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(54) Title: POROUS MEMBRANES AND RECORDING MEDIA COMPRISING SAME

(57) Abstract: The present invention relates to a porous membrane obtainable by polymerizing at least one type of curable epoxy-acrylate monomer that is soluble in a solvent wherein at least 50wt% of said solvent is water. The invention further relates to image recording materials, in which these porous membranes are used.

Title: Porous membranes and recording media comprising same

**Field of the invention**

The present invention relates to porous membranes obtained by curing compounds through radiation. The invention further relates to image recording materials in which these porous membranes are used, in particular 5 as an ink-receiving layer. The invention also relates to processes for preparing said membranes and said recording media, as well as to the use of said membranes and said recording media.

**Background of the invention**

10 Several methods exist to make porous membranes. Wet and dry phase inversion are among the most widely applied techniques for making membranes with small pore sizes in the range of 0.1 nm to 1  $\mu$ m. In the wet phase inversion method a polymer is dissolved in a solvent and contacted with a non-solvent, usually by immersion, to initiate precipitation of the polymer: 15 the solid polymer-rich phase forms the membrane structure while the liquid solvent rich phase forms the pores. In the dry phase inversion method the polymer is dissolved in a mixture of a solvent and a non-solvent whereby the solvent is more volatile than the non-solvent and by evaporation of the solvent the polymer starts to precipitate in the non-solvent. Both methods are limited 20 to specific combinations of polymers, solvents and non-solvents and because of relatively long contact times especially the wet phase inversion process is rather slow. And also because organic solvents are used environmental and safety issues make manufacturing troublesome and expensive.

25 Alternatively by the technique of ultraviolet or electron beam irradiation porous membranes or porous materials can be produced as is described in *e.g.* US-A-4 466 931, US-A-5 126 189, EP-A-216 622, EP-A-481 517 and EP-A-1 533 321. In practice a variety of organic solvents are applied to dissolve the monomers.

The technique of making porous structures by free radical polymerization (thermally or by UV irradiation) is disclosed in GB-A-932 126.

Others use free radical polymerization by UV irradiation for polymerization of the monomers and make the membrane by the conventional 5 technique of wet phase inversion, as described in *e.g.* EP-A-430 082 and EP-A-803 533.

Water soluble (also referred to as water reducible) epoxy acrylates are described for making non-porous coatings and films as disclosed in *e.g.* WO-A-02/081576, WO-A-2005/066231 and WO-A-2004/060689.

10 In the process of continuous optimization of membrane manufacturing there is a need for a fast, simple and efficient method that does not require extensive investments related to the field of environmental regulations and safety.

15 Several examples can be found in which the curing technique is used to produce inkjet recording media. WO-A-2001/092023, WO-A-03/016068 and WO-A-97/33758 disclose membranes comprising inorganic particles needed to achieve the porous character.

20 EP-A-0 704 315 mentions the possibility to improve the water resistance by adding a curable resin to the cationic resin layer of an inkjet recording medium. EP-A-0 547 806 describes an authentication-identification card wherein a writing layer contains a binder that can be a UV curable resin. However, in neither EP-A-0 704 315 nor EP-A-0 547 806 porosity is created by phase separation of the cured polymer.

25 In EP-A-1 401 664, WO-A-2006/037085 and US-A-2005/153147 inkjet recording media are disclosed in which one or more ink receptive layers are coated on top of a radiation-curable layer.

Another method to obtain porosity is the application of foamed layers as in for example EP-A-0 888 903.

30 In yet other methods to make inkjet recording media coated layers are irradiated by ultraviolet or electron beam radiation, but these layers are

not porous as in *e.g.* EP-A-709 438, WO-A-99/42296, WO-A-99/21723, GB-A-2182046 and WO-A-2001/091999.

Where porous membranes are used for making recording media high concentrations of organic solvents are required as described in *e.g.*

5 JP-A-2002178630 and JP-A-2001010221.

International application PCT/NL2006/000154 describes a process for making microporous membranes by curing compounds through radiation, as well as image recording materials, in which these microporous membranes are used.

10 One of the important properties of an ink receptive coating formulation is the liquid absorptivity. The majority, if not all, of the ink solvent has to be absorbed by the coating layer itself. Only when paper, cloth or cellulose is used as a support, some part of the solvent may be absorbed by the support. Another important property for an inkjet recording medium 15 having photographic quality, is the optical density of the images printed thereon.

When comparing the known solutions for providing an inkjet recording medium, including media with a porous receiving layer and media with a water swellable layer, these solutions have their positive and negative 20 characteristics.

On the one hand, the swellable type of inkjet recording media may exhibit high densities, but these generally dry slowly. On the other hand the porous inkjet recording media have excellent drying properties, but generally have lower densities than swellable media, especially those media that are 25 based on polymeric porous layers.

There remains a strong need for ink-jet recording media having excellent drying properties and which show minimal dye fading and have high image densities. In addition, these ink-jet recording media should preferably have properties such as suitable durability, good sheet feeding property in ink-30 jet printers, good gloss, as well as a good resolution.

The present invention seeks to fulfill, at least in part, this need.

### Detailed description

5 It is an object of this invention to provide a porous membrane that can be produced at low cost and at high coating speeds. It is a further object of this invention to provide a recording medium having excellent drying characteristics and also high image print densities. We unexpectedly found that these objectives can be met by providing a curable composition comprising 10 at least one type of epoxy acrylate compound soluble in an aqueous solvent wherein at least 50 wt% of that solvent is water. An epoxy acrylate compound is a (curable) compound having at least one epoxyacrylate group. Thus epoxy acrylate compounds are compounds comprising one or more epoxyacrylate groups. Epoxy acrylate groups are formed by reacting epoxygroups with acrylic acid whereby the epoxy group is converted into a 2-acryyoxy-1-hydroxy-ethyl group. In a first embodiment, the present invention is directed to a porous membrane based on at least one type of curable epoxyacrylate monomer that is soluble in a solvent comprising at least 50 wt.% of water. By this invention a porous membrane can be prepared for a variety of applications such as 15 separation, concentration and purification of gasses, liquids and mixtures. In a special embodiment a membrane is formed that can accommodate the high amounts of solvent associated with printing high density areas as in for example inkjet recording media while maintaining the benefits, as of for example high gloss and high image density, of a swellable layer, by careful 20 selection of the concentration and composition of a curable compound mixture, coating said mixture on a substrate, curing that curable compound mixture causing phase separation between the crosslinked compounds and the solvent after which a substrate provided with a porous layer is formed and subjecting the resulting composition to a washing and/or drying step. After removal of the 25 solvent a porous structure remains that has swelling properties as well. A 30

mixture in this context is defined as any kind of possible state of a compound in a solution. So mixtures comprise solutions, suspensions (including emulsions), dispersions and so on. Throughout the text the terms curable compound and (curable) monomer are used interchangeably.

5 When coating such a mixture comprising a curable compound on a substrate, followed by the subsequent steps of curing the mixture, washing and/or drying the resulting porous layer and optionally separating the porous layer from the substrate, a porous membrane can be obtained which can be used in various applications (e.g. liquid separation membrane of gas separation 10 membrane) and which is characterised by its high solvent flux and/or uptake capability. If separated the porous membrane of the present invention can be fixed afterwards to all kinds of supports. Separation from the substrate can be easily achieved by proper treatment of the substrate e.g. by applying a 'release' 15 layer comprising for instance a siloxane based polymer before coating the curable compound mixture on the substrate. The isolated porous membrane of this invention can be separately attached to a substrate via an adhesive layer. This adhesive layer can also impart certain properties to the resulting membrane.

In another embodiment substrate and porous layer are not 20 separated, but are used as formed e.g. a membrane coated on a porous support like a nonwoven support or on a glossy support in which the porous membrane can function as a colorant receiving layer when used in recording media. This can be for example an inkjet recording medium in which case the colorant is an 25 ink-solution. In case the substrate is porous (e.g. nonwoven), the porous layer according the invention can function as a separation layer when used as a fluid separation membrane. In these embodiments the porous layer is generally in direct contact with the support.

In another embodiment a substrate is coated with two or more 30 layers of the curable compound mixture. By this method porous membranes can be designed and prepared with varying properties throughout the porous

membrane. So an outer layer can be designed and prepared having colorant fixing properties, e.g. by introducing mordants in the outer layer, and an inner porous layer can be constructed having an optimised water uptake capability. Alternatively for the so-called backview option of backlit material the outer 5 layer is optimized for scratch resistance and the colorant fixing property is located in the layer closest to a transparent support. Or for separation membrane applications the porosity of the outer layer is controlled to determine the separation characteristics while the inner layer(s) are optimized to give both strength to the membrane and allow high solvent fluxes.

10 In general the dry thickness of the porous membrane of this invention in isolated form may typically be between 10 µm and 500 µm, more preferably between 30 and 300 µm. When adhered to a substrate the membrane need not give internal strength and the optimal thickness is based on properties such as solvent uptake capacity. In the latter case the dry 15 thickness is typically between 5 and 50 µm. When the substrate is impermeable to aqueous solvents the dry thickness is preferably between 20 and 50 µm, while when the substrate is able to absorb part of the solvent as is the case for e.g. (coated) base paper the preferred dry thickness is between 5 and 30 µm. When the porous layer is a multilayer the thickness of the various 20 layers can be selected freely depending on the properties one likes to achieve.

The curable composition of the invention comprises at least an epoxy acrylate compound and may further comprise other curable compounds. It was found that not all combinations of curable compounds yield porous membranes. For phase separation to occur it is necessary that upon curing 25 polymerization proceeds rapidly and that the resulting polymer is insoluble in the solvent. Surprisingly experiments showed that especially epoxy acrylates could initiate the phase separation process even at very low amounts. Highly reactive monomers give fast phase separation and are especially preferred. Although many epoxy acrylate monomers are capable of inducing phase 30 separation most preferred are those compounds that are soluble in aqueous

solutions, preferably those solutions comprising at least 50% of water. The main reason for this preference is ease of producibility. When the solvent comprises mainly water then less stringent measures are required for safety and for compliance with environmental regulations. Another advantage of 5 using epoxy acrylate monomers which are soluble in aqueous solvents is a higher water/aqueous ink absorption speed due to their hydrophilicity.

Monomers can have one, two or more acrylate groups in one molecule.

Preferably the monomers used in the invention have at least two acrylate groups per molecule.

10 Examples of suitable epoxy acrylate monomers are: oligo(ethylene glycol) glycerolate (di)acrylates (typically having a molar weight (MW) of <500), poly(propylene glycol) glycerolate (di)acrylate, glycerol triglycerolate triacrylate, glycerol diglycerolate diacrylate, oligo(propylene glycol) glycerolate (di)acrylate, poly(butylene oxide) glycerolate (di)acrylate, oligo(butylene oxide) 15 glycerolate (di)acrylate, ethoxylated bisphenol-A glycerolate (di)acrylates, Ethoxylated neopentylglycol glycerolate (di)acrylate, ethoxylated trimethylolpropane glycerolate acrylates (mono-, di-, or tri(meth)acrylates, typically having a molar weight (MW) of <500), ethoxylated glycerol 20 glycerolate acrylates (mono-, di-, or tri(meth)acrylates) (typically having a molar weight (MW) of <500), ethoxylated aliphatic diols (hexanediol, octanediol, decanediol, *etc.*) glycerolate (di)acrylates, *etc.* The epoxy acrylates of the invention preferably comprise one or more alkoxy groups, more preferably C<sub>2</sub>-C<sub>4</sub> alkoxy groups. By varying the number, type and size of the alkoxy groups in the molecule the solubility in the solvent can be optimized to 25 obtain a system with fast phase separation properties.

Examples of epoxy acrylate monomers not suitable due to their poor solubility in aqueous solvents are: epoxidised soya bean oil acrylates, fatty acid modified Bisphenol A epoxy acrylates, Bisphenol A diglycerolate diacrylate (= Bisphenol A glycerolate (1 glycerol/phenol) diacrylate), Bisphenol A

propoxylate glycerolate diacrylate (propoxylate/phenol<5), di-(3-acryloxy-2-hydroxypropyl)-ether of bisphenol-A (Celrad™ 3700), and the like.

For a rapid phase separation to occur it appeared sufficient that only small amounts of these reactive monomers are present in the curable 5 composition: for instance 0.5 wt% or even less of epoxy-acrylate based on the total composition was found to be sufficient to obtain the phase separation that leads to the porous membrane of the invention as long as the total concentration of curable monomers is high enough. In most cases however more than 0.5 wt% of epoxy-acrylates will be used, typically from 0.5 to 55 10 wt.%, *e.g.* 5 wt% or 10 wt% or 50 wt% of the curable composition. Next to the epoxy-acrylate any other type of curable monomer may be used. So the curable composition may comprise one, two, three or more types of curable monomers.

Curable compounds that can be used together with the epoxy acrylate monomers of the invention are described for example in "Development 15 of ultraviolet and electron beam curable materials" (edited by Y. Tabata, CMC publishing, 2003, ISBN 4882317915) and may be selected from, but are not limited to epoxy compounds, oxetane derivatives, lactone derivatives, oxazoline derivatives, cyclic siloxanes, or ethenically unsaturated compound such as acrylates, methacrylates, polyene-polythiols, vinyl ethers, vinylamides, 20 vinylamines, allyl ethers, allylesters, allylamines, maleic acid derivatives, itaconic acid derivatives, polybutadienes and styrenes. Preferably as the main component (meth)acrylates are used, such as alkyl-(meth)acrylates, polyester-(meth)acrylates, urethane-(meth)acrylates, polyether-(meth)acrylates, epoxy-(meth)acrylates, polybutadiene-(meth)acrylates, silicone-(meth)acrylates, 25 melamine-(meth)acrylates, phosphazene-(meth)acrylates, (meth)acrylamides and combinations thereof because of their high reactivity. These compounds can be used in the form of a mixture of the monomers *per se*, a mixture of oligomers comprising the monomers or a mixture of polymers comprising the monomers (*e.g.* monomer solution, monomer suspension, monomer dispersion,

oligomer solution, oligomer suspension, oligomer dispersion, polymer solution, polymer suspension and polymer dispersion).

