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(54) Title: COMPOSITE MEMBRANES

(57) Abstract: A process for preparing a composite membrane comprising the steps: a) applying a radiation-curable composition to a porous support; b) irradiating the composition present on the support, thereby forming a gutter layer of cured polymer; c) forming a discriminating layer on the gutter layer; and d) applying a radiation-curable composition to the discriminating layer and irradiating that composition, thereby forming a protective layer on the discriminating layer; wherein one or both of the radiation-curable compositions applied in steps a) and d) comprise a photo acid generator having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1*}cm^{-1}$. Also claimed are composite membranes and gas separation cartridges comprising the membranes.

COMPOSITE MEMBRANES

This invention relates to composite membranes and to processes for their preparation and use, particularly for separating gases.

The use of membranes to separate gases is known in the art. The known separation processes are based on differences in the relative permeability of two or more gases through a membrane. Typically a mixture of gasses is brought into contact with one side of a membrane through which at least one of the gases permeates faster than the other gases. In this way a gas stream is separated into two streams, one of which is enriched in the selectively permeating gas(es).

From a gas flux point of view, very thin membranes are preferred. However thin membranes are weaker than thicker membranes and run a greater risk of tearing, bursting and mechanical damage.

To improve the mechanical strength of membranes, without compromising gas flux rates, it is not uncommon to use composite membranes comprising a porous support and a thin, gas discriminating layer. The porous support does not discriminate between gases but instead it provides mechanical strength. The gas discriminating layer on the other hand performs the task of selectively allowing one or more gases to pass through more easily than other gases, providing a degree of gas separation and enrichment. In this way higher flux rates can be achieved than if an unsupported, thick discriminating membrane were used, while at the same time the mechanical strength and durability of the membrane is enhanced.

One of the problems faced by gas separation membranes is that the gases they come into contact with are often 'dirty' due to the environment in which they are used. For example, the gases contain significant quantities of higher hydrocarbons that damage membranes they come into contact with. Dirty gases can cause premature plasticization of the membranes and thereby reduce the membrane's selectivity. There is a need for composite membranes which retain good selectivity even when they have been in contact with dirty gases.

According to a first aspect of the present invention there is provided a process for preparing a composite membrane comprising the steps:

a) applying a radiation-curable composition to a porous support;

b) irradiating the composition present on the support, thereby forming a gutter layer of cured polymer;

c) forming a discriminating layer on the gutter layer; and

d) applying a radiation-curable composition to the discriminating layer and irradiating that composition, thereby forming a protective layer on the discriminating layer;

wherein one or both of the radiation-curable compositions applied in steps a) and d) comprise a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

The term 'curing' and the term 'crosslinking' are used interchangeably in this specification.

The gutter layer may also be referred to as a layer of cured polymer, but for brevity in this specification we usually refer to it as a "gutter layer" or "GL". Also in this specification the discriminating layer is sometimes abbreviated to DL and the protective layer is sometimes abbreviated to "PL".

In the statement of invention and claims, references to "that composition" refers to the radiation-curable composition present on the discriminating layer.

The photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$ is often abbreviated to "PAG" in this specification.

The absorbency coefficient Ɛ at 313 nm of photo acid generators may be measured using a spectrophotometer, e.g. on a 0.05 mmol/L solution of the photo acid generator under evaluation in MEK in a 1cm quartz cell. A suitable spectrophotometer is the Cary 100 UV-Vis Spectrophotometer from Agilent Technologies.

As will be understood, either or both of the compositions applied in steps a) and d) may contain a PAG. For example, the following options are available for performing the process:

1) the curable composition applied in step a) comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$ and the curable composition applied in step d) is free from photo acid generators having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$;
2) the curable compositions applied in step a) and in step d) each independently comprise a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$; and
3) the curable composition applied in step a) is free from photo acid generators having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$ and the curable composition applied in step d) comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

The primary purpose of the porous support is to provide mechanical strength to the discriminating layer without materially reducing the flux. Therefore the porous support is typically open pored, relative to the discriminating layer.

The porous support may be, for example, a microporous organic or inorganic membrane, or a woven or non-woven fabric. The porous support may be constructed from any suitable material. Examples of such materials include

polysulfones, polyethersulfones, polyimides, polyetherimides, polyamides, polyamideimides, polyacrylonitrile, polycarbonates, polyesters, polyacrylates, cellulose acetate, polyethylene, polypropylene, polyvinylidenefluoride, polytetrafluoroethylene, poly(4-methyl 1-pentene) and especially polyacrylonitrile.

One may use, for example, a commercially available, porous sheet material as the support. Alternatively one may prepare the porous support using techniques generally known in the art for the preparation of microporous materials. In one embodiment one may prepare a porous, non-discriminatory support by curing curable components, then applying further curable components to the formed porous support and curing such components thereby forming the layer of cured polymer and the discriminating layer on the already cured porous support.

The porous support is not limited to sheet form; also porous supports in tubular form like hollow fibres can be used.

One may also use a porous support which has been subjected to a corona discharge treatment, glow discharge treatment, flame treatment, ultraviolet light irradiation treatment or the like, e.g. for the purpose of improving its wettability and/or adhesiveness. Such a treatment may even be applied between steps b) and c) of the present process if desired.

The porous support preferably possesses pores which are as large as possible, consistent with providing a smooth surface for the gutter layer and subsequent discriminating layer. The porous support preferably has an average pore size of at least about 50% greater than the average pore size of the discriminating layer, more preferably at least about 100% greater, especially at least about 200% greater, particularly at least about 1000% greater than the average pore size of the discriminating layer.

The pores passing through the porous support typically have an average diameter of 0.001 to 10μm, preferably 0.01 to 1μm. The pores at the surface of the porous support will typically have a diameter of 0.001 to 0.1μm, preferably 0.005 to 0.05μm. The pore diameter may be determined by, for example, viewing the surface of the porous support by scanning electron microscopy ("SEM") or by cutting through the support and measuring the diameter of the pores within the porous support, again by SEM.

The porosity at the surface of the porous support may also be expressed as a % porosity, i.e.

$$\% \text{ porosity} = 100\% \times \frac{\text{(area of the surface which is missing due to pores)}}{\text{(total surface area)}}$$

The areas required for the above calculation may be determined by inspecting the surface of the porous support using a SEM. Thus, in a preferred

embodiment, the porous support has a % porosity >1%, more preferably >3%, especially >10%, more especially >20%.

The porosity of the porous support may also be expressed as a CO_2 gas permeance (units are $m^3(STP)/m^2.s.kPa$). When the composite membrane is intended for use in gas separation the porous support preferably has a CO_2 gas permeance of 5 to 150 x 10^{-5} $m^3(STP)/m^2.s.kPa$, more preferably of 5 to 100, most preferably of 7 to 70 x 10^{-5} $m^3(STP)/m^2.s.kPa$.

Alternatively the porosity is characterised by measuring the N_2 gas flow rate through the porous support. Gas flow rate can be determined by any suitable technique, for example using a Porolux™ 1000 device, available from Porometer.com. Typically the Porolux™ 1000 is set at the maximum pressure (about 34 bar) and one measures the flow rate (L/min) of N_2 gas through the porous support under test. The N_2 flow rate through the porous support at a pressure of about 34 bar for an effective sample area of 2.69 cm^2 (effective diameter of 18.5 mm) is preferably >1 L/min, more preferably >5 L/min, especially >10 L/min, more especially >25 L/min. The higher of these flow rates are preferred because this reduces the likelihood of the gas flux of the resultant composite membrane being reduced by the porous support.

The abovementioned % porosity and permeance refer to the porous support used to make the composite membrane (i.e. before step a) has been performed).

The porous support preferably has an average thickness of 20 to 500μm, preferably 50 to 400μm, especially 100 to 300μm.

One may use an ultrafiltration membrane as the porous support, e.g. a polysulfone ultrafiltration membrane, cellulosic ultrafiltration membrane, polytetrafluoroethylene ultrafiltration membrane, polyvinylidenefluoride ultrafiltration membrane and especially polyacrylonitrile ultrafiltration membrane. Asymmetric ultrafiltration membranes may be used, including those comprising a porous polymer membrane (preferably of thickness 10 to 150μm, more preferably 20 to 100μm) and optionally a woven or non-woven fabric support. The porous support is preferably as thin as possible, provided it retains the desired structural strength.

If desired, one may prevent the curable-composition applied to the porous support in step a) from permeating deeply into the porous support by any of a number of techniques. For example, one may select a curable composition which has a sufficiently high viscosity to make such permeation unlikely. With this in mind, the radiation-curable composition preferably has a viscosity of 0.1 to 500 Pa.s at 25°C, more preferably 0.1 to 100 Pa.s at 25°C.

Alternatively, the process optionally comprises the step of filling the pores of the porous support with an inert liquid before applying the radiation-curable

composition to the porous support. This technique has an advantage over the first technique mentioned above in that one may form thinner membranes and more application techniques are available for lower viscosity, radiation-curable compositions.

The PAG may be any compound which generates acid when irradiated with light of wavelength 313 nm and has an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$. Preferably the PAG has an absorbency coefficient Ɛ at 313 nm of more than $3 x 10^4$ $mol^{-1}*cm^{-1}$.

