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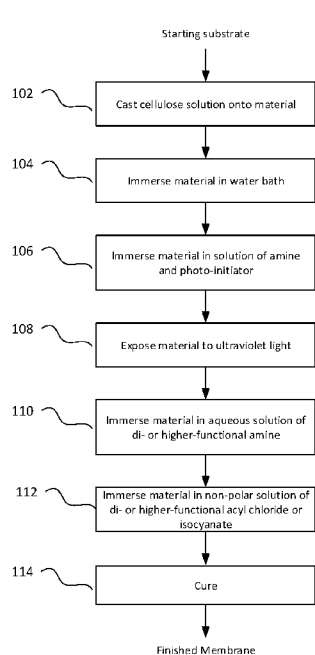


FIG. 4

(57) Abstract: Membranes for filtration and methods of making the same are disclosed. In embodiments, methods include casting a cellulose ester solution onto a material, which is immersed in a water bath and in an aqueous solution including an amine and a photoinitiator. The material is exposed to ultraviolet light to produce an amine-functionalized cellulose ester substrate. In embodiments, the substrate is immersed in an aqueous solution including a di- or higher-functional amine and in a non-polar solution including a di- or higher-functional acyl chloride or an isocyanate to produce an active layer on the substrate. The layer and substrate are cured to produce a thin film composite membrane.



AMINE FUNCTIONAL CELLULOSE SUBSTRATE FOR THIN FILM COMPOSITE MEMBRANES AND METHODS OF PREPARING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Patent Application No. 62/753,435, filed on 31 October 31 2018, the disclosure of which is incorporated herein, in its entirety, by this reference.

BACKGROUND

Thin film composite membranes

A commercial standard for reverse osmosis membranes is the thin film composite (TFC) membrane developed by John Cadotte at FILMTEC in the late 1970s. The membranes are prepared from an interfacially polymerized polyamide formed on a polysulfone substrate. Interfacial polymerization or interfacial synthesis refers to the preparation of a polymer film at the interface between immiscible solvents. For membrane separations, this polymer is often a polyamide but can also be a polyurea or polypiperamide. The immiscible solvents are often water and an alkane, or a mixture thereof. Commonly, the polyamide is prepared from a solution of 2% m-phenylenediamine (MPD) dissolved in water reacted with a solution of 0.1% 1,3,5-benzene tricarboxyl chloride (also known as trimesoyl chloride or TMC) dissolved in C₅-C₁₄ alkanes. The structure of a polyamide that may be formed from this chemistry is shown in Figure 1.

Figure 2 illustrates a method of preparing a polysulfone-supported thin film composite membrane. Interfacial polymerization of a polyamide, as shown in Figure 2, may be performed on polysulfone or other porous polymer substrates prepared by the non-solvent induced phase separation (NIPS) technique, whereby a polymer in solution with a water miscible solvent is drawn into a thin film over a substrate and immersed in a water bath. This substrate can be non-woven fabric, a woven fabric, or a nonporous surface, such as a glass plate. When the substrate and polymer solution film are immersed in water, the solvent of the polymer solution mixes with water. As the water and solvent mix, the water-insoluble polymer precipitates to form a porous film. After the preparation of this substrate, the polyamide active layer can be formed by bringing the porous polymer film into contact with an aqueous solution of MPD and kept in contact for a desired period of time. Next, the MPD solution is removed and any remaining droplets of the MPD solution are removed from the polymer substrate's surface by a rubber roller or an air knife. Then, the polymer

film is brought in contact with a TMC solution. While TMC has minimal solubility in water, MPD is soluble in alkanes. The defined phase separation between the water within the polymer and the alkane on the polymer's surface prevents MPD and TMC from mixing, but diffusive transport of the MPD into the alkane does occur. Owing to the high reactivity of primary amines and acyl chlorides, a spontaneous reaction between TMC and MPD occurs forming a dense and partially cross-linked film that serves as the active layer (also known as the selective layer) (see Figure 3) of the membrane, which provides its selective permeability of water over salt ions.

Asymmetric membranes

Asymmetric membranes having selectivity to water over dissolved salts (a.k.a. osmotic membranes) typically include three distinct regions, as shown in Figure 3. The densest and topmost region, during formation, of these membranes is the active (selective) layer, which imparts permselectivity of water to dissolved chemical species to osmotic membranes. The active layer of an asymmetric membrane is also typically the thinnest, which helps minimize mass transfer resistance to water flow and allows for more permeable membranes. Beneath and adjacent to the active layer is a support layer. The support layer typically includes two layers: a porous polymer layer and a fabric layer. The porous polymer support layer is often prepared by an induced phase separation either with a non-solvent (i.e., non-solvent induced phase separation, NIPS) or thermally (i.e., thermally induced phase separation, TIPS). Niche techniques involving fine fiber spinning have also been employed. The porous polymer is often formed on a non-woven fabric, which provides most of the mechanical strength for the asymmetric membrane structure. The fabric layer can be thick and in some seawater membranes represents ~70% of the entire thickness (see Figure 3, for which the dimensions are based on a seawater reverse osmosis membrane). In addition to their large relative thickness, some denser non-woven fabrics have low porosity. While generally not of great significance in reverse osmosis applications, low porosity of the support layer severely impairs water flux where an osmotic pressure difference drives water flow. Membranes for osmotically driven membrane processes may instead employ a woven support layer, which has a more open, thinner, and ordered structure as compared to the random fiber orientations in non-woven fabric. These characteristics of a woven support allow for the preparation of membranes that have improved water flux in osmotically driven membrane separations.

Transport in osmotically driven membrane processes

Water flow through a semipermeable membrane in osmotically driven membrane processes occurs primarily through an osmotic pressure difference between a feed solution and a draw solution. The draw solution is selected to have a higher osmotic pressure than the feed solution so that it draws water through the membrane separating the draw solution from the feed solution. The osmotic pressures of the draw and feed solutions are generally related to the concentration of dissolved solutes within them. Hydrostatic pressure difference across a membrane also influences rate of water flow. For example, a hydrostatic pressure can be applied to the draw solution to retard the flow of water (pressure retarded osmosis) or to the feed solution to increase the flow of water through the membrane (pressure assisted forward osmosis). Regardless of the magnitude of the transmembrane hydrostatic pressure difference, the flow of water through a membrane in an osmotically driven membrane process occurs due to both the osmotic pressure difference across the membrane and in the same direction as the osmotic pressure gradient. Separately, in an osmotically assisted reverse osmosis process, as in the reverse osmosis process, water flow occurs against an osmotic pressure difference. However, the osmotic pressure difference across the membrane is not exclusively impacted by membrane selectivity and is instead mediated by a solution with less salinity than the feed solution on the permeate side of the membrane.