In order to achieve the porous membrane of the invention the curable composition and the processing conditions have to be selected with care. Upon irradiation the monomers (or oligomers or prepolymers) crosslink to gradually form polymers. During this process the solubility of the growing polymer in the solvent decreases resulting in phase separation and by result the polymer separates from the solution into a solid polymer-rich phase. Finally the polymer forms a network with a porous structure wherein the liquid solvent-rich phase forms the pores. Upon drying the solvent is removed and a porous membrane remains. In certain embodiments the membrane is not dried but optionally washed and kept in a wet condition to prevent collapsing of the pores. To obtain an optimal structure of the porous membrane it is important to carefully select the concentration of the curable compound or mixture of curable compounds. When the concentration is too low it is assumed that upon curing no network structure is formed and when the concentration is too high experiments indicate that a more or less homogenous gelled layer may be formed that yields a non-porous, transparent layer after drying. Also when the monomers are too soluble in the solvent no phase separation occurs and then usually a gel structure is formed after polymerization. A porous structure is essential for a high solvent flux or a quick solvent uptake. In view of this the concentration of the curable compound or compounds in the solvent is preferably between 10 and 80 wt.%, more preferably between 20 and 70 wt.%, most preferably between 30 and 60 wt.%.

For example, in case of epoxy diacrylate (e.g. CN132) it was found that the concentration of monomer in water/isopropanol (in a ratio between about 6:1 to about 4:1 based on weight) is preferably  $38 \pm 15$  wt.%, more preferably  $38 \pm 10$  wt.% and most preferably  $38 \pm 5$  wt.%. The centre value of '38' in case of epoxy diacrylate may be different for other curable compounds or mixtures of curable compounds. For instance when the epoxy diacrylate is

partly replaced by a more water-soluble curable monomer it is possible to increase the water/isopropanol ratio and/or the concentration of the curable compounds.

It is also possible to tune the centre value by changing the monomer system, or by changing the solvent system, or by addition of additives. For example, the centre value of '50' can be achieved by using mixture of monomers CN132 and CN435 (in a ratio of 1/1) with water, or only CN132 with water/isopropanol mixture with a ratio of 9/1, or by addition of a surfactant like dodecyltrimethylammonium chloride or sodium dodecylbenzene sulfonate. The centre value of '60' can be achieved by using only CN132 with water. For each specific case, the skilled person can find non-separating mixtures beforehand by carrying out routine tests beforehand, without any undue burden.

It is impossible to predict this centre value for every possible curable compound and solvent combination since countless combinations of monomers or oligomers with solvent mixtures are possible. However, a skilled person can easily determine by experiment the concentration range for a given curable compound within which a porous membrane is obtained, now that it is clear that such a selection is essential to obtain a porous membrane.

Many curable compounds are hydrophobic in nature and require high concentrations of organic apolar solvents to obtain a clear solution. High concentrations of volatile organic solvents are not preferred since these may result in hazardous conditions in the production area during the drying phase of the membrane while non-volatile solvents are difficult to remove and are thus not preferred either. For safety reasons, and also for considerations of health and environment as well as from economic viewpoint water is the most preferred solvent. Suitable curable compounds are preferably water reducible to form an aqueous solution but can also be dispersible in water or an aqueous solution, or can be present as a suspension. A compound is regarded as "water reducible" when at 25 °C at least 2 wt% of water, more preferably at

least 4 wt%, is compatible with (*viz.* forms a stable mixture with) the curable compound. Preferably at least 10wt% of water is miscible with 90wt% of the curable compounds of the invention. A solvent comprising water is generally referred to as an aqueous solvent. The aqueous solvent of the invention

5 preferably comprises at least 50 weight percent of water, and may further comprise other polar or apolar co-solvents. In case the miscibility with water is not sufficient to dissolve the curable compound(s) completely admixing of a co-solvent is desirable. In a preferred embodiment the solvent contains at least 60 weight percent, preferably at least 70 weight percent and more preferably at

10 least 80 or even 90 weight percent of water. In a specific embodiment the solvent is water and does not contain organic co-solvents. For example, 10% CN132, 27.5% CN435 and 62.5% water; or 21.5% CN132, 21.5% CN435 and 57% water; or 60% CN132 and 40% water; or 49.75% CN132, 49.75% water and 0.5% dodecyltrimethylammonium chloride can give a favourable porous

15 matrix. CN132 and CN435 are curable monomers available from Cray Valley, France. CN132 is a low viscosity aliphatic epoxy acrylate. CN435 (available in the US as SR9035) is an ethoxylated trimethylolpropane triacrylate.

As co-solvents, polar volatile solvents that can be sufficiently removed by drying are preferred. Preferred co-solvents are lower alkyl alcohols, alkanones, alkanals, esters, or alkoxy-alkanes. The term "lower alkyl" means that the alkyl chain contains less than 7, preferably less than 6 and more preferably less than 5 carbon-atoms, most preferably 1-4 carbon atoms. In one embodiment the solvent is a mixture of isopropanol and water. Other suitable co-solvents are *e.g.* methanol, ethanol, 1-propanol, acetone, ethylacetate, dioxane, methoxy ethanol and dimethylformamide. Most preferred are co-solvents having a boiling point lower than that of water.

The solubility of the curable compound in the solvent is another parameter of importance. Preferably the curable composition is a clear solution. The solvent is preferably chosen such that the selected curable

30 compound or compound mixture is completely dissolved. It was found that a

clear solution is particularly important when a membrane with a high gloss is desired. When a matte surface is aimed at, a turbid solution may be used and the solvent can be selected accordingly. However a clear solution is more stable and is generally preferred. But a slight turbidity usually does not cause 5 instability and is in most cases acceptable. On the other hand for phase separation to occur the growing polymer should be insoluble in the solvent. This puts certain restrictions to the curable compounds that can be selected in combination with a certain solvent. Possible methods that can facilitate the selection of suitable combinations are described in e.g. EP-A-216622 (cloud 10 point) and US-A-3823027 (Hansen system).

When the porous membrane is used as a colorant receiving medium e.g. an inkjet recording medium, where aqueous inks are used to form images the membrane should have a hydrophilic character in order to rapidly absorb the aqueous solvents involved. In case the curable composition contains water 15 as main solvent the polymer formed must generally have hydrophobic character because incompatibility with the solvent is important for phase separation to occur. Also for solubility reasons the curable compounds preferably possess hydrophilic character. Although non-soluble monomers can be used in the form of an emulsion a clear solution is preferred. This implies 20 that for this application the membrane of the invention must have both hydrophilic character and hydrophobic character. These seemingly contradictory demands can be realized by selecting a curable compound that has an amphiphilic structure: a part of the molecule is hydrophilic and another part has a hydrophobic character. An amphiphilic monomer may have both 25 hydrophilic and hydrophobic groups or may have amphiphilic groups (e.g. a (1,2- or 1,3-) propylene oxide chain or a (1,2-, 1,3- or 1,4-) butylene oxide chain). Examples of hydrophobic groups are aliphatic or aromatic groups, alkyl chains longer than C3 and the like. An alternative approach is to include in the 30 curable composition curable compounds that are hydrophilic and those that are hydrophobic. The latter method allows the properties of the membrane to

be controlled by varying the ratio of both types of curable compounds. Hydrophilic monomers are for example water soluble monomers and monomers having hydrophilic groups such as hydroxy, carboxylate, sulfate, amine, amide, ammonium, ethylene oxide chain and the like. Amphiphilicity 5 can be obtained in several ways. Amphiphilic monomers can for instance be made by introducing a polar group (such as hydroxy, ether, carboxylate, sulfate, amine, amide, ammonium, *etc.*) into the structure of a hydrophobic monomer. On the other hand starting from a hydrophilic structure an 10 amphiphilic monomer can be made by increasing the hydrophobic character by introducing *e.g.* alkyl or aromatic groups.

The epoxy acrylates of the invention preferably comprise one or more alkoxy groups, more preferably C<sub>2</sub>-C<sub>4</sub> alkoxy groups. By varying the number, type and size of the alkoxy groups in the molecule the solubility in the solvent can be optimized to obtain a system with fast phase separation 15 properties.

Preferably the curable composition comprises between 1-100wt% of epoxy acrylate monomers, more preferably between 10-80wt%, most preferably between 40-70wt% based on the total amount of curable monomers. The curable composition may additionally comprise up to 99wt% of amphiphilic, 20 hydrophilic or hydrophobic monomers, preferably between 30-60wt% based on the total amount of curable monomers. At least one of the monomers in the curable composition is an epoxy-acrylate.

Good results are obtained when at least one of the curable compounds, preferably the epoxy acrylate monomer of the invention, has a 25 restricted water reducibility. Preferably water is miscible with the curable monomer at 25 °C in a weight ratio of between 2/98 and 50/50, more preferably between 4/96 and 50/50, even more preferably between 10/90 and 50/50. A suitable concentration of the monomer can be achieved by addition of a co-solvent, a surfactant, by adjusting the pH of the composition or by adding 30 monomers to the mixture, which monomers maintain a good solubility at

higher water loads. The miscibility ratios of water with the latter monomers are typically larger than 50 wt.% at 25 °C.

Suitable monomers exhibiting a miscibility with water at 25 °C in a ratio water/monomer between 2/98 and 50/50 are: poly(ethylene glycol) diacrylate (e.g. MW<500, e.g. triethylene glycol diacrylate, tetraethylene glycol diacrylate, etc.), ethylene glycol epoxylate dimethacrylate, glycerol diglycerolate diacrylate, oligo(ethylene glycol) glycerolate (di)(meth)acrylates (typically having a molar weight (MW) of <500), poly(propylene glycol) (di)(meth)acrylate, poly(propylene glycol) glycerolate (di)(meth)acrylate, 10 oligo(propylene glycol) (di)(meth)acrylate, glycerol triglycerolate triacrylate, glycerol diglycerolate diacrylate, propylene glycol glycerolate diacrylate, tripropylene glycol glycerolate diacrylate, oligo(propylene glycol) diacrylate, poly(propylene glycol) diacrylate, oligo(propylene glycol) glycerolate diacrylate, poly(propylene glycol) glycerolate diacrylate, oligo(butylene oxide) diacrylate, 15 poly(butylene oxide) diacrylate, oligo(butylene oxide) glycerolate diacrylate, poly(butylene oxide) glycerolate diacrylate, ethoxylated trimethylolpropane triacrylate (ethoxylation 3-10 mol), ethoxylated bisphenol-A diacrylate (ethoxylation 3-10 mol), 2-hydroxyethyl acrylate, 2-hydroxypropylacrylate, 2-hydroxy-3-phenoxy propyl acrylate, 2-(ethoxyethoxyl)ethylacrylate, N,N'- 20 (m)ethylene-bis(acrylamide) or combinations thereof. Also suitable are commercially available compounds such as CN129 (an epoxy acrylate), CN131B (a monofunctional aliphatic epoxy acrylate), CN133 (a trifunctional aliphatic epoxy acrylate), CN9245 (a trifunctional urethane acrylate), CN3755 (an amino diacrylate), CN371 (an amino diacrylate), all from Cray Valley, 25 France. All monomers may be applied alone or in combination with other monomers.

Additionally other curable monomers may be included in the curable composition such as monomers having a good miscibility with water (ratio water/monomer larger than 50/50 at 25 °C): poly(ethylene glycol) (meth)acrylates (e.g. MW>500), poly(ethylene glycol) di(meth)acrylates

(preferably MW>500), ethoxylated trimethylolpropane triacrylates (ethoxylation more than 10 mol), (meth)acrylic acid, (meth)acrylamide, 2-(dimethylamino)ethyl (meth)acrylate, 3-(dimethylamino)propyl (meth)acrylate, 2-(diethylamino)ethyl (meth)acrylate, 2-(dimethylamino)ethyl 5 (meth)acrylamide, 3-(dimethylamino)propyl (meth)acrylamide, 2-(dimethylamino)ethyl (meth)acrylate quartenary ammonium salt (chloride or sulfate), 2-(diethylamino)ethyl (meth)acrylate quartenary ammonium salt (chloride or sulfate), 2-(dimethylamino)ethyl (meth)acrylamide quartenary ammonium salt (chloride or sulfate), 3-(dimethylamino)propyl 10 (meth)acrylamide quartenary ammonium salt (chloride or sulfate) and monomers having a poor miscibility with water (ratio water/monomer smaller than 2/98 at 25 °C): alkyl (meth)acrylates (e.g. ethyl acrylate, n-butyl acrylate, n-hexylacrylate, octylacrylate, laurylacrylate), aromatic acrylates (phenol acrylate, alkyl phenol acrylate, etc.), aliphatic diol (di)(meth)acrylates (e.g. 1,4- 15 butanediol diacrylate, 1,6-hexanediol diacrylate, hydroxypivalic acid neopentylglycol diacrylate, neopentylglycol diacrylate, tricyclodecanedimethanol diacrylate), trimethylolpropane triacrylate, glyceryl triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, 20 ditrimethylolpropane tetraacrylate, styrene derivatives, divinylbenzene, vinyl acetate, vinyl alkyl ethers, alkene, butadiene, norbonene, isoprene, polyester acrylates having alkyl chain longer than C<sub>4</sub>, polyurethane acrylates having alkyl chain longer than C<sub>4</sub>, polyamide acrylates having alkyl chain longer than C<sub>4</sub>, and combinations thereof.

25 To obtain a large difference in solubility between the initial compounds and the resulting polymer and thus a fast phase separation preferably the molecular weight (MW) of the initial compounds is not too large, although also with high-MW polymers porous membranes can be realized by careful selection of the solvent. Preferably the MW of the curable monomers or 30 oligomers is less than 10 000 Dalton, more preferably less than 5000 Dalton.

Good results are obtained with compounds having a MW of less than 1000 Dalton.

Photo-initiators may be used in accordance with the present invention and can be mixed into the mixture of the curable compound(s), 5 preferably prior to applying the mixture to the support. Photo-initiators are usually required when the coated mixture is cured by UV or visible light radiation. Suitable photo-initiators are those known in the art such as radical type, cation type or anion type photo-initiators.

