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Composite membrane for the separation of water and method for its
manufacture

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The invention relates to a composite membrane for the separation of water, to its use as well as to a method for the manufacture of such a composite membrane in accordance with the preamble of the independent claim of the respective category.

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It is known to use the processes of pervaporation or of vapor permeation for the separation or deposition of water from fluid mixtures which contain organic components. Membranes are known for these processes which have at least one separation layer. A composite membrane is, for example,
20 disclosed in EP-A-0 096 339 which is made up of a carrier layer, a porous support layer and a separation layer of crosslinked polyvinyl alcohol (PVA).

A woven cloth or fleece usually serves as a carrier layer and has a high resistance with respect to chemicals and temperature. Polyester with a
25 smooth surface on one side is a preferred material for the carrier layer. A porous support layer which has the properties of an ultrafiltration membrane is applied to the carrier layer. Porous support layers of polyacrylic nitrile (PAN) or polysulfone (PS) are preferred.

The setting of the pore size and of the pore radius distribution can take place by corresponding conditions in the manufacture of the porous support layer.

- 5 The separation layer of such membranes is made up of crosslinked polyvinyl alcohol with a high degree of saponification and a mean molecular weight between 20,000 and 200,000 Daltons. The crosslinking operation of the polyvinyl alcohol of the separation layer takes place by esterification, etherification or acetalation or by a combination of these
- 10 processes. After the application of an aqueous solution of the polyvinyl alcohol and of the esterification means, the separation layer is dried, cured and crosslinked at a temperature of 120°C to 160°C. The process of the application of the aqueous solution and of the subsequent heat treatment can take place a plurality of times, for example twice, after one
- 15 another. The thickness of the separation layer typically amounts to 0.5 μm to 10 μm . Such membranes are operated at temperatures between 45°C to 95°C.

To allow higher operating temperatures and to achieve a better resistance

20 in particular toward bases and acids, it is known from DE-A-10 2004 060 857 to subject the separation layer of crosslinked polyvinyl alcohol to a post-crosslinking operation in a separate process step, with no acids or acid-releasing compounds being added. Even if these post-crosslinked membranes have proven themselves in practice, they are, however, subject

25 to the limitation that the duration of the post-crosslinking operation amounts to 6 to 48 hours, with the duration of 10 to 16 hours being preferred. This long treatment time makes the manufacture protracted.

A membrane of polyvinyl alcohol is known from EP-A-0 436 128 in which

30 the crosslinked (pre-crosslinked) membrane is post-crosslinked by the

effect or acids or of acid-releasing substances which act on the PVA over the vapor phase. Higher operating temperatures can also herewith be made possible and the resistance toward acids and bases is increased. It is, however, problematic in this manufacture that the process should be
5 carried out under reduced oxygen partial pressure in practice, which in particular gives rise to practical problems in larger productions facilities.

A method is disclosed in EP 0 307 636 for the manufacture of a composite membrane for pervaporation and vapor permeation with a separation layer
10 of polyvinyl alcohol, with the polyvinyl alcohol being crosslinked with a dialdehyde and an acid as a catalyst. The PVA solution contains simultaneously dialdehyde and acid as a catalyst for this purpose. Such solutions are as a rule very unstable and already react at room temperature, whereby the viscosity of the solution increases. A controlled
15 application, and in particular a machine application, of the solution is thereby hardly realizable in practice.

It has furthermore been shown that, when known composite membranes with a separation layer of crosslinked PVA are used, problems occur in the
20 dewatering of mixtures which contain aldehydes. The selectivity of the separation layer for water has already diminished dramatically after a comparatively short operating period. The selectivity of the membrane has thus, for example, fallen from an initial 99% to 80% after an operating period of 47 hours in a mixture of ethanol/water and 1% acetaldehyde.
25 These percentages substantially indicate the water content of the permeate.

Starting from this prior art, it is therefore an object of the invention to provide a composite membrane with a separation layer of polyvinyl alcohol
30 which also maintains a high selectivity and remains stable on the

dewatering of mixtures containing aldehydes. In addition, the composite membrane should also be operable at higher operating temperatures of up to 120°C. Furthermore, a method for the manufacture of such a composite membrane should be provided by the invention.

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The subjects of the invention satisfying this object are characterized by the independent claims of the respective category.