In the context of aqueous separations, an osmotically driven membrane process is characterized by the concentration dependence of the feed and draw solutions on osmotic pressure. Because of this dependence, a competition between solution convection and salt diffusion arises within the support layer of an asymmetric membrane, thereby reducing the osmotic pressure difference across the membrane. The reduced pressure difference limits water flux through the membrane, which results in internal concentration polarization (ICP). The detrimental effect of internal concentration polarization on water flux can be mitigated by increasing support layer porosity and reducing support layer thickness.

Polysulfone supported membranes in forward osmosis

While thin film composite chemistry performs well in pressure-driven separation of dissolved chemical species from water (i.e., reverse osmosis or nanofiltration), applicability of this chemistry to osmotically driven membrane processes has been less successful. Because pressure-driven separations generally require mechanically robust membranes, as

stated above, commercially produced TFC membranes are often supported by a relatively thick non-woven polyester fabric. This fabric enhances the mechanical strength of the TFC membrane but adds additional thickness that restricts diffusion through the support layer of the TFC membrane. Because osmotically driven membrane processes are influenced by concentrations on both sides of a membrane's selective layer, high mass transfer rates through a membrane's support layer are critical. While the detrimental effect on diffusion imparted by the fabric support layer can be mitigated by membrane design, polysulfone's hydrophobicity also impacts internal concentration polarization.

As a result of polysulfone's hydrophobicity, a membrane's support layer is not spontaneously and completely wetted by aqueous solutions. Incomplete wetting reduces the diffusive mass transfer coefficient through the support layer, which significantly reduces the driving force for water flow across the membrane in osmotically driven membrane processes. In academic applications, the hydrophobicity of the polysulfone can be mitigated by pre-wetting a TFC membrane with an alcohol or by adding a surfactant to the draw solution. In large commercial applications, these approaches may not be feasible. Therefore, membranes that are intrinsically hydrophilic and would be unaffected by reduced mass transfer due to poor pore wetting are needed.

Cellulose acetate forward osmosis membranes

Some commercially available membranes for osmotically driven membrane processes are constructed of cellulose acetates with varying degrees of acetate functionality up to and including cellulose triacetate. Developed in the 1950s and '60s, cellulose acetate membranes were amongst the first practical membranes for the desalination of seawater. Their continued usability for osmotically driven membrane processes is in part due to the innate hydrophilicity of a cellulose acetate when used in the preparation of semi-permeable membranes. This innate hydrophilicity ensures the membrane is more easily wetted when used for an osmotically driven membrane process, which produces a membrane with less severe internal concentration polarization than comparable thin film composite membranes. The active layer and porous mid-layer of a cellulose acetate membrane are chemically homogenous, and the two layers are formed simultaneously. As a result, active layer and support layer characteristics of these membranes must be carefully tailored in tandem, complicating fine tuning of the membrane design. Also, cellulose acetate membranes,

compared to TFC reverse osmosis membranes, have relatively thick selective layers resulting in reduced water permeance at comparable selectivity.

Use of cellulose esters as supports for thin film composite membranes

Preparation of a TFC membrane on a cellulose substrate has faced challenges, including in developing techniques for synthesizing a polyamide active layer on cellulose supports. While polysulfone (and the similar polyethersulfone) is aromatic (like both MPD and TMC), cellulose is not. As a result, one of the common routes of intermolecular attraction that may promote adhesion between layers, namely π - π stacking, is unavailable to TFCs prepared upon support layers of cellulosic materials such as cellulose esters. One publication proposed the covalent linking of a polyamide to a cellulosic support (U.S. Patent Application Publication No. 2013/0089727). The publication applied a polyamide film to cellulose acetate supports that had been hydrolyzed by caustic (i.e., potassium hydroxide or sodium hydroxide) and had subsequently been treated with TMC in a non-aqueous solvent (i.e., diethylene glycol diethyl ether). This technique sought to functionalize the surface of the cellulosic substrate with acyl chloride functional groups onto which a synthesized polyamide would grow by the subsequent introduction of an aqueous MPD solution followed by TMC in hexane. However, amine attack on the ester linkage formed between the TMC and hydroxyl groups on the cellulose substrate can break the ester linkage, instead forming an amide bond. As the ester linkages that would link the polyamide to the cellulose substrate are broken by exposure to the aqueous MPD solution, the synthesized polyamide is not covalently bonded to the cellulose substrate.

SUMMARY

Embodiments disclosed herein are directed to membranes for filtration and methods of making the same. In an embodiment, a method of preparing an amine-functionalized cellulosic substrate is disclosed. A cellulose ester solution is cast onto a material. The material is immersed in a water bath to produce a porous cellulose ester substrate. The substrate is immersed in an aqueous solution including an amine and a photo-initiator. The substrate is exposed to ultraviolet light to produce an amine-functionalized cellulose ester substrate.

In another embodiment, a method of preparing a cellulose-supported thin film composite membrane is disclosed. A cellulose ester solution is cast onto a material to produce a cellulosic support. The support is immersed in a water bath. The support is

immersed in an aqueous solution including an amine and a photo-initiator. The support is exposed to ultraviolet light to produce an amine-functionalized cellulosic support. The support is immersed in an aqueous solution including a di- or higher-functional amine. The support is immersed in a non-polar solution including a di- or higher-functional acyl chloride or an isocyanate to produce an active layer on the support. The layer and support are cured to produce a thin film composite membrane.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of a polyamide for use in thin film composite membranes.

FIG. 2 is a flow chart of a method of preparing a polysulfone-supported thin film composite membrane.

FIG. 3 is a schematic of an asymmetric osmotic membrane

FIG. 4 is a flow chart of a method of preparing a cellulose-supported thin film composite membrane according to embodiments.

FIG. 5 is a flow chart of a method of preparing a cellulose-supported thin film composite membrane according to embodiments.

FIG. 6 is a flow chart of a method of preparing a cellulose-supported thin film composite membrane according to embodiments.