Examples of radical type I photo-initiators are  $\alpha$ -hydroxyalkylketones, such as 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure<sup>TM</sup> 2959: Ciba), 1-hydroxy-cyclohexyl-phenylketone (Irgacure<sup>TM</sup> 184: Ciba), 2-hydroxy-2-methyl-1-phenyl-1-propanone (Sarcure<sup>TM</sup> SR1173: Sartomer), oligo[2-hydroxy-2-methyl-1-{4-(1-methylvinyl)phenyl}propanone] (Sarcure<sup>TM</sup> SR1130: Sartomer), 2-hydroxy-2-methyl-1-(4-tert-butyl-)phenylpropan-1-one, 2-hydroxy-[4'-(2-hydroxypropoxy)phenyl]-2-methylpropan-1-one, 1-(4-Isopropylphenyl)-2-hydroxy-2-methyl-propanone (Darcure<sup>TM</sup> 1116: Ciba);  $\alpha$ -aminoalkylphenones such as 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (Irgacure<sup>TM</sup> 369: Ciba), 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (Irgacure<sup>TM</sup> 907: Ciba);  $\alpha,\alpha$ -dialkoxyacetophenones such as  $\alpha,\alpha$ -dimethoxy- $\alpha$ -phenylacetophenone (Irgacure<sup>TM</sup> 651: Ciba), 2,2-diethoxy-1,2-diphenylethanone (Uvatone<sup>TM</sup> 8302: Upjohn),  $\alpha,\alpha$ -diethoxyacetophenone (DEAP: Rahn),  $\alpha,\alpha$ -di-(n-butoxy)acetophenone (Uvatone<sup>TM</sup> 8301: Upjohn); phenylglyoxolates such as methylbenzoylformate (Darocure<sup>TM</sup> MBF: Ciba); 15 benzoin derivatives such as benzoin (Esacure<sup>TM</sup> BO: Lamberti), benzoin alkyl ethers (ethyl, isopropyl, n-butyl, iso-butyl, etc.), benzylbenzoin benzyl ethers, Anisoin; mono- and bis-Acylphosphine oxides, such as 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (Lucirin<sup>TM</sup> TPO: BASF), ethyl-2,4,6-trimethylbenzoylphenylphosphinate (Lucirin<sup>TM</sup> TPO-L: BASF), bis(2,4,6-30 trimethylbenzoyl)-phenylphosphine oxide (Irgacure<sup>TM</sup> 819: Ciba), bis(2,6-

dimethoxybenzoyl)-2,4,4-trimethyl-pentylphosphineoxide (Irgacure<sup>TM</sup> 1800 or 1870). Other commercially available photo-initiators are 1-[4-(phenylthio)-2-(O-benzoyloxime)]-1,2-octanedione (Irgacure<sup>TM</sup> OXE01), 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-1-(O-acetylloxime)ethanone (Irgacure 5 OXE02), 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]-phenyl}-2-methyl-propan-1-one (Irgacure<sup>TM</sup> 127), oxy-phenyl-acetic acid 2-[2 oxo-2-phenyl-acetoxy-ethoxy]-ethyl ester (Irgacure<sup>TM</sup> 754), oxy-phenyl-acetic-2-[2-hydroxy-ethoxy]-ethyl ester (Irgacure<sup>TM</sup> 754), 2-(dimethylamino)-2-(4-methylbenzyl)-1-[4-(4-morpholinyl) phenyl]-1-butanone (Irgacure 379), 1-[4-[4-benzoylphenyl]thio]phenyl]-2-methyl-2-[(4-methylphenyl)sulfonyl]-1-propanone (Esacure<sup>TM</sup> 1001M from Lamberti), 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-bisimidazole (Omnirad<sup>TM</sup> BCIM from IGM).

Examples of type II photo-initiators are benzophenone derivatives such as benzophenone (Additol<sup>TM</sup> BP: UCB), 4-hydroxybenzophenone, 3-hydroxybenzophenone, 4,4'-dihydroxybenzophenone, 2,4,6-trimethylbenzophenone, 2-methylbenzophenone, 3-methylbenzophenone, 4-methylbenzophenone, 2,5-dimethylbenzophenone, 3,4-dimethylbenzophenone, 4-(dimethylamino)benzophenone, [4-(4-methylphenylthio)phenyl]phenyl-methanone, 3,3'-dimethyl-4-methoxy benzophenone, methyl-2-benzoylbenzoate, 4-phenylbenzophenone, 4,4-bis(dimethylamino)benzophenone, 4,4-bis(diethylamino)benzophenone, 4,4-bis(ethylmethyleamino)benzophenone, 4-benzoyl-N,N,N-trimethylbenzenemethanaminium chloride, 2-hydroxy-3-(4-benzoylphenoxy)-N,N,N-trimethyl-1-propanamium chloride, 4-(13-Acryloyl-1,4,7,10,13-pentaoxatridecyl)benzophenone (Uvecryl<sup>TM</sup> P36: UCB), 4-benzoyl-N,N-dimethyl-N-[2-(1-oxo-2-propenyl)oy]ethylbenzene-methanaminium chloride, 4-benzoyl-4'-methyldiphenyl sulphide, anthraquinone, ethylanthraquinone, anthraquinone-2-sulfonic acid sodium salt, dibenzosuberone; acetophenone derivatives such as acetophenone, 4'-phenoxyacetophenone, 4'-hydroxyacetophenone, 3'-hydroxyacetophenone, 3'-ethoxyacetophenone; thioxanthenone derivatives such as thioxanthenone, 2-

chlorothioxanthone, 4-chlorothioxanthone, 2-isopropylthioxanthone, 4-isopropylthioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthon-2-yloxy)-N,N,N-trimethyl-1-propanaminium chloride (Kayacure<sup>TM</sup> QTX: Nippon 5 Kayaku); diones such as benzyl, camphorquinone, 4,4'-dimethylbenzyl, phenanthrenequinone, phenylpropanedione; dimethylanilines such as 4,4',4"-methylidyne-tris(N,N-dimethylaniline) (Omnirad<sup>TM</sup> LCV from IGM); imidazole derivatives such as 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-bisimidazole; titanocenes such as bis(eta-5-2,4-cyclopentadiene-1-yl)-bis-[2,6-10 difluoro-3-1H-pyrrol-1-yl]phenyl]titanium (Irgacure<sup>TM</sup>784: Ciba); iodonium salt such as iodonium, (4-methylphenyl)-[4-(2-methylpropyl-phenyl)-hexafluorophosphate (1-). If desired combinations of photo-initiators may also be used.

For acrylates, diacrylates, triacrylates or multifunctional acrylates, 15 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-methylpropan-1-one, 1-hydroxycyclohexylphenylketone and oligo[2-hydroxy-2-methyl-20 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. Preferably the ratio of photo-initiator and curable compound(s) is 25 between 0.001 and 0.1, more preferably between 0.005 and 0.05, based on weight. It is preferred to apply as less as photo-initiator as possible, in other words preferably all photo-initiator has reacted after the curing step (or curing steps). Remaining photo-initiator may have adverse effects such as yellowing or degradation of dyes in case the membrane is used as a recording medium.

When applied as a separation membrane excessive washing may be required to wash out remaining photo-initiator.

When more than one layer is applied in each layer the type and concentration of photo-initiator can be chosen independently. For example, in a 5 multilayer structure the photo-initiator in the toplayer may be different from the photo-initiator in lower layer(s) which can give more efficient curing with low initiator concentrations than when a single initiator is applied throughout all layers. Some types of photo-initiator are more effective in curing the surface while other types cure much deeper into the layer when irradiated with 10 radiation. For the lower layers a good through cure is important and for a high efficiency of curing it is preferred to select a photo-initiator that has an absorption spectrum not fully overlapping with the spectrum of the photo-initiator applied in the toplayer. Preferably the difference in absorption maximum between photo-initiators in the top layer and in the bottom layer is 15 at least 20 nm. In the case UV radiation is used a light source can be selected having emissions at several wavelengths. The combination of UV light source and photo-initiators can be optimized so that sufficient radiation penetrates to the lower layers to activate the photo-initiators. A typical example is an H-bulb with an output of 600 Watts/inch (240 W/cm) as supplied by Fusion UV 20 Systems which has emission maxima around 220 nm, 255 nm, 300 nm, 310 nm, 365 nm, 405 nm, 435 nm, 550 nm and 580 nm. Alternatives are the V-bulb and the D-bulb which have a different emission spectrum. There needs to be sufficient overlap between the spectrum of the UV light source and that of the photo-initiators. From a choice of light sources and photo-initiators optimal 25 combinations can be made. This method allows for thicker layers to be cured efficiently with the same intensity of irradiation. Additionally by applying different types of photo-initiator characteristics such as gloss and porosity can be optimised to levels not possible with a single type of photo-initiator.

Curing rates may be increased by adding amine synergists to the 30 curable compound. Amine synergists are known to enhance reactivity and

retard oxygen inhibition. Suitable amine synergists are *e.g.* free alkyl amines such as triethylamine, methyldiethanol amine, triethanol amine; aromatic amine such as 2-ethylhexyl-4-dimethylaminobenzoate, ethyl-4-dimethylaminobenzoate and also polymeric amines as polyallylamine and its derivatives. Curable amine synergists such as ethylenically unsaturated amines (*e.g.* (meth)acrylated amines) are preferable since their use will give less odor, lower volatility and less yellowing due to its ability to be incorporated into the polymeric matrix by curing.

The amount of amine synergists is preferably from 0.1-10 wt.% based on the amount of curable compounds in the curable composition, more preferably from 0.3-3 wt.% based on the amount of curable compounds.

The curable compound mixture is preferably subjected to radiation to obtain the porous membrane. In principle (electromagnetic) radiation of any suitable wavelength can be used, such as for example ultraviolet, visible or infrared radiation, as long as it matches the absorption spectrum of the photo-initiator, when present, or as long as enough energy is provided to directly cure the curable compound without the need of a photo-initiator.

Curing by infrared radiation is also known as thermal curing. Thus curing polymerization may be effectuated by combining the ethylenically unsaturated monomers with a free radical initiator and heating the mixture. Exemplary free radical initiators are organic peroxides such as ethyl peroxide and benzyl peroxide; hydroperoxides such as methyl hydroperoxide, acyloins such as benzoin; certain azo compounds such as  $\alpha,\alpha'$ -azobisisobutyronitrile and  $\gamma,\gamma'$ -azobis( $\gamma$ -cyanovaleric acid); persulfates; peracetates such as methyl peracetate and tert-butyl peracetate; peroxalates such as dimethyl peroxalate and di(tert-butyl) peroxalate; disulfides such as dimethyl thiuram disulfide and ketone peroxides such as methyl ethyl ketone peroxide. Temperatures in the range of from about 23 °C to about 150 °C are generally employed. More often, temperatures in the range of from about 37 °C to about 110 °C are used.

Irradiation by ultraviolet light is preferred. Suitable wavelengths are for instance UV-A (400-320 nm), UV-B (320-280 nm), UV-C (280-200 nm), provided the wavelength matches with the absorbing wavelength of the photo-initiator, if present.

5 Suitable sources of ultraviolet light are 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  
10 the medium or high pressure mercury vapor type. Additional to mercury 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 450 nm are most suitable.

The energy output of the exposing device may be between 20 and  
15 240 W/cm, preferably between 40 and 150 W/cm but may be higher as long as the desired exposure dose can be realised. The exposure intensity is one of the parameters that can be used to control the extent of curing which influences the final structure of the membrane. Preferably the exposure dose is at least 40 mJ/cm<sup>2</sup>, more preferably between 40 and 600 mJ/cm<sup>2</sup>, most preferably  
20 between 70 and 220 mJ/cm<sup>2</sup> as measured by an High Energy UV Radiometer (UV Power Puck™ from EIT – Instrument Markets) in the UV-B range indicated by the apparatus. Exposure times can be chosen freely but need not be long and are typically less than 1 second.

In case no photo-initiator is added, the curable compound can be  
25 advantageously cured by electron-beam exposure as is known in the art. Preferably the output is between 50 and 300 keV. Curing can also be achieved by plasma or corona exposure.

The pH of the curable compositions is preferably chosen between a value of 2 and 11, more preferably between 3 and 8. The optimum pH depends  
30 on the used monomers and can be determined experimentally. The curing rate

appeared to be pH dependent: at high pH the curing rate is clearly reduced resulting in a less porous membrane. At low pH values (2 and lower) yellowing of the membrane occurs upon aging which is not desired when a good whiteness is preferred.

5        Where desired, a surfactant or combination of surfactants may be added to the aqueous composition as a wetting agent, to adjust surface tension, or for other purposes such as a good gloss. It is within the ability of one skilled in the art to employ a proper surfactant depending upon desired use and the substrate to be coated. Commercially available surfactants may be utilized,

10      including radiation-curable surfactants. Surfactants suitable for use in the curable composition include nonionic surfactants, ionic surfactants, amphoteric surfactants and combinations thereof. Preferred nonionic surfactants include ethoxylated alkylphenols, ethoxylated fatty alcohols, ethylene oxide/propylene oxide block copolymers, fluoroalkyl ethers, and the like. Preferred ionic surfactants include, but are not limited to, the following: alkyltrimethylammonium salts wherein the alkyl group contains from 8 to 22 (preferably 12 to 18) carbon atoms; alkylbenzyldimethylammonium salts wherein the alkyl group contains from 8 to 22 (preferably 12 to 18) carbon atoms, and ethylsulfate; and alkylpyridinium salts wherein the alkyl group

15      contains from 8 to 22 (preferably 12 to 18) carbon atoms. Surfactants may be fluorine based or silicon based. Examples of suitable fluorosurfactants are: fluoro C<sub>2</sub>-C<sub>20</sub> alkylcarboxylic acids and salts thereof, disodium N-perfluorooctanesulfonyl glutamate, sodium 3-(fluoro-C<sub>6</sub>-C<sub>11</sub> alkyloxy)-1-C<sub>3</sub>-C<sub>4</sub> alkyl sulfonates, sodium 3-(omega -fluoro-C<sub>6</sub>-C<sub>8</sub> alkanoyl-N-ethylamino)-1-

20      propane sulfonates, N-[3-(perfluorooctanesulfonamide)-propyl]-N,N-dimethyl-N-carboxymethylene ammonium betaine, perfluoro alkyl carboxylic acids (e.g. C<sub>7</sub>-C<sub>13</sub>-alkyl carboxylic acids) and salts thereof, perfluorooctane sulfonic acid diethanolamide, Li, K and Na perfluoro C<sub>4</sub>-C<sub>12</sub> alkyl sulfonates, Li, K and Na N-perfluoro C<sub>4</sub>-C<sub>13</sub> alkane sulfonyl-N-alkyl glycine, fluorosurfactants

25      commercially available under the name Zonyl® (produced by E.I. Du Pont)

that have the chemical structure of  $RfCH_2CH_2SCH_2CH_2CO_2Li$  or  $RfCH_2CH_2O(CH_2CH_2O)_xH$  wherein  $Rf = F(CF_2CF_2)_{3-8}$  and  $x = 0$  to  $25$ , N-propyl-N-(2-hydroxyethyl)perfluorooctane sulfonamide, 2-sulfo-1,4-bis(fluoroalkyl)butanedioate, 1,4-bis (fluoroalkyl)-2-[2-N,N,N-trialkylammonium] alkyl amino] butanedioate, perfluoro C<sub>6</sub>-C<sub>10</sub> alkylsulfonamide propyl sulfonyl glycinate, bis-(N-perfluorooctylsulfonyl-N-ethanolaminoethyl)phosphonate, mono-perfluoro C<sub>6</sub>-C<sub>16</sub> alkyl-ethyl phosphonates, and perfluoroalkylbetaine. Also useful are the fluorocarbon surfactants described e.g. in US-A-4 781 985 and in US-A-5 084 340.

