

Description

The invention relates to a semipermeable membrane which offers a high molecular transmission rate selectively to low-molecular-weight polar molecules while providing excellent resistance to pressure driven liquid flow. The composite membrane is generally useful as a barrier to liquid penetration while simultaneously allowing rapid molecular diffusion of certain polar molecules through the membrane. The high flux of low-molecular-weight polar molecules afforded by the semipermeable membrane is of value in separation applications where it is desired to concentrate a liquid by removal of low-molecular-weight polar molecules and/or where removal and/or collection of a low-molecular-weight species is desired. One particularly suitable use for this composite semipermeable membrane is in the area of rain protective garments.

Laminated materials which are both waterproof and breathable (i.e. which have the ability to transport interior moisture vapour to the external environment) and which are especially suited for use in rainwear or tents are disclosed in U.S. Patent 4,194,041, specifically incorporated by reference herein. That invention provided a layered article, for use in waterproof garments or tents, which is waterproof and resistant to surface-active agents in perspiration and yet still permits the evaporation of perspiration and the transfer of moisture vapour through the layered article.

That invention comprises a combination of at least two layers: (1) an interior, continuous, hydrophilic layer which readily allows water to diffuse through it, yet prevents the transport of surface-active agents and contaminating substances such as those found in perspiration; and (2) a hydrophobic outer layer which resists the flow of liquid water and simultaneously permits the transmission of water vapour therethrough, and also provides thermal insulating properties even when exposed to rain. Garments made of such materials are permanently waterproof from exterior water sources yet allow the evaporation of perspiration whenever the partial pressure of water vapour inside the garment exceeds that outside.

The hydrophilic layer used in the invention of U.S. Patent 4,194,041 has a moisture vapour transmission rate by the test method set forth therein exceeding $1,000 \text{ g/m}^2 \cdot 24 \text{ hours}$, and preferably above about $2,000 \text{ g/m}^2 \cdot 24 \text{ hours}$. It permits no detectable transmission of surface-active agents found in perspiration and preferably permits no detectable flow of liquid water at hydrostatic pressures up to 172 kN/m^2 (25 psig).

The hydrophobic layer used in that invention has a water vapour transmission rate, as measured by the test method set forth in that patent, exceeding $1,000 \text{ g/m}^2 \cdot 24 \text{ hours}$ and preferably exceeding $2,000 \text{ g/m}^2 \cdot 24 \text{ hours}$; an advancing water contact angle exceeding 90 degrees, and is preferably formed of a porous hydrophobic polymer, for example a film of porous expanded polytetrafluoroethylene (PTFE).

However, those skilled in the art have continued to seek semipermeable membranes, for use in rainwear and for other various separations, having a maximized transmission rate of the desired permeant with a simultaneous effective efficiency of separation from undesired species. In some separation practices the transmission rate of the permeant and the efficiency of separation can be tailored not only by the membrane used but also by the condition of the separation. In the area of separation, as applied to the breathable rainwear application where the environment is so variable, it is desirable to have a maximized transmission rate of water over as broad a range of conditions as possible. In general, the material described in U.S. Patent 4,194,041 has a water vapour transmission rate lower than that of the hydrophobic layer alone. It would be desirable to achieve a water vapour transmission rate comparable to the hydrophobic layer utilized alone while still achieving the desired protection of the hydrophobic layer provided by the hydrophilic layer used. The greater the capability of a garment material to transmit water vapour, the greater is the comfort range of that garment. Therefore, to those skilled in the art, there has been a continued effort to maximize the comfort range of a material by maximizing its transmission rate of water vapour throughout all conceivable conditions.

Likewise, those skilled in the art of membrane technologies have engaged in an ongoing, concerted effort to develop satisfactory membranes for commercial separation applications. In the development of new membranes, the flux of the desired permeant, selective semipermeability, mechanical strength and service life are criteria to be considered. Much of the technology has focused on achieving sufficient flux at economically suitable conditions to make an application commercially viable. In all membrane separations it is necessary to have the semipermeability adjusted so that the flux is not only sufficiently high for the desired permeant, but also that separation efficiency is sufficient to achieve the desired end results. For commercial viability, a membrane having sufficient flux and selectivity must have sufficient strength to be able to be handled and used in actual applications. Also, numerous additional physical and chemical considerations must be considered to provide a membrane with a reasonable service life. It is with these four considerations in mind, as well as the required economic considerations, that those skilled in the art have continued an ongoing effort to develop suitable commercially viable semipermeable membranes and commercially viable processes to produce those membranes to be used in membrane separation technology.

To maximize the flux of the permeant it is desirable to keep the thickness of the membrane to a minimum without compromising continuity. The membrane should have the highest possible diffusivity of the desired permeant through the membrane.

If the desired permeant is water, it would be desirable to improve the solubility of water in the

membrane by maximizing the hydrophilic nature of the chemical composition of the material and maximizing the amorphous content of the polymer. Historically, however, it has been difficult to obtain the required mechanical strength in a highly hydrophilic polymeric membrane to allow it to be useful commercially. Specifically, films of a highly hydrophilic polymer have tended to be weak and either easily torn or damaged by abrasion and/or flex or the stresses imposed upon them internally, especially when swollen with water. Accordingly, there is a need to increase the hydrophilicity of these membranes without concomitant deterioration in physical properties.

The requirement for chemical stability must be considered as it relates to service life in addition to the need for sufficient mechanical strength existing in a thin, highly hydrophilic membrane. For instance, with water as the permeant, it is recognized that water will be everywhere present and therefore the polymer must be resistant to hydrolysis to the degree required by the application. It is well known that ethers offer good resistance to hydrolysis. As well as resistance to the various modes of degradation encountered in a membrane application, it is important that the polymer be non-soluble to the systems encountered, or else service life will be brief. If the polymer is inherently soluble in the system in consideration, for example a highly hydrophilic polymer exposed to an aqueous environment, insolubility may be introduced to the overall system by crosslinking the polymer into an infinite three-dimensional network. The same four considerations that were discussed above must be applied in considering a crosslinked polymer is its entirety. For instance, it is known that crosslinking a polymeric network generally decreases the flux of the desired permeant as crosslink density increases. Conversely, selectivity typically improves. Also, the functional groups involved in crosslinking must be chemically stable to degradation as required by the application (similar to the considerations of the base polymer).

The addition of thiols to olefins to form thioethers is a reaction that is well known in the art. The thioether functionality affords chemical stability and hydrophilicity in many respects similar to those of its oxygen counterpart. This homolytic addition of the thiyl radical to carbon unsaturation proceeds by a free-radical chain-transfer mechanism and has been known to be photochemically induced. This chemical reaction has been reduced to commercial practice. The teachings of the prior art disclose the utility of utilizing Thiol/Ene chemistry for the curing of polymeric networks by a commercially viable processing technique, employing ultraviolet radiation.

Commercially available polythiols and polyenes and/or their packages do not meet the needs discussed above for the chemical composition of the desired fine hydrophilic film of this invention. Specifically, they are not of a sufficient hydrophilic nature nor are they hydrolytically stable. Commercially available thiols have the thiol function groups introduced into the desired polymer backbone through known hydrolytically sensitive functional groups such as esters, urethanes and ureas. Likewise, many of the commercial Thiol/Ene systems are used in conjunction with acrylate systems which also have the inherently hydrolytically unstable ester functional group.

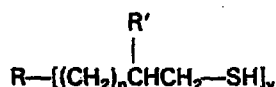
The present invention permits the production of improved semipermeable membranes for use in waterproof materials and in other membrane separation processes, the materials having much improved flux of low-molecular-weight polar molecules and hydrolytic stability, acceptable physical properties, and improved non-yellowing characteristics.

The present invention provides a crosslinkable chemical formulation comprising:
(a) a terminally unsaturated polyene component of the formula:



wherein $m=0$ or 1 and $x \geq 2$;

(b) a polythiol component of the formula:



wherein $n=0$ or 1 , $R'=H$ or OH and $y \geq 2$; and

(c) a free-radical initiator, wherein x and y are not both $=2$ and at least one R is polyoxyethylene and the other R is polyoxyethylene or a polyvalent organic moiety free from hydrolytically sensitive functional groups and other carbon-to-carbon unsaturation or thiol functional groups.

The invention further provides a flexible, layered composite semipermeable membrane comprising:

(a) a flexible film of microporous hydrophobic material having a water vapour transmission rate in excess of $10,000 \text{ g/m}^2 \cdot 24 \text{ hours}$, preferably above $100,000 \text{ g/m}^2 \cdot 24 \text{ hours}$, and an advancing water contact angle exceeding 90 degrees, and

(b) a continuous, crosslinked amorphous hydrophilic layer penetrated to an extent into the face of the hydrophobic layer and attached thereto, said hydrophilic layer comprising an essentially odorless solid polyether polythioether formed by the free-radical chain-extended reaction product of a suitable energy source, such as actinic radiation, and a crosslinkable chemical formulation in accordance with the invention, and said composite membrane having a transmission rate of water vapour exceeding 80% that of the hydrophobic material alone.

The hydrophilic layer, when appropriately located in the structure of the microporous hydrophobic material, may provide a composite membrane having a water vapour transmission rate of the complete ensemble which is comparable to and may even exceed 130% that of the hydrophobic material alone, having a glass-transition temperature well below expected use temperatures, and incorporating no hydrolytically sensitive functional groups along its crosslinked polymer backbone.

The composite membrane has sufficient strength which allows for the hydrophilic portion of the membrane to be maximized in its hydrophilicity. With the hydrophilic layer heavily impregnated into the porous hydrophobic layer, the physical properties of the composite, such as tear, flex and abrasion resistance, are provided substantially by the porous hydrophobic matrix. While the physical property requirements of the overall membrane are substantially provided by the hydrophobic film layer, the chemical requirements of the semipermeable hydrophilic layer are provided without the compromise normally due to physical property considerations.