FIG. 7 is an illustration of a polyamide covalently bound to an amide functionalized cellulose, prepared according to the method of FIG. 4, FIG. 5, or FIG. 6.

DETAILED DESCRIPTION

Embodiments disclosed herein are directed to methods of preparing an amine-functionalized cellulosic substrate. The amine functionalization may help produce a substrate capable of covalently bonding with other compounds that have amines as monomers, such as polyamides, polypiperamides, and polyureas. The ability to covalently bond with additional compounds may produce a substrate that can adhere well to another layer, such as an active layer in a thin film composite membrane.

Embodiments disclosed herein are also directed to methods of preparing thin film composite membranes on cellulosic supports. The cellulosic supports are amine functionalized, which may improve adhesion of synthesized polyamides. Improved adhesion may help layers of the membranes remain bound together. Improved adhesion may also prevent membranes from failing by separation of component layers.

Embodiments disclosed herein are also directed to methods of preparing amine-functionalized cellulose ester supports. Methods of constructing a thin film composite membrane having an active layer that is covalently bound to an amine functionality on a cellulose ester support layer are also disclosed.

Features from any of the disclosed embodiments may be used in combination with one another, without limitation. In addition, other features and advantages of the present disclosure will become apparent to those of ordinary skill in the art through consideration of the following detailed description.

Amine functionalization of cellulose using a photo-initiator

In some embodiments, to produce a membrane, an active layer is covalently bound to an amine functional group attached to a cellulose ester support by a method that employs a photo-initiator. With reference to Figure 4, the method 100 includes a step 102 of casting a cellulose solution onto a material, a step 104 of immersing the material in a water bath, a step 106 of immersing the material in a solution comprising an amine and a photo-initiator, a step 108 of exposing the material to ultraviolet light, a step 110 of immersing the material in an aqueous solution comprising a di- or higher-functional amine, a step 112 of immersing the material in a non-polar solution comprising a di- or higher-functional acyl chloride or an isocyanate, and a step 114 of curing the material.

In step 102, the material may be, for example, woven fabric, non-woven fabric, or a material having a non-porous surface, such as a glass plate. The cellulose solution may include a cellulose ester, such as cellulose acetate. The cellulose ester solution may include at least one alkene ($-\text{CH}=\text{CH}_2$ or $-\text{CH}=\text{CH}-$) functionalized cellulose, such as (acrylamidomethyl)cellulose acetate or cellulose acetate butyrate. In some examples, a cellulose ester may include a $-\text{CH}=\text{CH}_2$ or $-\text{CH}=\text{CH}-$ moiety, such as the derivatized cellulose ester of acrylamide, acrylate, or crotonate.

Step 104 may include the non-solvent induced phase separation (NIPS) technique, whereby a polymer in solution with a water miscible solvent is drawn into a thin film over

a substrate and immersed in a water bath. Step 104 may help form the porous structure that helps to minimize the membrane's resistance. In some embodiments, step 104 is excluded from the method 100.

In step 106, the amine may be a primary amine, which may have the formula $\text{CH}_2=\text{CH}-\text{R}-\text{NH}_2$. The amine may be, for example, a vinyl amine such as allylamine. Reaction of a vinyl amine with $-\text{CH}=\text{CH}_2$ (or $-\text{CH}=\text{CH}-$) groups on the cellulose ester backbone may impart amine functionality to a cellulose ester substrate. Also in step 106, the photo-initiator may be 2,2-dimethyl-1,2-diphenylethan-1-one.

In step 108, exposure to UV light may help bond a vinyl amine to $-\text{CH}=\text{CH}_2$ (or $-\text{CH}=\text{CH}-$) groups on the cellulose ester backbone.

In step 110, the di- or higher-functional amine may be m-phenylenediamine (MPD) or may be piperazine. The selection of a given amine may help produce a membrane with targeted permselectivity.

In step 112, the acyl chloride may be trimesoyl chloride (TMC) and/or the isocyanate may be toluene di-isocyanate. The selection of a given acyl chloride or isocyanate may help produce a membrane with targeted permselectivity. In some examples, the use of an isocyanate instead of an acyl chloride helps produce a polyurea membrane.

In step 114, curing the material may help tailor the thin film composite membrane selectivity.

Any or all of steps 110, 112, and 114 may include the interfacial polymerization of a polyamide, polypiperamide, or polyurea according to known methods in the art of constructing thin film composite membranes. In one example, 2% MPD is dissolved in water and is reacted with 0.1% TMC dissolved in $\text{C}_5\text{-C}_{14}$ alkanes.

Figure 7 illustrates an example of a polyamide covalently bound to an amide functionalized cellulosic substrate, produced by the method 100. In the illustrated example, a partially cross-linked aromatic polyamide is covalently bound to the polymer chains of an amine-functionalized cellulosic substrate. In the illustrated example, the method 100 included an (acrylamidomethyl)cellulose acetate solution, allylamine, MPD, and TMC.

In one implementation of the method 100, the di- or higher-functional amine is MPD and the acyl chloride is TMC. The TMC reacts with the amines on the functionalized

cellulose ester substrate and with the MPD. Amide bonds are formed in both reactions. The competition between amine functional groups on the functionalized cellulosic substrate and MPD can be modified by altering the concentration of each of TMC and MPD.

Amine functionalization of cellulose using a chemical initiator post-NIPS

In some embodiments, to produce a membrane, an active layer is covalently bound to an amine functional group attached to a cellulose ester support by a method that employs a chemical initiator following non-solvent induced phase separation (NIPS). With reference to Figure 5, the method 200 includes a step 202 of casting a cellulose solution onto a material, a step 204 of immersing the material in a water bath, a step 206 of immersing the material in a solution comprising an amine, a step 208 of immersing the material in a solution comprising a chemical initiator, a step 210 of immersing the material in an aqueous solution comprising a di- or higher-functional amine, a step 212 of immersing the material in a non-polar solution comprising a di- or higher-functional acyl chloride or an isocyanate, and a step 214 of curing the material.

In step 202, the material may be, for example, woven fabric, non-woven fabric, or a material having a non-porous surface, such as a glass plate. The cellulose solution may include a cellulose ester, such as cellulose acetate. The cellulose ester solution may include at least one alkene ($-\text{CH}=\text{CH}_2$ or $-\text{CH}=\text{CH}-$) functionalized cellulose, such as (acrylamidomethyl)cellulose acetate or cellulose acetate butyrate. In some examples, a cellulose ester may include a $-\text{CH}=\text{CH}_2$ or $-\text{CH}=\text{CH}-$ moiety, such as the derivatized cellulose ester of acrylamide, acrylate, or crotonate.

