, the membrane 42 and the support 11 are joined in a joining step 47, wherein the back surface 421 of the membrane 42 is brought in contact with the top surface 411 of the support 11 and possibly pressed against each other, such as by calendaring between rolls 48. Since the polymer chains in the surface interface layers are mobile by the action of the solvent(s), molecular interactions, such as interpenetration and entanglement of the polymer chains can readily take place. Afterwards, the solvent is removed in step 49 (e.g. by liquid phase separation in liquid bath 491 or by any other

suitable means), which causes the polymer chains to solidify and the interaction of the polymer chains to be made permanent.

**[0108]** It will be convenient to note that either one of the solvent treatment steps 45 and 46 can be omitted if a solvent or a mixture of solvents can be used able to soften or at least partially dissolve both the first polymer compound and the second polymer compound. By way of example, the solvent, or the mixture of solvents can be applied only to the top surface 411 of the support. When the back surface 421 of the membrane 42 is made to contact the top surface 411 following solvent application on the tops surface 411 (e.g. by application of pressure through calendering rolls 48), the solvent will soften and/or partially dissolve the first polymer compound at the back surface 421 as well. One can select a suitable contact time with the solvent before removing the solvent or the mixture of solvents in order to obtain suitable mobility of the polymer chains and hence suitable interaction.

**[0109]** Membrane elements according to aspects of the invention, such as the ones obtainable by any of the processes described above, hence feature an advantageously flat or planar support and one or more membranes, which cover either one or both opposite sides or faces of the support. The membranes and the support comprise suitable combinations of a first polymer compound and a second polymer compound respectively. Each membrane is solvent-bonded to the support through suitable molecular interactions between polymer chains of the first polymer compound and polymer chains of the second polymer compound.

**[0110]** An advantage of membrane elements according to aspects of the invention, is that there is a continuous bonding between membrane and support throughout the interface between the support and the membrane. There is advantageously no bonding at the through holes 115, where the membrane can be freely suspended in or across the through hole. This contrasts to cases in which the membrane is attached purely by mechanical anchoring, where membrane attachment is only at the through holes but not at the interface between membrane and support (such as in WO 2013/113928). The bonding between membrane and support according to aspects of the invention enables bonding over a larger surface area. This provides a uniform bonding throughout the membrane element. Advantageously, the adhesion between membrane and support is greater than the cohesive strength of the membrane itself, i.e. the membrane will tear apart before becoming loose from the support. Advantageously, solvent bonding allows for superior bonding compared to mechanical bonding, since mechanical bonding is limited by the strength of the membrane material at the anchor points. Membrane elements according to aspects of the invention advantageously do not negatively affect membrane performance and advantageously allow for reducing the amount of membrane material used.

**[0111]** A further advantage of membrane elements according to aspects of the invention over the prior art, is that a seal between membrane and support is automatically created along the edges of the membrane. There is hence no need of providing a special frame or adhesive with which to secure the membrane and support along the edges as known in the prior art. Hence, additional manufacturing steps can be omitted. An advantage of the sealing of the above kind, is that the membrane remains integer and can function in separating compounds even at the edge.

**[0112]** Advantageously, the outer layer of the support is formed as shown in Fig. 5. Fig. 5 shows a membrane element 50, in which a membrane 12 is bonded to an outer layer 111 of a support 11 according to aspects of the invention. The outer layer 111 comprises a peripheral region 117 surrounding a porous region 116. The porous region 116 is permeable for the compounds which membrane 12 is configured to separate from a feed, such as by through-holes 115 which are distributed throughout the porous region 116. The peripheral region 117 advantageously has a reduced permeability for the same compounds as compared to the porous region 116. By way of example, the peripheral region 117 is impermeable for said compounds, e.g. no through-holes are provided in peripheral region 117. The material of the outer layer 111 in the peripheral region 117 is advantageously solid or dense, e.g. without openings such as interconnected porosity through which the compounds may pass through the outer layer.

**[0113]** If the peripheral region 117 comprises the second polymer compound, a bonding between membrane and surface layer 111 can be obtained, at least in the peripheral region 117. Due to the reduced permeability of the peripheral region 117, the peripheral region effectively seals the internal parts of the support 11, such as the drainage compartment 114 of Fig. 1, and the only way to arrive in the drainage compartment is through the membrane 12.

**[0114]** Advantageously, as shown in Fig. 9, the membrane layer 12 comprises a skin 121, which forms an outer surface of the membrane layer 12. The skin comprises pores of determined size which determine the permselectivity of the entire membrane layer. The pores of the skin are typically smaller than the pores in the interior 122 of the membrane layer. Advantageously, the skin 121 extends to the surface layer 111, i.e. the skin forms an edge 123 in contact with the surface layer 111, along at least a portion of the circumference of the membrane layer 12. Advantageously, the skin forms an edge 123 in contact with the surface layer 111, the edge 123 completely enclosing or surrounding the membrane layer 12. It is obtained that the skin 121 seals the membrane layer 12 along the edge(s) 123, so that no additional sealing is required. Edge 123 is hence a sealing edge. Such an edge 123

can be obtained when the membrane is directly cast on the outer layer 111 as a polymeric solution.

**[0115]** Referring to Figs. 5 and 9, the surface layer 111 can furthermore comprise an edge region 118 provided at the outskirts of peripheral region 117. Advantageously, no membrane 12 is coated on the edge region, allowing for using the edge region 118 for handling or securing the element 50. Edge region 118 can extend along the total circumference of surface layer 111, or only along part of it.

**[0116]** It will be convenient to note that the porous region 116 can be made of a different material than the material of the peripheral region 117. The porous region 116 and the peripheral region 117 can for example be made of different parts which are assembled prior to coating of the membrane 12 on support 11.

**[0117]** By way of example, whereas the peripheral region can be made of a material comprising the second polymer compound, this compound can be absent in the material of which the porous region 116 is made.

**[0118]** An advantage of having frameless membrane elements 50 as in Fig. 5 is that there is no obstruction projecting from the membrane surface. The membrane elements 50 can hence be stacked closer to one another in fluid separation devices 60, and the feed 61 passing between them is not hindered by any projecting obstruction, as shown in Fig. 6. Since the membrane elements 50 have no obstructions projecting from the surface of the membranes 12, fluid 61 and air bubbles blown by aeration ducts 62, can pass between membrane elements 50 without hindrance.

**[0119]** Even though membrane elements have been described herein as being substantially planar or flat, this is no requirement for aspects of the invention, which can equally be applied to membrane elements having curved or tubular supports. One example is a multi-walled tubular support with annular integrated permeate channel interposed between concentric inner cylindrical outer cylindrical walls. Membrane layers can be solvent-bonded to the inner and/or outer cylindrical walls through known coating techniques.