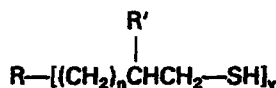
The invention further provides an essentially odorless solid polyether polythioether, useful as the hydrophilic layer herein, comprising a free-radical chain-extended reaction product of:

(a) a terminally unsaturated polyene of the formula:



wherein $m=0$ or 1 and $x \geq 2$;

(b) a polythiol component of the formula:



wherein $n=0$ or 1 , $R'=H$ or OH and $y \geq 2$;

(c) a free-radical initiator; and

(d) a suitable energy source,

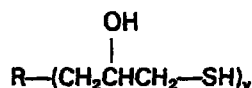
wherein x and y are not both $=2$ and at least one R is polyoxyethylene having a molecular weight preferably in the range from about 600 to 1,500 and the other R is polyoxyethylene or another polyvalent organic moiety free from hydrolytically sensitive functional groups and other carbon-to-carbon unsaturation or thiol functional groups. Specific examples of alternative R 's include an isocyanurate ring, polyoxypropylene, poly(tetramethylene oxide), pentaerythritol, diethyl ether and glycerol.

An essentially odorless, solid polyether polythioether, specifically useful as the hydrophilic layer in a semipermeable composite membrane in accordance with the invention, comprises a free-radical chain-extended reaction product of:

(a) a terminally unsaturated polyether polyene having a molecular weight preferably ranging from about 600 to about 1,500 of the formula:



(b) a polyether polythiol component having a molecular weight preferably ranging from about 600 to about 1,500 of the formula:

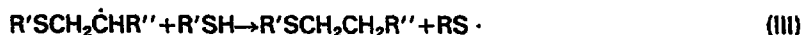
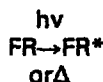


in which formulae R =polyoxyethylene and m , x and y are as defined above;

(c) a free-radical initiator; and

(d) a suitable energy source.

The free-radical addition of the polythiol to the polyene results in a chain extension through hydrolytically stable polythioether functional groups;



FR is a source for free radicals, such as an aromatic ketone which, when excited, FR^* , abstracts a

hydrogen radical from the thiol to initiate the chain-transfer addition of the polythiol to the polyene. Species I is the polythiol, supra. Species II is the polyene, supra.

Species III is the desired solid polyether polythioether useful in this invention as the hydrophilic layer. This polyether polythioether is a highly hydrophilic, substantially totally amorphous polymer system, hydrolytically stable, insoluble and low-yellowing.

Preferably both R's are polyoxyethylene but a satisfactory polythioether may also result from the reaction as described wherein the polyene or polythioether component (but not both) does not contain a polyoxyethylene backbone or other similar hydrophilic functionality, as long as the other component has sufficient hydrophilicity to impart to the hydrophilic layer a minimum hydrophilicity to practice this invention. For example, the hydrophilicity furnished by polyoxyethylene to the overall polymer has been found to be adequate when the polyoxyethylene is present in at least 40 percent by weight of the polymer. Preferably, however, the formulation contains at least 60 percent, and most preferably at least 80 percent polyoxyethylene by weight.

Suitable non-hydrophilic polyenes would be those which do not compromise other required properties of the final membrane, for example, triallylisocyanurate, pentaerythritol triallylether, butadiene, and -ene terminated polyoxypropylene and poly(tetramethylene oxide).

Suitable non-hydrophilic polythiols would be those which likewise do not compromise other required properties of the final membrane, for example, thiol-terminated polyoxypropylene and poly(tetramethylene oxide), pentaerythritol tris (γ -mercaptopropyl) ether, 2,2'-dimercapto diethyl ether, glycerol bis (γ -mercaptopropyl) ether, tris (2-mercaptoethoxy ethyl) isocyanurate, and tris (2-mercaptoethyl) isocyanurate.

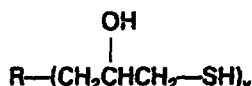
It is recognized that mercaptans have a characteristic odor that might make the lower molecular weight species commercially undesirable.

Likewise, it is contemplated that any polymeric network wherein polyoxyethylene is in excess of about 43 percent by weight of the final hydrophilic layer, preferably in excess of about 66 percent, and most preferably in excess of about 83 percent, would allow this invention to be practiced. An example, is a network formed through the reaction of a polyoxyethylene polythiol and polyoxyethylene polyepoxide, or the photoinitiated cationic polymerization of a similar polyoxyethylene polyepoxide alone.

A specific crosslinkable chemical formulation useful for obtaining an essentially odorless solid polyether polythioether in accordance with this invention is one in which the polyene component is a terminally unsaturated polyether, preferably having a molecular weight in the range from about 600 to about 1,500 of the formula:



and the polythiol component is a polyether, preferably having a molecular weight in the range from about 600 to about 1,500, of the formula:



in which formulae R=polyoxyethylene and m, x and y are as defined above.

Upon curing, for example by actinic radiation, the said formulation results in a cured solid polyether polythioether hydrophilic layer when the sum of x and y is greater than 4. The higher the sum of x and y, the higher the crosslink density of the hydrophilic polyether polythioether.

The invention also provides a method for forming a flexible composite semipermeable membrane comprising the steps of:

(a) forming a flexible layer of microporous hydrophobic material having a water vapour transmission rate exceeding $10,000 \text{ g/m}^2 \cdot 24 \text{ hours}$ and preferably exceeding $100,000 \text{ g/m}^2 \cdot 24 \text{ hours}$ and an advancing polar liquid (e.g. water) contact angle exceeding 90 degrees.

(b) casting a crosslinkable chemical formulation in accordance with the invention to form a thin yet continuous layer directly onto the microporous hydrophobic layer, the rheology of the formulation being such that, with sufficient hydraulic pressure applied, controllable penetration of the liquid composition is effected into the microporous hydrophobic layer.

(c) applying said hydraulic pressure.

(d) followed by curing of the crosslinking formulation to form a continuous solid polymeric hydrophilic layer impregnated to an extent into the pores of said microporous hydrophobic layer, said composite membrane having a water vapour transmission rate exceeding 80 percent that of said hydrophobic layer alone.

Penetration of the liquid composition into the microporous hydrophobic layer is preferably followed by a rapid, in situ curing of the hydrophilic layer to form a continuous crosslinked hydrophilic layer impregnated to an extent into the pores of the microporous hydrophobic film structure and continuously coating at least one face of the hydrophobic layer, the final hydrophilic film being cured (e.g. by actinic radiation) through the hydrophilic yet hydrolytically insensitive thioether functionality, the hydrophilic

layer of the composite membrane having a water vapour transmission rate approaching or exceeding that of the hydrophobic layer alone and wherein the cured hydrophilic layer is present within at least one face of the pore structure of the hydrophobic layer, thus mechanically attaching the hydrophilic layer into the hydrophobic layer.

5 Figure 1 shows the test configuration for determining the water vapor transmission rate (MVTR) of a sample composite membrane wherein the sample 2 is in direct contact with liquid water 16,

Figure 2 shows the test configuration for determining the MVTR of a membrane sample wherein the sample 2 is separated from liquid water 16 by a microporous expanded PTFE membrane 8,

10 Figure 3 shows the test configuration for determining the MVTR of a membrane sample 2 as described in ASTM-E96-80B,

Figure 4 shows the test configuration for determining the MVTR of a membrane sample 2 as described in ASTM-E96-80BW,

Figure 5 is a cross sectional view of a composite membrane 2 in accordance with the present invention,

Figure 6 depicts a process for making a composite membrane 2 of the present invention,

15 Figure 6A shows a process for making the composite membrane wherein the finished composite is washed in a bath of hydrogen peroxide.

In accordance with the invention, a flexible, composite semipermeable membrane is provided comprising a flexible layer of microporous hydrophobic material and a continuous hydrophilic layer penetrated to an extent into at least one face of the porous structure of the hydrophobic layer. When used 20 in rainwear, with an outer textile layer used for aesthetics and providing additional physical characteristics, the hydrophilic layer is generally an inner layer and the hydrophobic layer is oriented exterior to the hydrophilic layer.

For convenience, the following description relates to use of the semipermeable membrane of the present invention for separating water vapour from an aqueous solution as in a rainwear application. 25 Obviously, the semipermeable membrane of the present invention can be used in other applications to selectively separate low-molecular-weight polar molecules from solutions, such as required in distillation, waste concentration, concentration of citric juices or biological systems or in dialysis application, or wherever it is desired to concentrate a liquid by removal of low-molecular-weight polar molecules and/or where removal and/or collection of low-molecular-weight species is desired.

30 The microporous hydrophobic material has a water vapour transmission rate exceeding 10,000 g/m² · 24 hours, preferably exceeding 100,000 g/m² · 24 hours and an advancing water contact angle exceeding 90 degrees. The hydrophobic layer readily allows the flow of gases. The microporous hydrophobic layer is flexible and has sufficient physical strength throughout its structure to impart to the overall structure the required mechanical strength. The thickness of the microporous layer must be at least 35 as thick as the desired overall thickness of the final composite membrane. For maximum utility, the microporous material should be thicker than the continuous hydrophilic layer desired; the microporous layer generally has a thickness of from about 10 µm to about 125 µm, preferably from about 25 µm to about 75 µm.

40 Hydrophobic, as used here, means that water will not spread on the material and wick into its porous structure. A drop of water placed on the surface of a highly hydrophobic layer will remain in the form of a nearly spherical bead with an advancing water contact angle greater than 90 degrees. Water vapour, which evaporates or desorbs from the inner hydrophilic layer, is free to flow or diffuse as a gas through the pores of the hydrophobic layer to the exterior environment.

Where the external relative humidity is 100 percent, as it may be in raining conditions, a vapour 45 pressure differential occurs when the temperature inside the garment is higher than outside, the higher pressure being inside. For this reason, it is desirable to have an insulating layer outside the hydrophilic layer. This steepens the thermal gradient produced by body heat, increases the vapour pressure difference, and thus increases the moisture vapour transmission rate. If the inside surface of the garment is too cool, perspiration vapour will condense on the cool surface and wet the clothing and person within. Further, if 50 the outer covering of a garment is not hydrophobic, it will become wet through by rain, and thus allow the hydrophilic layer to chill, resulting in condensation of perspiration and wetting of the clothing and the person within.