Step 204 may include the non-solvent induced phase separation (NIPS) technique, whereby a polymer in solution with a water miscible solvent is drawn into a thin film over a substrate and immersed in a water bath. Step 204 may help form the porous structure that helps to minimize the membrane's resistance. In some embodiments, step 204 is excluded from the method 200.

In step 206, the amine may be a primary amine, which may have the formula $\text{CH}_2=\text{CH}-\text{R}-\text{NH}_2$. The amine may be, for example, a vinyl amine such as allylamine. Reaction of a vinyl amine with $-\text{CH}=\text{CH}_2$ (or $-\text{CH}=\text{CH}-$) groups on the cellulose ester backbone may impart amine functionality to a cellulose ester substrate.

In step 208, the chemical initiator may be a free radical initiator. In some examples, the chemical initiator is hydrogen peroxide. The chemical initiator may help bond the amine, such as allyamine, to the $-\text{CH}=\text{CH}_2$ (or $-\text{CH}=\text{CH}-$) on the cellulose ester substrate.

In step 210, the di- or higher-functional amine may be m-phenylenediamine (MPD) or may be piperazine. The selection of a given amine may help produce a membrane with targeted permselectivity.

In step 212, the acyl chloride may be trimesoyl chloride (TMC) and/or the isocyanate may be toluene di-isocyanate. The selection of a given acyl chloride or isocyanate may help produce a membrane with targeted permselectivity. In some examples, the use of an isocyanate instead of an acyl chloride helps produce a polyurea membrane.

Any or all of steps 210, 212, and 214 may include the interfacial polymerization of a polyamide, polypiperamide, or polyurea according to known methods in the art of constructing thin film composite membranes. In one example, 2% MPD is dissolved in water and is reacted with 0.1% TMC dissolved in $\text{C}_5\text{-C}_{14}$ alkanes.

In step 214, curing the material may help tailor the thin film composite membrane selectivity.

Figure 7 illustrates an example of a polyamide covalently bound to an amide functionalized cellulosic substrate, produced by the method 200. In the illustrated example, a partially cross-linked aromatic polyamide is covalently bound to the polymer chains of an amine-functionalized cellulosic substrate.

In one implementation of the method 200, the di- or higher-functional amine is MPD and the acyl chloride is TMC. The TMC reacts with the amines on the functionalized cellulose ester substrate and with the MPD. Amide bonds are formed in both reactions. The competition between amine functional groups on the functionalized cellulosic substrate and MPD can be modified by altering the concentration of each of TMC and MPD.

Amine functionalization of cellulose using a chemical initiator during NIPS

In some embodiments, to form a membrane, an active layer is covalently bound to an amine functional group attached to a cellulose ester in a method that employs a chemical initiator during a step of non-solvent induced phase separation. With reference to Figure 6, the method 300 includes a step 302 of casting a cellulose solution containing an amine

onto a material, a step 304 of immersing the material in an aqueous solution of a chemical initiator, a step 306 of immersing the material in an aqueous solution comprising a di- or higher-functional amine, a step 308 of immersing the material in a non-polar solution comprising a di- or higher-functional acyl chloride or an isocyanate, and a step 310 of curing the material to produce a membrane.

In step 302, the material may be, for example, woven fabric, non-woven fabric, or a material having a non-porous surface, such as a glass plate. The cellulose solution may include a cellulose ester, such as cellulose acetate. The cellulose ester solution may include at least one alkene ($-\text{CH}=\text{CH}_2$ or $-\text{CH}=\text{CH}-$) functionalized cellulose, such as (acrylamidomethyl)cellulose acetate or cellulose acetate butyrate. In some examples, a cellulose ester may include a $-\text{CH}=\text{CH}_2$ or $-\text{CH}=\text{CH}-$ moiety, such as the derivatized cellulose ester of acrylamide, acrylate, or crotonate.

In step 302, the amine may be a primary amine, which may have the formula $\text{CH}_2=\text{CH}-\text{R}-\text{NH}_2$. The amine may be, for example, a vinyl amine such as allylamine. Reaction of a vinyl amine with $-\text{CH}=\text{CH}_2$ (or $-\text{CH}=\text{CH}-$) groups on the cellulose ester backbone may impart amine functionality to a cellulose ester substrate.

In step 304, the chemical initiator may be a free radical initiator. In some examples, the chemical initiator is hydrogen peroxide. The chemical initiator may help to initiate a chemical reaction between the $-\text{CH}=\text{CH}_2$ (or $-\text{CH}=\text{CH}-$) groups on the cellulose ester and amine to help bond the amine to the cellulose ester.

In step 306, the di- or higher-functional amine may be m-phenylenediamine (MPD) or may be piperazine. The selection of a given amine may help produce a membrane with targeted permselectivity.

In step 308, the acyl chloride may be trimesoyl chloride (TMC) and/or the isocyanate may be toluene di-isocyanate. The selection of a given acyl chloride or isocyanate may help produce a membrane with targeted permselectivity. In some examples, the use of an isocyanate instead of an acyl chloride helps produce a polyurea membrane.

Any or all of steps 306, 308, and 310 may include the interfacial polymerization of a polyamide, polypiperamide, or polyurea according to known methods in the art of constructing thin film composite membranes. In one example, 2% MPD is dissolved in water and is reacted with 0.1% TMC dissolved in $\text{C}_5\text{-C}_{14}$ alkanes.

Figure 7 illustrates an example of a polyamide covalently bound to an amide functionalized cellulosic substrate, produced by the method 300. In the illustrated example, a partially cross-linked aromatic polyamide is covalently bound to the polymer chains of an amine-functionalized cellulosic substrate.

In one implementation of the method 300, the di- or higher-functional amine is MPD and the acyl chloride is TMC. The TMC reacts with the amines on the functionalized cellulose ester substrate and with the MPD. Amide bonds are formed in both reactions. The competition between amine functional groups on the functionalized cellulosic substrate and MPD can be modified by altering the concentration of each of TMC and MPD.

The methods 100, 200, and 300 may produce a cellulose substrate with greater water and amine tolerance than the method disclosed in U.S. Patent Application Publication No. 2013/0089727.