**[0120]** Example 1

A polycarbonate (= second polymer compound) film (Bayer®, Germany) having a thickness of 200 µm was coated with a membrane forming solution prepared by dissolving PES and PVP in the solvent NEP in relative amounts PES/PVP/NEP of 20/10/70 by weight. The solution was coated on the polycarbonate film using a doctor blade so as to obtain a wet coating thickness of 50 µm. After a contact time of about 5-10 s, the coated film was immersed in water to induce phase separation. A good bonding between PES/PVP membrane and PC film was observed. Figures 7A and 7B show scanning electron microscope (SEM) photographs of the interface 73 between the PES/PVP membrane 72

and the PC support 71. It can be seen that the support was partially made porous by the action of the solvent (at and below interface 73), indicating that the NEP solvated a surface layer 74 of the PC support 71. Table 1 lists reported values for Hildebrand solubility parameter and surface energy, from which it can be discerned that PC and PES have similar Hildebrand solubility parameters and PES has a lower surface energy than PC.

**[0121]** Example 2

The same procedure of Example 1 was followed, except that a membrane forming solution obtained by dissolving PVDF and PVP in the solvent NEP in relative amounts PVDF/PVP/NEP of 20/10/70 by weight was used. A good bonding between PVDF/PVP membrane and PC film was observed. From table 1 can be deduced that PVDF and PC have similar Hildebrand solubility parameters and PVDF has a lower surface energy than PC.

**[0122]** Example 3

The same procedure of Example 1 was followed, except that a membrane forming solution obtained by dissolving PC in the solvent NEP in relative amounts PC/NEP of 30/70 by weight was used. A good bonding between PC membrane and PC film was observed.

**[0123]** Example 4

The same procedure of Example 1 was followed, except that a membrane forming solution obtained by dissolving PEI in the solvent NEP in relative amounts PEI/NEP of 30/70 by weight was used to apply a 25 µm wet coating on a PEI film (Ultem®). A good bonding between PEI membrane 82 and PEI film 81 was observed, as shown in Figures 8A and 8B. One can observe the remarkably sharply defined interface 83 between support and membrane.

**[0124]** Comparative Example 5

In order to examine the difference with solvent bonding by thermal removal (evaporation) of solvent instead of phase separation, the following procedure was followed. A pre-formed, unsupported Zirfon® membrane layer was prepared by phase separation using a membrane forming solution which contained 85 wt.% $ZrO_2$ and 15 wt.% Udel® polysulfone type P1800 NT-11 (Solvay Specialty Polymers, US). NEP was used as solvent in forming this unsupported membrane. Next, a solvent solution was prepared by dissolving 5 wt% PSU (of same type as used for the membrane layer) in $CH_2Cl_2$ solvent and applying it on a side of an extruded polycarbonate support as shown in Fig. 1. The unsupported Zirfon® membrane layer was then pressed on the $CH_2Cl_2$ solvent-applied side and dried in an oven to evaporate the $CH_2Cl_2$ solvent. The bond interface between the membrane layer 92 and the support 91 obtained by this procedure is shown in Figs. 10A-B. One can see that the interface at the membrane side is denser in Example 5.

**Table 1: Values of Hildebrand solubility parameter and Surface energy**

| Polymer | Hildebrand solubility parameter ($MPa^{1/2}$) | Surface energy (mN/m) |
|---|---|---|
| Polycarbonate (PC) | 19.8 | 42 |
| Polyethersulfone (PES) | 22.1-24.1 | 33 |
| Polyvinylidene fluoride (PVDF) | 19.2-22.7 | 25 |
| Polyvinylpyrrolidone (PVP) | 25.6 | 47 |
| Polyether imide (PEI) | 22.9 | 50 |

## CLAIMS

**1.** Membrane element (10, 50) for selective transport of one or more compounds, comprising a polymeric membrane layer (12, 13) and a support (11), wherein:

the polymeric membrane layer (12, 13) is operable for selectively transporting the one or more compounds through the membrane layer and comprises a first polymer compound,

the support (11) has a thickness of at least 200 µm and comprises a support layer (111, 112) provided with through-holes (115) through the support layer, the through-holes having a diameter of at least 25 µm thus enabling the one or more compounds to permeate through the support layer, wherein the support layer comprises a second polymer compound,

the membrane layer (12, 13) is obtained by application of a solution of the first polymer compound on the support layer (111, 112), wherein the solution at least partially fills the through-holes (115), and forming the membrane layer through phase separation of the first polymer compound from the solution, such that the membrane layer (12, 13) extends in the through-holes (115),

the membrane layer and the support layer share an interface (73, 83), characterised in that

the first and second polymer compounds are such that the membrane layer is solvent bonded to the support layer through molecular interaction between the first and second polymer compounds at the interface when the membrane layer is formed.

**2.** Membrane element of claim 1, wherein the first and the second polymer compounds have Hildebrand solubility parameters, wherein the absolute value of the difference between the Hildebrand solubility parameters of the first polymer compound and of the second polymer compound is 4 $MPa^{1/2}$ or less.

**3.** Membrane element of claim 1 or 2, wherein, when the solution of the first polymer compound is applied on the support layer, the second polymer compound is in an at least partially dissolved or swollen state at the interface, which causes the first and second polymer compounds to interact at the interface.

**4.** Membrane element of any one of the preceding claims, wherein the support layer is a polymeric film or a wall (111, 112) of a multi-walled board (11).

**5.** Membrane element of any one of the preceding claims, wherein the support layer (111, 112) is a solid polymeric layer which is liquid impermeable, except at the through-holes (115).

**6.** Membrane element of any one of the preceding claims, wherein the membrane layer (12) extends in the through-holes (115) without forming undercuts.

**7.** Membrane element of any one of the preceding claims, wherein no adhesive is used to bond the membrane layer to the support layer.

**8.** Membrane element of any one of the preceding claims, wherein the support layer (111, 112) does not have an interconnected porosity other than through holes (115).

**9.** Membrane element of any one of the preceding claims, wherein the through-holes (115) have a diameter of at least 50 µm.

**10.** Membrane element of any one of the preceding claims, wherein the through-holes (115) have substantially cylindrical or prismatic shape.

**11.** Membrane element of claim 10, wherein the through-holes (115) have axes perpendicular to the interface.

**12.** Membrane element of any one of the preceding claims, wherein the first polymer compound and the second polymer compound are different chemical species.

**13.** Membrane element of any one of the claims 1 to 11, wherein the second polymer compound is the first polymer compound.

**14.** Membrane element of any one of the preceding claims, wherein the first polymer compound is one or a blend of: polysulfone, polyethersulfone, polyvinylidene fluoride, polyvinylidene chloride, polyvinyl chloride, chlorinated polyvinyl chloride, polyaryletherketone, polyether ether ketone, sulfonated polyether ether ketone, polychlorotrifluoroethene, polyether imide, polyimide, polyamide imide, polyacrylonitrile, polyurethane, polyphenylene sulphide, cellulose acetate, cellulose triacetate, a grafted variant of any of these polymers, and a copolymer of any of these polymers.