10           Silicon based surfactants are preferably polysiloxanes such as polysiloxane-polyoxyalkylene copolymers. Such copolymers may be for example dimethylsiloxane-methyl (polyoxyethylene) copolymer, dimethylsiloxane-methyl (polyoxyethylene-polyoxypropylene) siloxane copolymer, trisiloxane alkoxylate as a copolymer of trisiloxane and polyether, and siloxane

15           propoxylate as a copolymer of siloxane and polypropylene oxide. The siloxane copolymer surfactants may be prepared by any method known to those having skill in the art and can be prepared as random, alternate, block, or graft copolymers. The polyether siloxane copolymer preferably has a weight-average molecular weight in a range of 100 to 10,000. Examples of polyether siloxane

20           copolymers commercially available in the market include SILWET DA series, such as SILWET 408, 560 or 806, SILWET L series such as SILWET-7602 or COATSIL series such as COATSIL 1211, manufactured by CK WITCO; KF351A, KF353A, KF354A, KF618, KF945A, KF352A, KF615A, KF6008, KF6001, KF6013, KF6015, KF6016, KF6017, manufactured by SHIN-ETSU;

25           BYK-019, BYK-300, BYK-301, BYK-302, BYK-306, BYK-307, BYK-310, BYK-315, BYK-320, BYK-325, BYK-330, BYK-333, BYK-331, BYK-335, BYK-341, BYK-344, BYK-345, BYK-346, BYK-348, manufactured by BYK-CHEMIE; and GLIDE series such as GLIDE 450, FLOW series such as FLOW 425, WET series such as WET 265, manufactured by TEGO.

Surfactants may be added in the curable composition and/or may be introduced by impregnation of the membrane for the purpose of improving printer transportability, blocking resistance and waterproofness. The surfactant, when used, preferably is present in an amount between 0.01 and 5 2% based on the dry weight of the membrane, more preferably between 0.02 and 0.5%. Preferably the surfactants are soluble in the composition in the concentration used. When an aqueous solvent is used preferably the solubility of the surfactant in water at 25°C is at least 0.5%.

For a fast uptake of especially aqueous inks the surface needs to be 10 hydrophilic. The hydrophilicity of the surface is suitably expressed by measuring the contact angle of water drops. Values below 80° are indicative for hydrophilic surfaces and are preferred for applications as ink receiving layer.

In accordance with the present invention, a membrane is referred to as "porous" if it contains a substantial amount of pores preferably having a 15 diameter of between 0.0001 and 2.0 µm. More preferably the majority of the pores of the porous membrane of the invention have a size of between 0.001 and 1.0 µm, even more preferably between 0.003 and 0.7 µm. For selected embodiments the average pore diameter is preferably between 0.01 and 1.0 µm, more preferably between 0.03 and 0.4 µm. For other embodiments very 20 small average pore sizes are preferred e.g. between 0.0001 and 0.01 µm. The latter embodiments include reversed osmosis and nanofiltration. There is no preference for the pore shape. The pores can be spherical or irregular or a combination of both. Preferably the pores are inter-connected, since this will contribute to a high flux or quick solvent absorption.

25 The porosity of the membrane is preferably between 5 and 90 percent as determined by analysing SEM cross-section images. The porosity is determined by the following formula:

(Dry thickness / coated amount of solids per m<sup>2</sup> \* 100 %) – 100 % wherein the density of the coated solids is assumed to be 1 kg/dm<sup>3</sup>. More

preferably the porosity is between 10 and 70 percent, even more preferably between 20 and 50%.

For membranes applied as ink receiving layer it is important to exhibit a high gloss for which the surface layer is preferably smooth and the size and total area of the pores on the surface of the membrane must be controlled within certain limits. A good gloss without loss in ink absorption speed can be obtained by controlling the area occupied by pores to preferably between 0.1 and 30%. More preferably the pore area is between 0.2 and 25%, even more preferably between 0.3 and 18% for maximum gloss with high ink absorption speed. Pore area is determined by diameter and amount of pores. This means that for a certain pore area the amount of pores varies depending on the pore diameter. In general a low frequency of large pores is less preferred than a high frequency of small pores. The absolute average pore diameter of the surface pores is preferably smaller than 1.2  $\mu\text{m}$ , more preferably between 0.02 and 1  $\mu\text{m}$ , even more preferably between 0.05 and 0.7  $\mu\text{m}$ . For selected embodiments a range between 0.06 and 0.3  $\mu\text{m}$  is preferred. Good gloss can be additionally expressed in a surface roughness (Ra) value. Ra values are influenced by pore diameter/pore area. Preferred Ra values for membranes having a good gloss are below 0.8  $\mu\text{m}$ , more preferably below 0.5  $\mu\text{m}$ , even more preferably below 0.3  $\mu\text{m}$  and most preferably below 0.2  $\mu\text{m}$ . A glossy appearance is thought to be determined mainly by the smoothness of the surface area between the pores. In ISO 13565-1 (1998) and JIS B0671-1 (2002) a method is described by which it is possible to determine the Ra value of the surface eliminating the contribution of the pores to the calculation. In a special embodiment the membrane is composed of distinct structures: an isotropic bulk matrix in the form of an open polymer network and a thin surface layer of a completely different structure. This surface layer or skin layer is a continuous layer having pores that are not connected and can be described as a perforated continuous layer. By varying the process and recipe conditions the number and size of surface pores can be controlled according to

desired specifications. This surface layer is thought to contribute to the gloss of the membrane. For applications such as reversed osmosis it may be preferred that there are no pores at all at the surface or only pores of a very small diameter, which means that the skin layer can be regarded as a closed

5 continuous layer. For the application as ink receiving layer the surface layer is assumed to prevent the dyes present in the ink from being absorbed deep into the membrane which would lead to a low optical density of the printed image. So the surface layer contributes to a high optical density. On the other hand a skin layer reduces the flow rate through the membrane which may result in

10 worse drying properties. Therefore preferably this skin layer is thin, having a thickness less than 0.5  $\mu\text{m}$ , more preferably the thickness of the skin layer is less than 0.2  $\mu\text{m}$ . Except for the thin skin layer the membrane is preferably symmetric, although an asymmetric structure to some extent is allowable.

An important characteristic of the membrane is the swellability of

15 the porous layer. In addition to the porosity the swellability contributes to the speed and capacity of solvent uptake. Depending on the desired properties, a certain balance can be selected between the porosity and the swellability. To attain a certain level of solvent uptake a high porosity can be combined with a low swelling behaviour or *vice versa*. This enables a large variation in

20 membrane structures all with a good solvent uptake speed. For membranes applied as ink receiving layer the swelling preferably is between 1 and 50  $\mu\text{m}$ , more preferably between 2  $\mu\text{m}$  and 30  $\mu\text{m}$ , most preferably between 3 and 20  $\mu\text{m}$ . Because the dry thickness of the porous layer may vary depending on the desired application the swelling is more appropriately expressed in a relative

25 way as a percentage of the dry thickness. Preferably the swelling is at least 5%, more preferably between 6 and 150% of the dry thickness of the porous membrane, even more preferably between 10 and 80%. The swelling in this invention is determined by subtracting the dry thickness of the layer before swelling from the swollen thickness of the layer after swelling, wherein the

30 swollen thickness represents the thickness of the layer after immersion in

20 °C distilled water for 3 minutes, and dry thickness represents the thickness of the layer being allowed to stand at 23 °C and 60%RH for more than 24 hours. The thickness of the layer can be determined by various methods. For example, there is a method in which after a sample is immersed in distilled 5 water at a given temperature for a given time to swell the layer, while the swelling process is observed by touching the swollen layer continuously with a needle positioning sensor. There is also a method to measure the height of the swollen layer by optical sensor without touching the surface, and subtracting the height of the dry layer to know the swelling amount of the layer. The 10 degree of swelling can be controlled by the types and ratio of monomers, the extent of curing/cross-linking (exposure dose, photo-initiator type and amount) and by other ingredients (e.g. chain transfer agents, synergists).

Surprisingly the membrane due to its swelling character showed high image densities when used as an ink receiving layer and an improved 15 ozone fastness. Without wishing to be bound by theory, the researchers assume that due to swelling the colorants are incorporated in the polymer network structure and after drying are protected against the influences of ozone and other gasses. In a porous network without swelling capability the colorants can penetrate deep into the layer while by swelling the colorants are 20 thought mainly to be trapped in the surface region of the layer explaining the increased density observed.

A disadvantage of a strongly swelling porous layer is a rather weak scratch resistance. A large swellability is achieved by a low degree of crosslinking which makes the structure of the membrane sensitive to physical 25 disturbance. Surprisingly it was found that a second curing treatment of the dry membrane after drying is completed, is more effective for enhancing the robustness than intensifying the curing of the wet coated layer. Again, without wishing to be bound by theory, the inventors suggest that by drying the unreacted curable double bonds are moving closer to each other, thereby 30 increasing the probability of crosslinking upon curing. This second curing step

may be done by UV-curing, but also other methods are suitable such as EB-curing or other sources of radiation, *e.g.* those mentioned hereinabove. In case UV curing is applied for the second curing at least part of the photo-initiator need to remain in reactive form after the first curing step. On the other hand it

5 is important that finally essentially all photo-initiator has reacted because remaining photo-initiator may lead to yellowing of the membrane due to aging which is undesirable for certain applications. This can be easily achieved by tuning the initial concentration of the photo-initiator in the recipe.

Alternatively the photo-initiator for the second curing is added separately *e.g.*

10 by impregnation.

In stead of a second curing of the membrane in the dry state, in another embodiment the membrane is cured while being wet. To this end, the second curing can be done shortly after the first curing without an intermediate drying step. Another way is to prewet the dried membrane by a

15 liquid that may contain one or more ingredients such as surfactants. An advantage of this procedure is that in the wet state the membrane structure changes upon curing when the membrane is swellable in the liquid applied. So properties as porosity can be modified by performing a second curing step when the membrane is in the swollen state. By this method a wider range of

20 materials and process conditions become suitable since tuning of the structure remains possible after the initial curing step. In between both curing steps an impregnation can be carried out. By impregnation compounds can be brought into the membrane that are not very well compatible with the curable composition of the first curing step. When the structure of the membrane after

25 the first curing is already good, a second curing is superfluous and just drying after impregnation is generally sufficient. But when it is desired to fix the compounds brought in by impregnation to the matrix a second curing step is the preferred method of crosslinking. Preferably the membrane is partly dried before an impregnation step is executed. By partial drying the compounds

30 introduced by impregnation *e.g.* by coating, spraying or dipping, can deeper

penetrate into the membrane. By partial drying part of the solvent is removed, e.g. 25% or 50% and in some cases up to 80% of the solvent is removed prior to impregnation. With a good process design more than two curing steps will in general not result in improved properties, however certain circumstances such 5 as limited UV intensity may make multiple curing beneficial.

Preferably the exposure dose in the second curing step is between 80 and 300 mJ/m<sup>2</sup>, more preferably between 100 and 200 mJ/m<sup>2</sup> as measured by an High Energy UV Radiometer (UV Power Puck™ from EIT – Instrument Markets) in the UV-B range indicated by the apparatus.

10 The porous membrane may also comprise one or more non-curable water soluble polymers and/or one or more hydrophilic polymers that are not crosslinked by exposure to radiation. The non-curable water soluble polymer may be added to the curable compound mixture before curing or applied to the cured membrane after curing.

15 In addition to a non-curable water soluble polymer, crosslinking agent may be added, preferably up to 20 wt.%, more preferably between 0.5 and 5 wt.%, based on the amount of non-curable water soluble polymer in the layer. Suitable crosslinking agents are described in EP-A-1 437 229. Thus the crosslinking agent may be one or more of aldehyde-based compounds such as 20 formaldehyde, glyoxal, glutaraldehyde and the like; a ketone-based compound such as diacetyl, cyclopentanedione and the like; an activated halide such as bis(2-chlorethylurea)-2-hydroxy-4,6-dichloro-1,3,5-triazine, 2,4-dichloro-6-S-triazine sodium salt and the like; an activated vinyl compound such as divinylsulfonic acid, 1,3-vinylsulfonyl-2-propanol, N,N'- 25 ethylenebis(vinylsulfonylacetamide), 1,3,5-triacryloylhexahydro-S-triazine and the like; an N-methylol compound such as dimethylol urea, methylol dimethylhydantoin and the like; a melamine resin (for example, methylol melamine, alkylated methylol melamine); an epoxy resin; an isocyanate compound such as 1,6-hexamethylene diisocyanate and the like; aziridine 30 compound described in US-A-3 017 280 and US-A-2 983 611; a carboxyimide

compound described in US-A-3 100 704; an epoxy-based compound such as glycerol triglycidyl ether and the like; an ethyleneimino-based compound such as 1,6-hexamethylene -N,N'-bisethylene urea and the like; a halogenated carboxyaldehyde-based compound such as mucochloric acid,

5 mucophenoxychloric acid and the like; a dioxane-based compound such as 2,3-dihydroxydioxane and the like; a boron compound such as boric acid, borax and borate; a metal-containing compound such as titanium lactate, aluminum sulfate, chromium alum, potassium alum, zirconyl acetate, chromium acetate and the like, a polyamine compound such as tetraethylene pentamine, a

10 hydrazide compound such as adipic acid dihydrazide, a low molecular weight compound or polymer having two or more oxazoline group and the like. These crosslinking agents can be used alone or in combination.

In one embodiment at least two mixtures are coated on a substrate of which at least one is a curable compound mixture, which after curing and

15 drying results in a medium comprising at least one top layer and at least one bottom layer that is closer to the substrate than the top layer. At least the top layer, and preferably also the bottom layer comprises the porous membrane of this invention. For a two-layer membrane structure the bottom layer preferably has a dry thickness of between 3 and 50 µm, preferably between 7

20 and 40 µm, most preferably between 10 and 30 µm and the toplayer preferably between 1 and 30 µm, preferably between 2 and 20 µm, most preferably between 4 and 15 µm.

In another embodiment a substrate is coated with at least three layers of which at least one layer, preferably the top (outer) layer comprises a

25 curable compound mixture. After applying the curable compositions to the substrate, curing and drying, a medium comprising at least three layers is formed, which three layers then comprise at least one bottom layer with a dry thickness of between 3 and 50 µm, preferably between 5 and 40 µm, most preferably between 7 and 30 µm, at least one middle layer with a dry thickness

30 of between 1 and 30 µm, preferably between 2 and 20 µm, most preferably

between 3 and 15  $\mu\text{m}$ , and at least one toplayer above the middle layer. The top layer preferably has a dry thickness of less than 10  $\mu\text{m}$ , preferably of between 0.1 and 8  $\mu\text{m}$ , most preferably between 0.4 and 4  $\mu\text{m}$ .