Examples

The following working examples set forth methods of preparing thin film composite membranes having a polyamide covalently bound to an amine functionalized cellulose ester support. The method 100 is performed by casting an (acrylamidomethyl)cellulose acetate solution onto a fabric support, immersing the support in a water bath, immersing the support in an aqueous solution comprising allylamine and 2,2-dimethyl-1,2-diphenylethan-1-one as a photo-initiator, exposing the support to ultraviolet light, immersing the support in an aqueous solution of MPD, immersing the material in a solution of TMC in C₅-C₁₄ alkanes, and curing the substrate to produce a membrane.

The method 200 is performed by casting an (acrylamidomethyl)cellulose acetate solution onto a fabric support, immersing the support in a water bath, immersing the support in an aqueous solution comprising allylamine, immersing the support in a solution of hydrogen peroxide, immersing the support in an aqueous solution of MPD, immersing the material in a solution of TMC in C₅-C₁₄ alkanes, and curing the substrate to produce a membrane.

The method 300 is performed by casting an (acrylamidomethyl)cellulose acetate solution comprising allylamine onto a fabric support, immersing the support in an aqueous solution of hydrogen peroxide, immersing the support in an aqueous solution of MPD, immersing the material in a solution of TMC in C₅-C₁₄ alkanes, and curing the substrate to produce a membrane.

While various aspects and embodiments have been disclosed herein, other aspects and embodiments are contemplated. The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting.

CLAIMS

1. A method of preparing an amine-functionalized cellulosic substrate, the method comprising:
 - casting a cellulose ester solution onto a material;
 - immersing the material in a water bath to produce a porous cellulose ester substrate;
 - immersing the substrate in an aqueous solution comprising an amine and a photo-initiator; and
 - exposing the substrate to ultraviolet light to produce an amine-functionalized cellulose ester substrate.
2. The method of claim 1, wherein the cellulose ester solution includes at least one cellulose ester having one or more functional groups selected from acetate, propionate, butyrate, acrylamide, acrylate, and crotonate.
3. The method of claim 1, wherein the cellulose ester solution includes at least one alkene functionalized cellulose.
4. The method of claim 1, wherein the amine includes an alkene functional group.
5. The method of claim 1, wherein the material is selected from the group consisting of a woven fabric, a non-woven fabric, and a material having a non-porous surface.
6. A method of preparing a cellulose-supported thin film composite membrane, the method comprising:
 - casting a cellulose ester solution onto a material to produce a cellulosic support;
 - immersing the support in a water bath;
 - immersing the support in an aqueous solution comprising an amine and a photo-initiator;
 - exposing the support to ultraviolet light to produce an amine-functionalized cellulosic support;
 - immersing the support in an aqueous solution comprising a di- or higher-functional amine;
 - immersing the support in a non-polar solution comprising a di- or higher-functional acyl chloride or an isocyanate to produce an active layer on the support; and
 - curing the layer and support to produce a thin film composite membrane.
7. The method of claim 6, wherein the cellulose ester solution includes a cellulose ester.
8. The method of claim 7, wherein the cellulose ester includes cellulose acetate.

9. The method of claim 6, wherein the cellulose ester solution includes an alkene functionalized cellulose.
10. The method of claim 6, wherein the amine includes an alkene functional group.
11. The method of claim 6, wherein the material is selected from the group consisting of a woven fabric, a non-woven fabric, and a material having a non-porous surface.
12. The method of claim 6, wherein the di- or higher-functional amine includes m-phenylenediamine (MPD).
13. The method of claim 6, wherein the di- or higher-functional acyl chloride includes trimesoyl chloride (TMC).
14. The method of claim 6, wherein the active layer is produced on the support by interfacial polymerization of the di- or higher-functional amine.
15. The method of claim 6, wherein the di- or higher-functional amine is covalently bound to an amine group of the amine-functionalized cellulosic support.