It is undesirable for the outer layer to lose most of its thermal insulating properties when it becomes wet with rain. Therefore, the outer layer is preferred to be both hydrophobic and waterproof. It is preferred 55 that this layer be waterproof at water pressures exceeding 172 kN/m² so as to retain its thermal insulating properties and not become wet even when it is subjected to high-velocity windblown rain, and/or mechanical flexing and rubbing.

In rainwear applications, usually the interior face of the composite semipermeable membrane is the continuous hydrophilic layer. The hydrophilic layer of this invention, when appropriately located within the 60 pores of the microporous hydrophobic material, provides to the composite semipermeable membrane a moisture vapour transmission rate of the complete ensemble which is comparable to or exceeds that of the microporous hydrophobic material alone. This high flux of water molecules afforded by the composite membrane is highly surprising and unexpected. This is further significant and valuable when it is considered that an additional separation technology is provided by the composite membrane over that 65 provided by the microporous hydrophobic material alone, yet there is not a concomitant decrease of water

vapour transmission rate despite the imposition of an additional transport phenomenon necessitated by the addition of the hydrophilic layer. For rainwear applications, the hydrophilic layer forms a barrier to passage of surface-tension-lowering agents such as body oils which would, if present in the hydrophobic layer, tend to reduce the waterproofness of the hydrophobic layer.

The term "hydrophilic" is a relative term and has been used by others in reference to several different characteristics of material, which include the following:

- (1) Materials which absorb substantial amounts of water when immersed in it;
- (2) Materials which absorb moisture from the atmosphere;
- (3) Porous materials which wet through easily when brought in contact with water;
- (4) Porous materials which absorb water into their structure when brought in contact with it;
- (5) Materials which have surfaces easily wetted with water;
- (6) Materials which are permeable to water vapour.

As used in reference to this invention, "hydrophilic" denotes a material which rapidly equilibrates with the water vapour pressure to which it is exposed and has a high solubility of water in itself.

The term "hydrophilic layer" used in reference to this invention is restricted to dense, continuous layers of an amorphous polymer, wherein application temperatures are above the glass transition of the polymer. The term "dense" as used in this specification implies that there are no intentional pores of microscopic dimensions in the hydrophilic layer and that all unoccupied volume is simply free space between the segments of the macromolecular chains.

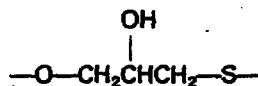
The hydrophilic layer transfers large amounts of water through the film by a diffusion mechanism driven by the difference in partial pressure of water vapour across the layer. If a continuous layer of this hydrophilic material is exposed to air containing substantial water vapour on one side of the layer (inside) and to air containing less water vapour on the other side (outside), the side of the layer exposed to the higher water vapour concentration will absorb or solubilize water molecules which will then be transported, via diffusion, through the layer and are then evaporated or desorbed on the side exposed to the lower water vapour concentration. Thus, water vapour is effectively transmitted through the dense hydrophilic film on a molecule-by-molecule basis.

The hydrophilic materials of this invention are selective in absorbing and transporting water and other low-molecular-weight polar molecules, and not surface-active agents and other non-polar or high-molecular-weight polar organic materials generally. Nor do they allow gases such as oxygen, air and nitrogen to flow through them readily under hydrostatic pressure. They are also resistant to hydraulic flow of liquids, including water. These continuous, hydrophilic layers are unique in transporting water by the solution/diffusion mechanism. They do not transfer water by capillary action or by wicking. Water molecules are not believed to be transferred in association with other water molecules but rather as individual molecules. Advantageously, the present invention of a composite hydrophilic film layer and a hydrophobic film layer provides a membrane having a water vapour transmission rate of the complete ensemble which is comparable to the porous hydrophobic material alone. Indeed, the composite semipermeable membrane, in combination with any fabric used as a support, forms a usefully waterproof sheet which possesses a water vapour transmission rate that is generally not greatly lower than the water vapour transmission rate of the fabric used as the support.

An effective hydrophilic layer has been achieved through the formation of an infinite, three-dimensional polyoxyethylene polythioether network. Hydrophilicity is obtained through the incorporation of hydrophilic functional groups along the network's backbone, specifically:



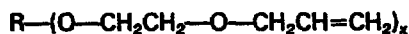
or



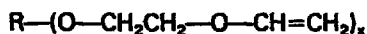
A polythioether network provides for a mechanism wherein desired hydrophilic functional groups in the backbone may be cured resulting in hydrolytically stable and hydrophilic functional groups.

The preferred polyoxyethylene polythioether network is a free-radical chain-extended reaction product of a polyoxyethylene polyene and a polyoxyethylene polythiol, the reaction initiated in the presence of ultraviolet light via a photoinitiator.

Suitable terminally unsaturated polyene components can be prepared from any of the commercially available polyoxyethylenes and allyl halides or allyl alcohol via the well known Williamson ether synthesis procedure or any other organic synthesis procedure that yields an allyl ether structure of the formula:



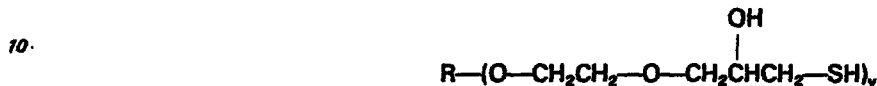
wherein $x \geq 2$ and R=polyoxyethylene; additionally suitable terminally unsaturated polyenes may be those provided by a vinyl ether synthesis route providing a structure of the formula:



wherein $x \geq 2$ and R=polyoxyethylene.

A preferred polyene component is the allyl ether of a trifunctional polyoxyethylene of molecular weight approximately 1,000.

Suitable polythiol components can be prepared by the art discussed in U.S. Patent 3,258,495 and U.S. Patent 3,278,496. Desired polythiols as employed herein comprise the formula:



wherein $y \geq 2$ and R=polyoxyethylene.

A preferred polythiol component is the thiol-terminated structure depicted above of a trifunctional polyoxyethylene of molecular weight approximately 1,000.

Suitable photoinitiators are well known in the art and include, either independently or in combination, benzophenone, acetophenone(s), dibenzosuberone, 1-hydroxycyclohexylphenyl ketone, benzoin isopropyl ether.

Preferred photoinitiators in this invention are benzophenone and 1-hydroxycyclohexylphenyl ketone.

A preferred source of energy herein is that provided by commercially available ultraviolet light sources.

In order to achieve the desired infinite three-dimensional polyoxyethylene polythioether network, the polyoxyethylene polyene and polyoxyethylene polythiol must have functionalities, when summed, that are greater than 4. In general, it is also preferred to operate with the ratio of polythiol to polyene being approximately 1 to 1 on an equivalency basis.

The amount of photoinitiator used, based on the total weight of the polythiol and polyene combined, is from about 0.01 percent to about 10 percent, preferably from 0.5 percent to 2 percent. Of course, as will be obvious to one of ordinary skill in the art, the level of photoinitiator can be varied to vary the rate of reaction, and may also influence final properties.

A microporous, expanded, polytetrafluoroethylene (PTFE) film has been found to be an excellent casting surface upon which a very thin, i.e. about 3 microns and up, coating can be cast of an extremely continuous nature. Penetration into the porous matrix has been achieved in a controllable, industrial manner to provide the semipermeable membrane the flexibility required to achieve the desired flux and separation efficiency, the PTFE film providing for sufficient strength and other physical properties desired in the composite.

In accordance with the invention, the hydrophilic layer is preferably heavily penetrated into the porous structure of the expanded PTFE hydrophobic layer on one face thereof resulting in mechanical attachment of the hydrophilic layer to the hydrophobic layer upon curing. By thus anchoring the hydrophilic layer to the hydrophobic layer and locating it within the porous structure of the hydrophobic layer, it has been found that the hydrophilicity of the hydrophilic layer can be successfully maximized by adjusting the hydrophilic layer's chemistry without concomitant deterioration in physical properties required for the application.

Anchoring is accomplished as illustrated in Figure 6, by dispensing or metering a known amount of the hydrophilic formulation in flowable liquid form directly onto the flexible microporous hydrophobic layer 4, and then via sufficient hydraulic pressure generally provided by nip rollers 40, 42, the hydrophilic formulation penetrates heavily into the porous structure of the hydrophobic layer to thus impregnate the hydrophilic formulation into one surface of the hydrophobic layer.

The viscosity of the reactive liquid formulation of polyene, polythiol, and photoinitiator at the point of application of the hydraulic pressure is from about 100 mPa · s to 4,000 mPa · s, preferably from about 200 mPa · s to 1,500 mPa · s. Preferably, but not essentially, the formulation is liquid at room temperature.

The percentage depth of penetration (dp), Figure 5, of the hydrophilic layer 6 into the hydrophobic layer 4 is calculated by the ratio of the thickness of penetration (tp) of the hydrophilic layer into the hydrophobic layer to the overall thickness (T) of the hydrophilic layer 6, multiplied by 100, i.e.,

$$dp = \frac{tp}{T} \times 100$$

The desired depth of penetration should be in excess of about 75 percent, 100 percent being optimum.

The attachment is secured by curing the continuous impregnated hydrophilic formulation after casting. Figure 6, preferably by using ultraviolet radiation 44, e.g. from a medium-pressure mercury lamp, by conventional means. Other methods of actinic radiations or those methods which can be used to generate free radicals are feasible, apart from radiation which would cause concomitant deterioration of the hydrophobic layer.

Anchoring the hydrophilic layer into the matrix of the hydrophobic layer fulfills the need of the

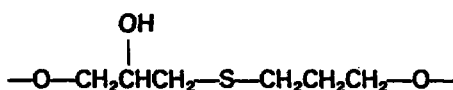
membrane to have physical characteristics required by the application, such as being physically strong, flexible, abrasion-resistant and tear-resistant. This anchoring allows immense latitude for adjusting the chemistry of high-vapour-transmission dense amorphous polymers to provide a maximum flux without compromising physical characteristics and handling characteristics of the final film.

5 If the hydrophilic layer and hydrophobic layer of this invention do not function as a composite, but rather as a "laminate" of the two layers, the results found in the composite structure are not obtainable. A non-penetrated layer of highly hydrophilic material when swollen by water will undergo stresses, crack and disintegrate under conditions of use or, in some cases, simply exposure to water. A hydrophilic material of adequate physical strength for end-use applications or a "laminate" of the two layers will result in a
10 significant lowering of moisture vapour transfer of the overall membrane versus that of the microporous hydrophobic layer above.