In a preferred embodiment, the substrate is coated with two, three 5 or more curable compound mixtures, which after curing and drying results in a recording medium in which all layers are layers comprising a porous membrane of the invention. Said mixtures may have the same or different compositions depending on the results one likes to achieve. Furthermore the curable compound mixtures might be coated simultaneously and then cured or 10 might be coated consecutively and cured. Consecutively means, that a first mixture is coated, then cured; then a second mixture is coated, cured and so on. In the latter situation it is likely that at least a part of the second mixture is impregnating the first layer so care has to be taken that the pores of the resulting membrane do not become blocked.

15 Preferably the top layer and the middle layer comprising the porous membrane of the present invention are essentially free from organic or inorganic particles that are capable of absorbing solvent. Essentially free means here that the amount or location of particles is such that there is no significant decrease in gloss or colour density. A quantity of less than 0.1 g/m<sup>2</sup> 20 is regarded as essentially free. Preferably all porous layers are essentially free from particles. An exception are matting agents, that are added to prevent handling problems such as blocking, caused by a too smooth surface and which preferably are added in the top layer of the medium in a low amount. Usually less than 0.5% of the total solid content of the porous layer(s) is formed by 25 matting agents.

It may be desirable to add in the toplayer a matting agent (also known as anti-blocking agents) to reduce friction and to prevent image transfer when several printed inkjet media are stacked. Very suitable matting agents have a particle size from 1 to 20  $\mu\text{m}$ , preferably between 2 and 10  $\mu\text{m}$ . 30 The amount of matting agent is from 0.005 to 1 g/m<sup>2</sup>, preferably from 0.01 to

0.4 g/m<sup>2</sup>. In most cases an amount of less than 0.1 g/m<sup>2</sup> is sufficient. The matting agent can be defined as particles of inorganic or organic materials capable of being dispersed in an aqueous composition. The inorganic matting agents include oxides such as silicon oxide, titanium oxide, magnesium oxide and aluminium oxide, alkali earth metal salts such as barium sulphate, calcium carbonate, and magnesium sulphate, and glass particles. Furthermore inorganic matting agents can be used, e.g. those disclosed in DE-A-2 529 321, GB-A-760 775 and GB-A-1 260 772, and U.S. Pat. Nos. 1 201 905, 2 192 241, 3 053 662, 3 062 649, 3 257 296, 3 322 555, 3 353 958, 10 3 370 951, 3 411 907, 3 437 484, 3 523 022, 3 615 554, 3 635 714, 3 769 020, 4 021 245 and 4 029 504. Suitable organic matting agents include starch, cellulose esters such as cellulose acetate propionate, cellulose ethers such as ethyl cellulose, and synthetic resins. The synthetic resins are water insoluble or sparingly soluble polymers which include a polymer of an 15 alkyl(meth)acrylate, an alkoxyalkyl(meth)acrylate, a glycidyl(meth)acrylate, a (meth)acrylamide, a vinyl ester such as vinyl acetate, acrylonitrile, an olefin such as ethylene, or styrene and a copolymer of the above described monomer with other monomers such as acrylic acid, methacrylic acid, alpha, beta - unsaturated dicarboxylic acid, hydroxyalkyl(meth)acrylate, 20 sulfoalkyl(meth)acrylate and styrene sulfonic acid. Further, a benzoguanamin-formaldehyde resin, an epoxy resin, polyamide, polycarbonates, phenol resins, polyvinyl carbazol or polyvinylidene chloride can be used. Organic matting agents can be used as well, for instance the compounds disclosed in GB-A-1 055 713, U.S. Pat. Nos. 1 939 213, 2 221 873, 2 268 662, 2 322 037, 25 2 376 005, 2 391 181, 2 701 245, 2 992 101, 3 079 257, 3 262 782, 3 443 946, 3 516 832, 3 539 344, 3 591 379, 3 754 924 and 3 767 448, JP-A- 49106821 (corresponding to US-A-4 056 396) and JP-A-57014835 (corresponding to US-A-4 396 706). The matting agents may be used alone or in combination.

Usually the porous membrane has an opaque appearance due to the 30 porous structure of the matrix. Investigations revealed that a higher image

density can be obtained when the outer layer or layers are somewhat transparent. This can be achieved by modifying the structure of the outer layer in such a way that the porosity is less. An additional advantage of a less porous toplayer is a better gloss. Because solvent absorption speed is among 5 others dependent on porosity it is preferred that this more transparent toplayer is rather thin. Because the thickness of the more transparent layer usually does not correspond with the thickness of the toplayer as coated it may be more correct to refer to this layer as top region. Most effect of the transparency of the top region on image density is obtained when the colorants 10 are fixed in the upper layers of the membrane, preventing diffusion of the colorant to lower layers. Fixing can be achieved by incorporating into the membrane mordant functionality. For instance a curable mordant can be added to the curable composition or mordants that are non-curable can be added. Mordants are preferably added in the outer layer or layers e.g. in the 15 top layer and/or in the layer just below the toplayer. Preferably the mordants are cationic making them suitable to form complexes with anionic colorants and may be organic or inorganic. The organic and inorganic mordants may be employed alone independently or in combination with each other. A very suitable method to fix the mordants in the outer layer is to introduce negative 20 charges in the outer layer, for instance by applying anionic curable compounds in the curable composition.

A cationic mordant described above is preferably a polymeric mordant having a primary to tertiary amino group or a quaternary ammonium salt as a cationic group; a cationic non-polymeric mordant may also be 25 employed. Such a polymeric mordant is preferably a homopolymer of a monomer (mordant monomer) having a primary to tertiary amino group or a salt thereof, or a quaternary ammonium salt, as well as a copolymer or a condensation polymer of such a mordant monomer with other monomers (hereinafter referred to as a non-mordant monomers). Such a polymeric 30 mordant may be in the form either of a water-soluble polymer or a water-

dispersible latex particle, e.g. a dispersion of a polyurethane. Suitable mordant monomers are for example alkyl- or benzyl ammonium salts comprising one or more curable groups such as vinyl, (di)allyl, (meth)acrylate, (meth)acrylamide and (meth)acryloyl groups such as trimethyl-p-vinylbenzylammonium chloride, 5 trimethyl-m-vinylbenzylammonium chloride, triethyl-m-vinylbenzylammonium chloride, N,N-dimethyl-N-ethyl-N-p-vinylbenzylammonium chloride, N,N-diethyl-N-methyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-n-propyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-n-octyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-benzyl-N-p-vinylbenzylammonium chloride, N,N-diethyl-N-benzyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-(4-methyl)benzyl-N-p-vinylbenzylammonium chloride, N,N-dimethyl-N-phenyl-N-p-vinylbenzylammonium chloride; trimethyl-p-vinylbenzylammonium bromide, 10 15 trimethyl-m-vinylbenzylammonium bromide, trimethyl-p-vinylbenzylammonium sulfonate, trimethyl-m-vinylbenzylammonium sulfonate, trimethyl-p-vinylbenzylammonium acetate, trimethyl-m-vinylbenzylammonium acetate, N,N,N-triethyl-N-2-(4-vinylphenyl)ethylammonium chloride, N,N,N-triethyl-N-2-(3-vinylpheuyl)ethylammonium chloride, N,N-diethyl-N-methyl-N-2-(4-vinylphenyl)ethylammonium chloride, N,N-diethyl-N-methyl-N-2-(4-vinylphenyl)ethylammonium acetate; N,N-dimethylaminoethyl(meth)acrylate, 20 25 N,N-diethylaminoethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylamide, N,N-diethylaminoethyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, N,N-diethylaminopropyl(meth)acrylamide methyl chloride, ethyl chloride, methyl bromide, ethyl bromide, methyliodide or ethyliodide or ethyl iodide-derived, 30 anatomized substance or sulfonate, alkylsulfonate, acetate or alkyl

carboxylates thereof formed as a result of the substitution of its anion.

Preferred mordant monomers are monomethyldiallylammonium chloride, trimethyl-2-(methacryloyloxy)ethylammonium chloride, triethyl-2-(methacryloyloxy)ethylammonium chloride, trimethyl-2-

5 (acryloyloxy)ethylammonium chloride, triethyl-2-(acryloyloxy)ethylammonium chloride, trimethyl-3-(methacryloyloxy)propylammonium chloride, triethyl-3-(methacryloyloxy)propylammonium chloride, trimethyl-2-(methacryloylamino)ethylammonium chloride, triethyl-2-(methacryloylamino)ethylammonium chloride, trimethyl-2-

10 (acryloylamino)ethylammonium chloride, triethyl-2-(acryloylamino)ethylammonium chloride, trimethyl-3-(methacryloylamino)propylammonium chloride, triethyl-3-(methacryloylamino)propylammonium chloride, trimethyl-3-(acryloylamino)propylammonium chloride, triethyl-3-

15 (acryloylamino)propylammonium chloride, N,N-dimethyl-N-ethyl-2-(methacryloyloxy)ethylammonium chloride, N,N-diethyl-N-methyl-2-(methacryloyloxy)ethylammonium chloride, N,N-dimethyl-N-ethyl-3-(acryloylamino)propylammonium chloride, trimethyl-2-(methacryloyloxy)ethylammonium bromide, trimethyl-3-

20 (acryloylamino)propylammonium bromide, trimethyl-2-(methacryloyloxy)ethylammonium sulfonate, trimethyl-3-(acryloylamino)propylammonium acetate and the like. Copolymerizable monomers such as N-vinylimidazole and N-vinyl-2-methylimidazole may also be used.

25 Other suitable mordants are allylamine, diallylamine and derivatives or salts thereof. Suitable salts are for example, hydrochloride, acetate, sulfate and the like. Examples of these compounds include diallylmethylamine and its salt, diallylethylamine and its salt, diallyldimethylammonium salt (wherein the counteranion may *e.g.* be chloride, 30 acetate ion and sulfate ion) and the like. Any of these allylamine and

diallylamine derivatives is usually polymerized in the form of a salt because of its polymerizability in the form of an amine, which is generally too low. It may then be desaltsed after polymerization if necessary. It is also possible to use N-vinylacetamide or N-vinylformamide units which are subsequently hydrolyzed 5 to yield vinylamine units after polymerization, and salts of such units may also be employed.

A non-mordant monomer as described above is a monomer which does not contain a basic or cationic moiety such as a primary to tertiary amino group or its salt, or quaternary ammonium salt and which exhibits no or 10 substantially slight interaction with a dye contained in the ink jet printing ink. Such a non-mordant monomer may for example be alkyl (meth)acrylates; cycloalkyl (meth)acrylates such as cyclohexyl (meth)acrylate; aryl (meth)acrylates such as phenyl (meth)acrylate; aralkyl esters such as benzyl (meth)acrylate; aromatic vinyls such as styrene, vinyltoluene and alpha - 15 methylstyrene; vinyl esters such as vinyl acetate, vinyl propionate and vinyl versatate; allyl esters such as allyl acetate; halogen-containing monomers such as vinylidene chloride and vinyl chloride; olefins such as ethylene and propylene and the like. Such an alkyl (meth)acrylate is preferably an alkyl (meth)acrylate whose number of the carbon atoms in its alkyl moiety is 1 to 18, 20 such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate and the like. Among those listed above, methyl acrylate, ethylacrylate, methyl 25 methacrylate, ethyl methacrylate and hydroxyethyl methacrylate are preferred. Any of the non-mordant monomers listed above may be employed alone or in combination with each other.

A preferred polymeric mordant may be polydiallyldimethylammonium chloride, polymethacryloyloxyethyl beta 30 hydroxyethyl dimethylammonium chloride, polyethyleneimide, polyallylamine

and its derivative, polyamide-polyamine resin, cationized starch, dicyanediimide formalin condensate, dimethyl-2-hydroxypropylammonium salt polymerization product, polyamidine, polyvinylamine, dicyanediimide-formalin polymeric condensate and other dicyane-based cationic resins, 5 dicyaneamide-diethylenetriamine polymeric condensate and other polyamine-based cationic resins, epichlorohydrin-dimethylamine addition polymerization product, dimethyldiamineammonium chloride-SO<sub>2</sub> copolymerization product, diallylamine salt-SO<sub>2</sub> copolymerization product, (meth)acrylate-containing polymer having in its ester moiety a quaternary ammonium base-substituted 10 alkyl group, styryl polymer having a quaternary ammonium base-substituted alkyl group and the like.

Preferred organic mordants are polyamine or polyallylamine and its derivatives whose weight mean molecular weight is preferably 100 000 or less. A polyamine or its derivative may be any known amine polymer and its 15 derivative. Such a derivative may for example be a salt of a polyamine with an acid (acid may for example be an inorganic acid such as hydrochloric acid, sulfuric acid, phosphoric acid and nitric acid, an organic acid such as methanesulfonic acid, toluenesulfonic acid, acetic acid, propionic acid, cinnamic acid, (meth)acrylic acid and the like, a combination thereof, or those 20 in which a part of the amine is converted into a salt), a derivative of a polyamine obtained by a polymeric reaction, a copolymer of a polyamine with other copolymerizable monomers (such monomers may for example be (meth)acrylates, styrenes, (meth)acrylamides, acrylonitrile, vinyl esters and the like). Typically, the poly(allyl)amine and its derivative may for example be 25 the compounds described in JP-B-62-31722, JP-B-2-14364, JP-B-63-43402, JP-B-63-43403, JP-B-63-45721, JP-B-63-29881, JP-B-1-26362, JP-B-2-56365, JP-B-2-57084, JP-B-4-41686, JP-B-6-2780, JP-B-6-45649, JP-B-6-15592, JP-B-4-68622, Japanese Patent No.3199227, Japanese Patent No.3008369, JP-A-10-330427, JP-A-11-21321, JP-A-2000-281728, JP-A-2001-106736, JP-A-62-30 256801, JP-A-7-173286, JP-A-7-213897, JP-A-9-235318, JP-A-9-302026, JP-A-

11-21321, WO99/21901, WO99/19372, JP-A-5-140213, JP-W-11-506488 and the like.