In accordance with the invention, a composite membrane is therefore
10 proposed for the separation of water having at least one separation layer of crosslinked polyvinyl alcohol, with the separation layer being subjected in a separate process step to a post-crosslinking operation with an acid or an acid-releasing compound and at least one dialdehyde.

15 It has surprisingly been shown that a pre-crosslinked separation layer which is manufactured in a manner known per se by esterification, etherification or acetalation of the polyvinyl alcohol or by a combination of these methods and is not yet thermally post-crosslinked leads by a post-crosslinking operation with a dialdehyde and an acid or an acid-releasing
20 compound serving as a catalyst to a composite membrane which also has a very good stability with respect to mixtures containing aldehydes at an elevated operating temperature.

The post-crosslinking operation provided as a separate step preferably
25 takes place by means of an aqueous solution which contains both the acid or the acid-releasing compound and the dialdehyde. The acid-dialdehyde solution is very stable in this connection since it does not contain any polyvinyl alcohol.

The post-crosslinking operation advantageously takes place at an elevated temperature which is preferably in the range from 150°C to 220°C and particularly preferably from 160°C to 200°C.

- 5 The duration of the post-crosslinking operation is in particular between one and 30 minutes, preferably between 5 and 15 minutes.

The post-crosslinking operation preferably takes place by means of a solution in which the dialdehyde is contained in quantities between 1%
10 and 30%, preferably between 5% and 10%.

Glutaric dialdehyde is in particular suitable as the dialdehyde.

- 15 With respect to the acid content for the post-crosslinking operation it has proven successful if the post-crosslinking operation takes place by means of a solution in which the acid is contained in quantities from 0.1% to 1%, preferably from 0.3% to 0.6%.

20 A preferred acid for the post-crosslinking operation is sulfuric acid.

It is furthermore advantageous if the post-crosslinking operation takes place by means of an aqueous solution which contains water in quantities from 70% to 95%, preferably from 85% to 95%.

- 25 The solution for the post-crosslinking operation can contain up to 30% alcohol, preferably from 5% to 15% alcohol, with the alcohol preferably being ethanol.

30 In a particularly preferred embodiment, the post-crosslinking operation takes place using an aqueous solution containing at least one alcohol,

with the water-alcohol mixture serving as the solvent for the dialdehyde and the acid.

5 A particularly preferred use of the composite membrane in accordance with the invention is that for the separation of water from fluid mixtures which contain organic components by means of pervaporation or vapor permeation.

10 A method is furthermore proposed by the invention for the manufacture of a composite membrane having at least one separation layer of polyvinyl alcohol. The method includes the following steps:

- application of a starting solution containing polyvinyl alcohol to a support layer;
- pre-crosslinking of the polyvinyl alcohol;
- 15 - application of a solution for the post-crosslinking of the polyvinyl alcohol, wherein the solution contains an acid or an acid-releasing compound as well as at least one dialdehyde;
- post-crosslinking of the separation layer.

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It is advantageous with respect to the crosslinking of the PVA if the starting solution contains at least one dicarboxylic acid and in particular a dicarboxylic acid without a double bond and a dicarboxylic acid with a double bond.

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Glutaric dialdehyde is a preferred dialdehyde for the post-crosslinking operation.

30 The solution for the post-crosslinking operation preferably contains sulfuric acid as the acid.

Further advantageous measures and preferred embodiments of the invention result from the dependent claims.

- 5 The invention will be explained in more detail in the following with reference to embodiments and to the drawing. There is shown in the drawing

Fig. 1 a schematic sectional representation of an embodiment of a
10 composite membrane in accordance with the invention.

Fig. 1 shows in a schematic sectional representation an embodiment of a composite membrane in accordance with the invention which is designated as a whole by the reference numeral 1. The composite
15 membrane 1 has a carrier layer 2 on which a porous support layer 3 is applied. A separation layer of polyvinyl alcohol (PVA) is provided on the support layer 3.

The carrier layer 2 is made up in a known manner from a woven cloth or
20 from a fleece or from a porous ceramic material. All materials of sufficient resistance with respect to the operating temperature to be expected or aimed for and to the chemicals present in the fluid to be separated can be used as the material for the support layer 2. The preferred material for the carrier layer 2 is polyester with a smooth surface on one side. Further
25 suitable materials for the cloth or for the fleece are, for example, polyphenyl sulfide, polymide and polyvinylidene difluoride. Glass fibers or carbon fibers, metals or ceramic materials are preferred as the inorganic materials.