The radiation-curable composition applied in step a) and the radiation-curable composition applied in step d) preferably each independently comprise 0.01 to 5 wt%, more preferably 0.1 to 4 wt% and especially 0.15 to 3.5 wt% of PAG.

The PAG may be ionic or non-ionic. Ionic PAGs comprise an anion and a cation, preferably a cation having a solubility parameter value ("δ") greater than 22, more preferably greater than 24 $(J/cm^3)^{0.5}$. The δ of a cation may be determined by converting the PAG to the neutral (e.g. to the free base form to give a neutralised PAG) and then using Fedors's method to give the Fedors' solubility parameter, e.g. by performing the calculation as described by Fedors in Polymer engineering and Science, February 1974, Vol. 14, no.2:

$$\delta = (\Delta Ev/V)^{½}$$

wherein:

ΔEv is the energy of vaporization of the neutralized PAG, measured at a temperature of 25 ^0C; and

V is the molar volume of the neutralized PAG.

One may calculate V from the molecular weight and density of the neutralized PAG.

For ionic PAGs comprising an anion and a cation, the anion is preferably tetrakis(pentafluorophenyl)borate, hexafluorophosphate, hexaflurorantimonate, or trifluoromethanesulfonate.

For ionic PAGs comprising an anion and a cation, the cation preferably comprises a sulphonium group.

As an example of suitable PAGs there may be mentioned (4-phenylthiophenyl)diphenylsulfonium triflate; triphenylsulfonium triflate; Irgacure(R) 270 (available from BASF); triarylsulfonium hexafluoroantimonate; triarylsulfonium hexafluorophosphate; CPI-100P (available from SAN-APRO); CPI-210S (available from SAN-APRO) and especially Irgacure(R) 290 ((having an absorbency coefficient Ɛ at 313 nm of 44,239 and a cation δ of 25.2) (available from BASF) and CPI-100P from San-Apro Limited of Japan (having an absorbency coefficient

Ɛ at 313 nm of 16,497 and a cation δ of 23.2). Preferably the radiation-curable composition(s) further comprise a partially crosslinked, radiation-curable polymer comprising epoxy groups and siloxane groups and a photoinitiator. In this specification the partially crosslinked, radiation-curable polymer comprising epoxy groups and siloxane groups is often abbreviated in this specification to "the PCP Polymer". Optionally the PCP Polymer is substantially free from mono-epoxy compounds (i.e. compounds which have only one epoxy group).

Another option for ensuring the curable composition applied to the porous support in step a) does not permeate excessively into the porous support is to increase the hydrodynamic radius (R_{hyd}) of the PCP Polymer. R_{hyd} may be increased by increasing the extent to which the PCP Polymer is crosslinked. R_{hyd} can be suitably determined by dynamic light scattering.

Preferably the R_{hyd} of the PCP Polymer is more than half the average diameter of at least 50% of the pores at the surface of the porous support. Some degree of permeation is preferred to achieve a good adhesion.

The process of the present invention optionally further comprises the step of preparing the PCP Polymer. For example, one may partially cure a composition comprising one or more curable components (e.g. monomers, oligomers and/or polymers), at least one of which comprises epoxy groups.

Preferably the partial cure is performed by a thermally initiated polymerisation process.

In a preferred embodiment, at least one of the curable components comprises a group which is both thermally curable and radiation-curable. This is because one may then use a thermally initiated process for preparing the PCP Polymer and subsequently use a radiation initiated process for forming the gutter layer in step b).

Alternatively, the thermally curable group and the radiation-curable groups are different groups and are part of the same component used to from the PCP Polymer.

As thermal curing is a relatively slow process, one may partially cure the curable components thermally to form the PCP Polymer, then stop or slow down the thermal cure process, then apply a composition containing the PCP Polymer to the support (step a)) in the form of a composition comprising an inert solvent, and then irradiate the composition on the support to form a gutter layer on the support (step b)). The thermal cure process may be stopped or slowed down simply by cooling (e.g. to below 30°C) and/or diluting the composition used to make the PCP Polymer at an appropriate time.

The use of two distinct mechanisms for preparing the PCP Polymer and for the final curing after the PCP Polymer has been applied to the porous support in

step a) and/or to the discriminating layer in step d) makes the process more flexible and suitable for large scale production.

Groups which are curable both thermally and by irradiation include epoxy groups and ethylenically unsaturated groups such as (meth)acrylic groups, e.g. (meth)acrylate groups and (meth)acrylamide groups.

Typically the components used to form the PCP Polymer are selected such that they are reactive with each other. For example, a component having an epoxy group is reactive with a component comprising, for example, an amine, alkoxide, thiol or carboxylic acid group. One or more of the components used to form the PCP Polymer may also have more than one curable group. Components having an ethylenically unsaturated group may be reacted with other components by a free radical mechanism or, alternatively, with a nucleophilic component having for example one or more thiol or amine groups.

The PCP Polymer is preferably obtained by thermally curing a composition comprising:

(i) a component which is both thermally curable and radiation-curable and which comprises dialkoxysilane groups and at least three epoxy groups;

(ii) a crosslinking agent which is copolymerisable with component (i) when heated; and

(iii) inert solvent; and optionally

(iv) a catalyst.

Preferably the amount of inert solvent present in the composition is from 5 to 95wt%, more preferably 10 to 80wt%, especially 30 to 70wt%. For convenience, the inert solvent present in the above composition may also act as the inert solvent present in the composition applied in step a) of the present process.

Component (i) preferably comprises at least three radiation-curable groups per molecule.

The alkyl groups in the dialkylsiloxane groups are preferably each independently C_{1-4}-alkyl groups, especially methyl groups.

Preferably component (i) is free from phenyl siloxane groups (e.g. of formula $-(Si(Ph)_2-O)-$ groups wherein Ph is a phenyl or phenylene group).

Component (i) preferably has a number average molecular weight ("NAMW"), of 1 to 500 kDa, preferably 1 to 100 kDa, especially 2 to 50 kDa. The NAMW may be determined by any technique known in the art such as dynamic light scattering or size exclusion chromatography.

Component (i) is preferably present in an amount of 1 to 95wt%, more preferably 5 to 75, especially 10 to 50wt%, relative to the weight of the composition used to make the PCP Polymer.

As examples of component (i) there may be mentioned polydimethylsiloxane epoxy (meth)acrylates, epoxy modified polydimethylsiloxane (meth)acrylates, and allyl modified, vinyl modified, (meth)acrylic modified, epoxy-modified polydimethylsiloxanes and mixtures comprising two or more thereof.

Component (i) also comprises one or more thermally curable groups. This is necessary so that component (i) can cure thermally to provide the PCP Polymer.

Examples of crosslinking agents which may be used as component (ii) include: polydimethylsiloxane comprising two or more reactive groups, for example two or more groups selected from carboxylic acid, hydroxyl, thiol and/or anhydride groups, preferably polydimethylsiloxane having at least two of such groups (e.g. at both ends); (cyclo)aliphatic or aromatic di-, tri- or poly-carboxylic acids, e.g. succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, trimesic acid; (cyclo)aliphatic or aromatic di-, tri- or poly-thiols, e.g. 1,2-ethanedithiol, 1,4-butanedithiol, 1,6-hexanedithiol, benzene-1,2-dithiol, benzene-1,3-dithiol, benzene-1,4-dithiol, 1,2-benzenedimethanethiol, 1,3-benzenedimethanethiol, 1,4-benzenedimethanethiol or toluene-3,4-dithiol; (cyclo)aliphatic or aromatic di-, tri- or poly-amines, e.g. ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, cadaverine, hexamethylenediamine, 1,8-diaminooctane, 1,2-bis(3-aminopropylamino)ethane, 1,2-diaminocyclohexane, 4-aminobenzylamine, o-xylylenediamine, o-phenylenediamine, m-phenylenediamine, p-phenylenediamine; or (cyclo)aliphatic or aromatic anhydrides, e.g. succinic anhydride, 3,3-dimethylglutaric anhydride, ethylenediaminetetraacetic dianhydride, glutaric anhydride, phenylsuccinic anhydride, pyromellitic dianhydride, or phthalic anhydride; metal alkoxides, e.g. alkoxides of zirconium, titanium or niobium, especially titanium (IV) isopropoxide, titanium (IV) ethoxide, zirconium propoxide and/or niobium ethoxide. Preferably the crosslinking agent comprises two (i.e. two and not more than two) reactive groups.

The composition used to make the PCP polymer preferably satisfies the equation:

$$(Mii \times Nii)/(Mi \times Ni) = Y$$

wherein:

- Y is 0.01 to 0.99;
- Mi is the number of moles of component (i);
- Ni is the average number of thermally curable groups per mole of component (i).
- Mii is the number of moles of component (ii); and
- Nii is the average number of thermally curable groups per mole of component (ii).

Preferably Y is 0.02 to 0.50, more preferably 0.02 to 0.20.

The identity of thermally curable groups is not particularly limited and includes, for example epoxy groups, ethylenically unsaturated groups, benzoxazine groups, naphthoxazine groups, hydroxyl groups, isocyanate groups, propargyl groups, ethynyl groups and acetylene groups. Ethylenically unsaturated groups or epoxy groups may also be used to ensure the resultant PCP Polymer is radiation-curable.