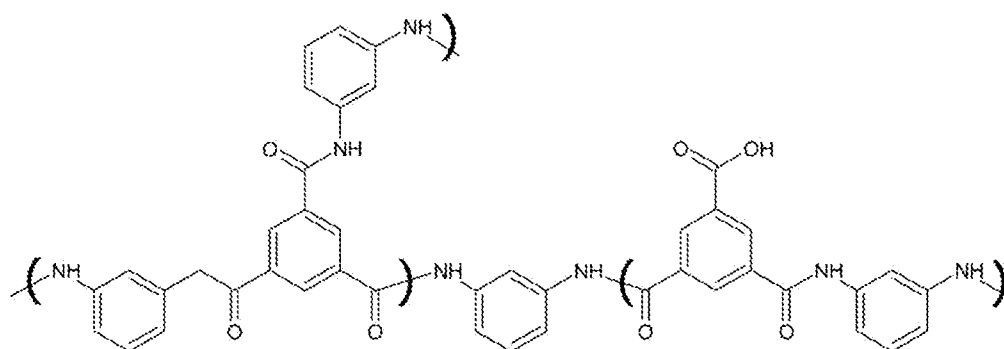


FIG. 1

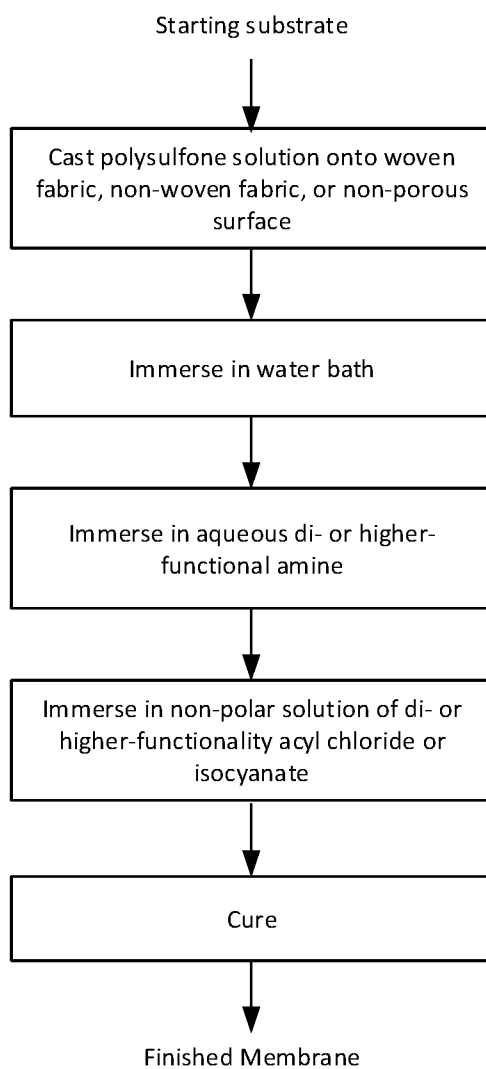
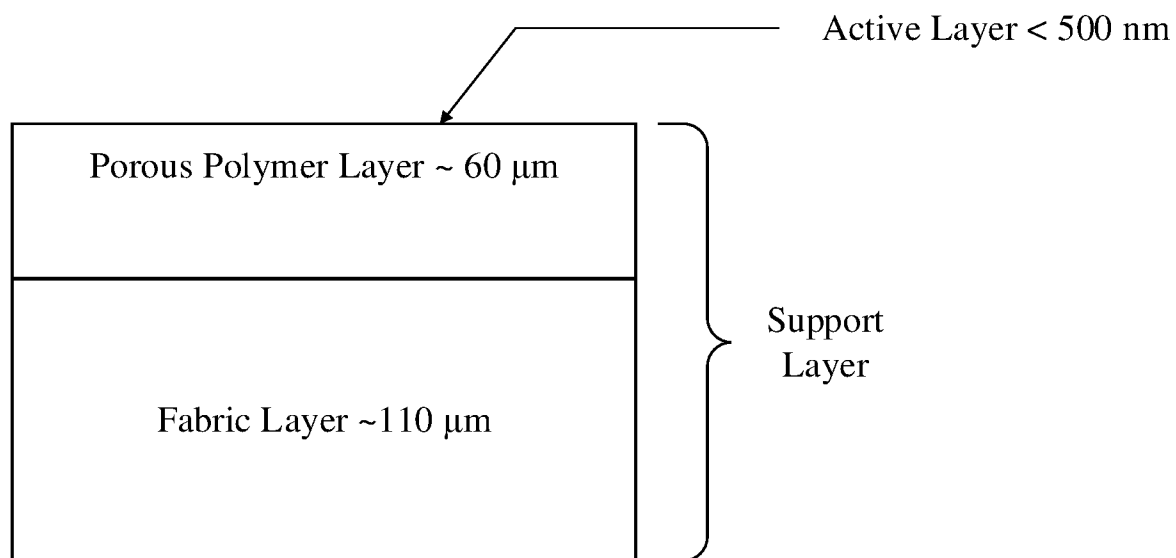