The composite semipermeable membrane produced in accordance with the invention possesses numerous desirable properties. The most evident is the high water vapour transmission rate through a continuous dense film, herein attributable in the preferred hydrophilic layer to a maximization of
15 hydrophilic functional groups, specifically:



but also, in the preferred polythioether:



20 The functionality of the chemistry used herein, for the preferred embodiments of the hydrophilic portion of the semipermeable membrane; results in materials of a polyether or polythioether nature which are extremely stable chemically, particularly to hydrolysis. Additionally, the preferred semipermeable membranes are non-yellowing and are non-soluble. Also, the maximum hydrophilicity of the final cured hydrophilic layer is achieved by the polymer being locked into a totally amorphous nature by the infinite
25 three-dimensional network formed in the curing reaction, and by the base polymer used having a glass transition well below the use temperature of the final composite semipermeable membrane. As used herein, the term amorphous content refers to macromolecules being of a non-crystalline nature having neither definite form nor structure.

The composite semipermeable membrane of this invention can be tailored by the hydrophilic
35 chemistry and the microporous hydrophobic layer to have the required flux and the required separation efficiency. As is well known in the art, crosslink density of a continuous dense amorphous polymer network will affect these characteristics. The higher the crosslink density, generally, the lower the water vapour transmission rate and the greater the separation ability. Within the scope of the present invention, it is believed that these parameters are controlled not only by the crosslink on a molecular level but also on the
40 microscopic level by the porous structure of the hydrophobic layer. The tighter and smaller the pore structure, the less swelling of the hydrophilic layer with concomitant decrease in water vapour transmission rate and increase in separation ability.

For convenience and clarity, this discussion has been with reference to the separation of water vapour from an aqueous solution, as in a rainwear type application. It should be noted, however, that the
45 hydrophilic layer will transport rapidly molecules of sufficiently low-molecular-weight and capable of offering a hydrogen for hydrogen-bonding, for example, alcohols, hydrogen sulphide, mercaptans, carboxylic acids, inorganic acids, chloroform and aldehydes. In addition, the composite membrane offers two mechanisms of separation: that imposed by the microporous layer and that imposed by the continuous dense amorphous polymer layer, and as such is capable of numerous separation operations as
50 mentioned. Flux can be achieved in either direction through the composite membrane, thus inverting the order of separation as most desired by the application.

It is contemplated that the practice of this invention can use other microporous hydrophobic structures, for example, those made from coagulation, stretching, foaming, etching, or phase-separation of poly(vinyl chloride), polyurethane, polypropylene, polycarbonate, polystyrene, polyethylene, polyamide,
55 or any process and polymer that results in the hydrophobic requirements as discussed herein. Expanded, microporous polytetrafluoroethylene is preferred.

The following examples illustrate the present invention and include the best mode presently known of carrying it out. It should be emphasized, however, that the examples given herein are purely illustrative in character and this invention is not to be limited to the details set out therein since variations in said details
60 are possible without departing from the scope of the invention as defined in the accompanying claims.

A description of the tests employed to measure water vapour transmission rate (MVTR) follow. There are four basic methods employed to measure MVTR herein: two ASTM procedures and two other procedures as described below. The variations in the test methods simulate different service conditions and provide a broader basis for understanding the benefits of the composite semipermeable membrane of
65 this invention. Agreement should not be assumed between the various methods.

1. Wet Modified Desiccant Method (MDM)

The test apparatus for determining MVTR according to the procedure described herein, as the wet MDM method is shown in Figure 1. This method is appropriate for waterproof materials which are to be in contact with liquid water. The MVTR values set forth in all claims herein below are values determined by this method.

In the procedure, approximately 70 ml of a saturated salt solution of potassium acetate and distilled water 12 is placed into a 120 ml (4.5 ounces) polypropylene cup 10, having an inside diameter of 6.5 cm at the mouth. An expanded PTFE membrane 8, having a Gurley number of 5.5 seconds, a bubble point of 185 kN/m² (26.8 psig), thickness of 25 micrometers and a weight of 12 g/m², available from W. L. Gore & Associates, Incorporated, Elkton, Maryland, U.S.A., product designation PN 10300NA, is heat-sealed to the lip of the cup to create a taut, leakproof, microporous barrier containing the salt solution. The membrane 2, to be tested, is placed taut within a 15 cm (six inch) diameter embroidery hoop 14, and floated upon the surface of the water 16, with the hydrophilic face 6 in direct contact with the water. The water bath assembly is jacketed for temperature control and provides movement of the test water via gentle stirring. A controlled environment for the cup assembly is accomplished via an enclosed headspace above the water of the bath. The entire apparatus is controlled at 23±0.1°C, utilizing a temperature-controlled room and water-circulating bath. After allowing the membrane to equilibrate with the water for 15 minutes, the cup assembly is weighed to the nearest 0.001 g and placed in an inverted manner on the centre of the floating sample, as shown in Figure 1.

Water transport is provided by the driving force between the water 16 and the saturated solution, providing water flux by diffusion in the direction indicated by the arrows in Figure 1. The sample is tested for 15 minutes and then the cup assembly is removed and weighed again to the nearest 0.001 g.

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

2. Dry Modified Desiccant Method (MDM)

The test apparatus for determining MVTR according to the procedure described herein as the dry MDM method is shown in Figure 2. This method provides a high relative humidity in contact with the sample without direct liquid contact with the composite membrane.

The procedure is similar to the wet MDM method and utilizes the same cup assembly as described previously. An expanded PTFE membrane 8, product designation PN 10300NA, as characterized above, is mounted taut in a 15 cm (six inch) embroidery hoop 14, and floated upon the surface of the water 16. The composite membrane 2 is mounted taut in an 8 cm (three inch) diameter embroidery hoop 18, with the hydrophilic face 6 oriented down on the surface of the floating PTFE membrane.

The test is conducted and the MVTR calculated according to the weight gain of the cup assembly as described in the wet MDM method.

3. ASTM EW 96-80BW Inverted water method.

Figure 3 shows the test assembly for determining MVTR according to the procedure referred to hereafter as the inverted water method, and discussed in detail under ASTM for Water Transmission of Materials, ASTM EW 96-80BW.

The sample is secured with clamp 26 into a Thwing-Albert Vapometer Cup 10, manufactured for this test method and previously filled to a height of 2.5 cm (one inch) of distilled water 30, having the hydrophilic face 6 mounted toward the inside of the cup. The entire cup assembly is then weighed to the nearest 0.01 g, inverted, and placed onto the lip 22 of the opening provided for the cup in the Controlled Air Flow Water Vapour Test Chamber 20, available from W. L. Gore & Associates, Incorporated, identified above.

The chamber 20 provides a free-stream air velocity 24 of 2.8±0.25 m/s (550 FPM±50 FPM), measured 5 cm (two inches) from the sample and at least 5 cm (two inches) from any other surface in the channel. The entire chamber is located in a room environmentally controlled to 23±1°C and 50±2 percent relative humidity, providing a driving force in the direction as indicated. The sample is tested for two hours after which the cup assembly is removed and weighed again to within 0.01 g.

The MVTR of the sample is calculated from the weight loss of the cup assembly and is expressed in grammes of water per square meter of sample surface area per 24 hours.

4. ASTM EW 96-80B upright water method

Figure 4 shows the test assembly for determining MVTR according to the procedure referred to herein as the upright water method, and discussed in detail under the ASTM for Water Transmission of Materials, ASTM EW 96-80B.

The sample 2 is mounted similarly as in the inverted water method wherein the cup 10 has been filled with distilled water 30 to provided a 1.9 cm (0.75 inch) air gap 28 between the surface of the water 30 and the composite sample 2. The cup assembly is weighed to the nearest 0.01 g and placed upright onto the lip 22 of the Controlled Air Flow Test Chamber 20, similar to that described earlier. Transfer of water vapour through the sample is in the direction indicated in Figure 4, and, in this configuration, is limited by the stagnant air gap, 28, to an estimated MVTR upper limit of 1,000 g/m² · 24 hours. The sample is tested for 24

hours, the cup assembly removed and weighed again to within 0.01 g. The MVTR is calculated from the weight loss of the cup assembly and is expressed in grammes of water per square meter of sample surface area per 24 hours.

Generally, a method of making the composite membrane of this invention is as shown in Figure 6 wherein the liquid formulation 45 which will form the hydrophilic layer of the composite, comprising the specified polyene and polythiol, together with the photoinitiator, is metered from the dispenser 38 (which may be a gravure roller) onto the surface of rubber roll 40 and thence carried to the surface of the hydrophobic porous solid layer 4, moving in the direction of the arrows as shown, to form a liquid layer or desired thickness thereon. Hydraulic pressure generated between the nip rollers 40 and 42 forces this liquid into the pores of the hydrophobic layer 4. The hydrophobic membrane 4 with the liquid formulation 45 penetrated therein is then conveyed through housing 44 and the surface having the liquid formulation thereon is exposed to radiation by lamps 50 to effect curing of the liquid formulation to a solid, continuous hydrophilic layer. The composite membrane 2 thus formed is characterized by a solid hydrophilic layer 6 having thickness (T) and penetrated into hydrophobic layer 4 to a thickness of penetration (tp), shown in detail in Figure 5. Figure 6A shows the finished composite 2 preferably guided through a bath 54 of 3 percent H_2O_2 in water to substantially eliminate certain residual odors, followed by drying by conventional means, not shown.

Example 1

Synthesis of a polyene was accomplished by a Williamson ether route. The reaction was effected in a one-liter, four-neck, water-jacketed reaction kettle, equipped with a stirrer, nitrogen purge, condenser, additional funnel and thermocouple, 46.8 g (1.17 equivalents) of technical grade flaked NaOH was charged to the reaction kettle, followed by the complete addition of 300 g (0.90 equivalents) of a polyoxyethylene having an average functionality of 3 and a molecular weight of approximately 1,000.