The porous support layer 3 is applied to the carrier layer 2 in a manner known per se with a pore width which is as uniform as possible. Poly acrylic nitrile (PAN), polysulfone (PS), polyether sulfone and polyether etherketone are preferred among the polymers as materials for the porous support layer. If the carrier layer 2 is made of ceramic material, the porous support layer 3 is preferably made of ceramic material. The porous support layer 3 has the properties of an ultrafiltration membrane.

The separation layer 4 is formed from crosslinked polyvinyl alcohol which is preferably applied to the surface of the support layer 3 from an aqueous starting solution. The starting solution contains crosslinking means which crosslink the polyvinyl alcohol by etherification, esterification or acetalation or by a combination of these three processes and also make it insoluble in boiling water. Acid can be added to accelerate the crosslinking operation. In particular formaldehyde and dicarboxylic acids (biacids) are suitable as crosslinking agents. It is particularly advantageous if the starting solution contains a dicarboxylic acid without a double bond, e.g. malonic acid, as well as a dicarboxylic group with a double bond, e.g. maleic acid.

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The separation layer 4 can be applied in one work step or in a plurality of work steps. The separation layer 4 is dried and crosslinked after every application, which advantageously takes place at temperatures between 80°C and 190°C over a time period of 3 minutes up to one hour.

25 Temperatures from 150°C to 160°C with a duration of six minutes have proven to be particularly advantageous.

The separation layer 4 prepared in this manner is called a "separation layer of pre-crosslinked polyvinyl alcohol". In accordance with the invention, a post-crosslinking operation now takes place in a separate

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method step using an acid or an acid-releasing compound and at least one dialdehyde.

In a preferred embodiment, the acid/acid-releasing compound and the
5 dialdehyde are applied to the separation layer 4 of pre-crosslinked
polyvinyl alcohol in an aqueous solution for the post-crosslinking
operation. The acid serves as a catalyst in the post-crosslinking operation.
This solution for post-crosslinking, which contains the acid/acid-releasing
compound as well as the dialdehyde, is very stable because it does not
10 contain any PVA. The post-crosslinking operation takes place at an
elevated temperature of 120°C up to 220°C, preferably at at least 150°C
and particularly preferably at a temperature in the range from 160°C up to
200°C. The duration of the post-crosslinking operation amounts to
between one minute and 30 minutes.

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It has been shown that separation layers 4 of PVA post-crosslinked in this
manner maintain their high selectivity and remain stable. This also in
particular applies when the fluid mixture which acts on the composite
membrane 1 for the purpose of separation from water contains aldehydes,
20 in particular acetaldehyde.

Generally all substances are suitable as the dialdehyde for the post-
crosslinking operation which have two functional groups which can each
react with an OH group. Glutaric dialdehyde is preferably used as the
25 dialdehyde. Malonic dialdehyde or other water-soluble dialdehydes are
likewise suitable. The quantity of dialdehyde in the aqueous solution for
the post-crosslinking operation preferably amounts to 1% to 30%.

A mixture of water (100%-70%) and alcohols such as ethanol, isopropanol,
30 butanol, ethylene glycol and glycerin is preferably used as the solvent for

the dialdehyde or the dialdehydes as well as for the acid(s)/acid-releasing compound(s).

Suitable acids for the post-crosslinking operation are in particular:

- 5 sulfuric acid, hydrochloric acid, hydrobromic acid, phosphoric acid, with the preferred acid being sulfuric acid.

The examples explain the invention.

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Example 1

A support layer 3 which is made as a PAN ultrafiltration membrane and which is provided on the carrier layer 2 was coated with a 5% PVA solution in accordance with the prior art and pre-crosslinked at 150°C
15 during a period of six minutes. The separation layer 4 was then coated with a solution for post-crosslinking with 0.3% sulfuric acid, 5% glutaric dialdehyde and 24.7% ethanol and 70% water and is crosslinked at 160°C over a period of ten minutes. The composite membrane was measured with a mixture of 10% water and 90% ethanol by means of pervaporation
20 at 105°C.