The identity of the radiation-curable group(s) is not particularly limited and includes, for example, epoxy groups or ethylenically unsaturated groups such as allylic, vinylic, and (meth)acrylic groups.

The thermal cure step used to make the PCP Polymer, when performed, preferably takes place at a temperature in the range 60 to 150°C, more preferably 75 to 125°C. The thermal cure reaction may be stopped by cooling and/or diluting the thermally-curable composition as described above to give the desired PCP Polymer. For dilution, preferably the same material is used as for component (ii).

The crosslinking agent is useful for increasing the hydrodynamic radius of the resultant PCP Polymer, for example to a size which is more than the average pore size at the surface of the porous support. In this way, penetration of the curable composition into the pores of the porous support is reduced without having to impregnate the porous support with an inert solvent.

Examples of crosslinking agents which may be used as component (ii) include: alkoxides of zirconium, titanium or niobium, e.g. titanium (IV) isopropoxide, titanium (IV) ethoxide, zirconium propoxide and/or niobium ethoxide; polydimethylsiloxane comprising carboxylic acid, thiol or anhydride groups; (cyclo)aliphatic or aromatic di-, tri- or poly-carboxylic acids, e.g. succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, trimesic acid; (cyclo)aliphatic or aromatic di-, tri- or poly-thiols, e.g. 1,2-ethanedithiol, 1,4-butanedithiol, 1,6-hexanedithiol, benzene-1,2-dithiol, benzene-1,3-dithiol, benzene-1,4-dithiol, 1,2-benzenedimethanethiol, 1,3-benzenedimethanethiol, 1,4-benzenedimethanethiol or toluene-3,4-dithiol; (cyclo)aliphatic or aromatic di-, tri- or poly-amines, e.g. ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, cadaverine, hexamethylenediamine, 1,8-diaminooctane, 1,2-bis(3-aminopropylamino)ethane, 1,2-diaminocyclohexane, 4-aminobenzylamine, o-xylylenediamine, o-phenylenediamine, m-phenylenediamine, p-phenylenediamine; or (cyclo)aliphatic or aromatic anhydrides, e.g. succinic anhydride, 3,3-dimethylglutaric anhydride, ethylenediaminetetraacetic dianhydride, glutaric anhydride, phenylsuccinic anhydride, pyromellitic dianhydride, or phthalic anhydride.

The function of the inert solvent (iii) is to provide the composition used to make the PCP Polymer with a concentration suitable for the thermal crosslinking reaction to proceed efficiently. Typically the inert solvent used as component (iii) comprises one or more organic solvents, especially water-immiscible organic solvent(s). The inert solvent is referred to as "inert" because it is not curable.

As examples of inert solvents there may be mentioned: C_5-C_{10} (cyclo)alkanes, benzene, alkylbenzenes (e.g. toluene), C_3-C_{10} (optionally branched) ketones, C_4-C_{10} cyclic ketones, C_4-C_{10} (optionally branched) esters, C_4-C_{10} cyclic esters, C_4-C_{10} (optionally branched) ethers, C_4-C_{10} cyclic ethers and especially n-heptane and n-octane. Preferably the inert solvent comprises one or more, especially from 1 to 8, of the abovementioned preferred inert solvents.

Suitable catalysts (IV) include, for example, amine, phosphonium and metal compounds, e.g. amines such as 2-ethylhexylamine, bis(2-ethylhexyl)amine, dodecyldimethylamine, n,n-dimethylbenzylamine, 2-ethylimidazole, 1,8-diazabicyclo[5.4.0]undec-7-ene, tetramethyl guanidine, tetrabutylammonium chloride, benzyltrimethyl ammonium bromide, benzyltrimethyl ammonium hydroxide, tetrabutyl ammonium hydroxide, crosslinked polyvinylpyridine, and polymer bound amines such as polymer bound 1,4-diazabicyclo[2.2.2]octane hydrochloride, polymer bound 1,8-diazabicyclo[5.4.0] undec-7-ene and polymer bound tetraalkylammonium carbonate; phosphonium compounds such as tetrabutyl phosphonium bromide, pentyltriphenylphosphonium bromide, polymer bound triphenylphosphonium chloride; metal compounds such as titanium (iv) isopropoxide, diisopropoxytitanium-bis-(acetylacetonate), titanium (iv) 2-ethylhexyloxide, titanium (iv) butoxide, titanium butylphosphate, zirconium (iv) propoxide, zirconium (iv) ethoxide, zirconium (iv) acetylacetonate, zirconium (iv) bis(diethyl citrato)-dipropoxide, niobium ethoxide, aluminum acetylacetonate, aluminum lactate, bismuth octoate, calcium octoate, cerium naphthenate, chromium (iii) 2-ethylhexanoate, cobalt octoate, copper (ii) acetylacetonate, iron (iii) acetylacetonate, magnesium 2,4-pentadionate, manganese naphthenate, nickel acetylacetonate, stannous octoate, titanium ethyl acetoacetate chelate, titanium acetylacetonate chelate, titanium triethanolamine chelate, zinc acetate, zinc acetylacetonate, zinc di-2-ethylhexyldithio-phosphate, zinc nitrate, zinc octoate, zirconium 6-methylhexanedione, zirconium octoate, zirconium (iv) trifluoroacetylacetone, and the like. Catalysts generally are used in concentrations ranging from about 0.004 to about 1 wt%, preferably from about 0.01 to about 0.5 wt%, relative to the total weight of curable components.

The radiation-curable composition applied in step a) and/or step d) preferably comprises:

(1) 0.5 to 50 wt% of PCP Polymer;

(2) 0.01 to 5 wt% of PAG; and

(3) 50 to 99.5 wt% of inert solvent.

When the radiation-curable composition used in only one of steps a) and d) comprises a PAG and the radiation-curable composition used in the other of steps a) and d) does not comprise a PAG it is preferred that the radiation-curable composition used in the other of steps a) and d) which does not comprise a PAG comprises a photoinitiator, e.g. in the amounts indicated above for the PAG.

In order for the PCP Polymer to be radiation-curable, it preferably has at least at least two epoxy groups. Epoxy groups are preferred because their cure is usually not inhibited by presence of oxygen. The PCP polymers often have a high affinity for oxygen and this oxygen can sometimes inhibit the curing of other curable groups.

The PCP Polymer optionally comprises further radiation-curable groups, in addition to the at least two epoxy groups. Such further radiation-curable groups include ethylenically unsaturated groups (e.g. (meth)acrylic groups (e.g. CH_2=CR-C(O)- groups), especially (meth)acrylate groups (e.g. CH_2=CR-C(O)O- groups) and/or (meth)acrylamide groups (e.g. CH_2=CR-C(O)NR- groups), wherein each R independently is H or CH_3). The preferred ethylenically unsaturated groups are acrylate groups because of their fast polymerisation rates, especially when the irradiation in step b) uses UV light. Many compounds having acrylate groups are also easily available from commercial sources.

Commercially available photo-initiators often contain mono-epoxy compounds comprising a C-$_{10\text{-}16}$-alkyl group. These are included in the photo-initiators to act as a reactive diluent. By substantially removing such compounds from the photo-initiator, or by using photo-initiators which are free from such compounds, the CO_2/CH_4 selectivity of the membranes derived from PCP Polymers can often be increased.

Preferably the photo-initiator is a type I and/or type II photo-initiator.

Examples of radical type I photo-initiators are as described in WO 2007/018425, page 14, line 23 to page 15, line 26, which are incorporated herein by reference thereto.

Examples of radical type II photo-initiators are as described in WO 2007/018425, page 15, line 27 to page 16, line 27, which are incorporated herein by reference thereto.

For PCP Polymers comprising one or more acrylate group, type I photo-initiators are preferred. Especially alpha-hydroxyalkylphenones, such as 2-hydroxy-2-methyl-1-phenyl propan-1-one, 2-hydroxy-2-methyl-1-(4-tert-butyl-) phenylpropan-1-one, 2-hydroxy-[4´-(2-hydroxypropoxy)phenyl]-2-methylpropan-1-one, 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl propan-1-one, 1-hydroxycyclohexylphenylketone and oligo[2-hydroxy-2-methyl-1-{4-(1-methylvinyl)phenyl}propanone], alpha-aminoalkylphenones, alpha-

sulfonylalkylphenones and acylphosphine oxides such as 2,4,6-trimethylbenzoyl-diphenylphosphine oxide, ethyl-2,4,6-trimethylbenzoyl-phenylphosphinate and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, are preferred.

Cationic photo-initiators are preferred because the PCP Polymer comprises curable groups such as epoxy-modified groups and may comprise other curable groups as oxetane, other ring-opening heterocyclic groups or vinyl ether groups.

Preferred cationic photo-initiators include organic salts of non-nucleophilic anions, e.g. hexafluoroarsinate anion, antimony (V) hexafluoride anion, phosphorus hexafluoride anion, tetrafluoroborate anion and tetrakis (2,3,4,5,6-pentafluorophenyl)boranuide anion.

If it is desired that the photo-initiator is substantially free from mono-epoxy compounds, one may select a commercially available photo-initiator which is free from such compounds, or one may remove such compounds from a commercially available photo-initiator which contains such compounds.