The entire reaction assembly was purged briefly with nitrogen and then the reagents were stirred and allowed to react for one hour at approximately room temperature. To the thus formed sodium alkoxide was added, via the addition funnel, 89.5 g (1.17 equivalents) of allyl chloride, while maintaining the reaction temperature less than 28°C by controlling the addition rate of the allyl chloride and cooling of the jacketed kettle. After addition of the allyl chloride was effected, the reaction mixture was stirred for 17 hours, maintaining the temperature below 28°C and a nitrogen blanket throughout.

Purification was effected by vacuum-stripping the allyl chloride from the reaction kettle, decanting the polyene product from the settled solids and subsequent filtration to remove the remaining solids. The polyene product was analyzed by C^{13} NMR and found to have 96 percent conversion of the polyol hydroxy functionality to allyl ether and a viscosity of about 85 mPa · s at 250°.

The polyene thus formed is hereinafter referred to as Polyene A, and is the preferred polyene herein.

Example 2

A reaction similar to Example 1, employing a polyoxyethylene of an approximate molecular weight 600 and a functionality of 2, yielded a 97 percent converted polyene, having a viscosity of about 49 mPa · s at 25°C and hereinafter referred to as Polyene B.

Example 3

A polyoxyethylene polythiol was obtained from Diamond Shamrock Corporation made according to the teachings of U.S. Patent 3,258,495 and U.S. Patent 3,278,496 from the same polyoxyethylene of Example 1. The polythiol was analyzed by C^{13} NMR and found to have 86 percent conversion of the polyol hydroxy functionality to mercaptan functionality. The polythiol thus obtained had a viscosity of about 1034 mPa · s at 25°C and is hereinafter referred to as Polythiol C, and is the preferred polythiol.

Example 4

A polythiol was obtained from the same polyoxyethylene utilized in Example 2, by the manner described in Example 3. The polythiol was 70 percent converted, had a viscosity of about 6450 mPa · s at 25°C and is hereinafter referred to as Polythiol D.

Example 5

6.1 g (2 percent) benzophenone was heated to 50°C and then added warm to 152 g of Polyene A and 151 g of Polythiol C at room temperature. The entire solution was stirred and was found to have a viscosity of about 258 mPa · s at 25°C and is hereinafter referred to as Formulation E.

Example 6

Equal amounts of benzophenone and 1-hydroxycyclohexylphenyl ketone were added to a glass beaker, heated and stirred to effect solution, 11.4 g of this mixture were then added to 285 g of Polyene A and 284 g of Polythiol C. The entire solution was stirred, was found to have a viscosity of about 269 mPa · s at 25°C and is hereinafter referred to as Formulation F, and is the preferred curable formulation.

Example 7

11.0 g of the 50 percent mixture of benzophenone and 1-hydroxycyclohexylphenyl ketone were added to 285 g of Polyene A and 264 g of Polythiol D similarly to Example 6. This mixture, having a viscosity of about 343 mPa · s at 25°C, is hereinafter referred to as Formulation G.

Example 8

10.1 g of the 50 percent mixture of benzophenone and 1-cyclohexylphenyl ketone were added to 83 g of triallyl isocyanurate and 420 g of Polythiol C. This mixture, having a viscosity of about 677 mPa · s at 25°C, is hereinafter referred to as Formulation H. The polyene in Formulation H is not hydrophilic.

Example 9

8.7 g of the 50 percent mixture of benzophenone and 1-cyclohexylphenyl ketone was added to 83 g of triallyl isocyanurate and 352 g of Polythiol D. This mixture, having a viscosity of about 415 mPa · s at 25°C, is hereinafter referred to as Formulation I.

Example 10A

10.8 g of the 50 percent mixture of benzophenone and 1-hydroxycyclohexylphenyl ketone was added to 255 g of Polyene B and 284 g of Polythiol C. This mixture, having a viscosity of about 213 mPa · s at 25°C, is hereinafter referred to as Formulation J.

Example 10B

8.7 g of the 50 percent mixture of benzophenone and 1-hydroxycyclohexylphenyl ketone was added to 255 g of Polyene B and 264 g of Polythiol D. This mixture, having a viscosity of about 222 mPa · s at 25°C, is hereinafter referred to as Formulation K.

Example 11

Formulation F was metered onto a Thiokol (RTM) rubber roll by the use of a gravure roll to effect a continuous liquid layer of the desired amount. Hydraulic pressure generated between the rubber roll and a backing roll was adjusted to drive the formulation into the matrix of an expanded PTFE membrane, commercially available from W. L. Gore & Associates, Incorporated, product designation PN 11124NA, having a Gurley number of 4.8 seconds, a bubble point of 162 kN/m² (23.5 psig), thickness of 37.5 micrometers, width of 1.67 m and a weight of 15.8 g/m². The membrane with the formulation penetrated into its structure was then conveyed at 0.15 m/s (30 FPM) through two banks of medium-pressure mercury vapour lamps, 118 watts per linear centimeter (300 watts per linear inch) UV lamps to effect curing of the liquid formulation to a solid, continuous hydrophilic layer. The composite membrane thus formed was characterized by Scanning Electron Microscopy (SEM) to have a hydrophilic layer of 9.5 micrometers thickness (T) and 9.5 micrometers thickness of penetration (tp), as shown in Figure 5.

Example 12

The composite membrane of Example 11 was tested for MVTR by the 4 methods earlier described and compared to the hydrophobic layer alone and the layered article prepared according to the teachings of U.S. Patent 4,194,041.

MVTR	Expanded PTFE PN 11124NA	Layered article of U.S. Patent 4,194,041	Composite semipermeable membrane
Wet MDM (MVTR, as claimed)	127,356	62,997	154,359
Dry MDM	91,512	20,613	62,665
Upright water method	1,023	799	971
Inverted water method	12,086	12,125	13,846

Example 13

Formulations E, G, H, I, J and K were processed in a manner similar to Example 11 with the expanded PTFE membrane, PN 11124NA similar to Example 11 having a Gurley number of 4.8 seconds, a bubble point of 145 kN/m² (21.1 psig), thickness of 50 micrometers and a weight of 18.9 g/m² and a 122,975 g/m² · 24 hours wet MDM MVTR. These composite semipermeable membranes were characterized as follows:

EP 0 160 473 B1

Formulation	E	G	H	I	J	K
(T)	14.5	17.3	15.4	20.4	18.2	30.0
(tp)	14.5	17.3	15.4	20.4	18.2	30.0
Wet MDM (MVTR, as claimed)	162,853	167,842	118,921	181,085	177,535	185,737
Dry MDM	50,760	53,985	27,571	37,278	47,736	70,028

Example 14

Formulation F was processed according to the manner of Example 11 with an expanded PTFE membrane, product designation CH224-211, having a Gurley number of 4.4 seconds, a bubble point of 169 kN/m² (24.5 psig), thickness of 47.5 micrometers, width of 1.67 m, a weight of 18.9 g/m² and a wet MDM of 119,832 g/m² · 24 hours. The composite membrane herein was characterized by SEM to have a hydrophilic layer of 17.3 micrometers thickness (T) and 17.3 micrometers thickness of penetration (tp) and having a wet MDM of 173,622 g/m² · 24 hours.

Example 15

Formulation F was processed according to the manner of Example 11 with expanded unsintered PTFE membrane PN 11316NA, having a Gurley member of 350 seconds, a bubble point of 324 kN/m² (47 psig), thickness of 1.0×10⁵ micrometers, width of 0.44 m, a weight of 77.7 g/m² and a wet MDM of 26,993 g/m² · 24 hours. The composite membrane herein was characterized by SEM to have a hydrophilic layer of 25.0 micrometers thickness (T) and 22.7 micrometers thickness of penetration (tp) and having a wet MDM of 30,479 g/m² · 24 hours.

Example 16

Formulation F was processed according to the manner of Example 11 with expanded PTFE membrane PN 10300NA, having a Gurley number of 4.6 seconds, a bubble point of 174 kN/m² (25.3 psig), thickness of 23.8 micrometers, width of 1.67 m and a weight of 12.0 g/m² and a wet MDM of 152,351 g/m² · 24 hours. The composite membrane herein was characterized by SEM to have a hydrophilic layer of 14.5 micrometers thickness (T) and 14.5 micrometers thickness of penetration (tp) and having a wet MDM of 193,708 g/m² · 24 hours.

Example 17

A three layer laminate was made consisting of a composite membrane prepared in a manner similar to Example 16. The composite membrane herein was characterized by SEM to have a hydrophilic layer of approximately 13 micrometers thickness (T) and approximately 13 micrometers thickness of penetration (tp) and having a wet MDM of 113,323 g/m² · 24 hours. The composite membrane was sandwiched between an outer woven shell fabric of approximately 95 g/m² (2.8 ounces per yard) nylon Teslan (RTM) and an inner knit tricot of approximately 51 g/m² (1.5 ounces per yard). The layers were bonded together by an adhesive applied in a dot pattern so as not to occlude more than half of the membrane surface area of either side. The shell side of the laminate was then treated with a water repellent.

A 15 cm (six inch) square sample of this laminate was then sewn into the back of two T-shirts. Each T-shirt was worn over a period of five days for a total of approximately five hours of jogging to subject it to perspiration. The T-shirts were worn by two persons known to previously experience loss of waterproofness due to contamination after half to one hour of like jogging conditions using a laminate containing a layer of microporous PTFE alone.

After each one hour of perspiration exposure, the samples were tested for leakage by a hydrostatic water head of 76 cm (30 inches) for three minutes, as specified in FED-STD-191, Method 5516. Both samples subjected to this test were found not to leak, indicating the hydrophobic layer had not been contaminated. Likewise, the hydrophobic layer had remained white and opaque, whereas if contaminated it would be expected to look clarified. The test was discontinued after about five hours of exposure.

Example 18

In an effort to test the MVTR of the hydrophilic layer independent from the composite structure of this invention, a film of Formulation F approximately 250 micrometers thick was hand-cast onto polyester film. The formulation was then cured upon exposure to a non-focused UV light source of 100 watts for approximately two minutes. In an effort to remove the slightly adhered cured hydrophilic layer from the polyester, the hydrophilic layer was moistened with water. As the hydrophilic layer swelled instantly, stresses were introduced which caused the hydrophilic film to crack and literally disintegrate immediately into innumerable pieces.