It is also possible to employ an inorganic mordant as a mordant, including a polyvalent water-soluble metal salt or a hydrophobic metal salt 5 compound. Typically, the inorganic mordant may for example be a salt or complex of a metal selected from the group consisting of magnesium, aluminium, calcium, scandium, titanium, vanadium, manganese, iron, nickel, copper, zinc, gallium, germanium, strontium, yttrium, zirconium, molybdenum, indium, barium, lanthanum, cerium, praseodymium, 10 neodymium, samarium, europium, gadolinium, dysprosium, erbium, ytterbium, hafnium, tungsten and bismuth. Those exemplified typically are calcium acetate, calcium chloride, calcium formate, calcium sulfate, barium acetate, barium sulfate, barium phosphate, manganese chloride, manganese acetate, manganese formate dihydrate, ammonium manganese sulfate 15 hexahydrate, cupric chloride, copper (II) ammonium chloride dihydrate, copper sulfate, cobalt chloride, cobalt thiocyanate, cobalt sulfate, nickel sulfate hexahydrate, nickel chloride hexahydrate, nickel acetate tetrahydrate, ammonium nickel sulfate hexahydrate, nickel amidosulfate tetrahydrate, aluminium sulfate, aluminium alum, basic polyaluminium hydroxide, 20 aluminium sulfite, aluminium thiosulfate, polyaluminium chloride, aluminium nitrate nonahydrate, aluminium chloride hexahydrate, ferrous bromide, ferrous chloride, ferric chloride, ferrous sulfate, ferric sulfate, zinc phenolsulfonate, zinc bromide, zinc chloride, zinc nitrate hexahydrate, zinc sulfate, titanium tetrachloride, tetraisopropyl titanate, titanium 25 acetylacetone, titanium lactate, zirconium acetylacetone, zirconyl acetate, zirconium sulfate, ammonium zirconium carbonate, zirconyl stearate, zirconyl octylate, zirconyl nitrate, zirconium oxychloride, zirconium hydroxychloride, chromium acetate, chromium sulfate, magnesium chloride hexahydrate, magnesium citrate nonahydrate, sodium phosphorus tungstate, tungsten 30 sodium citrate, 12 tungstophosphoric acid n-hydrate, 12 tungstosilicic acid 26-

hydrate, molybdenum chloride, 12 molybdenophosphoric acid n-hydrate, gallium nitrate, germanium nitrate, strontium nitrate, yttrium acetate, yttrium chloride, yttrium nitrate, indium nitrate, lanthanum benzoate, cerium chloride, cerium sulfate, cerium octylate, praseodymium nitrate, neodymium nitrate, samarium nitrate, europium nitrate, gadolinium nitrate, dysprosium nitrate, erbium nitrate, ytterbium nitrate, hafnium nitrate, bismuth nitrate and the like. An inorganic mordant of the invention is preferably an aluminium-containing compound, titanium-containing compound, zirconium-containing compound, a compound of a metal in the series of Group IIIB in the periodic table (salt or complex). Certain multivalent metal ions are known to be flocculating agents; well known example are aluminum and iron(III) salts such as poly(aluminum chloride) and the sulfates of both ions. These compounds may also be applied as mordants. At high concentrations these compounds may flocculate in the presence of other compounds in aqueous solution but at lower concentrations application as a clear solution is possible.

The amount of mordant is preferably from 0.01 to 5 g/m<sup>2</sup>, more preferably from 0.1 to 3 g/m<sup>2</sup>.

If the mordant is a relatively small molecule the mordant or the mordant-colorant complex may diffuse within the layer or to other layers causing reduced sharpness. This problem is also referred to as long term bleeding. A very good method to prevent diffusion of the mordant molecule is to incorporate negative charges into the polymer matrix of the porous membrane. Preferably curable compounds bearing a negative charge are added to the curable composition. Examples of these negatively charged curable compounds are ethenically unsaturated compounds having sulfonic or carboxylic or phosphoric acid groups, or their metal (or ammonium) salts. Sulfonic acid derivatives are more preferred due to stronger binding with mordants. For example, (meth)acrylic acid-(sulfoalkyl)esters such as sulfopropyl acrylic acid and sulfopropyl methacrylic acid, (meth)acryl-(sulfoalkyl)amides such as 2-acryloylamido-2-methylpropane-1-sulfonic acid,

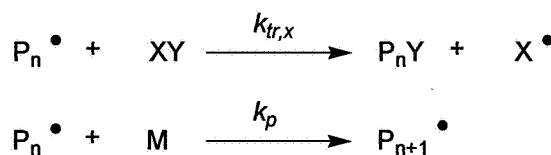
styrenesulfonic acid, itaconic acid-(alkylsulfonic acid)ester, itaconic acid-bis-(alkylsulfonic acid)ester, maleic acid-(alkylsulfonicacid)ester, maleic acid-bis-(alkylsulfonicacid)ester, alkylsulfonic acid allyl ether, mercapto compounds such as, mercaptoalkylsulfonic acid and their metal/ammonium salts.

5 When applied these negatively charged curable compounds are preferably added up to an amount of 30 wt.%, more preferably in an amount between 0.5 and 10 wt.% based on the weight of the curable compounds in the curable composition, most preferably between 1 and 5 wt.%. Better than by wt.% the introduced negative charges are expressed by equivalents since a 10 monomer molecule may contain more than one negatively charged group and the MW of monomers may very significantly. Preferably the porous membrane of the invention comprises up to 10 milli equivalents (meq) per m<sup>2</sup> with a minimum of 0.1 meq/m<sup>2</sup>, more preferably between 0.3 and 5 meq/m<sup>2</sup>, most preferably between 0.5 and 3 meq/m<sup>2</sup>. The negatively charged compounds may 15 be added to one composition or to the compositions for more than one layer.

Especially preferred are anionic curable compounds that comprise one or more functional thiol groups. These compounds then act as chain transfer agents which are known to be less sensitive to oxygen inhibition and have a remarkable effect on the structure of the membrane: the porosity is less 20 and the surface becomes smoother. Surprisingly the image density increases when chain transfer agents are applied, even in relatively low amounts. An additional advantage of the use of chain transfer agents is that the tackiness of the surface of the membrane after curing becomes less and the structure becomes more rigid. Examples include mercaptoacetic acid, mercaptopropionic 25 acid, alkyl mercaptopropionate, mercapto-propylsulfonate, ethyldithiocarbonato-S-sulfopropylester, dimercaptopropane sulfonate and mercaptobenzimidazole sulfonate.

Alternatively chain transfer agents that are non-ionic can be added in addition to or in stead of the negatively charged curable compounds to 30 obtain similar effects on structure and surface properties.

Chain transfer is a reaction in radical polymerization by which a radical center on a growing polymer chain is transferred to another molecule, in this case to a chain transfer agent. Chain transfer agents can be characterized by a so-called chain transfer constant which is defined as the 5 ratio of the chain transfer rate constant and the propagation rate constant. Thus the chain transfer constant is defined as  $C_x = k_{tr,x} / k_p$ , where  $k_{tr,x}$  and  $k_p$  are rate constants of the following reactions.



10 Where  $P_n \cdot$  and  $P_{n+1} \cdot$  are propagating polymer radicals, XY is a chain transfer agent (X, Y can be any atom or organic group) and M is a monomer.

Chain transfer agents can be characterized by a so-called chain transfer constant which is preferably larger than 0.1 with styrenes, methacrylates, or acrylates, for example styrene, methyl methacrylate, methyl 15 acrylate, ethyl acrylate, butyl acrylate and acrylonitrile, more preferably larger than 1.0. For transfer constants lower than 0.1 no or only very limited effects are achieved. Optimum quantities depend very much on the composition of the curable composition, on the type of the chain transfer agent (reactivity) and on the irradiation dose so the optimum concentration has to be 20 determined case by case. At high levels of chain transfer agents it was found that adhesion problems may occur if the compound is in the layer adjacent to the support. When a multilayer membrane is made the chain transfer agent is preferably in the toplayer where the effect on image density is expected to be the highest. Very high levels may retard the crosslinking reaction too much 25 resulting in a dense non-porous layer or even a layer that is still uncured. Preferably the chain transfer agent is present in an amount between 0.001 and 1.0 mmol/g curable compound. For most compounds the preferred range will be between 0.005 and 0.1 mmol/g curable compound. If the membrane consists of

more than one layer the mentioned range apply to the layer or layers comprising the chain transfer agent.

In accordance with the present invention, chain transfer agents may be used having a chain transfer constant for the reaction with a reference 5 compound of at least 0.1, preferably more than 1.0. These reference compounds are preferably selected from the group consisting of styrene, methyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate and acrylonitrile. The chain transfer constant of the chain transfer agent is preferably at least 0.1 for at least one of the reference compounds. More preferably it is at least 10 0.1 for more than one of the reference compounds, and even more preferably it is at least 0.1 for all of the reference compounds.

Chain transfer agents or classes of chain transfer agents are described for example in J. Brandrup, E. H. Immergut and E.A. Grulke, "Polymer Handbook" Fourth edition, 1999 (ISBN 0-471-48171-8), page II-97 – 15 II-168; P. Flory, "Principles of Polymer Chemistry", Cornell University Press (ISBN 0-8014-0134-8); and George Odian, "Principles of Polymerization", Fourth edition (2004), John Wiley & Sons (ISBN 0-471-27400-3).

Classes of compounds that comprise suitable substances are mercaptans, polymethacrylates, polyhalo alkanes, benzoquinones, oximes, 20 anthracenes, disulfides, sulfonyl chlorides, sulfoxides, phosphines, alkyl anilines, alkyl amines and metal compounds (such as aluminum, iron, cobalt, copper salts or complexes). Preferred compounds are mercaptoethanol, mercaptoethylether, mercaptobenzimidazole, ethyldithioacetate, butanethiol, dimethyldisulfide, tetrabromomethane, dimethylaniline, 25 ethylenedioxydiethanethiol and triethylamine.

A special class of chain transfer agents are so-called RAFT agents (RAFT = Reversible Addition-Fragmentation chain Transfer). These can also be suitably employed in the present invention. This RAFT reaction is a controlled radical polymerization and generally leads to very narrow molecular 30 weight distributions. Suitable RAFT agents comprise a dithioester group of the

formula  $R_1-C(=S)-S-R_2$ , a xanthate group of the formula  $R_1-O-C(=S)-S-R_2$  or a thioxanthate (trithiocarbonate) group of the formula  $R_1-S-C(=S)-S-R_2$ , a dithiocarbamate group of the formula  $R_1-NR-C(=S)-S-R_2$  where R,  $R_1$  and  $R_2$  are selected from an alkyl group, a cycloalkyl group, an aryl group, a 5 heterocyclic group or an arenyl group. Examples are ethyldithioacetate, benzyl dithiobenzoate, cumyl dithiobenzoate, benzyl 1-pyrrolecarbodithioate, cumyl 1-pyrrolecarbodithioate, o-ethyldithiocarbonato-S-(3-sulfopropyl) ester, N,N-dimethyl-S-thiobenzoylthiopropionamide, N,N-dimethyl-S-thiobenzoylthioacetamide, trithiocarbonates and dithiocarbamates.

10 For adequate colorant fixing properties it is important to have a surplus of positive charges that can bind the negatively charged colorant molecules. Preferably the ratio of negative charges present in the anionic curable compounds and positive charges present in the cationic compounds (e.g. mordants) is at least 1:1 and more preferably between 1:2 and 1:10.

15 Cationic mordants may coagulate with the negatively charged curable compounds if added to the curable composition. Therefore it is generally desirable not to add the mordants to the composition but to apply the mordants to the porous membrane after curing. This may be done by impregnation after partial drying or after complete drying. Impregnation can 20 be performed e.g. by coating or by spraying a solution onto the membrane or by dipping the membrane into a solution. Metering coating such as slide or slot coating is preferred. After drying a porous membrane remains wherein the mordant molecules are trapped at the site where the negative charges are build in into the matrix.

25 In a preferred embodiment (part of the) cationic mordants are not introduced after curing but are combined with anionic curable compounds in the curable composition. These anionic and cationic compounds form complexes in solution which surprisingly do not precipitate but remain in solution. Those complexes appear to have a better solubility in monomer 30 mixtures that have a limited compatibility with water. This limited

compatibility with water makes these monomer mixtures very suitable to initiate phase separation. The single ionic compounds are thought to be more hydrophilic due to their charge than the complexes in which the charges are shielded. Also a combination of both methods (introduction in the curable 5 composition and by impregnation) can be used. When after the membrane is made there is no surplus of positive charges or the surplus is insufficient to fix the dyes at high printing densities additional cationic compounds may be added in a subsequent step, e.g. by impregnation, after the membrane has been formed. So initially in the curable composition the ratio of negative 10 charges present in the anionic curable compounds and positive charges present in the cationic compounds may be larger than 1, e.g. 2:1. Preferably this ratio is reduced in a subsequent step as described above by introducing more cationic charges.

In general mordants are applied to fix the colorants (dyes) from ink. 15 Since at least three colours are used in a colour printer and there exist many brands of ink usually a combination of mordants is required to fix all colorants. Ideally such a mix of mordants is capable of fixing all existing dyes. Alternatively a medium is developed that is dedicated to certain types of ink by which a higher quality may be realized than with a medium suitable for all 20 types of ink.

Additives of different sorts may be brought into the porous membrane by impregnation. Preferably these additives are water soluble or may be dispersed or added as an emulsion. To maintain the porous character the total quantity of additives added should generally be lower than the total 25 pore volume of the membrane, in other words the pores should not be completely filled with additives. The pH of the impregnation solution preferably is comparable to the pH of the porous membrane or if necessary may be adjusted to obtain a clear solution. The impregnation solution may be applied in a wide range of concentrations depending on the type of additives. A 30 suitable concentration is between 1 and 20 wt.%, between 5 and 15 wt.% is

more preferred. The impregnation coating may constitute a single layer but may also be a multilayer. A multilayer is very suitable to direct one or more compounds to a desired region in the membrane. Compounds such as mordants and optical brighteners are preferably present in the top region of the

5 membrane; by impregnating the membrane by a multilayer wherein these compounds are present in the toplayer these compounds will be located near the surface of the membrane. The toplayer of the impregnation solution is preferably an aqueous solution and may comprise mordants, optical brighteners, surfactants, curable monomers, amine synergists, water soluble

10 polymers, transportability improving/ friction reducing agents, UV-absorbers, dye fading prevention agents (radical scavengers, light stabilisers, anti-oxidants), cross-linking agents and conventional additives such as pH regulators, viscosity regulators, biocides, organic solvents. The subsequent second curing fixates the membrane structure through which the final state is

15 obtained.

Also the non-curable water soluble polymer(s) mentioned above can be brought into the porous membrane by impregnation.

Other additives that may be added to one or more of the curable compositions or may be included by impregnation are UV absorbing agents, 20 brightening agents, anti-oxidants, light stabilising agents, radical scavengers, anti-blurring agents, antistatic agents and/or anionic, cationic, non-ionic, and/or amphoteric surfactants.

Suitable optical brighteners are disclosed in *e.g.* RD11125, RD9310, RD8727, RD8407, RD36544 and Ullmann's Encyclopedia of industrial 25 chemistry (Vol. A18 p153-167), and comprise thiophenes, stilbenes, triazines, imidazolones, pyrazolines, triazoles, bis(benzoxazoles), coumarins and acetylenes. Preferred optical brightening agents to be used in the invention are water-soluble and comprise compounds selected from the classes 30 distyrylbenzenes, distyrylbiphenyls, divinylstilbenes, diaminostilbenes, stilbenyl-2H-triazoles, diphenylpyrazolines, benzimidazoles and benzofurans.