A flow of 1.4 kg/m²h was measured and 99% water was found in the permeate. 1% acetaldehyde was then added to the water/ethanol mixture and the membrane was subjected to an endurance test at 105°C. A flow of
25 1.7 kg/m²h was measured and 95% water was found in the permeate after 120 hours operating time.

Example 2

A support layer 3 which is made as a PAN ultrafiltration membrane and which is provided on the carrier layer 2 was coated twice with a 3% PVA solution in accordance with the prior art. After the first coating, a pre-crosslinking operation took place at 150°C over a time period of six
5 minutes. After the second coating, a pre-crosslinking operation took place at 160°C over a time period of six minutes. The pre-crosslinked separation layer 4 was then coated with a post-crosslinking solution with 0.5% sulfuric acid, 10% glutaric dialdehyde and 89.5% water and was post-crosslinked at 180°C for five minutes.

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The composite membrane was measured with a mixture of 10% water and 90% ethanol by means of pervaporation at 105°C.

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A flow of 1.1 kg/m²h was measured and 99,0% water was found in the permeate. 1% acetaldehyde was then added to the water/ethanol mixture and the membrane was subjected to an endurance test at 105°C. A flow of 1.4 kg/m²h was measured and 97% water was found in the permeate after 120 hours operating time.

Claims

1. A composite membrane for the separation of water having at least one separation layer (4) of pre-crosslinked polyvinyl alcohol,
5 characterized in that the separation layer (4) is subjected in a separate method step to a post-crosslinking operation with an acid or an acid-releasing compound and at least one dialdehyde.
2. A composite membrane in accordance with claim 1, wherein the
10 post-cross-linking takes place at an elevated temperature which is preferably in the range from 150°C to 220°C and particularly preferably from 160°C to 200°C.
3. A composite membrane in accordance with any one of the preceding
15 claims, wherein the duration of the post-crosslinking operation lies between one and 30 minutes, preferably between 5 and 15 minutes.
4. A composite membrane in accordance with any one of the preceding
20 claims, wherein the post-crosslinking operation takes place by means of a solution in which the dialdehyde is contained in quantities between 1% and 30%, preferably between 5% and 10%.
5. A composite membrane in accordance with any one of the preceding
25 claims in which the dialdehyde is glutaric dialdehyde.
6. A composite membrane in accordance with any one of the preceding
30 claims, wherein the post-crosslinking operation takes place by means of a solution in which the acid is contained in quantities from 0.1% to 1%, preferably from 0.3% to 0.6%.

7. A composite membrane in accordance with any one of the preceding claims in which the acid for the post-crosslinking operation is sulfuric acid.
- 5 8. A composite membrane in accordance with any one of the preceding claims, wherein the post-crosslinking operation takes place by means of a solution which contains water in quantities from 70% to 95%, preferably from 85% to 95%.
- 10 9. A composite membrane in accordance with any one of the preceding claims, wherein the post-crosslinking operation takes place by means of a solution which contains up to 30% alcohol, preferably from 5% to 15% alcohol, and wherein the alcohol is preferably ethanol.
- 15 10. Use of a composite membrane in accordance with any one of the preceding claims for the separation of water from fluid mixtures which contain organic components by means of pervaporation or vapor permeation.
- 20 11. A method for the manufacture of a composite membrane having at least one separation layer (4) from polyvinyl alcohol including the following steps:
 - application of a starting solution containing polyvinyl alcohol to a
 - 25 support layer (3)
 - pre-crosslinking of the polyvinyl alcohol;
 - application of a solution for the post-crosslinking of the polyvinyl alcohols, with the solution containing an acid or an acid-releasing compound as well as at least one dialdehyde;
 - 30 - post-crosslinking of the separation layer (4).

12. A method in accordance with claim 11, wherein the starting solution contains at least one dicarboxylic acid.
- 5 13. A method in accordance with one of the claims 11 or 12, wherein the starting solution contains a dicarboxylic acid without a double bond and a dicarboxylic acid with a double bond.
- 10 14. A method in accordance with any one of the claims 11 to 13, wherein the dialdehyde is glutaric dialdehyde.
- 15 15. A method in accordance with any one of the claims 11 to 14, wherein the solution for the post-crosslinking operation contains sulfuric acid.