Examples of commercially available photo-initiators which are free from mono-epoxy compounds include, for example, hexafluoroantimonate salts, pentafluorohydroxyantimonate salts, hexafluorophosphate salts and hexafluoroarsenate salts. Among these photo-initiators, sulphonium salts and iodonium salts are preferably used. The PAG may be used in addition to such a photoinitiator or in place of such a photoinitiator.

Examples of suitable sulphonium salts include triphenylsulphonium hexafluorophosphate, triphenylsulphonium hexafluoroantimonate, triphenylsulphonium tetrakis(pentafluorophenyl)borate, 4,4'-bis[diphenylsulphonio]diphenylsulfide bishexafluorophosphate, 4,4'-bis[di(beta-hydroxyethoxy)phenylsulphonio]diphenylsulfide bishexafluoroantimonate, 4,4'-bis[di(beta-hydroxyethoxy)phenylsulphonio]diphenylsulfide bishexafluorophosphate, 7-[di(p-toluyl)sulphonio]-2-isopropylthioxanthone hexafluoroantimonate, 7-[di(p-toluyl)sulphonio]-2-isopropylthioxanthone tetrakis(pentafluorophenyl)borate, 4-phenylcarbonyl-4'-diphenylsulphonio-diphenylsulphide hexafluorophosphate, 4-(p-tert-butylphenylcarbonyl)-4'-diphenylsulphonio-diphenylsulphide hexafluoroantimonate, and 4-(p-tert-butylphenylcarbonyl)-4'-di(p-toluyl)sulphonio-diphenylsulphide tetrakis(pentafluorophenyl)borate (e.g. DTS-102, DTS-103, NDS-103, TPS-103 and MDS-103 from Midori Chemical Co. Ltd.).

Examples of suitable iodonium salts include phenyliodonium hexafluoroantimonate (e.g. CD-1012 from Sartomer Corp.), diphenyliodonium tetrakis(pentafluorophenyl)borate, diphenyliodonium hexafluorophosphate, diphenyliodonium hexafluoroantimonate, bis(dodecylphenyl)iodonium hexafluoroantimonate, and di(4-nonylphenyl)iodonium hexafluorophosphate.

MPI-103, BBI-103 from Midori Chemical Co. Ltd. may also be used, as may certain iron salts (e.g. Irgacure™ 261 from Ciba).

Preferred commercially available photo-initiators free from epoxy compounds include 4-isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl) borate ($(C_{40}H_{18}BF_{20}I)$) available under the name I0591 from TCI) and 4-(octyloxy)phenyl](phenyl) iodonium hexafluoroantimonate ($C_{20}H_{26}F_6IOSb$, available as AB153366 from ABCR GmbH Co).

The presence/absence and amount of mono-epoxy compounds may be determined by, for example, gas-liquid chromatography and/or mass spectroscopy.

One may substantially remove mono-epoxy compounds found photo-initiators which contain such compounds by standard purification techniques, for example by column chromatography or recrystallisation as appropriate.

The preferred curable composition contains less than 0.1wt%, more preferably less than 0.05wt%, especially less than 0.01wt% of mono-epoxy compounds. Most preferably the curable composition is free from mono-epoxy compounds.

Preferably the weight ratio of photo-initiator/PAG to radiation-curable components present in the radiation-curable composition(s) is between 0.001 and 0.2 to 1, more preferably between 0.01 and 0.1 to 1. It is preferred to minimize the amount of photo-initiator/PAG used, in other words preferably all photo-initiator/PAG has reacted after step b). A single type of photo-initiator or PAG may be used but also a combination of several different types.

The function of the inert solvent (3) is to provide the radiation-curable composition with a viscosity suitable for the particular method used to apply the curable composition to the porous support. For high speed application processes one will usually choose an inert solvent of low viscosity. The number of parts of component (3) is preferably 70 to 99.5wt%, more preferably 80 to 99wt%, especially 90 to 98wt%.

The inert solvent is preferably selected from the solvents described above for the preparation of the PCP Polymer.

The radiation-curable composition may contain other components, for example surfactants, surface tension modifiers, viscosity enhancing agents, biocides, other components capable of co-polymerisation with the PCP Polymer or other ingredients.

The radiation-curable composition may be applied to the porous support in step a) and/or to the discriminating layer in step d) by any suitable coating technique, for example by curtain coating, meniscus type dip coating, kiss coating, pre-metered slot die coating, reverse or forward kiss gravure coating, multi roll gravure coating, spin coating and/or slide bead coating.

Conveniently the radiation-curable composition may be coated onto the support in step a) and/or to the discriminating layer in step d) by a multilayer coating method, for example using a consecutive multilayer coating method to perform steps a) and c) either side of an irradiation source for performing step b).

In a preferred consecutive multilayer process a layer of the radiation-curable composition, the discriminating layer (or a composition used to form the discriminating layer) and optionally the protective layer are applied consecutively to the support, with the radiation-curable composition used in step b) being applied before the discriminating layer and the radiation-curable composition used in step d) being applied after the discriminating layer.

In order to produce a sufficiently flowable composition for use in a high speed coating machine, the radiation-curable composition preferably has a viscosity below 4000mPa·s when measured at 25°C, more preferably from 0.4 to 1000mPa·s when measured at 25°C. Most preferably the viscosity of the radiation-curable composition is from 0.4 to 500mPa.s when measured at 25°C. For coating methods such as slide bead coating the preferred viscosity is from 1 to 100mPa.s when measured at 25°C. The desired viscosity is preferably achieved by controlling the amount of solvent in the radiation-curable composition and/or by the conditions for preparing the radiation-curable polymer.

In the multi-layer coating methods mentioned above one may optionally apply a lower inert solvent layer to the porous support followed by applying the radiation-curable composition.

With suitable coating techniques, coating speeds of at least 5m/min, e.g. at least 10m/min or even higher, such as 15m/min, 20m/min, or even up to 100m/min, can be reached. In a preferred embodiment the radiation-curable composition is applied to the support at one of the aforementioned coating speeds.

The thickness of the cured polymer arising from step b) and step d) may be influenced by controlling the amount of curable composition per unit area applied to the support. For example, as the amount of curable composition per unit area increases, so does the thickness of the resultant gutter layer. The same principle applies to formation of the discriminating layer and the protective layer.

While it is possible to practice the invention on a batch basis with a stationary porous support, to gain full advantage of the invention it is much preferred to perform the process on a continuous basis using a moving porous support, e.g. the porous support may be in the form of a roll which is unwound continuously or the porous support may rest on a continuously driven belt. Using such techniques the radiation-curable composition can be applied to the porous support on a continuous basis or it can be applied on a large batch basis. Removal of the inert solvent from the radiation-curable composition can be

accomplished at any stage after the radiation-curable composition has been applied to the support, e.g. by evaporation.

Thus in a preferred process, the radiation-curable composition is applied continuously to the porous support in step a) by means of a manufacturing unit comprising a radiation-curable composition application station, step b) is performed using an irradiation source located downstream from the radiation-curable composition application station, the discriminating layer is formed on the layer of cured polymer in step c) by a discriminating layer application station and the resultant composite membrane is collected at a collecting station, wherein the manufacturing unit comprises a means for moving the porous support from the radiation-curable composition application station to the irradiation source and to the discriminating layer application station and to the composite membrane collecting station.

Optionally the discriminating layer is formed on the gutter layer by a radiation curing process. Under such circumstances, the manufacturing unit preferably further comprises an irradiation source or a heater located downstream from the discriminating layer application station, thereby radiation- or thermally-curing the components used to form the discriminating layer.

The radiation-curable composition application station may be located at an upstream position relative to the irradiation source and the irradiation source is located at an upstream position relative to the discriminating layer application station, such that the process steps occur in the order (b), (c), (d).

If desired step c) may be performed using a different manufacturing unit from that used to perform step a). Thus one may perform steps a) and b), store the product of step b), then perform step c) and step d) later either using the same manufacturing unit used for steps a) and b) or a different manufacturing unit.

The gutter layer (formed in step b)) usually has the function of providing a smooth and continuous surface for the discriminating layer. While it is preferred for the gutter layer to be pore-free, the presence of some pores usually does not reduce the permselectivity of the final membrane because the discriminating layer is often able to fill minor defects in the gutter layer.

The gutter layer preferably has a thickness of 25 to 800nm, preferably 30 to 600nm, especially 50 to 500nm, e.g. 70 to 400nm, or 80 to 300nm, or 90 to 200nm. The thickness may be determined by cutting through the layer and examining its cross section using a scanning electron microscope. “Thickness” refers to the part of the gutter layer which is present on top of the porous support and is an average value. The part of the radiation-curable composition which is present within the pores of the support is not taken into account.

The gutter layer is preferably essentially nonporous, i.e. any pores present therein have an average diameter <1nm. This does not exclude the presence of

defects which may be significantly larger. Defects may be corrected by the discriminating layer as described above.

The irradiation step b) may be performed using any source which provides the wavelength and intensity of radiation necessary to cause the radiation-curable composition to polymerise. For example, electron beam, UV, visible and/or infra red radiation may be used to cure the composition, the appropriate radiation being selected to match the composition. For UV curing a mercury arc lamp is particularly effective, but light emitting diodes can also be used.