FIG. 2

**FIG. 3**

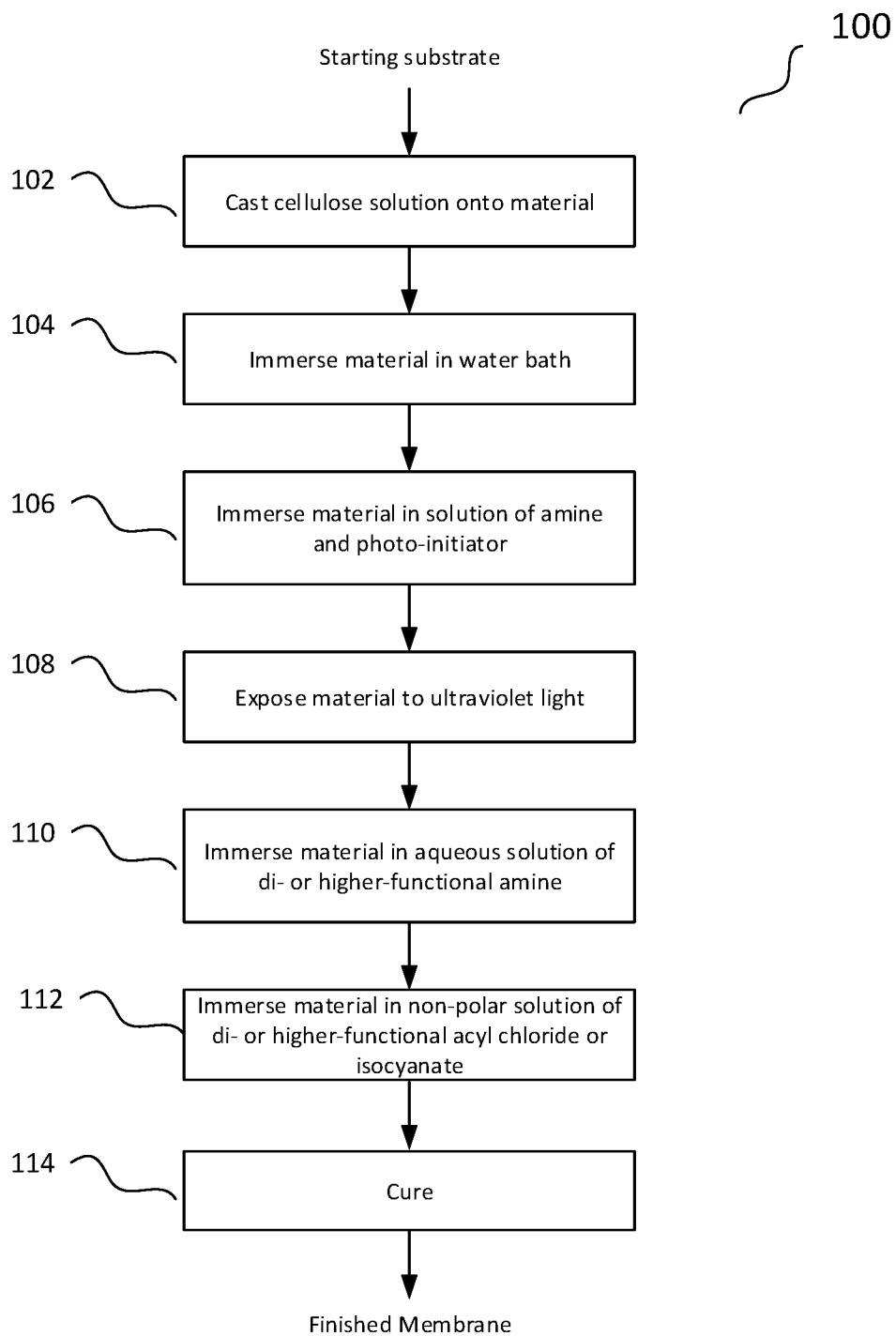


FIG. 4

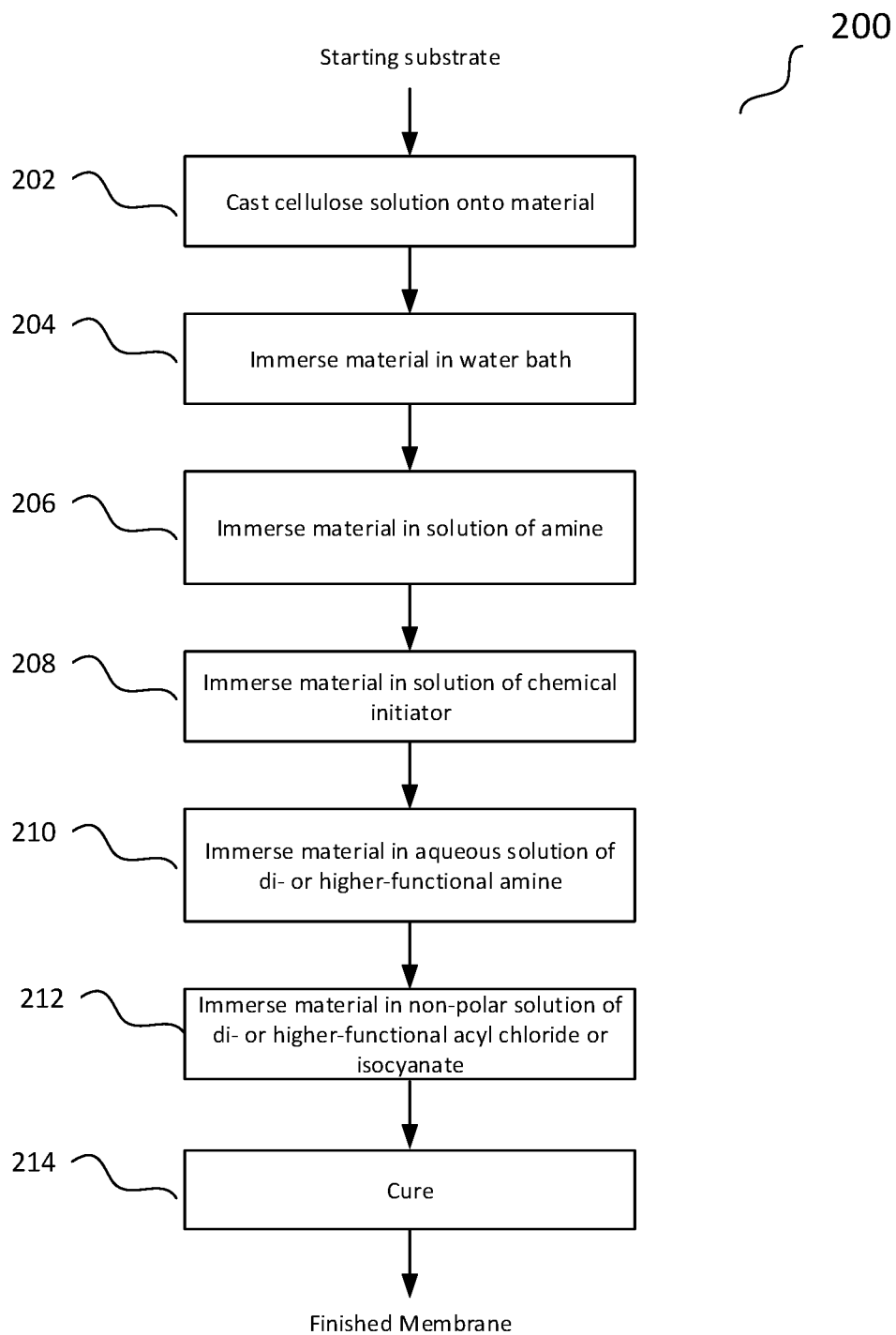


FIG. 5

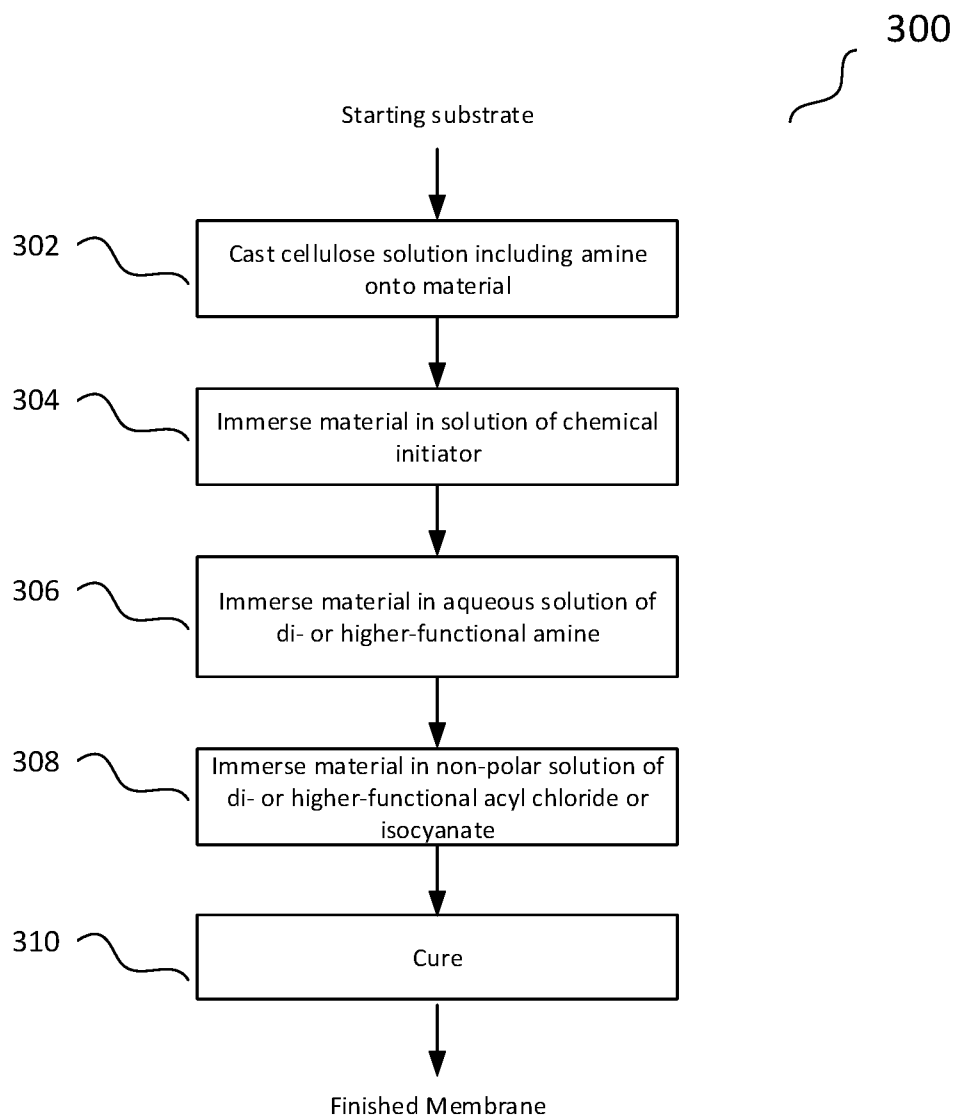


FIG. 6

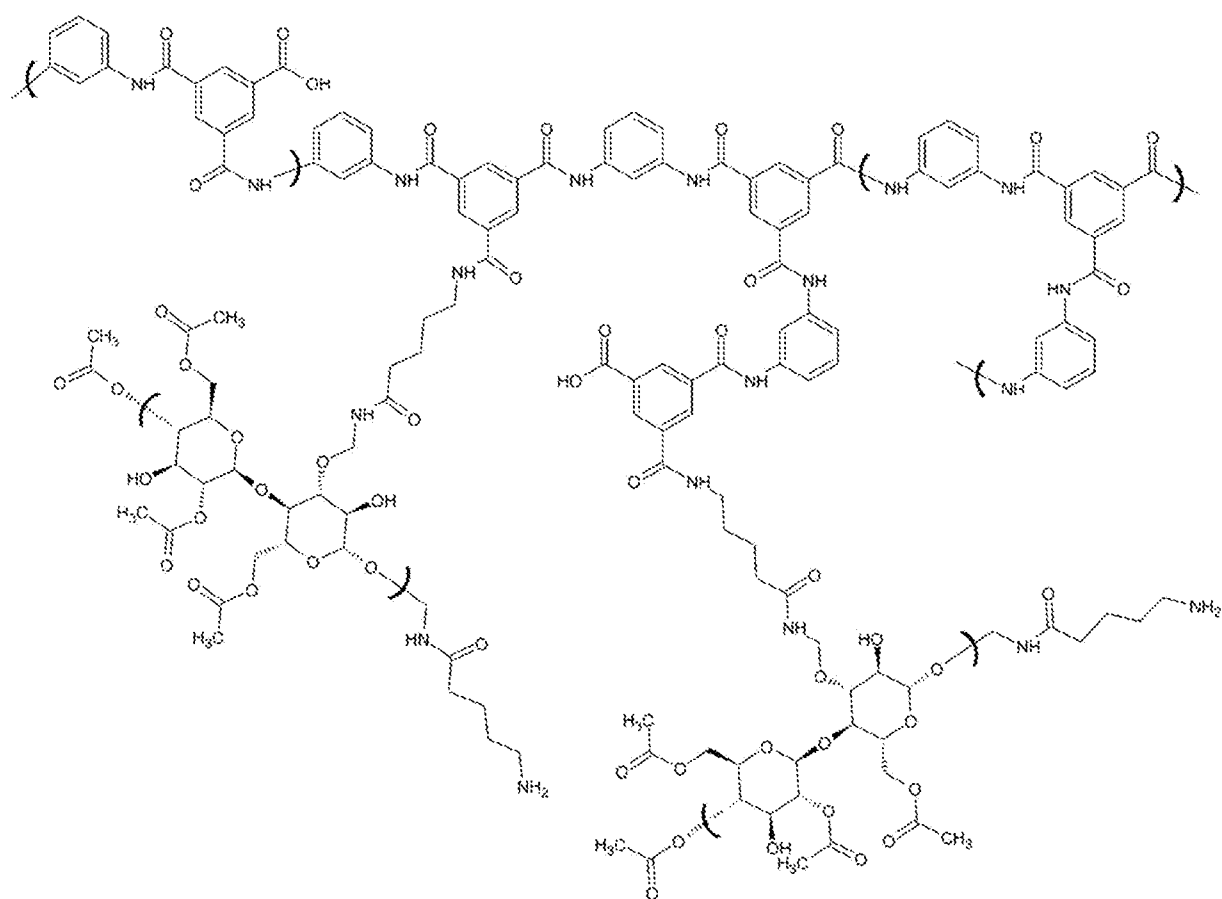


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US19/56906

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B01D 69/10, 69/12, 71/10, 71/12, 71/16, 71/56, 71/60 (2019.01)

CPC - B01D 67/0002, 67/0006, 67/0011, 69/10, 69/12, 69/125, 71/10, 71/12, 71/16, 71/56, 71/60

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)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 9,022,227 B2 (NA, Y-H, et al.) 02 May 2015; abstract; figures 1-2; column 2, lines 4-15; column 3, lines 21-35, 42-45; column 4, column 4, lines 23-26, 34-35, 39-41, 60-67; column 5, lines 1-15; column 9, lines 30-33; column 10, lines 29-32; column 17, lines 1-12; column 28, lines 13-14; table 2	1-15
Y	- CN 105,327,623 A (CHINESE ACAD INST CHEMISTRY) 17 February 2016; see machine translation; abstract; claims 1-2; paragraphs [0003], [0008], [0012]-[0013], [0033]	1-15
Y	WO 2016/113518 A1 (FUJIFILM MANUFACTURING EUROPE BV) 21 July 2016; page 10, lines 32-40; page 12, lines 22-28; page 16, lines 9-10, 25-26; page 17, lines 21-28	1-15
Y	↗ EP 0,312,943 B1 (W.R. GRACE AND CO.) 23 March 1994; page 4, lines 5-7, 24-26; page 7, lines 44-50	3, 9
Y	- CN 101,239,284 B (UNIV TIANJIN) 28 July 2010; see machine translation; abstract	4, 10



Further documents are listed in the continuation of Box C.



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"&" document member of the same patent family

Date of the actual completion of the international search

03 December 2019 (03.12.2019)

Date of mailing of the international search report

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Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

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