Example 19

Six laminates were made at the same time in like manner to the laminate made described in Example 17 without, however, the water repellent applied.

The different laminates were both two-layer (i.e. without knit) and three-layer (i.e. with knit) Antron (RTM) laminates of the hydrophobic layer alone, the layered article prepared according to the teachings of U.S. Patent 4,194,041 and the composite membrane of this invention. The composite membrane was characterized by SEM to have a hydrophilic layer of 12.7 micrometers thickness (T) and 8.2 micrometers thickness of penetration (tp) and a Wet MDM of 108,057. These laminates are summarized in the table. The laminates were tested for MVTR by the four methods earlier described.

Laminate:	L	M	N	O	P	Q
Shell fabric:	← 58 g/m ² (1.7 ounces per yard) Antron Knit →					
Membrane:	Expanded PTFE PM 11124NA		Layered Article of U.S. Patent 4,194,041		Composite semipermeable membrane	
Knit:	Two-layer	Three-layer	Two-layer	Three-layer	Two-layer	Three-layer
MVTR Test*						
Wet MDM	34,920	24,114	29,858	17,445	34,943	35,530
Dry MDM	29,376	14,178	15,911	5,779	27,074	13,455
Upright water method	1,258	1,206	867	732	1,159	1,027
Inverted water method	6,552	6,102	7,353	4,537	7,921	8,155

*Units: g/m² · 24 hours

Claims

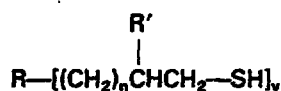
1. A crosslinkable chemical formulation comprising:

(a) a terminally unsaturated polyene component of the formula:



wherein m=0 or 1 and x≥2;

(b) a polythiol component of the formula:



wherein n=0 or 1, R'=H or OH and y≥2; and

(c) a free-radical initiator; wherein x and y are not both=2 and at least one R is polyoxyethylene and the other R is polyoxyethylene or a polyvalent organic moiety free from hydrolytically sensitive functional groups and other carbon-to-carbon unsaturation or thiol functional groups.

2. A crosslinkable chemical formulation as claimed in claim 1 which contains at least 40 percent by weight polyoxyethylene.

3. A crosslinkable chemical formulation as claimed in claim 2 which contains at least 60 percent by weight polyoxyethylene.

4. A crosslinkable chemical formulation as claimed in claim 3 which contains at least 80 percent by weight polyoxyethylene.

5. A crosslinkable chemical formulation as claimed in claim 1 in which both R's are polyoxyethylene.

6. A crosslinkable chemical formulation as claimed in claim 1 in which one R is polyoxyethylene and the other R is at least a divalent moiety consisting of an isocyanurate, polyoxypropylene, poly(tetramethylene oxide), pentaerythritol, diethyl ether or glycerol.

7. A crosslinkable chemical formulation as claimed in claim 5 in which the polyene component is a terminally unsaturated polyether of the formula:



Example 19

Six laminates were made at the same time in like manner to the laminate made described in Example 17 without, however, the water repellent applied.

The different laminates were both two-layer (i.e. without knit) and three-layer (i.e. with knit) Antron (RTM) laminates of the hydrophobic layer alone, the layered article prepared according to the teachings of U.S. Patent 4,194,041 and the composite membrane of this invention. The composite membrane was characterized by SEM to have a hydrophilic layer of 12.7 micrometers thickness (T) and 8.2 micrometers thickness of penetration (tp) and a Wet MDM of 108,057. These laminates are summarized in the table. The laminates were tested for MVTR by the four methods earlier described.

Laminate:	L	M	N	O	P	Q
Shell fabric:	← 58 g/m ² (1.7 ounces per yard) Antron Knit →					
Membrane:	Expanded PTFE PM 11124NA		Layered Article of U.S. Patent 4,194,041		Composite semipermeable membrane	
Knit:	Two-layer	Three-layer	Two-layer	Three-layer	Two-layer	Three-layer
MVTR Test* Wet MDM	34,920	24,114	29,858	17,445	34,943	35,530
Dry MDM	29,376	14,178	15,911	5,779	27,074	13,455
Upright water method	1,258	1,206	867	732	1,159	1,027
Inverted water method	6,552	6,102	7,353	4,537	7,921	8,155

*Units: g/m² · 24 hours

35 Claims

1. A crosslinkable chemical formulation comprising:
 - (a) a terminally unsaturated polyene component of the formula:



wherein $m=0$ or 1 and $x \geq 2$;

- (b) a polythiol component of the formula:



wherein $n=0$ or 1 , $R'=H$ or OH and $y \geq 2$; and

- (c) a free-radical initiator; wherein x and y are not both $=2$ and at least one R is polyoxyethylene and the other R is polyoxyethylene or a polyvalent organic moiety free from hydrolytically sensitive functional groups and other carbon-to-carbon unsaturation or thiol functional groups.

2. A crosslinkable chemical formulation as claimed in claim 1 which contains at least 40 percent by weight polyoxyethylene.

3. A crosslinkable chemical formulation as claimed in claim 2 which contains at least 60 percent by weight polyoxyethylene.

4. A crosslinkable chemical formulation as claimed in claim 3 which contains at least 80 percent by weight polyoxyethylene.

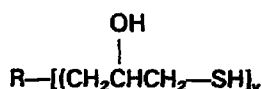
5. A crosslinkable chemical formulation as claimed in claim 1 in which both R 's are polyoxyethylene.

6. A crosslinkable chemical formulation as claimed in claim 1 in which one R is polyoxyethylene and the other R is at least a divalent moiety consisting of an isocyanurate, polyoxypropylene, poly(tetramethylene oxide), pentaerythritol, diethyl ether or glycerol.

7. A crosslinkable chemical formulation as claimed in claim 5 in which the polyene component is a terminally unsaturated polyether of the formula:



and the polythiol component is a polyether of the formula:



in which formulae R=polyoxyethylene and m, x and y are as defined in claim 1.

8. A crosslinkable chemical formulation as claimed in any one of the preceding claims in which the polyoxyethylene has a molecular weight in the range from 600 to 1,500.

9. A crosslinkable chemical formulation as claimed in any one of the preceding claims which is photocurable and contains one or more photoinitiators selected from the class consisting of benzophenone, acetophenone(s), dibenzosuberone, 1-hydroxycyclohexylphenyl ketone and benzoin isopropyl ether.

10. A photocurable chemical formulation as claimed in claim 9 in which the photoinitiator is a combination of benzophenone and 1-hydroxycyclohexylphenyl ketone.

11. A method for forming a flexible, layered composite semipermeable membrane comprising the steps of:

(a) forming a flexible layer of a microporous hydrophobic material having a water vapour transmission rate exceeding $10,000 \text{ g/m}^2 \cdot 24 \text{ hours}$ and an advancing polar liquid contact angle exceeding 90 degrees,

(b) casting a crosslinkable formulation as claimed in any preceding claim to form a continuous layer directly onto the microporous hydrophobic layer, the rheology of the crosslinkable formulation being such that, with sufficient hydraulic pressure applied, controllable penetration of the formulation into the microporous hydrophobic layer is achieved,

(c) applying said hydraulic pressure

(d) followed by curing of the crosslinkable formulation to form a continuous solid polymeric hydrophilic layer impregnated to an extent into the pores of said microporous hydrophobic layer, said composite membrane having a water vapour transmission rate exceeding 80 percent that of said hydrophobic layer alone.

12. A method as claimed in claim 11, wherein the hydrophobic microporous material is polytetrafluoroethylene, polypropylene, poly(vinyl chloride), polyurethane, polycarbonate, polystyrene, polyethylene or polyamide.

13. A method as claimed in claim 12 in which the hydrophobic microporous material is expanded, microporous polytetrafluoroethylene.

14. A flexible, layered composite semipermeable membrane comprising:

(a) a flexible film of a microporous hydrophobic material having a water vapour transmission rate in excess of $10,000 \text{ g/m}^2 \cdot 24 \text{ hours}$, and an advancing water contact angle exceeding 90 degrees, and

(b) a continuous, hydrophilic layer penetrated to an extent into the face of the hydrophobic layer and attached thereto, said hydrophilic layer comprising an essentially odorless solid polyether polythioether formed by the free-radical chain-extended reaction product of an actinic energy source and a crosslinkable chemical formulation as claimed in any one of claims 1 to 7, and said composite membrane having a transmission rate of water vapour exceeding 80 percent that of the hydrophobic material alone.

15. A composite semipermeable membrane as claimed in claim 14 having a water vapour transmission rate exceeding that of said hydrophobic material alone.

16. A composite semipermeable membrane as claimed in claim 15 having a water vapour transmission rate exceeding 130 percent that of said hydrophobic material alone.

17. A composite semipermeable membrane as claimed in any one of claims 14 to 16, in which the microporous hydrophobic material is polytetrafluoroethylene, polypropylene, poly(vinyl chloride), polyurethane, polycarbonate, polystyrene, polyethylene or polyamide.

18. A composite semipermeable membrane as claimed in claim 17 in which the hydrophobic material is expanded, microporous polytetrafluoroethylene.

19. A composite semipermeable membrane as claimed in any one of claims 14 to 18 in which the hydrophilic layer is impermeable to air.

20. A composite semipermeable membrane as claimed in any one of claims 14 to 19 having at least one additional textile layer affixed to at least one surface thereof and in laminate attachment thereto.

21. A method of separating molecules of low molecular weight capable of offering a hydrogen for hydrogen bonding in which such molecules are transported through a composite semipermeable membrane as claimed in any one of claims 14 to 20.

22. A synthetic polymer comprising an essentially odorless solid polyether polythioether comprised of the free-radical chain-extended reaction product of:

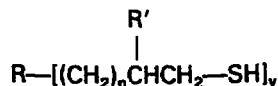
(a) a terminally unsaturated polyene comprising the formula:



wherein $m=0$ or 1 and $x \geq 2$;

(b) a polythiol component of the formula:





5 wherein $n=0$ or 1 , $\text{R}'=\text{H}$ or OH and $y \geq 2$;

(c) a free-radical initiator; and

(d) a suitable energy source,

wherein x and y are not both equal to 2 and at least one R is polyoxyethylene and the other R is polyoxyethylene or a polyvalent organic moiety free from hydrolytically sensitive functional groups and other carbon-to-carbon unsaturation or thiol functional groups.