**15.** Membrane element of any one of the preceding claims, wherein the second polymer compound is one or a blend of: polycarbonate, polyester, poly(methyl methacrylate), nylon, polystyrene, acrylonitrile-butadiene-styrene, polychlorotrifluoroethylene, polybutyrene terephthalate, polyethylene, polypropylene, poly(ethylene terephthalate), polysulfone, polyethersulfone, polyvinylidene fluoride, polyvinylidene chloride, polyvinyl chloride, chlorinated polyvinyl chloride, polyaryletherketone, polyether ether ketone, sulfonated polyether ether ketone, polychlorotrifluoroethene, polyether imide, polyimide, polyamide imide, polyacrylonitrile, polyurethane, polyphenylene sulphide, cellulose acetate, cellulose triacetate, a grafted variant of any of these polymers, and a copolymer of any of these polymers.

**16.** Membrane element (50) of any one of the preceding claims, wherein the support layer (111) comprises a peripheral region (117) surrounding a permeable region (116), wherein the peripheral region (117) is impermeable for the one or

more compounds, wherein the peripheral region of the support layer comprises the second polymer compound, wherein the membrane layer (12) and the peripheral region (117) share the interface such that the membrane layer is solvent bonded to the support layer in the peripheral region thereby sealing the permeable region (116).

**17.** Membrane element (10) of any one of the preceding claims, wherein the support (11) comprises an integrated permeate channel (114) interposed between opposite spaced apart support layers (111, 112) and spacing members extending between the opposite support layers and through the integrated permeate channel to secure the opposite support layers to each other.

**18.** Membrane element (10) of claim 17, wherein the opposite support layers (111, 112) are each provided with the through-holes, and wherein the membrane layer (12, 13) is provided on each of the opposite support layers.

**19.** Membrane element (10, 50) of any one of the preceding claims, wherein the interface is porous.

**20.** Method of manufacturing a membrane element (10) operable for selective transport of one or more compounds, comprising:

- preparing a membrane forming solution (24) comprising a first polymer compound and a first solvent of the first polymer compound,
- providing a support (11) having a thickness of at least 200 µm and comprising a support layer (111, 112) comprising a second polymer compound, the support layer being provided with through-holes (115) through the support layer, the through-holes having a diameter of at least 25 µm and enabling the one or more compounds to permeate through the support layer,
- applying the membrane forming solution (24) on the support layer to form a coating on the support layer, wherein the support layer and the coating share an interface, and
- forming the membrane layer (12, 13) by phase separation of the first polymer compound from the membrane forming solution which removes the first solvent from the coating,

characterised in that the second polymer compound is brought in a swollen or at least partially solvated state at the interface, and the first polymer compound and the second polymer compound are selected, such that molecular interactions between the first polymer compound and the second polymer compound occur at the interface, such that the membrane layer solvent bonds to the support layer when the membrane layer is formed.

**21.** Method of claim 20, wherein in the step of applying the membrane forming solution, the solution at least partially fills the through-holes (115), and the membrane layer (12, 13) extends in the through-holes (115) when formed.

**22.** Method of claim 20 or 21, wherein the second polymer compound is brought in the swollen or at least partially solvated state by the first solvent.

**23.** Method of claim 20 or 21, wherein the second polymer compound is brought in the swollen or at least partially solvated state by a second solvent applied prior to applying the membrane forming solution.

**24.** Method of claim 20 or 21, wherein the second polymer compound is brought in the swollen or at least partially solvated state by a second solvent which is mixed with the first solvent in the membrane forming solution.

**25.** Method of any one of the claims 20 to 24, wherein the second polymer compound brought in the swollen or at least partially solvated state at the interface is subjected to phase separation when forming the membrane layer, in order to remove a solvent.