Preferably radiation curing of the radiation-curable composition begins within 7 seconds, more preferably within 5 seconds, most preferably within 3 seconds, of the radiation-curable composition being applied to the porous support.

Preferably the curing is achieved by irradiating the radiation-curable composition for less than 30 seconds, more preferably less than 10 seconds, e.g. less than 5 seconds.

In steps b) and d) the radiation-curable composition is preferably irradiated with ultraviolet light or an electron beam.

Preferably the irradiation referred to in step b) or d) uses ultraviolet light. Suitable wavelengths are for instance UV-A (400 to >320nm), UV-B (320 to >280nm), UV-C (280 to 200nm), provided the wavelength matches with the absorbing wavelength of the photo-initiator or PAG included in the composition. For compositions comprising a PAG UV-B is preferred (320 to >280nm),

Suitable sources of ultraviolet light include mercury arc lamps, carbon arc lamps, low pressure mercury lamps, medium pressure mercury lamps, high pressure mercury lamps, swirlflow plasma arc lamps, metal halide lamps, xenon lamps, tungsten lamps, halogen lamps, lasers and ultraviolet light emitting diodes. Particularly preferred are ultraviolet light emitting lamps of the medium or high pressure mercury vapour type. In addition, additives such as metal halides may be present to modify the emission spectrum of the lamp. In most cases lamps with emission maxima between 200 and 450nm are particularly suitable.

The energy output of the irradiation source is preferably from 20 to 1000W/cm, preferably from 40 to 500W/cm but may be higher or lower as long as the desired exposure dose can be realized.

The discriminating layer preferably has pores of average diameter below 2 nm, preferably below 1nm, and preferably is substantially non-porous. Preferably the discriminating layer has a very low permeability to liquids.

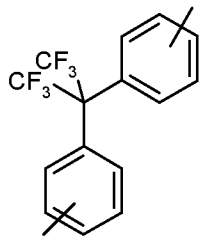
The discriminating layer preferably has a dry thickness of 10 to 300nm, more preferably 10 to 150nm, especially 20 to 100nm.

The dry thickness may be determined by cutting through the composite membrane and measuring the thickness of the discriminating layer above the gutter layer using a scanning electron microscope.

The composition used to make the discriminating layer preferably comprises a polymer, an inert solvent and optionally an initiator. The inert solvent may be any solvent capable of dissolving the polymer used to form the discriminating layer. Suitability of the solvent is determined by the properties of the polymer and the concentration desired. Suitable solvents include water, C_{5-10}-alkanes, e.g. cyclohexane, heptane and/or octane; alkylbenzenes, e.g. toluene, xylene and/or C_{10}-C_{16} alkylbenzenes; C_{1-6}-alkanols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and/or cyclohexanol; linear amides, e.g. dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, e.g. acetone, methyl ether ketone, methyl isobutyl ketone, cyclohexanone and/or diacetone alcohol; ethers, e.g. tetrahydrofuran and/or dioxane; diols, preferably diols having from 2 to 12 carbon atoms, e.g. pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and/or thiodiglycol; oligo- and poly-alkyleneglycols, e.g. diethylene glycol, triethylene glycol, polyethylene glycol and/or polypropylene glycol; triols, e.g. glycerol and/or 1,2,6-hexanetriol; mono-C_{1-4}-alkyl ethers of diols, preferably mono-C_{1-4}-alkyl ethers of diols having 2 to 12 carbon atoms, e.g. 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and/or ethyleneglycol monoallylether; cyclic amides, e.g. 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and/or 1,3-dimethylimidazolidone; cyclic esters, e.g. caprolactone; sulphoxides, e.g. dimethyl sulphoxide and/or sulpholane; and mixtures comprising two or more of the foregoing.

The discriminating layer is generally polymeric in nature. Preferred discriminating layers comprise a polyimide, cellulose acetate, polybenzoxazole, polyethyleneoxide or polyetherimide, especially a polyimide comprising trifluoromethyl groups.

A particularly preferred discriminating layer comprises a polyimide comprising groups of the Formula (1):



Formula (1).

Polyimides comprising trifluoromethyl groups may be prepared by, for example, the general methods described in U.S. Pat. Reissue No. 30,351 (based on US 3,899,309) US 4,717,394 and US 5,085,676.

The composition used to prepare the discriminating layer preferably comprises less than 0.1 wt%, more preferably less than 0.05 wt%, especially less than 0.01 wt% of mono-epoxy compounds. Most preferably the composition used to prepare the discriminating layer is free from mono-epoxy compounds.

When the discriminating layer is cured after applying it to the gutter layer the composition used to prepare the discriminating layer preferably comprises an initiator, preferably a thermal initiator or a photo-initiator. The initiator may be selected from those described above for the gutter layer.

Preferably the discriminating layer is obtained from a composition which is free from mono-epoxy compounds comprising a C_{-10-16}-alkyl group, more preferably free from epoxy compounds having a molecular weight below 300 or 400 Daltons.

The discriminating layer may be formed on the gutter layer by any suitable technique, for example by a process comprising any of the coating methods described above in relation to preparation of the gutter layer.

For improving the adhesion of the discriminating layer to the gutter layer the latter may be treated by a corona discharge or plasma treatment before forming the discriminating layer thereon. For the corona or plasma treatment generally an energy dose of 0.5 to 100 kJ/m^2 will be sufficient.

The protective layer may be formed on the discriminating layer by any suitable technique, for example by a process comprising any of the coating methods described above in relation to preparation of the gutter layer.

The protective layer, when present, preferably is highly permeable to the gases or vapours that are to be separated. Preferably the protective layer comprises dialkylsiloxane groups.

The radiation-curable composition used to prepare the protective layer in step d) may be any radiation-curable composition, although a radiation-curable composition as independently described above for preparation of the gutter layer is preferred. Thus the radiation-curable composition applied to the discriminating layer in step d) may be the same as or different to the radiation-curable composition applied to the porous support in step a) and both compositions preferably fall within the above description of preferred radiation-curable compositions. Furthermore, the radiation-curable composition applied to the discriminating layer in step d) may be irradiated in a different or in an analogous manner to that described above for irradiating the radiation-curable composition in step b). Thus the method used to cure the radiation-curable composition in step d) may be the same as or different to the method used in step b).The protective layer optionally has surface characteristics which influence the functioning of the composite membrane, for example by making the membrane surface more hydrophilic or hydrophobic. The composite membrane preferably has a water

permeability at 20°C of less than 6.10^{-8} $m^3/m^2.s.kPa$, more preferably less than 3.10^{-8} $m^3/m^2.s.kPa$.

The overall dry thickness of the composite membrane will typically be 20 to 500µm, preferably from 30 to 300µm.

Steps a) to d) are preferably performed sequentially as part of a continuous process for preparing the composite membrane.

In one embodiment, step a) comprises meniscus type dip coating of the radiation-curable composition onto the porous support and the discriminating layer (or the components from which the discriminating layer is derived) is applied to the cured polymer in step c) by reverse kiss gravure coating, meniscus type dip coating or pre-metered slot die coating. Alternatively the radiation-curable composition may be applied to the support by pre-metered slot die coating or multi roll gravure coating. The radiation-curable composition and the discriminating layer may also be applied by curtain coating.

For production on a small scale, it is convenient to perform all of steps a), c) and d) by reverse kiss gravure coating, forward kiss gravure coating, meniscus type dip coating, pre-metered slot die coating or spin coating.

A three-roll offset gravure coating may also be used, especially when the compositions to be applied to the support etc. have relatively high viscosity.

The process of the present invention may contain further steps if desired, for example washing and/or drying one or more of the various layers and removing the inert solvent from the composite membrane, e.g. by evaporation.

According to a second aspect of the present invention there is provided a composite membrane obtained by a process according to the first aspect of the present invention.

A preferred composite membrane according to the present invention comprises:

i) a porous support;

ii) a gutter layer;

iii) a discriminating layer on the gutter layer; and

iv) a protective layer;

wherein one or both of the gutter layer ii) and the protective layer iv) comprise a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

Although irradiation of the radiation-curable composition(s) during preparation of the composite membrane causes some of the PAG to release acid and be converted to an irradiated PAG, not all of the PAG is converted and some PAG remains in the layer(s) obtained by irradiating the radiation-curable composition(s) containing a PAG. Thus the following options are available for the composite membranes of the present invention:

1) (a) the gutter layer ii) comprises an photo acid generator having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$; and (b) the protective layer iv) is free from photo acid generators having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$;

2) the gutter layer ii) and the protective layer iv) each independently comprises an photo acid generator having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$; and

3) (a) the gutter layer ii) is free from photo acid generators having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$; and (b) the protective layer iv) comprises an photo acid generator having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

In a preferred embodiment both the gutter (ii) and the protective layer iv) comprise an PAG (i.e. a photo acid generator having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$). The protective layer preferably comprises 0.01 to 5 wt%, more preferably 0.1 to 4 wt% and especially 0.15 to 3.5 wt% of PAG and/or irradiated PAG.

The preferences for the porous support, gutter layer, discriminating layer, protective layer and for the PAG are as described above in relation to the first aspect of the present invention (the protective layer preferably comprising a PAG and/or an irradiated PAG in the amounts described above).