In a preferred embodiment the optical brightening agents are cationic and are trapped by negative sites present in the matrix. An effective method of applying these agents is by impregnation as described above. The positively charged optical brightening agents are preferentially trapped in the top region 5 of the porous membrane where they have the most effect. Then lower amounts are sufficient compared with anionic agents that tend to diffuse through the complete layer of the membrane (or all layers in case of a multilayer membrane). Commercially available examples of suitable cationic optical brightening agents are Blankophor<sup>TM</sup> ACR (Bayer) and Leucophor<sup>TM</sup> FTS 10 (Clariant).

Whiteness is suitably expressed by the b-value of the CIELAB color model. CIE L\*a\*b (CIELAB) is a color model used conventionally to describe all the colors visible to the human eye. It was developed for this specific purpose by the International Commission on Illumination (*Commission Internationale d'Eclairage*, hence the *CIE* acronym in its name). The three 15 parameters in the model represent the luminance of the color (**L**, the smallest L represents black), its position between red and green (**a**, the smallest a represents green) and its position between yellow and blue (**b**, the smallest b represents blue). For very white membranes low b-values are preferred, values 20 between -5 and -8 indicate a very bright white appearance. Relatively high values (-4 and higher) indicate a more yellowish colour and are less preferred. Membranes with lower values (-8 and lower) tend to be bluish and are 25 generally less preferred. The amount of optical brightening agent is preferably lower than 1 g/m<sup>2</sup>; more preferably between 0.004 and 0.2 g/m<sup>2</sup>; most preferably between 0.01 and 0.1 g/m<sup>2</sup>.

Further the porous membrane may comprise one or more light stabilising agents such as sterically hindered phenols, sterically hindered amines, and compounds as disclosed in GB-A-2088777, RD 30805, RD 30362 and RD 31980. Especially suitable are water-soluble substituted piperidinium 30 compounds as disclosed in WO-A-02/55618 and compounds such as CGP-520

(Ciba Specialty Chemicals, Switzerland) and Chisorb 582-L (Double Bond Chemical, Taiwan). Other additives may be one or more plasticizers, such as (poly)alkylene glycol, glycerol ethers and polymer lattices with low Tg-value such as polyethylacrylate, polymethylacrylate and the like and one or more 5 conventional additives, such as described for example in EP-A-1 437 229 and EP-A-1 419 984, and in international patent applications WO-A-2005/032832, WO-A-2005/032834 and WO-A-2006/011800 such as acids, biocides, pH controllers, preservatives, viscosity modifiers c.q. stabilisers, dispersing agents, inhibitors, anti-blurring agents, antifoam agents, anti-curling agents, 10 water resistance-imparting agents and the like in accordance with the objects to be achieved.

The above-mentioned additives (UV absorbers, antioxidants, anti-blurring agents, plasticizers, conventional additives) may be selected from those known in the art and are preferably added in an amount of about 0.01 to 15 10 g/m<sup>2</sup>. Any of the components mentioned above may be employed alone or in combination with each other. They may be added after being solubilized in water, dispersed, polymer-dispersed, emulsified, converted into oil droplets, or may be encapsulated in microcapsules.

The porous membrane of the invention may be produced by the 20 following steps:

- providing at least one mixture of at least one epoxy acrylate compound and optionally other curable compounds in an aqueous solvent comprising at least 50% of water;
- applying said mixture to a support;
- curing said mixture by exposure to radiation of a suitable wavelength and intensity, thereby causing phase separation between the crosslinked curable compound(s) and the solvent;
- removing said solvent by drying and/or washing the resulting porous membrane;
- optionally separating the porous membrane from said support.

When high intensity UV light is applied for cross-linking the curable composition heat is generated by the UV lamp(s). In many systems cooling by air is applied to prevent the lamps from becoming overheated. Still a 5 significant dose of IR light is irradiated together with the UV-beam. In one embodiment the heating-up of the coated support is reduced by placing an IR reflecting quartz plate in between the UV lamp(s) and the coated layer that is guided underneath the lamp(s).

With this technique coating speeds of up to 200 m/min (3.33 m/s) or 10 even higher can be reached. To reach the desired dose more than one UV lamp in sequence may be required, so that the coated layer is successively exposed to more than one lamp. When two or more lamps are applied all lamps may give an equal dose or each lamp may have an individual setting. For instance the first lamp may give a higher dose than the second and following lamps or the 15 exposure intensity of the first lamp may be lower. Surprisingly at constant dose the relative intensities appeared to have subtle effects on the photopolymerisation reaction which influences the porosity and the structure. By varying the exposure conditions a person skilled in the art can determine optimum settings for the process depending on the properties one wishes to 20 achieve.

The invention can be carried out as a batch process with a stationary support surface, while obtaining full advantage of the invention. However, it is much preferred to practice the invention on a continuous basis using a moving support surface such as a roll-driven continuous web or belt. Using such 25 apparatus the curable composition can be made on a continuous basis or it can be made on a large batch basis, and the composition poured or otherwise applied continuously onto the upstream end of the driven continuous belt support surface, the irradiation source being located above the belt downstream of the composition application station and the membrane removal 30 station being further downstream of the belt, the membrane being removed in

the form of a continuous sheet thereof. Removal of the solvent from the membrane can be accomplished either before or after the membrane is taken from the belt. For this embodiment and all others where it is desired to remove the porous membrane from the support surface, it is, of course, preferable that 5 the support surface be such as to facilitate as much as possible the removal of the membrane therefrom. Typical of the support surfaces useful for the practice of such embodiments are smooth, stainless steel sheet or, better yet, teflon or teflon-coated metal sheet. Rather than using a continuous belt, the support surface can be of an expendable material, such as release paper or the 10 like (but not soluble in the solvent), in the form of a roll thereof such that it can be continuously unrolled from the roll, upstream of the solution application station, as a continuous driven length and then rerolled, with the porous membrane thereon, downstream of the radiation station.

It is also within the purview of the invention to form the thin layer 15 of solution as a coating on or intermingled with and supported by a porous sheet or fibrous web to which the resulting membrane remains bounded and which can function, for example, as a strengthening reinforcement or backing for the porous membrane. Such porous support surface of which the porous membrane is formed should, of course, be of a material which is insoluble in 20 the solvent used. Typical of the porous support surfaces which can be used for the practice of such embodiments are paper, woven and nonwoven fabric, and the like.

Embodiments are also recognized in which the porous material is not to be separated from a solid support, but in which the two bonded together 25 are the desired final product. Examples of such embodiments are polyester film supported porous membranes which are utilized in electrophoretic separations, membranes attached to a transparent or opaque sheet to be used as recording media for images and the like.

As the support, any of a transparent support composed of a transparent material such as a plastic, and an opaque support composed of an opaque material such as a paper can be used. For most membrane applications the support – if present – must be porous to allow the passing of fluids or 5 gasses. These porous supports can be paper, woven and nonwoven fabric. Examples of nonwoven fabric are materials based on cellulose, polyamide, polyester, polypropylene and the like.

As a material which can be used in the transparent support for recording media, materials which are transparent and have the nature of 10 enduring the radiated heat upon use in Overhead Projection (OHP) and back light display are preferred. Examples of these materials include polyesters such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), triacetate cellulose (TAC), polysulfone, polyphenylene oxide, polyethylene, polypropylene, polyvinylchloride, polyimide, polycarbonate, polyamide and the 15 like. Other materials that may be used as support are glass, polyacrylate and the like. *Inter alia*, polyesters are preferable, and polyethylene terephthalate is particularly preferable.

The thickness of the transparent support is not particularly limited, however 50 to 200  $\mu\text{m}$  is preferable from the viewpoint of the final products 20 handling properties.

As an opaque support having high gloss, a support with the surface on which a colorant receiving layer is provided, having a gloss of at least 5% - preferably 15% or larger – is preferable. The gloss is a value that can for instance be obtained by measuring the specular surface gloss of the support at 25 75° (TAPPI T480).

Embodiments include paper supports having high gloss such as resin coated (RC) paper, baryta paper which are used in art paper, coated paper, cast coated paper, supports as used for silver salt photographic paper and the like; films having high gloss by making opaque plastic films such as 30 polyesters, such as polyethylene terephthalate (PET), cellulose esters such as

nitrocellulose, cellulose acetate, cellulose acetate butyrate, polysulfone, polyphenylene oxide, polyimide, polycarbonate, polyamide and the like (which may have the surface subjected to calender treatment), by containing of a white pigment or the like; or supports in which a covering layer of polyolefin 5 containing or not containing a white pigment is provided on the surface of the aforementioned various paper supports, the aforementioned transparent support or films containing a white pigment or the like. An example of a suitable embodiment includes a white pigment-containing expanded polyester film (e.g. expanded PET which contains polyolefin fine particles and in which a 10 void is formed by stretching).

The thickness of the opaque support is not particularly limited, however 50 to 300  $\mu\text{m}$  is preferable from the viewpoint of the final products handling properties.

As already mentioned an important characteristic of a recording 15 medium is the gloss. The gloss is preferably larger than 20% at 20°, more preferably larger than 30% as measured by a Dr. Lange Refo 3-D reflectometer. It has been found that the gloss of the medium can be improved by selecting the appropriate surface roughness of the used support. It was found, that providing a support having a surface roughness characterised by 20 the value Ra being less than 1.0  $\mu\text{m}$ , preferably below 0.8  $\mu\text{m}$  a very glossy medium can be obtained. A low value of the Ra indicates a smooth surface. The Ra is measured according to DIN 4776 using a UBM equipment, software package version 1.62, with the following settings:

(1) Point density 500 P/mm, (2) Area  $5.6 \times 4.0 \text{ mm}^2$ , (3) Cut-off wavelength 0.80 25 mm, (4) Speed 0.5 mm/sec.

In case paper is used as the support for the present invention the paper is selected from materials conventionally used in high quality printing paper. Generally it is based on natural wood pulp and if desired, a filler such as talc, calcium carbonate,  $\text{TiO}_2$ ,  $\text{BaSO}_4$ , and the like can be added. Generally 30 the paper also contains internal sizing agents, such as alkyl ketene dimer,

higher fatty acids, paraffin wax, alkenylsuccinic acid, such as kymene, epichlorhydrin fatty acid amid and the like. Further the paper may contain wet and dry strength agents such as a polyamine, a poly-amide, polyacrylamide, poly-epichlorohydrin or starch and the like. Further additives 5 in the paper can be fixing agents, such as aluminium sulphate, starch, cationic polymers and the like. The Ra value for a normal grade base paper is usually below 2.0  $\mu\text{m}$  and may typically have values between 1.0 and 1.5  $\mu\text{m}$ . The porous layer of the present invention or layers of which at least one comprises the porous layer of this invention can be directly applied to this base paper.

10 In order to obtain a base paper with a Ra value below 1.0  $\mu\text{m}$  such a normal grade base paper can be coated with a pigment. Any pigment can be used. Examples of pigments are calcium-carbonate,  $\text{TiO}_2$ ,  $\text{BaSO}_4$ , clay, such as kaolin, styrene-acrylic copolymer, Mg-Al-silicate, and the like or combinations thereof. The amount being between 0.5 and 35.0  $\text{g/m}^2$  more preferably between 15 2.0 and 25.0  $\text{g/m}^2$ . The paper can be coated on one side or on both sides. The amount mentioned before is the amount coated on one side. If both sides are coated the total amount preferably is between 4.0 and 50  $\text{g/m}^2$ . This pigmented coating can be applied as a pigment slurry in water together with suitable binders like styrene-butadiene latex, styrene-acrylate latex, methyl 20 methacrylate-butadiene latex, polyvinyl alcohol, modified starch, polyacrylate latex or combinations thereof, by any technique known in the art, like dip coating, roll coating, blade coating, bar coating, size press or film press. The pigment coated base paper may optionally be calendered. The surface roughness can be influenced by the kind of pigment used and by a combination 25 of pigment and calendering. The base pigment coated paper substrate has preferably a surface roughness between 0.4 and 0.8  $\mu\text{m}$ . If the surface roughness is further reduced by super calendering to values below 0.4  $\mu\text{m}$  the thickness and stiffness values will in general become rather low.

The porous layer or layers of which at least one comprises the porous layer of this invention, can be directly applied to the pigment coated base paper.

In another embodiment, the pigment coated base paper having a 5 pigmented top side and a back-side is provided on at least the topside with a polymer resin through high temperature co-extrusion giving a laminated pigment coated base paper. Typically temperatures in this (co-) extrusion method are above 280 °C but below 350 °C. The preferred polymers used are poly olefins, particularly polyethylene. In a preferred embodiment the polymer 10 resin of the top side comprises compounds such as an opacifying white pigment e.g. TiO<sub>2</sub> (anatase or rutile), ZnO or ZnS, dyes, colored pigments, including blueing agents, e.g. ultramarine or cobalt blue, adhesion promoters, optical brighteners, antioxidant and the like to improve the whiteness of the laminated pigment coated base paper. By using other than white pigments a 15 variety of colors of the laminated pigment coated base paper can be obtained. The total weight of the laminated pigment coated base paper is preferably between 80 and 350 g/m<sup>2</sup>. The laminated pigment coated base paper shows a very good smoothness, which after applying the porous layer or layers comprising the porous layer or layers of the present invention results in a 20 recording medium with excellent gloss.

On the other hand, depending on the product one wants to make a polyethylene-coated paper can be used with a matt surface or silky surface such as is well known in the art. Such a surface is obtained by conducting an embossing treatment upon extruding a polyethylene on a paper substrate.

25 As is evident from the description given above, the recording media comprising the porous layer of this invention can be a single layer or a multi-layer applied onto a support. It can also comprise layers, which are non porous and are located below the porous layer.

The media including the inventive porous layer or layers, can be coated in one single step or in successive steps as long as the preferred pore sizes, and porosity is obtained.

As a coating method, any method can be used. For example, curtain 5 coating, extrusion coating, air-knife coating, slide coating, roll coating method, reverse roll coating, dip coating, rod bar coating. This coating can be done simultaneously or consecutively, depending on the embodiments used. In order to produce a sufficiently flowable composition for use in a high speed coating machine, it is preferred that the viscosity should not exceed 4,000 mPa.s at 25 10 °C, more preferably that it should not exceed 1,000 mPa.s at 25 °C.

Before applying the coating to the surface of the support material described above this support may be subjected to a corona discharge treatment, glow discharge treatment, flame treatment, ultraviolet light irradiation treatment and the like, for the purpose of improving the wettability 15 and the adhesiveness.