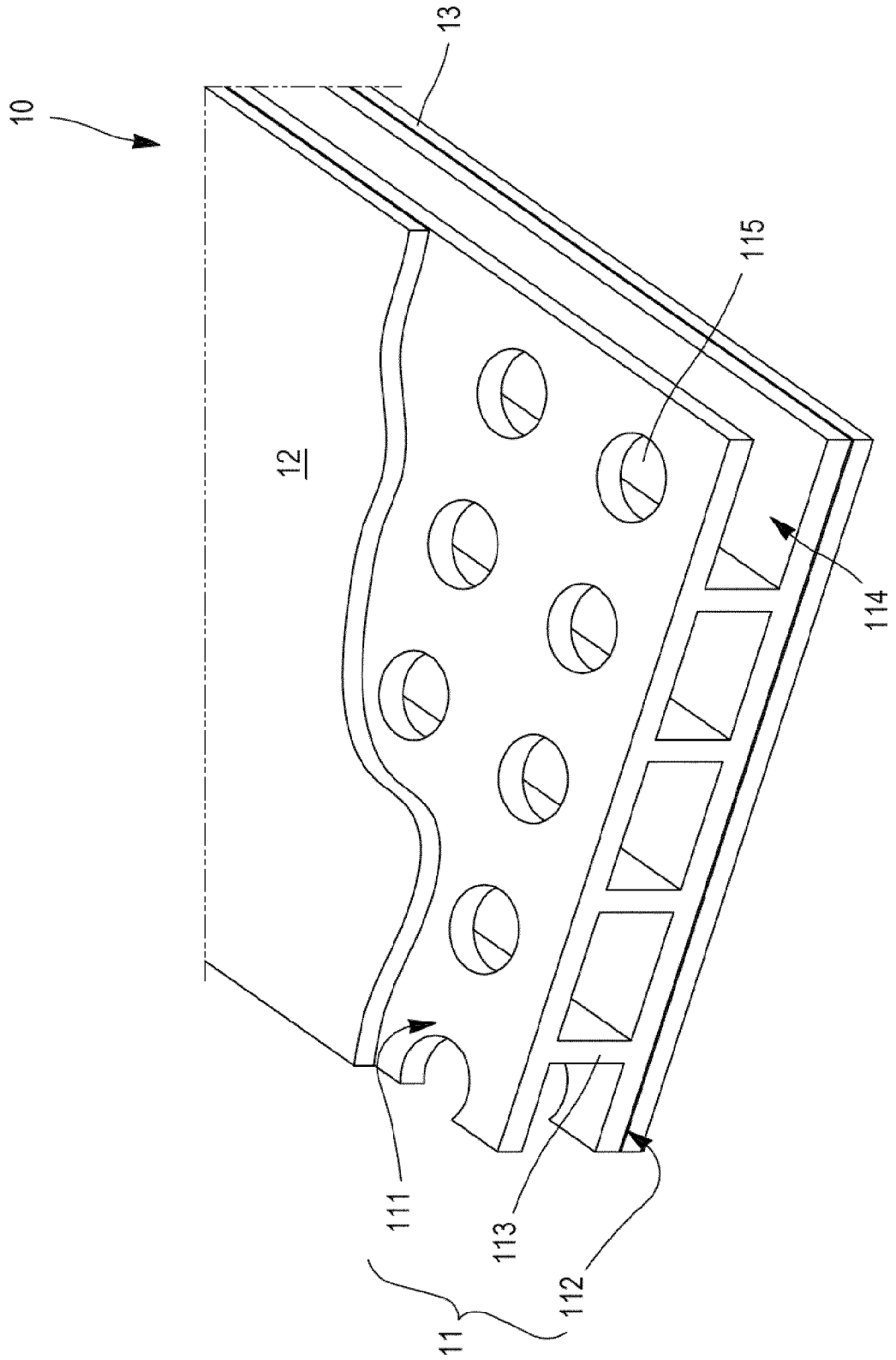



FIG 1

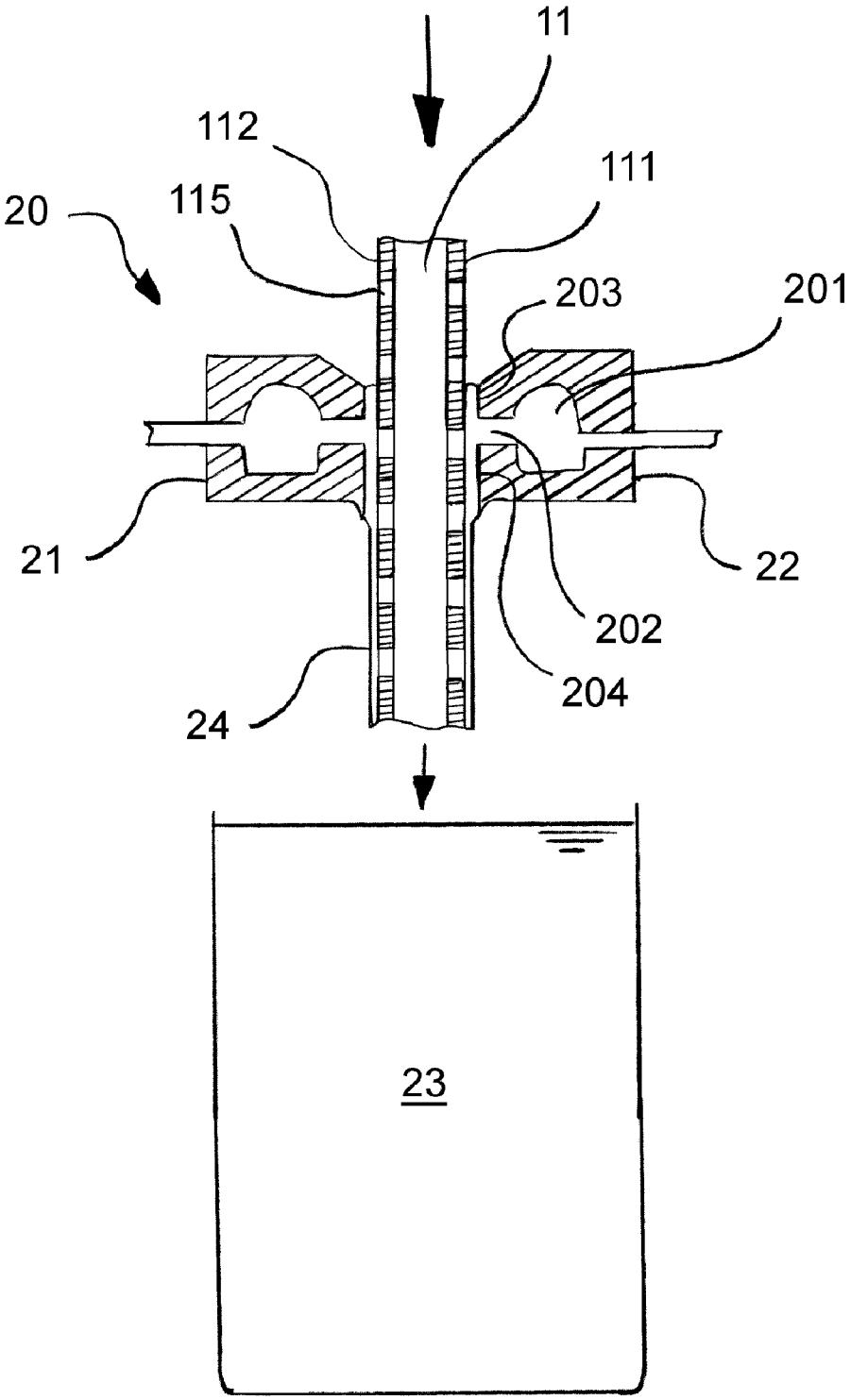



FIG 2

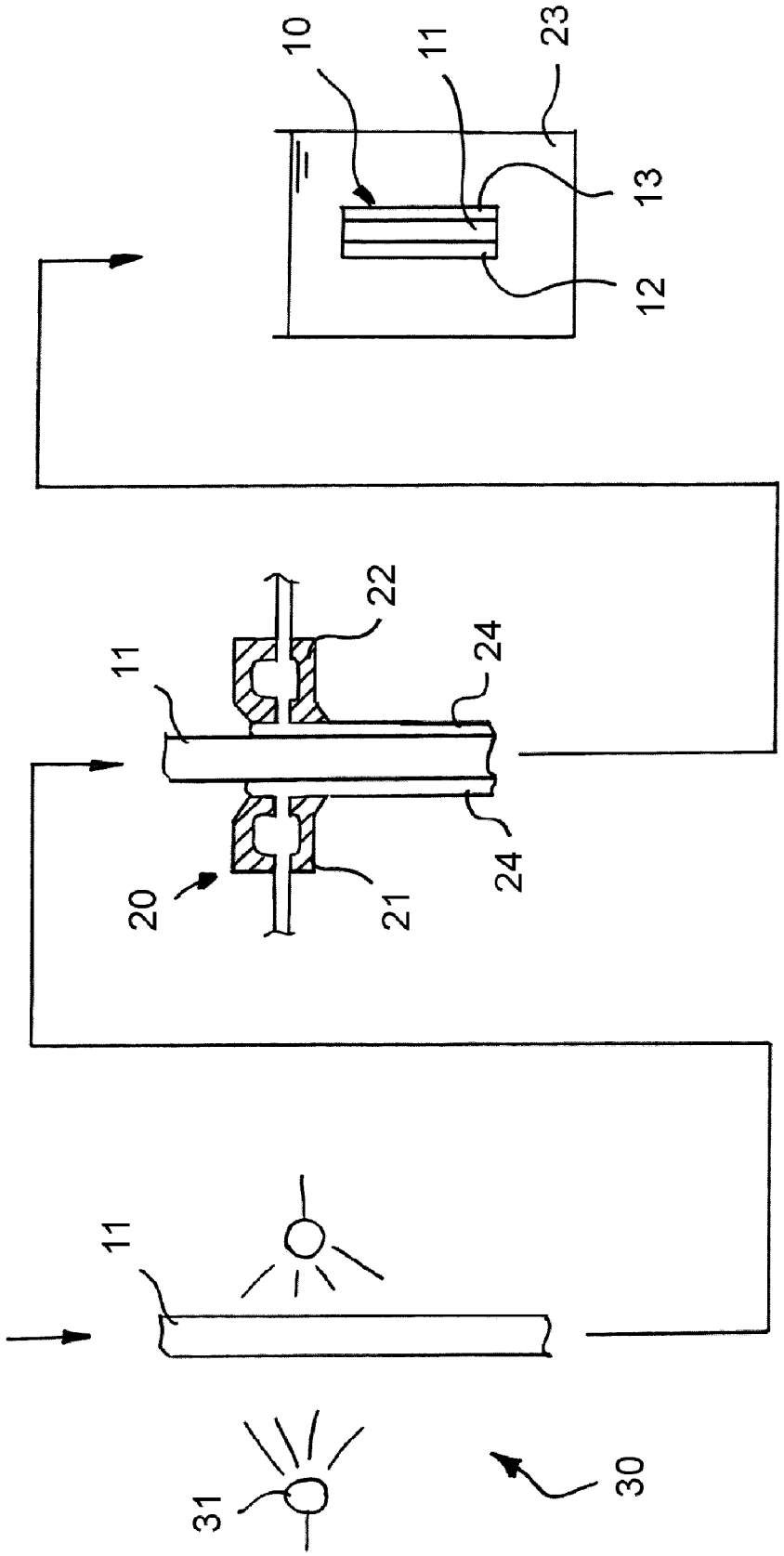



FIG 3

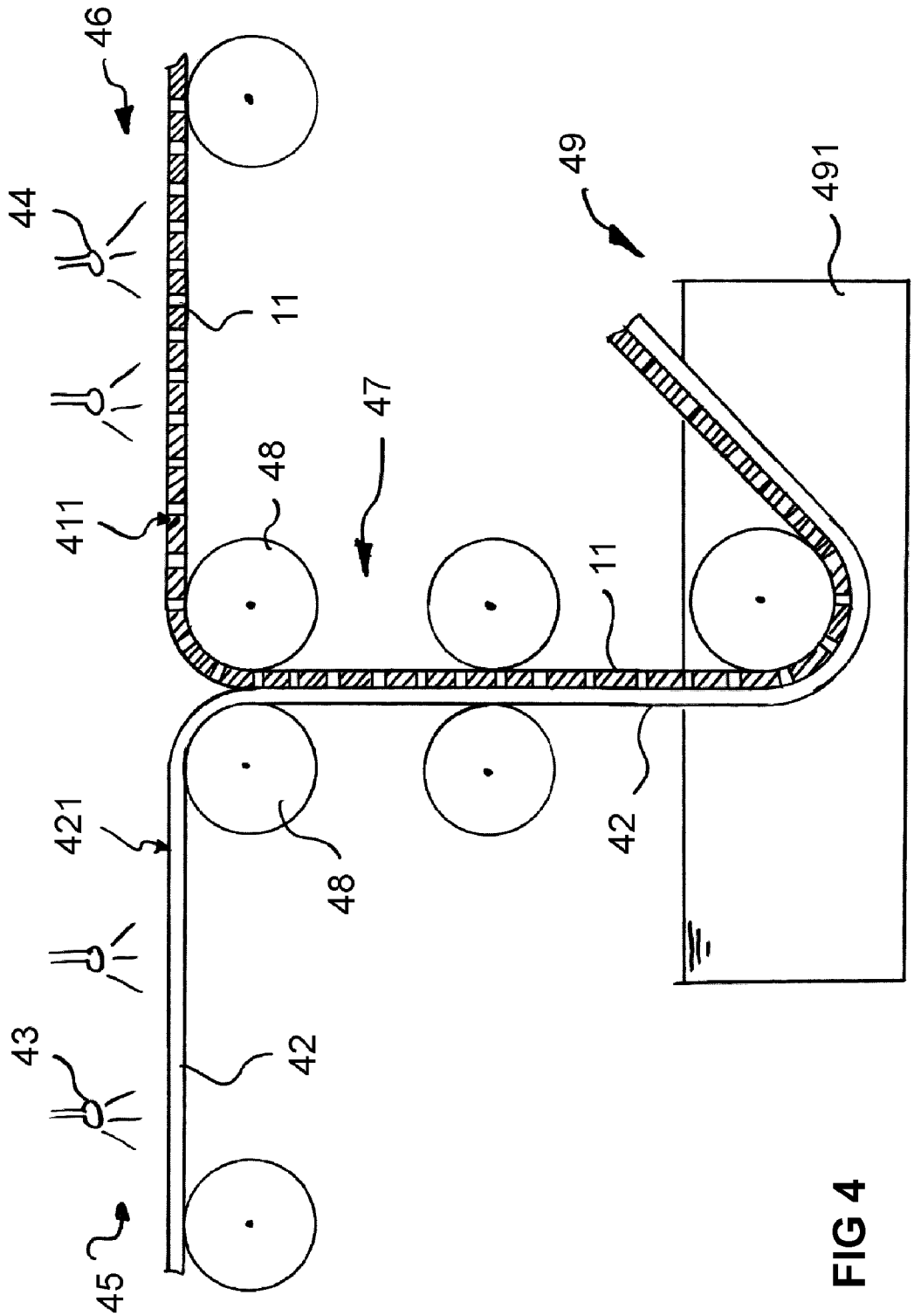



FIG 4

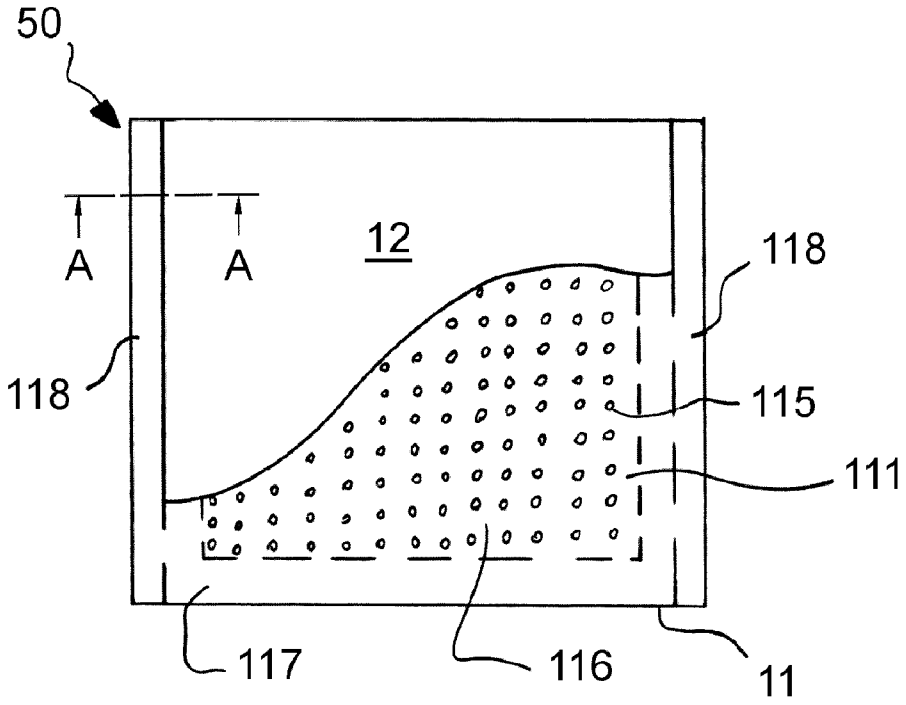



FIG 5

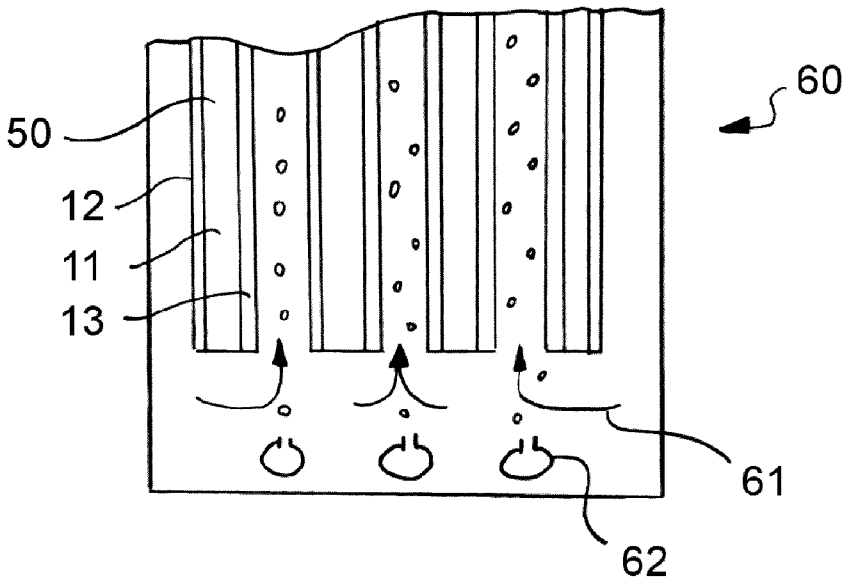



FIG 6

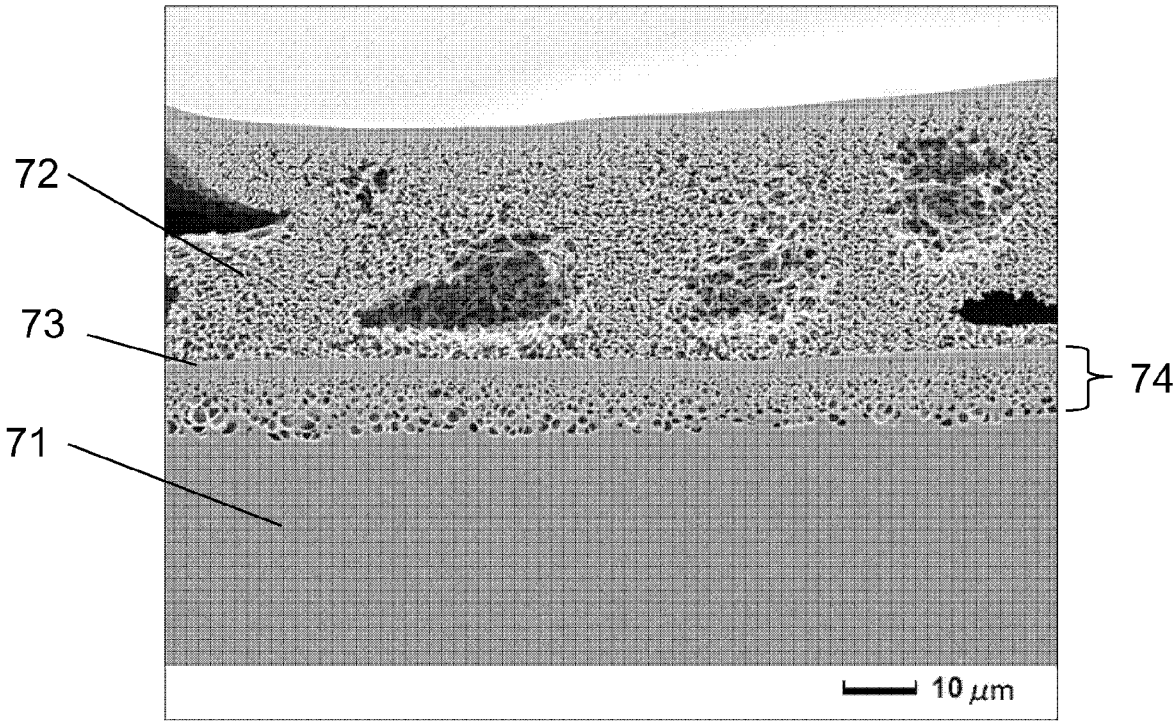