In the composite membranes of the present invention, the irradiated PAG is preferably a PAG which has been irradiated with radiation having a wavelength and intensity which causes the PAG to release acid, e.g. radiation of a wavelength 280 to 380 nm, especially 300 to 330 nm.

Preferably the discriminating layer in the composite membrane according to the second aspect of the present invention has been obtained from a composition which is substantially free from mono-epoxy compounds.

The porous support, gutter layer and discriminating layer of the composite membrane according to the second aspect of the present invention are preferably as described above in relation to the first aspect of the present invention.

Preferably the composite membrane according to the second aspect of the present invention is obtained by a process according to the first aspect of the present invention.

The discriminating layer preferably comprises a polyimide, especially a polyimide comprising trifluoromethyl groups. Preferably the discriminating layer is free from PAGS and irradiated PAGs.

A further aspect of the present invention provides a gas separation module for separating a feed gas containing a target gas into a gas stream rich in the target gas and a gas stream depleted in the target gas, the module comprises a

housing and one or more cartridges comprising a composite membrane according to the second aspect of the present invention.

A still further aspect of the present invention provides a gas separation cartridge comprising a composite membrane according to the second aspect of the present invention.

The composite membrane (which may also be referred to as a gas separation element) is preferably in tubular or, more preferably, in sheet form. Tubular forms of membrane are sometimes referred to as being of the hollow fibre type. Membranes in sheet form are suitable for use in, for example, spiral-wound, plate-and-frame and envelope cartridges.

The composite membranes are particularly suitable for separating a feed gas containing a target gas into a gas stream rich in the target gas and a gas stream depleted in the target gas. For example, a feed gas comprising polar and non-polar gases may be separated into a gas stream rich in polar gases and a gas stream depleted in polar gases. In many cases the membranes have a high permeability to polar gases, e.g. CO_2, H_2S, NH_3, SO_x, and nitrogen oxides, especially NO_x, relative to non-polar gases, e.g. alkanes, H_2, and N_2.

The target gas may be, for example, a gas which has value to the user of the composite membrane and which the user wishes to collect. Alternatively the target gas may be an undesirable gas, e.g. a pollutant or 'greenhouse gas', which the user wishes to separate from a gas stream in order to protect the environment.

The composite membranes are particularly useful for purifying natural gas (a mixture which comprises methane) by removing polar gases (CO_2, H_2S); for purifying synthesis gas; and for removing CO_2 from hydrogen and from flue gases. Flue gases typically arise from fireplaces, ovens, furnaces, boilers, combustion engines and power plants. The composition of flue gases depend on what is being burned, but usually they contain mostly nitrogen (typically more than two-thirds) derived from air, carbon dioxide (CO_2) derived from combustion and water vapour as well as oxygen. Flue gases also contain a small percentage of pollutants such as particulate matter, carbon monoxide, nitrogen oxides and sulphur oxides. Recently the separation and capture of CO_2 has attracted attention in relation to environmental issues (global warming).

The composite membranes of the invention are particularly useful for separating the following: a feed gas comprising CO_2 and N_2 into a gas stream richer in CO_2 than the feed gas and a gas stream poorer in CO_2 than the feed gas; a feed gas comprising CO_2 and CH_4 into a gas stream richer in CO_2 than the feed gas and a gas stream poorer in CO_2 than the feed gas; a feed gas comprising CO_2 and H_2 into a gas stream richer in CO_2 than the feed gas and a gas stream poorer in CO_2 than the feed gas, a feed gas comprising H_2S and CH_4 into a gas stream richer in H_2S than the feed gas and a gas stream poorer in H_2S than the feed gas;

and a feed gas comprising H_2S and H_2 into a gas stream richer in H_2S than the feed gas and a gas stream poorer in H_2S than the feed gas; especially such feed gases which are dirty, e.g. such feed gases which further comprise one or more of ethane, propane, n-butane, n-heptane and toluene.

Preferably the composite membrane has a CO_2/CH_4 selectivity ($\alpha CO_2/CH_4$) >20. Preferably the selectivity is determined by a process comprising exposing the membrane to a 13:87 mixture by volume of CO_2 and CH_4 at a feed pressure of 6000 kPa and a temperature of 40°C.

Preferably the composite membrane has a CO_2/N_2 selectivity ($\alpha CO_2/N_2$) >35. Preferably the selectivity is determined by a process comprising exposing the membrane to CO_2 and N_2 separately at feed pressures of 6000 kPa and a temperature of 40°C. The CO_2/N_2 selectivity ($\alpha CO_2/N_2$) and CO_2/CH_4 selectivity ($\alpha CO_2/CH_4$) may be measured for both clean gas and dirty gas, as illustrated in the Examples. The preferred selectivities described above apply to both clean gases and dirty gases. While this specification emphasises the usefulness of the composite membranes of the present invention for separating gases, especially polar and non-polar gases, it will be understood that the composite membranes can also be used for other purposes, for example providing a reducing gas for the direct reduction of iron ore in the steel production industry, dehydration of organic solvents (e.g. ethanol dehydration), pervaporation and vapour separation and also for breathable apparel.

The invention is now illustrated by the following non-limiting examples in which all parts and percentages are by weight unless otherwise specified. ("Comp" means Comparative).

The following materials were used in the Examples:

MAT is a porous support polyacrylonitrile L14 ultrafiltration membrane from GMT Membrantechnik GmbH, Germany.

UV-9300 is SilForce™ UV9300 from Momentive Performance Materials Holdings. This is thermally curable copolymer comprising at least 3 epoxy groups and linear polydimethyl siloxane chains. Furthermore, this copolymer cures rapidly when irradiated with UV light in the presence of a photo-initiator.

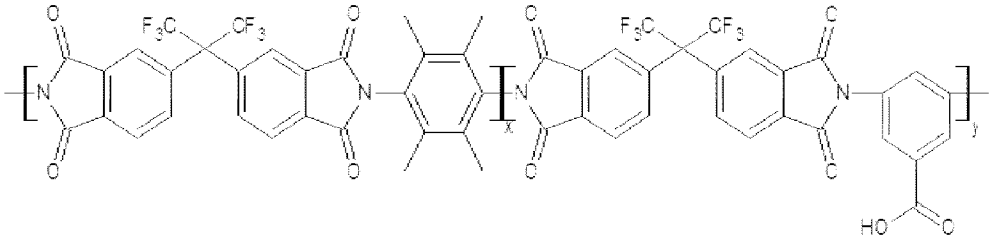
UV9390C is SilForce™ UV-9390C - a cationic photo-initiator (a solution of a bis(4-alkylaryl)iodonium hexafluoroantimonate salt, a photosensitizer and about 28 wt% of mono epoxy compounds (a mixture glycidyl C_{12}, C_{14} or C_{16} –alkyl ether, as judged by GC-MS). This material has an

absorbency coefficient Ɛ at 313 nm of 850.

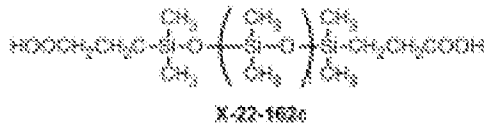
n-Heptane is n-heptane from Brenntag Nederland BV

MEK is 2-butanone from Brenntag Nederland BV

PI is 6FDA-TeMPD x /DABA y, x/y=20/80; obtained from FUJIFILM Finechemicals Co., Ltd, having the following structure:



X-22-162C is a dual end reactive silicone having carboxylic acid reactive groups, a viscosity of 220 mm^2/s and a reactive group equivalent weight of 2,300 g/mol] from Shin-Etsu Chemical Co., Ltd. (MWT 4,600):

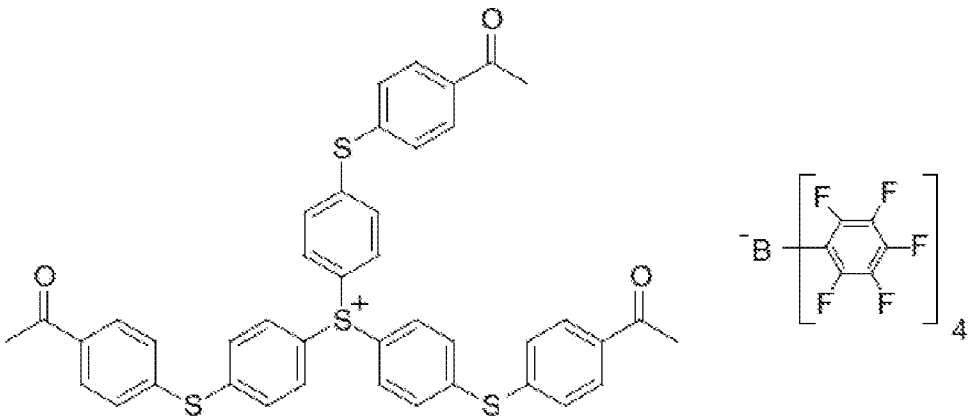


X-22-162C

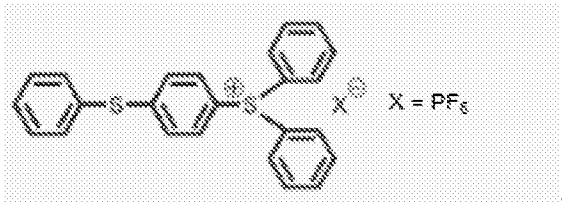
DBU is 1,8-diazabicycloundec-7-ene from Sigma-Aldrich.