If desired, *e.g.* for improving curling or blocking behaviour or transportability properties in printing machines, one or more coating layers may be applied onto the backside of the support, *i.e.* the side opposite to the side to which the porous membrane is adhered. These backside coating layers 20 may contain polymeric binders and particles or beads and may be composed in such a way that a desired level of smoothness and gloss is obtained. When used as recording media the membranes of the present invention can be used for a multitude of recording applications so it is within the scope of the present invention to provide recording media that are suitable for creating high quality 25 images by using techniques as for example Giclée printing, color copying, screen printing, gravure, dye-sublimation, flexography, ink jet and the like.

Except for application in (inkjet) recording media, the porous membranes find use in variety of other applications, such as in membranes for water treatment, in the chemical and petrochemical industry, for ultra 30 filtration processes in the electrocoating of paint, in the food industry such as

in the production process of cheese, clarification of fruit juice and in beer production, in the pharmaceutical industry where a high resistivity membrane for organic solvents is required, and in the biotechnology industry especially where flux reduction due to fouling by protein needs to be avoided. The 5 membrane can be made suitable for nanofiltration or reversed osmosis by selecting appropriate ingredients and process conditions. The hydrophilic character of the porous membrane according to this invention may result in a significant reduction of the fouling rate of the membrane and makes it suitable for all kind of other application where conventional micro- and ultra filtration 10 is applied.

The present invention will be illustrated in more detail by the following non-limiting examples. Unless stated otherwise, all given ratios and amounts are based on weight.

15 Examples

Curable compositions are prepared containing 7.5 g compound, 0.2 g photo-initiator (Irgacure<sup>TM</sup> 2959, supplied by CIBA Specialty Chemicals) and 12.3 g solvent mixture as specified in table 1. Total weight of the composition 20 is 20 g.

The curable compositions were coated as a single layer using a bar coater on a transparent substrate (cellulose triacetate film) resulting in a layer with a wet thickness of about 40 µm. The coated sheet was placed in a box covered with a transparent UV translucent polypropylene foil to protect the 25 coated sheet from the cooling air flow from the lamp. The coated sheet was fed underneath a UV-light emitting lamp (Light Hammer<sup>TM</sup> 6 fitted in a bench-top conveyer LC6E, both supplied by Fusion UV) at a speed of 24 m/min (0.4 m/s) at a power level of 80%. The time between coating and curing was kept within 30 sec. After curing the coated sheet was dried at 60 °C for 20 minutes.

Table 1: The occurrence of phase separation depending on curable compound

Example	curable compound	PW (g)	IPA (g)	Curing solution	miscibility with water* (wt%)	phase separation after curing
1A	CN132	10.5	1.8	Homogeneous	45.5	yes
1B	CN133	7.3	5.0	Homogeneous	13.8	yes
1C	G-epoxy-DA	7.7	4.6	Homogeneous	15.0	yes
1D	PG-epoxy-DA	8.6	3.7	Homogeneous	12.8	yes
1E	TPG-epoxy-DA	7.8	4.5	Homogeneous	15.7	yes
1F ref	TPG-DA	6.3	6.0	Homogeneous	2.4	no
1G ref	PPG-540-DA	5.1	7.2	Homogeneous	2.6	no
1H ref	PPG-900-DA	5.0	7.3	Homogeneous	2.8	no
1I ref	BPA-PO-epoxy-DA	5.0	7.3	Homogeneous	<2	yes
1J ref	BPA-PO-epoxy-DA	6.1	6.2	Heterogeneous	<2	yes
1K ref	BPA-epoxy-DA	5.0	7.3	Heterogeneous	<2	yes
1L ref	BPA-epoxy-DA	6.1	6.2	Heterogeneous	<2	yes

\* The values given are the maximum amount of water that is miscible with the curable compound (weight percentage) at 25°C yielding a clear solution.

CN-132 is an aliphatic epoxy acrylate monomer supplied by Cray Valley, France.

CN-133 is a trifunctional aliphatic epoxy acrylate monomer supplied by Cray Valley, France.

5 G-epoxy-DA is glycerol-1,3-diglycerolate diacrylate supplied by Aldrich.

PG-epoxy-DA is propylene glycol glycerolate diacrylate supplied by Aldrich.

10 TPG-epoxy-DA is tri(propylene glycol) glycerolate diacrylate supplied by Aldrich.

TPG-DA is tri(propylene glycol) diacrylate supplied by Aldrich.

PPG-540-DA and PPG-900-DA are poly(propylene glycol) diacrylates with a MW of respectively 540 and 900, supplied by Aldrich.

15 BPA-PO-epoxy-DA is Bisphenol A propoxylate glycerolate diacrylate, supplied by Aldrich.

BPA-epoxy-DA is Bisphenol A glycerolate (1 glycerol/phenol) diacrylate, supplied by Aldrich.

Isopropanol (IPA) is supplied by Shell.

20 The ratio of PW and IPA is chosen so as to obtain a clear solution, whereby the amount of IPA used is as small as possible (for samples 1A to 1I). The formation of a porous membrane is characterized by the occurrence of phase separation upon irradiation of the curable composition by UV light. As a result a white opaque layer is formed. For the references 1F, 1G and 1H no porous membrane is formed, probably because the formed polymer is still 25 compatible with the solvent mixture resulting in a transparent film. The reaction is too slow to initiate coagulation. For reference 1I which is an epoxy acrylate and is highly reactive, phase separation does occur, but a large amount of IPA (>50%) is required to obtain a clear solution. Reference 1J indicates that a water/IPA ratio of about 1:1 is not capable of dissolving BPA-

PO-epoxy-DA, while BPA-epoxy-DA does not dissolve in both tested solvents (ref. 1K and 1L).

Several epoxy acrylates are tested in a system with 2 curable monomers. The composition comprises 7.5 g curable compounds (4.5 g epoxy acrylate and 3.0 g CN-435), 0.1 g photo-initiator (Irgacure<sup>TM</sup> 2959) and 12.4 g solvent mixture as specified in table 2. Total weight of the composition is 20 g. CN435 is an ethoxylated trimethylolpropane triacrylate, supplied by Cray Valley.

10

Table 2: The occurrence of phase separation depending on curable compound for a mixture of curable compounds

Example	epoxy acrylate	PW (g)	IPA (g)	phase separation
2A	CN132	9.9	2.5	yes
2B	TPG-epoxy-DA	8.4	4.0	yes
2C	PG-epoxy-DA	8.9	3.5	yes
2D ref	TPG-DA	4.9	7.5	no
2E ref	PPG-540-DA	4.9	7.5	no

15

Also for these compositions the minimum amount of IPA was chosen for which a clear solution is obtained. The curable solutions were coated by the method described for the first experiment. Again only the compositions containing epoxy acrylates show phase separation upon irradiation with UV light indicative for the formation of a porous membrane.

20

In the third experiment the amount of epoxy acrylate was varied while keeping the total amount of curable compound constant at 7.5 g. As second curable monomer CN435 was chosen. In this experiment low amounts of epoxy acrylate were tested and since CN435 is well soluble in water there was no need to add co-solvents. So the composition contained 12.4 g of water as solvent and 0.1 g of Irgacure<sup>TM</sup> 2959 as photo-initiator. Total weight of the composition is 20 g. The curable solutions were coated by the method described

for the first experiment. Purpose is to determine the quantity of epoxy acrylate needed to obtain a porous membrane.

5 Table 3: The occurrence of phase separation depending on the amount of epoxy acrylate

Example	epoxy acrylate	quantity (g)	CN435 (g)	phase separation
3A ref	none	0	7.5	no
3B	CN132	0.1	7.4	yes
3C	CN132	0.2	7.3	yes
3D	CN132	0.5	7.0	yes
3E	CN132	1.0	6.5	yes
3F	TPG-epoxy-DA	0.2	7.3	yes
3G	TPG-epoxy-DA	0.5	7.0	yes
3H	TPG-epoxy-DA	1.0	6.5	yes
3I	PG-epoxy-DA	0.2	7.3	yes
3J	PG-epoxy-DA	0.5	7.0	yes
3K	PG-epoxy-DA	1.0	6.5	yes

When only CN435 is present no porous membrane is formed.

Already with 0.1 g (1.3 wt% of total amount of monomers) of CN132 phase separation occurs and a porous membrane is formed. In general 0.2 g of epoxy acrylate is sufficient. Depending on desired properties several curable compounds of which at least one is an epoxy acrylate can be combined in a curable composition to form a porous membrane of the invention.

15 By making a porous membrane adhered to a support two inkjet recording media are prepared (examples 4A and 4B). Both examples are two layer constructs and comprise CN132 as epoxy acrylate. Example 4B has one additional compound versus example 4A which affects the optical density, but

both examples show that the membrane is very suitable as an inkjet recording medium.

Table 4: composition for a 2-layer membrane

Ingredient	bottom layer (g)	toplayer (g)
CN132	22.07	20.65
CN435	14.48	14.48
isopropanol (IPA)	9.00	9.85
KIP100F (20% solution in IPA)	0.96	
Irgacure™ 2959		0.29
Orgasol™ 10 solution		1.56
Zonyl™ FSN (3 wt.%)		7.31
Water	53.50	46.89

5 Esacure™ KIP 100F is a photo-initiator supplied by Lamberti Spa.

Orgasol™ 10 solution is a mixture containing Orgasol™ 10 (10 gram), CN132 (608.55 gram) and IPA (227.62 gram); Orgasol™ 10 is supplied by Arkema.

Zonyl™ FSN is a fluoro-surfactant supplied by DuPont.

10

Both layers were coated simultaneously with a slide bead coater with the following conditions and subsequently cured by UV irradiation:

flow for the bottom layer = 37.5 cc/m<sup>2</sup> ; (cc is 10<sup>-6</sup> m<sup>3</sup>)

flow for the toplayer = 22.5 cc/m<sup>2</sup>

15

coating speed 30 m/min (0.5 m/s)

UV lamp (model Light Hammer™, H-bulb, Fusion UV Systems), power level 80%.

coating/curing conditions: 25 °C, 5 % RH

Drying at 40°C, 8% RH for 2 minutes

20

Evaluation

The samples were printed by using a HP325 printer (with the settings paper: HP photo Paper and print quality: best) and black density was measured 3-4 hours after printing by a X-Rite™ DTP41 spectrophotometer.

5

Table 5: optical black density of the porous membrane after printing thereon

Example	additive to the top layer	gram	optical black density
4A	none	-	1.58
4B	MPS	1.51	1.85

MPS is 3-Mercaptopropane sulfonic acid, sodium salt, supplied by Raschig.

Claims

1. Porous membrane obtainable by polymerizing a curable composition comprising at least one type of epoxyacrylate monomer soluble in an aqueous solvent wherein at least 50 wt% of said solvent is water.
2. Porous membrane according to claim 1 wherein the miscibility of water with said epoxyacrylate monomer at 25 °C is between 4 weight% and 50 weight%.
3. Porous membrane according to any of the previous claims, wherein the porosity of said membrane is between 5 and 90 %.
4. Porous membrane according to any of the previous claims, wherein the diameter of a substantial amount of the pores is between 0.0001 and 2.0  $\mu\text{m}$ .
5. Porous membrane according to any of the previous claims wherein said epoxyacrylate monomer comprises at least one C<sub>2</sub>-C<sub>4</sub> alkoxy group.
6. Porous membrane according to any of the previous claims wherein said epoxyacrylate monomer has at least two acrylate groups.
7. Porous membrane according to any of the previous claims wherein the amount of said epoxyacrylate monomer is from 1 to 100% based on the total amount of curable compounds.
8. Porous membrane according to any of the previous claims wherein the solvent comprises one or more organic co-solvents.
9. Porous membrane according to any of the previous claims wherein the membrane further comprises a surfactant and a photo-initiator.
10. Porous membrane according to any of the previous claims wherein said membrane comprises a polyether modified polysiloxane derivative.
- 25 11. Porous membrane according to any of the previous claims wherein the swellability of said membrane in water is between 5 and 100% based on the dry thickness of said membrane.

12. Porous membrane according to any of the previous claims wherein said membrane comprises at least two layers.
13. Porous membrane according to any of the previous claims wherein said porous membrane is essentially free from inorganic or organic particles 5 that are capable of absorbing aqueous solvents.
14. Process for preparing a porous membrane comprising the steps of:
  - providing at least one mixture of at least one epoxy acrylate compound and optionally other curable compounds in an aqueous solvent comprising at least 50% of water;
  - 10 • applying said mixture to a support;
  - curing said mixture by exposure to radiation of a suitable wavelength and intensity, thereby causing phase separation between the crosslinked curable compound(s) and the solvent;
  - removing said solvent by drying and/or washing the resulting porous 15 membrane;
  - optionally separating the porous membrane from said support.
15. Recording medium comprising a support and the porous membrane according to any of the previous claims.
16. Medium according to claim 15 wherein said support is a transparent 20 support suitable for back-lit applications and is selected from the group consisting of polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polysulfone, polyphenylene oxide, polyimide, polycarbonate and polyamide.
17. Medium according to claim 15, wherein said support is a reflective 25 support and is selected from the group consisting of a paper support, a plastic film and a support in which a covering layer of polyolefin optionally containing a white pigment is provided.
18. Use of a medium according to any of the claims 15-17 for printing images or characters thereon, using Giclée printing, colour copying, screen 30 printing, gravure, dye-sublimation, flexography, and/or ink jet printing.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/NL2007/050388

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. B41M5/52 B41M5/50 B01D67/00 B01D71/40

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)  
B41M B42D B01D

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

Electronic data base consulted during the international search (name of data base and, where practical, 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	US 4 466 931 A (G.B.TANNY) 21 August 1984 (1984-08-21) cited in the application column 2, line 36 - line 45 column 2, line 43 column 3, line 16 - line 53 column 4, line 12 - line 22 column 7, line 28 - line 39 column 8, line 25 - line 50 claims 1-7 -----	1-18
P, X	WO 2006/101390 A (FUJI PHOTO FILM COMPANY LIMITED) 28 September 2006 (2006-09-28) cited in the application page 1, line 3 - line 6 page 7, line 14 - page 8, line 3 page 9, line 3 - line 19 page 30, line 21 - page 35, line 27 claims 1-13 -----	1-18



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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- \*E\* earlier document but published on or after the international filing date
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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
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- \*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 October 2007	16/10/2007
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  Bacon, Alan

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No  
PCT/NL2007/050388

Patent document cited in search report	Publication date		Patent family member(s)		Publication date
US 4466931	A	21-08-1984	CA 1231318 A1 DE 3325412 A1 FR 2531440 A1 GB 2124973 A JP 59062648 A JP 63065220 B		12-01-1988 09-02-1984 10-02-1984 29-02-1984 10-04-1984 15-12-1988
WO 2006101390	A	28-09-2006	NONE		