10 23. A synthetic polymer is claimed in claim 22 in which both R' 's are polyoxyethylene.

24. A synthetic polymer according to claim 23 in which the polyene component is a terminally unsaturated polyether of the formula:



and the polythiol component is a polyether of the formula:



in which formulae R is polyoxyethylene and m , x and y are as defined in claim 23.

25 25. A polymer as claimed in claim 22 in which said polyoxyethylene has a molecular weight in the range from 600 to $1,500$.

26. A polymer according to claim 22 wherein one R is polyoxyethylene and the other R is an isocyanurate, polyoxypropylene, poly(tetramethylene oxide), pentaerythritol, diethyl ether or glycerol.

27. A polymer according to claim 22 which is photocurable and contains one or more photoinitiators selected from the class consisting of benzophenone, acetophenone(s), dibenzosuberone, 1-hydroxycyclohexylphenyl ketone and benzoin isopropyl ether.

28. A polymer as claimed in claim 27 wherein the photoinitiator is a combination of benzophenone and 1-hydroxycyclohexylphenyl ketone.

35 Patentansprüche

1. Vernetzbare chemische Formulierung umfassend

(a) eine endständig ungesättigte Polylenkomponente der Formel



worin $m=\text{Null}$ oder 1 und $x \geq 2$;

(b) eine Polythiolkomponente der Formel



worin $n=\text{Null}$ oder 1 , $\text{R}'=\text{H}$ oder OH und $y \geq 2$; und

50 (c) einen Freiradikalinitiator;

wobei x und y nicht beide 2 sind und mindestens ein R Polyoxyäthylen bedeutet und das andere R Polyoxyäthylen oder eine mehrwertige organische Gruppierung ist, die frei von hydrolytisch empfindlichen funktionellen Gruppen und anderen Kohlenstoff-Kohlenstoff-Doppelbindungen oder funktionellen Thiolgruppen ist.

55 2. Vernetzbare chemische Formulierung, wie in Anspruch 1 beansprucht, die mindestens 40 Gew.% Polyoxyäthylen enthält.

3. Vernetzbare chemische Formulierung, wie in Anspruch 2 beansprucht, die mindestens 60 Gew.% Polyoxyäthylen enthält.

4. Vernetzbare chemische Formulierung, wie in Anspruch 3 beansprucht, die mindestens 80 Gew.% Polyoxyäthylen enthält.

60 5. Vernetzbare chemische Formulierung, wie in Anspruch 1 beansprucht, in der beide R Polyoxyäthylen sind.

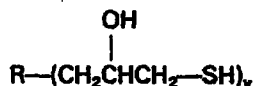
6. Vernetzbare chemische Formulierung, wie in Anspruch 1 beansprucht, in der ein R Polyoxyäthylen ist und das andere R mindestens eine zweiwertige Gruppierung darstellt, die aus einem isocyanurat, Polyoxypropylen, Poly(tetramethylenoxid), Pentaerythrit, Diäthyläther oder Glycerin besteht.



7. Vernetzbare chemische Formulierung, wie in Anspruch 5 beansprucht, in der die Polyenkomponente ein endständig ungesättigter Polyäther der Formel



ist und die Polythiolkomponente ein Polyäther der Formel



ist, in welchen Formeln R Polyoxyäthylen bedeutet und m, x und y wie in Anspruch 1 definiert sind.

8. Vernetzbare chemische Formulierung, wie in einem der vorhergehenden Ansprüche beansprucht, in der das Polyoxyäthylen ein Molgewicht im Bereich von 600 bis 1500 aufweist.

9. Vernetzbare chemische Formulierung, wie in einem der vorhergehenden Ansprüche beansprucht, die photohärtbar ist und einen oder mehrere Photoinitiatoren ausgewählt aus der Gruppe bestehend aus Benzophenon, Acetophenon(en), Dibenzosuberon, 1-Hydroxycyclohexylphenylketon und Benzoinisopropyläther enthält.

10. Photohärtbare chemische Formulierung, wie in Anspruch 9 beansprucht, in der der Photoinitiator eine Kombination von Benzophenon und 1-Hydroxycyclohexylphenylketon ist.

11. Verfahren zum Herstellen einer flexiblen schichtförmigen semipermeablen Verbundmembran, das folgende Schritte umfaßt:

(a) Bilden einer flexiblen Schicht eines mikroporösen hydrophoben Materials mit einer Wasserdampftransmissionsrate von mehr als $10\,000\text{ g/m}^2 \cdot 24\text{ Stunden}$ und einem ansteigenden polaren Flüssigkeitsberührungswinkel von mehr als 90° ,

(b) Gießen einer vernetzbaren Formulierung, wie in einem vorhergehenden Anspruch beansprucht, direkt auf die mikroporöse hydrophobe Schicht unter Bildung einer kontinuierlichen Schicht, wobei die Rheologie der vernetzbaren Formulierung derart ist, daß bei Ausüben von ausreichendem hydraulischen Druck ein regulierbares Eindringen der Formulierung in die mikroporöse hydrophobe Schicht erzielt wird,

(c) Ausüben des genannten hydraulischen Druckes und

(d) anschließendes Härten der vernetzbaren Formulierung unter Bildung einer kontinuierlichen festen polymeren hydrophilen Schicht, die bis zu den Poren der genannten mikroporösen hydrophoben Schicht imprägniert ist, wobei die Verbundmembran eine Wasserdampftransmissionsrate aufweist, die 80% jener der hydrophoben Schicht allein übersteigt.

12. Verfahren, wie in Anspruch 11 beansprucht, worin das hydrophobe mikroporöse Material Polytetrafluoräthylen, Polypropylen, Poly(vinylchlorid), Polyurethan, Polycarbonat, Polystyrol, Polyäthylen oder Polyamid ist.

13. Verfahren, wie in Anspruch 12 beansprucht, worin das hydrophobe mikroporöse Material expandiertes mikroporöses Polytetrafluoräthylen ist.

14. Flexible schichtförmige semipermeable Verbundmembran umfassend

(a) einen flexiblen Film eines mikroporösen hydrophoben Materials mit einer Wasserdampftransmissionsrate von mehr als $10\,000\text{ g/m}^2 \cdot 24\text{ Stunden}$ und einem ansteigenden Wasserberührungswinkel von mehr als 90° und

(b) eine kontinuierliche hydrophile Schicht, die bis zur Vorderseite der hydrophoben Schicht gedrungen ist und daran haftet, welche hydrophile Schicht einen im wesentlichen geruchlosen festen Polyätherpolythioäther umfaßt, der vom kettenverlängerten Freiradikalreaktionsprodukt einer aktinischen Energiequelle und einer vernetzbaren chemischen Formulierung, wie in einem der Ansprüche 1 bis 7 beansprucht, gebildet ist, und die Verbundmembran eine Wasserdampftransmissionsrate aufweist, die 80% jener des hydrophoben Materials allein übersteigt.

15. Semipermeable Verbundmembran, wie in Anspruch 14 beansprucht, mit einer Wasserdampftransmissionsrate, die jene des hydrophoben Materials allein übersteigt.

16. Semipermeable Verbundmembran, wie in Anspruch 15 beansprucht, mit einer Wasserdampftransmissionsrate, die 130% jener des hydrophoben Materials allein übersteigt.

17. Semipermeable Verbundmembran, wie in einem der Ansprüche 4 bis 16 beansprucht, in der das mikroporöse hydrophobe Material Polytetrafluoräthylen, Polypropylen, Poly(vinylchlorid), Polyurethan, Polycarbonat, Polystyrol, Polyäthylen oder Polyamid ist.

18. Semipermeable Verbundmembran, wie in Anspruch 17 beansprucht, in der das hydrophobe Material expandiertes mikroporöses Polytetrafluoräthylen ist.

19. Semipermeable Verbundmembran, wie in einem der Ansprüche 14 bis 18 beansprucht, in der die hydrophile Schicht luftundurchlässig ist.

20. Semipermeable Verbundmembran, wie in einem der Ansprüche 14 bis 19 beansprucht, mit mindestens einer weiteren Textilschicht, die an mindestens einer Oberfläche derselben und in Laminatverbindung daran befestigt ist.

21. Verfahren zum Trennen von Molekülen mit niedrigem Molgewicht, die zum Anbeiten eines Wasserstoffatoms zur Wasserstoffbindung imstande sind, in dem solche Moleküle durch eine



semipermeable Verbundmembran, wie in einem der Ansprüche 14 bis 20 beansprucht, transportiert werden.

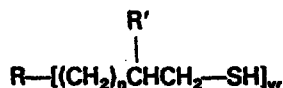
22. Synthetisches Polymer umfassend einen im wesentlichen geruchlosen festen Polyätherpolythioäther bestehend aus dem kettenverlängerten Freiradikalreaktionsprodukt

(a) eines endständig ungesättigten Polyens der Formel



worin $m=0$ oder 1 und $x \geq 2$;

(b) einer Polythiolkomponente der Formel



worin $n=0$ oder 1 , $R'=M$ oder OH und $y \geq 2$; und

(c) eines Freiradikalinitiators und

(d) einer geeigneten Energiequelle,

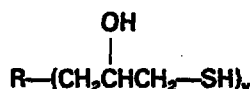
worin x und y nicht beide 2 sind und mindestens ein R Polyoxyäthylen bedeutet und das andere R Polyoxyäthylen oder eine mehrwertige organische Gruppierung, die frei von hydrolytisch empfindlichen funktionellen Gruppen und anderen Kohlenstoff-Kohlenstoff-Doppelbindungen oder funktionellen Thiolgruppen ist.

23. Synthetisches Polymer, wie in Anspruch 22 beansprucht, in dem beide R Polyoxyäthylen sind.

24. Synthetisches Polymer nach Anspruch 23, in dem die Polylenkomponente ein endständig ungesättigter Polyäther der Formel



ist und die Polythiolkomponente ein Polyäther der Formel



ist, in welchen Formeln R Polyoxyäthylen bedeutet und m , x und y wie in Anspruch 23 definiert sind.