Tyzor(R) TPT is tetraisopropyl orthotitanate from Sigma-Aldrich.

Irgacure(R) 290 is a PAG from BASF having an absorbency coefficient Ɛ at 313 nm of 44,239 and having the following structure:



CPI-100P is a PAG from San-Apro having an absorbency coefficient Ɛ at 313 nm of 16,497 and having the following structure:



I0591 is 4-isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl) borate ($C_{40}H_{18}BF_{20}I$) from TCI (a comparative photo acid generator having an absorbency coefficient Ɛ at 313 nm of 6,915).

APTMS is 3-trimethoxysilyl propan-1-amine from Sigma Aldrich.

DIOX is 1,3-dioxolane from Brenntag Nederland BV.

Clean Gas and Dirty Gas have the compositions shown in the table below:

	Gas composition vol %						
	CO_2	CH_4	ethane	propane	n-butane	n-heptane	Toluene
Dirty Gas	9.00	82.12	4.50	3.00	1.00	0.30	0.08
Clean Gas	9.00	91.00	0.00	0.00	0.00	0.00	0.00

Performance means the CO_2 flux and permselectivity of CH_4 of the composite membrane under evaluation, measured as described below in sections (A) and (B).

Evaluation of Gas Permeability & Selectivity

In the following Examples gas permeability and selectivity of the composite membranes was determined as follows:

(A) Gas flux

The flux of Clean Gas and Dirty Gas through the obtained composite membrane was measured at 40°C and gas feed pressure of 6000 kPa using a gas permeation cell with a measurement diameter of 3.0 cm and a feed gas composition of 9 v/v % CO_2 and 91 v/v % CH_4.

Flux of each gas through a composite membrane under test was determined after a period of 5 minutes continuous use using the following equation:

$$Q_i = (\theta_{Perm} \cdot X_{Perm,i})/(A \cdot (P_{Feed} \cdot X_{Feed,I} - P_{Perm} \cdot X_{Perm,i}))$$

wherein:

Q_i = Flux of the relevant gas (i.e. CO_2 or CH_4) (m^3(STP)/m^2·kPa·s);

θ_{Perm} = Permeate flow (m^3(STP)/s);

$X_{Perm,i}$ = Volume fraction of the relevant gas in the permeate;

A = Membrane area (m^2);

P_{Feed} = Feed gas pressure (kPa);

$X_{Feed,i}$ = Volume fraction of the relevant gas in the feed;

P_{Perm} = Permeate gas pressure (kPa); and

STP is standard temperature and pressure, which is defined here as 25.0°C and 1 atmosphere (101.325 kPa).

(B) Selectivity

Selectivity ($\alpha_{CO2/CH4}$) was calculated from Q_{CO2} and Q_{CH4} calculated above, based on following equation:

$$\alpha_{CO2/CH4} = Q_{CO2}/Q_{CH4}$$

Viscosity was measured using a Brookfield LVDV-II + PCP viscosity meter, using either spindle CPE-40 or CPE-52 depending on viscosity range.

Measurement of the absorbency coefficient Ɛ at 313 nm

In the Examples the absorbency coefficient Ɛ at 313 nm of the photo acid generators under evaluation were measured using 0.05 mmol/L solutions of the photo acid generator under evaluation in MEK in a 1cm quartz cell using a Cary 100 UV-Vis Spectrophotometer from Agilent Technologies.

Measurement of the Solubility Parameter Value (δ)

In the Examples the solubility parameter value (δ) of the photo acid generators under evaluation was calculated using the Fedors method, as described in detail in the article by Fedors, R. F. (1974), entitled "A method for estimating both the solubility parameters and molar volumes of liquids", Polym Eng Sci, 14: 147–154. doi: 10.1002/pen.760140211. The atomic group contribution method was used.

Examples and Comparative Examples

Stage a) Preparation of the PCP Polymer

A solution of a PCP Polymer (“PCP Polymer 1”) was prepared by heating the components described in Table 1 together for 105 hours at 95°C. The resultant solution of PCP Polymer 1 had a viscosity of about 64,300 mPas when measured at 25°C.

Table 1- Ingredients used to prepare PCP Polymer 1

Ingredient	Amount (w/w%)
UV-9300	46.4%
X-22-162C	13.6%
n-Heptane	40.0%
DBU	0.0%
Total	100.0%

Stage b) Preparation of Radiation-curable Compositions ("RCC"s) 1 to 4

Portions of the solution of PCP Polymer 1 obtained in stage a) above were cooled to 20°C, diluted with n-heptane and then filtered through a filter paper having an average pore size of 2.7µm. The ingredients indicated in Table 2 below were added to make RCC1 to 4 as indicated in Table 2 below wherein the % are w/w% (weight/weight%).

Table 2

Ingredient	RCC1	RCC2	RCC3	RCC4
PCP Polymer 1	16.67%	16.67%	16.67%	16.67%
n-Heptane	81.00%	62.97%	63.06%	63.02%
MEK	2.00%	20.00%	20.00%	20.00%
Tyzor(R) TPT	0.22%	0.22%	0.22%	0.22%
I0591	0.11%	-	-	-
Irgacure(R) 290	-	0.14%	-	-
CPI-100P	-	-	0.05%	-
UV9390C	-	-	-	0.09%
Total	100.0%	100.0%	100.0%	100.0%
Solids content	10%	10%	10%	10%
PAG content mmol/g	0.00104	0.00104	0.00104	0.00104

Stage c) Preparation of The Composition Used to Form a Discriminating Layer

Composition DSL1 was prepared by mixing the components shown in Table 3 (wherein the % are w/w%) and filtering the mixture through a filter paper having an average pore size of 2.7 µm.

Table 3

Ingredient	DSL1
PI	1.00%
MEK	94.0%
DIOX	5.0%
APTMS	0.0100%
Total	100.01%

Stage d) Preparation of Compositions Used to Form a Protective Layer

Compositions PL1 to PL4 were prepared by mixing the components shown in Table 4 (wherein the % are w/w%) and filtering the mixture through a filter paper having an average pore size of 2.7 µm.

Table 4

Ingredient	PL1	PL2	PL3	PL4
PCP polymer	11.67%	11.67%	11.67%	11.67%
n-Heptane	86.11%	68.08%	68.14%	68.12%
MEK	2.00%	20.00%	20.00%	20.00%
Tyzor(R) TPT	0.15%	0.15%	0.15%	0.15%
I0591	0.07%	-	-	-
Irgacure(R) 290	-	0.10%	-	-
CPI-110P	-	-	0.04%	-
UV9390C	-	-	-	0.06%
Total	100.0%	100.0%	100.0%	100.0%
Solid content	7%	7%	7%	7%
PAG content mmol/g	0.00073	0.00073	0.00073	0.00073

Stage e) Preparation of Composite Membranes

Composite membranes were prepared using the combinations of radiation-curable composition and discriminating layers described in Table 5.

The radiation-curable compositions RCC1 to RCC4 were applied to a MAT (step a)) at a speed of 10m/min by a meniscus dip coating and irradiated. Irradiation (step b)) was performed using a Light Hammer LH10 from Fusion UV Systems fitted with a D-bulb and irradiating with an intensity of 16.8 kW/m (70%). The resultant gutter layers had a dry thickness of 300nm. Discriminating layers were formed on the gutter layers (step c)) using the compositions DSL1 as indicated in Table 4, using a meniscus type coating T 10 m/min coating speed. In Examples 1 to 5 the GL and/or PL comprised a photo acid generator having an

absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-}1$. In Comparative Examples CEx1 and CEx2 both the GL and PL were free from photo acid generators having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

After steps a) to d) had been completed, the resultant composite membranes were dried and tested. The tests were performed on circular patches of the composite membrane having a diameter of 47 mm and the patches were exposed to the relevant gases (clean or dirty) for a continuous period of 5 minutes by applying the gases to one side of the membrane under test at a pressure of 60 bar while the other side of the membrane was open to the atmosphere and therefore was subjected to air at a pressure of 1 atmosphere. The test results are shown in Table 5 below.