FIG 7 A

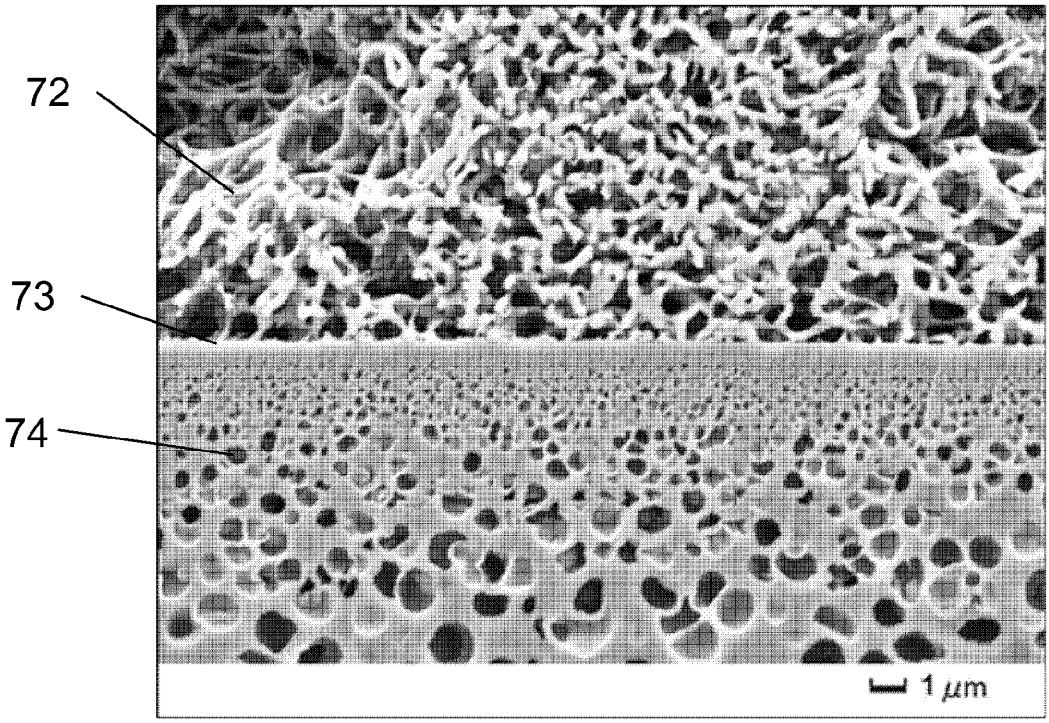



FIG 7 B

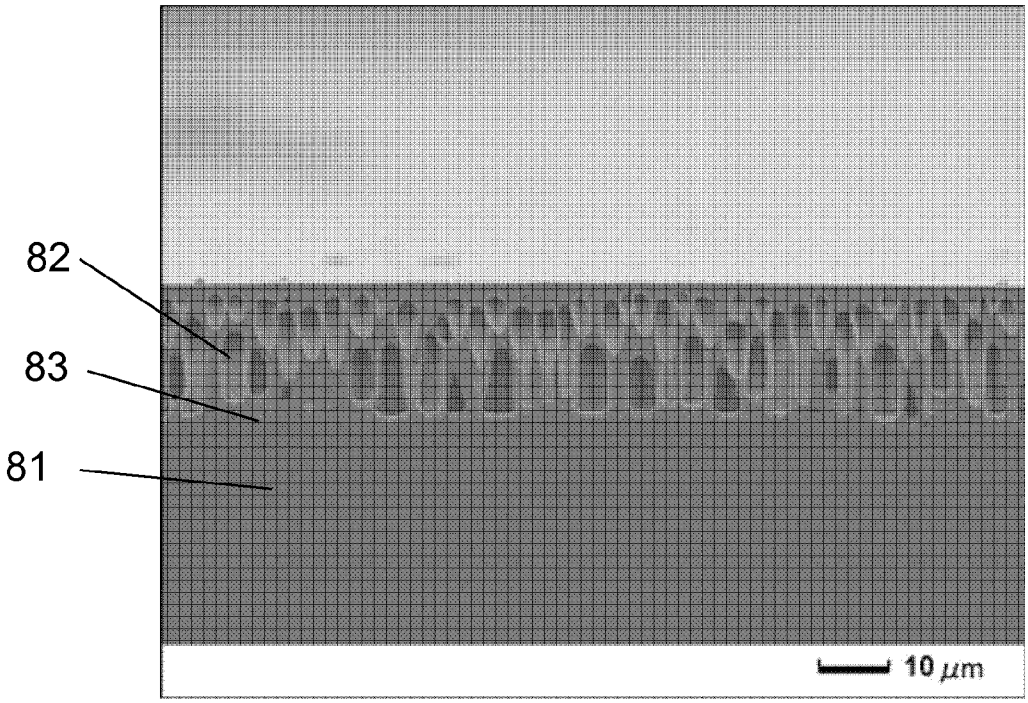



FIG 8 A

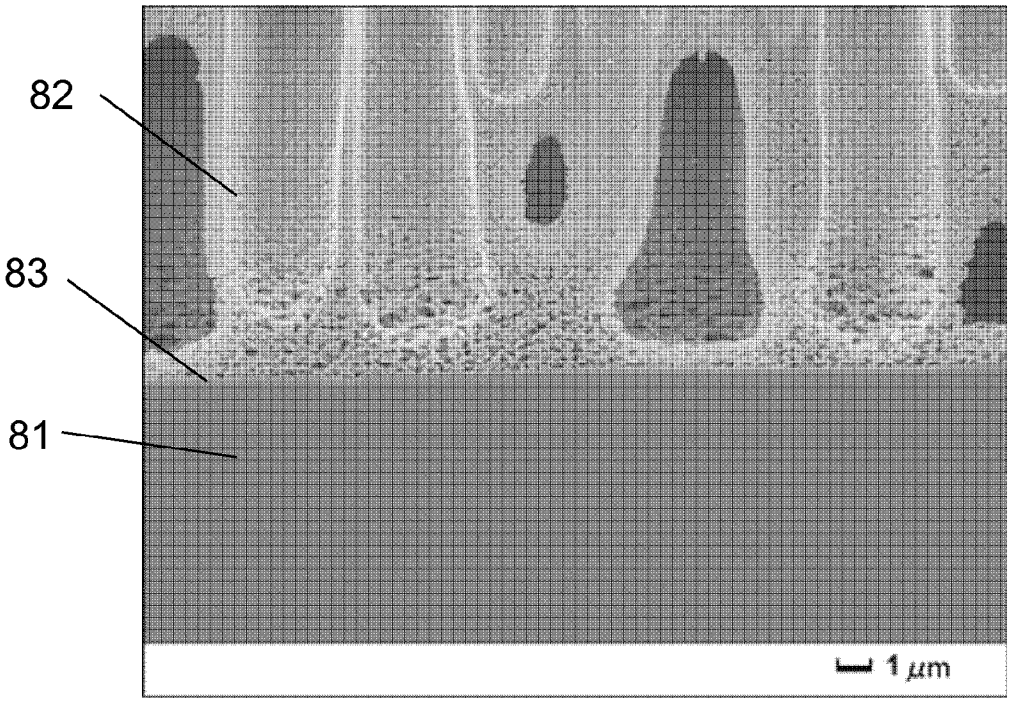



FIG 8 B

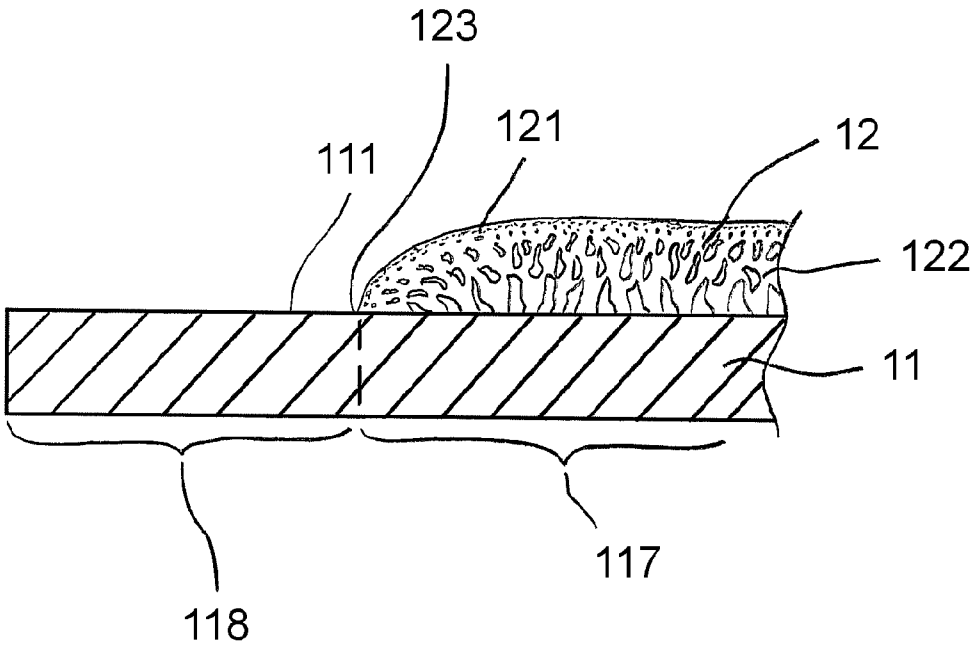



**FIG 9: A-A**

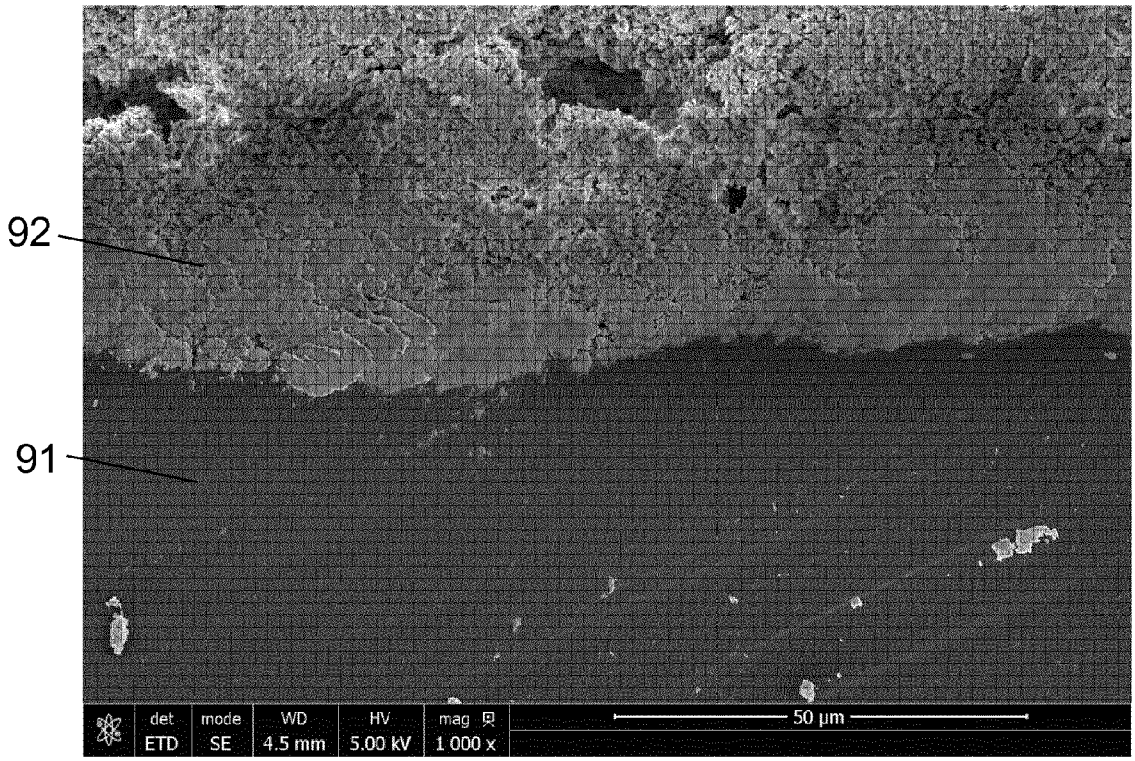



FIG 10A

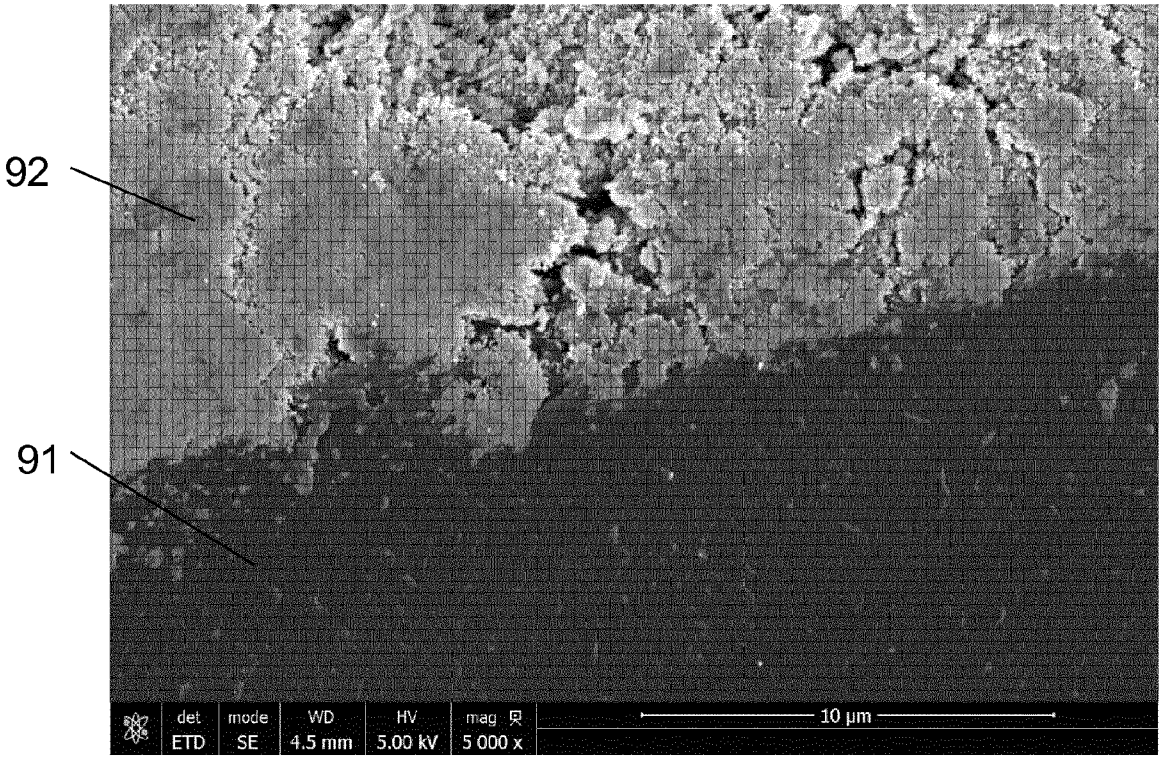



FIG 10B

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/056162

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D65/00 B01D69/10
ADD.

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)
B01D

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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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

[X] See patent family annex.

* Special categories of cited documents :

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"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

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"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

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 5 June 2015 | 25/06/2015 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Hennebrüder, K |

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Form PCT/ISA/210 (second sheet) (April 2005)

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/056162

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No
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