25. Polymer, wie in Anspruch 22 beansprucht, in dem das Polyoxyäthylen ein Molgewicht im Bereich von 600 bis 1500 aufweist.

26. Polymer nach Anspruch 22, in dem ein R Polyoxyäthylen bedeutet und das andere R ein Isocyanurat, Polyoxypropylen, Poly(tetramethylenoxid), Pentaerythrit, Diäthyläther oder Glycerin ist.

27. Polymer nach Anspruch 22, das photohärtbar ist und einen oder mehrere Photoinitiatoren ausgewählt aus der Gruppe bestehend aus Benzophenon, Acetophenon(en), Dibenzosuberone, 1-Hydroxycyclohexylphenylketon und Benzoinisopropyläther enthält.

28. Polymer, wie in Anspruch 27 beansprucht, worin der Photoinitiator eine Kombination von Benzophenon und 1-Hydroxycyclohexylphenylketon ist.

Revendications

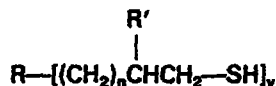
1. Formulation chimique réticulable comprenant

(a) un composant de polyène terminalement insaturé de la formule:



dans laquelle $m=0$ ou 1 et $x \geq 2$;

(b) un composant de polythiol de la formule:



dans laquelle $n=0$ ou 1 , $R'=H$ ou OH et $y \geq 2$; et

(c) un initiateur à radicaux libres, x et y n'étant pas tous deux égaux à 2 et au moins un R représente du polyoxyéthylène et l'autre R représente du polyoxyéthylène ou un fragment organique polyvalent exempt de groupe fonctionnels hydrolytiquement sensibles et autre insaturation carbone-carbone ou de groupes fonctionnels thiol.



2. Formulation chimique réticulable suivant la revendication 1, caractérisée en ce qu'elle contient au moins 40% en poids de polyoxyéthylène.

3. Formulation chimique réticulable suivant la revendication 2, caractérisée en ce qu'elle contient au moins 60% en poids de polyoxyéthylène.

5 4. Formulation chimique réticulable suivant la revendication 3, caractérisée en ce qu'elle contient au moins 80% en poids de polyoxyéthylène.

5. Formulation chimique réticulable suivant la revendication 1, caractérisée en ce que les deux R représentent du polyoxyéthylène.

6. Formulation chimique réticulable suivant la revendication 1, caractérisée en ce qu'un R représente du polyoxyéthylène et l'autre R représente au moins un fragment bivalent se composant d'un isocyanurate, de polyoxypropylène, de poly(oxyde de tétraméthylène), de pentaérythritol, d'éther diéthylique ou de glycérol.

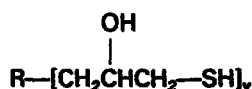
7. Formulation chimique réticulable suivant la revendication 5, caractérisée en ce que le composant de polyène est un polyéther terminalement insaturé de la formule:

15



et le composant de polythiol est un polyéther de la formule:

20



formules dans lesquelles R=polyoxyéthylène et m, x et y sont tels que définis dans la revendication 1.

25 8. Formulation chimique réticulable suivant l'une quelconque des revendications précédentes, caractérisée en ce que le polyoxyéthylène a un poids moléculaire de l'ordre de 600 à 1,500.

9. Formulation chimique réticulable suivant l'une quelconque des revendications précédentes, caractérisée en ce qu'elle est photodurcissable et contient un ou plusieurs photoinitiateurs choisis dans la classe comprenant la benzophénone, l'acétophénone ou les acétophénones, la dibenzosubérone, la 30 l'hydroxycyclohexylphényl cétone et l'éther isopropylique de benzoïne.

10. Formulation chimique photodurcissable suivant la revendication 9, caractérisée en ce que le photoinitiateur est une combinaison de benzophénone et de l'hydroxycyclohexylphényl cétone.

11. Procédé de formation d'une membrane semiperméable composite stratifiée, souple comprenant les étapes suivantes:

35 (a) la formation d'une couche souple d'une matière hydrophobe microporeuse ayant une vitesse de transmission de vapeur d'eau excédant 10,000 g/m² · 24 heures et un angle de contact avec un liquide polaire en mouvement excédant 90 degrés.

(b) la coulée d'une formulation réticulable suivant l'une quelconque des revendications précédentes pour former une couche continue directement sur la couche hydrophobe microporeuse, la rhéologie de la 40 formulation réticulable étant telle qu'avec l'application d'une pression hydraulique suffisante, en obtient une pénétration contrôlable de la formulation dans la couche hydrophobe microporeuse,

(c) l'application de cette pression hydraulique,

(d) suivie d'un durcissement de la formulation réticulable pour former une couche hydrophile polymère solide continue imprégnée à un certain degré dans les pores de la couche hydrophobe 45 microporeuse, la membrane composite ayant une vitesse de transmission de vapeur d'eau excédant 80% de celle de la couche hydrophobe seule.

12. Procédé suivant la revendication 11, caractérisé en ce que la matière microporeuse hydrophobe est du polytétrafluoréthylène, du polypropylène, du poly(chlorure de vinyle), du polyuréthane, du polycarbonate, du polystyrène, du polyéthylène ou du polyamide.

50 13. Procédé suivant la revendication 12, caractérisé en ce que la matière microporeuse hydrophobe est du polytétrafluoréthylène microporeux, expansé.

14. Membrane semi-perméable composite stratifiée, souple comprenant:

(a) une pellicule souple d'une matière hydrophobe microporeuse ayant une vitesse de transmission de 55 vapeur d'eau excédant 10,000 g/m² · 24 heures et un angle de contact avec de l'eau en mouvement excédant 90 degrés, et

(b) une couche hydrophile, continue ayant pénétré à un certain degré la face de la couche hydrophobe et fixée à celle-ci, cette couche hydrophile comprenant un polyéther polythioéther dense, essentiellement sans odeur formé par le produit de réaction d'allongement de chaîne à radicaux fibres d'une source d'énergie actinique et d'une formulation chimique réticulable suivant l'une quelconque des revendications 1 à 7, et cette membrane composite ayant une vitesse de transmission de vapeur d'eau excédant 80% de 60 celle de la matière hydrophobe seule.

15. Membrane semi-perméable composite suivant la revendication 14, ayant une vitesse de transmission de vapeur d'eau excédant celle de la matière hydrophobe seule.

65 16. Membrane semi-perméable composite suivant la revendication 15, ayant une vitesse de transmission de vapeur d'eau excédant 130% de celle de la matière hydrophobe seule.



17. Membrane semi-perméable composite suivant l'une quelconque des revendications 14 à 16, caractérisée en ce que la matière hydrophobe microporeuse est du polytétrafluoréthylène, du polypropylène, du poly(chlorure de vinyle), du polyuréthane, du polycarbonate, du polystyrène, du polyéthylène ou du polyamide.

18. Membrane semi-perméable composite suivant la revendication 17, caractérisée en ce que la matière hydrophobe est du polytétrafluoréthylène microporeux, expansé.

19. Membrane semi-perméable, composite suivant l'une quelconque des revendications 14 à 18, caractérisée en ce que la couche hydrophile est imperméable à l'air.

20. Membrane semi-perméable composite suivant l'une quelconque des revendications 14 à 19, ayant au moins une couche de matière textile additionnelle fixée à au moins une de ses surfaces et en attachement stratifié à cette dernière.

21. Procédé de séparation de molécules de bas poids moléculaire pouvant offrir un hydrogène pour la liaison d'hydrogène, caractérisé en ce que ces molécules sont transportées à travers une membrane semi-perméable composite suivant l'une quelconque des revendications 14 à 20.

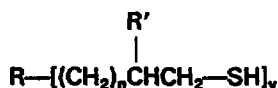
22. Polymère synthétique comprenant un polyéther polythioéther dense essentiellement sans odeur, formé du produit de réaction d'allongement de chaîne à radicaux libres:

(a) d'un polyène terminalement insaturé répondant à la formule:



dans laquelle $m=0$ ou 1 et $x \geq 2$;

(b) d'un composant de polythiol de la formule:



dans laquelle $n=0$ ou 1 , $R'=H$ ou OH et $y \geq 2$;

(c) d'un initiateur à radicaux libres; et

(d) d'une source d'énergie appropriée,

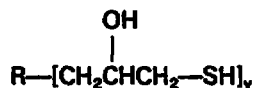
x et y n'étant pas tous deux égaux à 2 et au moins un R représentant du polyoxyéthylène et l'autre R représentant du polyoxyéthylène ou un fragment organique polyvalent exempt de groupes fonctionnels hydrolytiquement sensibles et autre insaturation carbone-carbone ou de groupes fonctionnels-thiol.

23. Polymère synthétique suivant la revendication 22, caractérisé en ce que les deux R sont du polyoxyéthylène.

24. Polymère synthétique suivant la revendication 23, caractérisé en ce que le composant de polyène est un polyéther terminalement insaturé de la formule:



et le composant de polythiol est un polyéther de la formule:



formules dans lesquelles R représente du polyoxyéthylène et m , x et y sont tels que définis dans la revendication 23.

25. Polymère suivant la revendication 22, caractérisé en ce que le polyoxyéthylène a un poids moléculaire de l'ordre de 600 à 1.500 .

26. Polymère suivant la revendication 22, caractérisé en ce qu'un R représente du polyoxyéthylène et l'autre R représente un isocyanurate, le polyoxypropylène, le poly(oxyde de tétraméthylène), le pentaérythritol, l'éther diéthylique ou le glycérol.

27. Polymère suivant la revendication 22, caractérisé en ce qu'il est photodurcissable et contient un ou plusieurs photoinitiateurs choisis dans la classe comprenant la benzophénone, l'acétophénone ou les acétophénones, la dibenzosubérone, la l'hydroxycyclohexylphényl cétone et l'éther isopropylique du benzoïne.

28. Polymère suivant la revendication 27, caractérisé en ce que le photoinitiateur est une combinaison de benzophénone et de l'hydroxycyclohexylphényl cétone.