Table 5

	CEx1	Ex1	Ex2	Ex3	Ex4	Ex5	CEx2
Porous Support	GMT	GMT	GMT	GMT	GMT	GMT	GMT
Radiation-curable composition used to form the GL	RCC1	RCC1	RCC2	RCC1	RCC3	RCC2	RCC4
Coating speed used to form the GL	10 m/min	10 m/min	10 m/min	10 m/min	10 m/min	10 m/min	10 m/min
Amount of radiation-curable composition applied to the porous support to form the GL	6 mL/m2	6 mL/m2	6 mL/m2	6 mL/m2	6 mL/m2	6 mL/m2	6 mL/m2
UV bulb used to irradiate the radiation-curable composition	H-bulb	H-bulb	H-bulb	H-bulb	H-bulb	H-bulb	H-bulb
Dry thickness of the resultant GL	600 nm	600 nm	600 nm	600 nm	600 nm	600 nm	600 nm
Composition used to form the DL	DSL1	DSL1	DSL1	DSL1	DSL1	DSL1	DSL1
Amount of composition applied to the GL to form the DL	10 mL/m^2	10 mL/m^2	10 mL/m^2	10 mL/m^2	10 mL/m^2	10 mL/m^2	10 mL/m^2
Dry thickness of the resultant DL	100 nm	100 nm	100 nm	100 nm	100 nm	100 nm	100 nm
Composition used to form the PL	PL1	PL2	PL2	PL3	PL3	PL1	PL4
Coating speed used to form the PL	10 m/min	10 m/min	10 m/min	10 m/min	10 m/min	10 m/min	10 m/min
Amount of composition applied to the DL to form the PL	9 mL/m^2	9 mL/m^2	9 mL/m^2	9 mL/m^2	9 mL/m^2	9 mL/m^2	9 mL/m^2
UV bulb used to irradiate the composition used to form the PL	H-bulb	H-bulb	H-bulb	H-bulb	H-bulb	H-bulb	H-bulb
Dry thickness of the resultant PL	595 nm	595 nm	595 nm	595 nm	595 nm	595 nm	595 nm
Ɛ at 313 nm ($mol^{-1}*cm^{-1}$) of PAG in GL	6,915	6,915	**44,239**	6,915	**16,497**	**44,239**	850
δ of PAG cation in GL	20.60	20.60	25.20	20.60	23.20	23.20	19.00
Ɛ at 313 nm ($mol^{-1}*cm^{-1}$) of PAG in PL	6,915	**44,239**	**44,239**	**16,497**	**16,497**	6,915	850
δ of PAG cation in PL	20.60	25.20	25.20	23.20	23.20	20.60	19.00

(Table 5 continued) **RESULTS:**							
	CEx1	Ex1	Ex2	Ex3	Ex4	Ex5	CEx2
Clean Gas evaluation: 60bar, 40°C							
CO_2 flux (GPU)	52	44	38	48	41	36	55
CO_2/CH_4 selectivity	27	32	32	26	26	33	23
Dirty Gas evaluation: 60bar, 40°C							
CO_2 flux (GPU)	48	35	30	43	38	32	60
CO_2/CH_4 selectivity	17	26	29	19	20	24	13
Relative Performance: Dirty Gas evaluation vs. Clean Gas evaluation:							
Selectivity ratio (Dirty Gas/Clean Gas)	0.63	0.81	0.91	0.73	0.77	0.73	0.57

In Table 5 GL means gutter layer, DL means discriminating layer and PL means protective layer.

As can be seen from Table 5, Comparative Examples 1 and 2 in which the GL and PL were both free from photo acid generators having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$ suffered from much lower selectivity for dirty gas than for clean gas. However the Examples of the invention in which the GL and/or PL comprised a photo acid generator having an absorbency coefficient ε at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$ retained good selectivity even when the gas was a dirty gas.

CLAIMS

1. A process for preparing a composite membrane comprising the steps:
a) applying a radiation-curable composition to a porous support;
b) irradiating the composition present on the support, thereby forming a gutter layer of cured polymer;
c) forming a discriminating layer on the gutter layer; and
d) applying a radiation-curable composition to the discriminating layer and irradiating that composition, thereby forming a protective layer on the discriminating layer;
wherein one or both of the radiation-curable compositions applied in steps a) and d) comprise a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

2. A process according to claim 1 wherein the radiation-curable composition applied in step a) comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

3. A process according to claim 1 wherein the radiation-curable composition applied in step a) comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$ and the radiation-curable composition applied in step d) is free from photo acid generators having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

4. A process according to claim 1 wherein the radiation-curable compositions applied in step a) and in step d) each independently comprise a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

5. A process according to claim 1 wherein the radiation-curable composition applied in step a) is free from photo acid generators having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$ and the radiation-curable composition applied in step d) comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

6. A process according to any one of the preceding claims wherein the photo acid generator has an absorbency coefficient Ɛ at 313 nm of more than 3×10^4 $mol^{-1}*cm^{-1}$.

7. A process according to any one of the preceding claims wherein the photo acid generator is a compound which generates acid when irradiated with light of wavelength 313 nm.

8. A process according to any one of the preceding claims wherein the photo acid generator comprise an anion and a cation.

9. A process according to any one of the preceding claims wherein the photo acid generator comprise a cation having a solubility parameter value greater than 22 $(J/cm^3)^{0.5}$.

10. A process according to any one of the preceding claims wherein the photo acid generator comprise an anion and a cation anion and the cation comprises a sulphonium group.

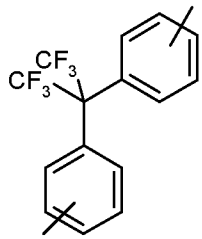
11. A process according to any one of the preceding claims wherein the radiation-curable composition(s) applied in step (a) and/or (d) comprise 0.01 to 5 wt % of the said photo acid generator.

12. A process according to any one of the preceding claims wherein the protective layer is formed on the discriminating layer in step d) from a radiation-curable composition comprising a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

13. A process according to any one of the preceding claims wherein the discriminating layer comprises a polyimide, cellulose acetate, polybenzoxazole, polyethyleneoxide or polyetherimide.

14. A process according to any one of the preceding claims wherein the discriminating layer comprises a polyimide comprising trifluoromethyl groups.

15. A process according to claim 14 wherein the polyimide comprises groups of the Formula (1):



Formula (1).

16. A process according to any one of the preceding claims which further comprises the step of treating the gutter layer with corona discharge or a plasma treatment before forming the discriminating layer thereon.

17. A process according to any one of the preceding claims wherein:
the radiation-curable composition is applied continuously to the porous support in step a) by means of a manufacturing unit comprising a radiation-curable composition application station, step b) is performed using an irradiation source located downstream from the radiation-curable composition application station, the discriminating layer is formed on the layer of cured polymer in step c) by a discriminating layer application station, and the resultant composite membrane is collected at a collecting station, wherein the manufacturing unit comprises a means for moving the porous support from the radiation-curable composition application station to the irradiation source and to the discriminating layer application station and to the composite membrane collecting station.

18. A process according to claim 17 wherein the porous support is continuously unwound from a spool and the resultant composite membrane is continuously wound onto a spool.

19. A process according to any of the previous claims wherein step a) and/or step c) is or are performed by curtain coating, meniscus type dip coating, kiss coating, pre-metered slot die coating, reverse or forward kiss gravure coating, multi roll gravure coating, spin coating and/or slide bead coating.

20. A composite membrane comprising:
i) a porous support;
ii) a gutter layer;
iii) a discriminating layer on the gutter layer; and
iv) a protective layer;

wherein one or both of the gutter layer ii) and the protective layer iv) comprise a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

21. A composite membrane prepared by the method according claims 1 to 19.

22. A composite membrane according to claim 20 or 21 wherein the gutter layer ii) comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

23. A composite membrane according to claim 20 or 21 wherein (a) the gutter layer ii) comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$; and (b) the protective layer iv) is free from photo acid generators having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

24. A composite membrane according to claim 20 or 21 wherein the gutter layer ii) and the protective layer iv) each independently comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

25. A composite membrane according to claim 20 or 21 wherein (a) the gutter layer ii) is free from photo acid generators having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$; and (b) the protective layer iv) comprises a photo acid generator having an absorbency coefficient Ɛ at 313 nm of more than $1x10^4$ $mol^{-1}*cm^{-1}$.

26. A gas separation cartridge comprising the composite membrane according to any one of claims 20 to 25 wherein the cartridge is of plate-and-frame, spiral-wound, hollow-fibre, tubular or envelope type.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/050738

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D67/00 B01D53/22 B01D69/10 B01D69/12 B01D71/16
B01D71/62 B01D71/64
ADD. B01D63/08 B01D63/10 B01D69/04 B01D69/06 B01D69/08
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 B41M

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/001795 A1 (FUJIFILM MFG EUROPE BV [NL]; FUJIFILM IMAGING COLORANTS LTD [GB]) 3 January 2014 (2014-01-03)	1-5,7,8, 10-26
Y	the whole document -----	6,9
Y	Basf Factsheet: "July 2015 Rev 3 Electronic Specialties Industrial Coatings Printing & Packaging", , 31 July 2015 (2015-07-31), XP055378422, Retrieved from the Internet: URL:https://worldaccount.basf.com/wa/NAFTA~en_US/Catalog/Additives/doc4/BASF/PRD/30508825/.pdf?asset_type=pi/pdf&language=EN&urn=urn:documentum:eCommerce_sol_EU:09007bb2801793db.pdf [retrieved on 2017-06-02] the whole document ----- -/--	6,9

[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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 June 2017	26/06/2017

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

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/050738

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2014/001792 A1 (FUJIFILM MFG EUROPE BV [NL]; FUJIFILM IMAGING COLORANTS LTD [GB]) 3 January 2014 (2014-01-03) abstract -----	6,9
A	EP 1 859 855 A1 (MILLIPORE CORP [US]) 28 November 2007 (2007-11-28) paragraph [0020] - paragraph [0021] -----	1-26

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2017/050738

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		US 2015298071 A1	22-10-2015
		US 2015343389 A1	03-12-2015
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		WO 2014001798 A1	03-01-2014
WO 2014001792 A1	03-01-2014	NONE	
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		US 2007272607 A1	29-11-2007