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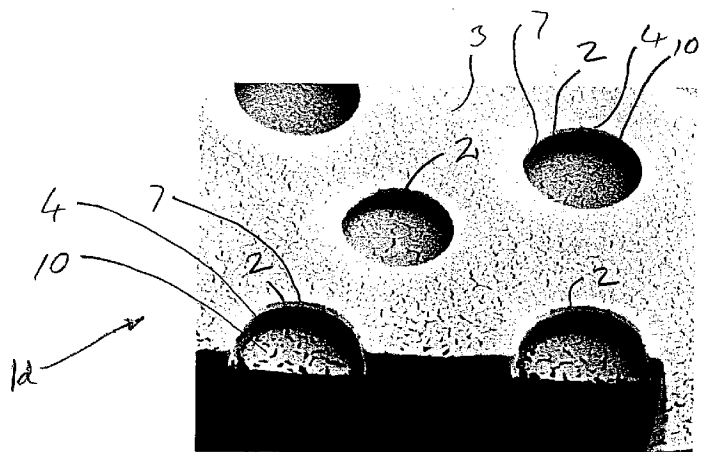
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(54) Title: A METHOD FOR PRODUCING A POLYMER FILM WITH AN ARRAY OF CAVITIES THEREIN



(a) FIG 6

(57) Abstract: A method for producing an array of cavities (2) in a polymer film (1) comprises preparing a polymer/solvent solution and drop casting a thin film (6) of the solution on a substrate. The film solution (6) is subjected to three gas flows. An initial gas flow of a relatively low relative humidity is passed over the film solution (6) to evaporate solvent from the polymer/solvent solution (6) to reduce the surface temperature of the film solution (6) below the dew point temperature of the next gas flow, namely, an intermediate gas flow. The intermediate gas flow of relatively high relative humidity forms droplets on the surface of the film solution (6) which grow into the film solution to form the cavities (2) therein. A final gas flow evaporates droplets from the formed cavities (6) as well as further solvent from the film solution (6), but maintains the level of solvent in the film solution (6) at a level, when the droplets have been evaporated to the extent that they no longer influence the formation of the cavities (2), so that the glass transition temperature of the polymer/film solution adjacent

the cavities (2) is below the temperature of the film solution (6) in order to permit local polymer flow adjacent the cavities (2) to determine the final shape of the cavities (2).

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“A method for producing a polymer film with an array of cavities therein”

The present invention relates to a method for producing a polymer film with an array of cavities therein, and to a polymer film produced by the method.

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Films comprising arrays of cavities of micron and sub-micron size are required in many fields of technology, for example, in photonics, in microfluidics and other technological fields where cavities of micron and sub-micron sizes are required. For example, films comprising cylindrical cavities of micron and sub-micron sizes are used as photonic light delays and filters, as are spherical cavities and cavities of other shapes. In general, in the field of photonics, such films comprising cavities of micron and sub-micron sizes are formed of silicon, glass, quartz and the like, and the cavities are formed using reactive ion etching, electrochemical processes and electron beam lithography. The cavities thus formed are then coated or functionalised as required. While these methods do result in the formation of micron and sub-micron size cavities, the initial capital investment and the running costs of apparatus for carrying out such processes in silicon, glass and quartz are relatively high, and the processes are relatively labour intensive and time consuming.

20 Methods for producing a polymer film comprising arrays of micron and sub-micron cavities are known. In general, such methods are known for producing cavities of spherical or cylindrical shape. However, in general, where cavities are required of shapes other than spherical, the formation of such cavities in a polymer film is problematical. For example, in the formation of cylindrical cavities in a polymer film, the base of such cylindrical cavities, in general, when formed using known methods, is of concave shape when viewed into the cavity through an open mouth of the cavity. This is undesirable, since in many applications a cylindrical cavity comprising a flat base is more desirable. Additionally, in such known methods it is relatively difficult to form cavities of shapes other than spherical and cylindrical in a polymer film. This, thus, limits the use of such processes.

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In U.S. published Patent Application Specification No. 2003/0106487 of Wen-Chiang

Huang, a method is disclosed for producing a photonic crystal material which requires initially producing a porous template of polymer material. In the method of Huang a polymer, an oligomer or a non-polymeric organic substance is dissolved in a volatile solvent to form an evaporative solution. A film of the solution is deposited
5 on a substrate, and a moisture containing gas is passed over the film solution in order to evaporate the solvent. Moisture in the gas condenses on the surface of the film solution to form water droplets in an ordered array, which in turn sink into the film solution to form spherical water filled voids. When the solvent has been fully evaporated, water in the spherical voids is then evaporated thereby producing a thin
10 polymer with ordered arrays of spherical micron cavities. Other prior art documents which disclose methods for producing micron and sub-micron cavities in a polymer film are published PCT Application Specification No. WO 2009/069110, U.S. Published Patent Application Specification No. 2003/0129311, U.S. Published Patent Application Specification No. 2004/0138323, U.S. Published Patent Application
15 Specification No.2002/0143073, PCT Published Application Specification No. WO 2007/086421, PCT Published Application Specification Application No. WO 2006/112358, Chinese Patent Abstract No. CN1676204 and Chinese Patent Abstract No. CN1511874. However, none of these documents disclose a method for forming a cavity in a polymer film where the formation of the base and/or the final
20 shape of the cavity can be relatively accurately controlled.

There is therefore a need for a method for producing a polymer film comprising an array of cavities which addresses at least some of the problems of prior art methods.

25 The present invention is directed towards providing such a method, and the invention is also directed towards providing a polymer film comprising an array of cavities.

According to the invention there is provided a method for producing a polymer film
30 with an array of cavities therein, the method comprising forming a film of a polymer/solvent solution on a substrate, subjecting the film solution to a first environment adjacent a gas/film interface of the film solution, the first environment

being adapted to accelerate solvent evaporation from the film solution through the gas/film interface of the film solution to establish a polymer concentration gradient in the film solution with the polymer concentration decreasing in a direction into the film solution from the gas/film interface so that the polymer concentration gradient is
5 suitable for facilitating growth of liquid droplets into the film solution through the gas/film interface, subjecting the film solution to a second environment adjacent the gas/film interface thereof on establishment of the polymer concentration gradient, the second environment being adapted to condense a liquid on the gas/film interface surface to form droplets of the liquid thereon with the droplets growing into the film
10 solution through the gas/film interface to form the cavities, and subjecting the film solution adjacent the gas/film interface thereof to a third environment adapted to inhibit further droplet growth and to evaporate the droplets from the cavities, the third environment being further adapted to control the rate of evaporation of the solvent from the polymer/solvent solution, so that when the liquid of the droplets is
15 evaporated to an extent that the droplets no longer solely determine the shape and size of the cavities, the level of the solvent remaining in the polymer/solvent solution is sufficient to maintain the glass transition temperature of the film solution at a level below the temperature of the film solution adjacent the cavities to permit local polymer flow adjacent the cavities for determining the shape of the cavities.

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The glass transition temperature of a polymer or other material is the temperature at which the material loses its glass-like, more rigid properties and becomes rubbery and more flexible in nature.

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In one embodiment of the invention the rate of evaporation of the solvent from the film solution is controlled by the third environment so that when the droplets no longer solely determine the shape and size of the cavities, the level of the solvent remaining in the film solution is sufficient to maintain the glass transition temperature of the film solution adjacent the bases of the cavities below the actual temperature of
30 the film solution adjacent the bases of the cavities.

In another embodiment of the invention the film solution is subjected to the third

environment until substantially all of the solvent is evaporated from the polymer/solvent solution of the film solution.

5 In a further embodiment of the invention the film solution is subjected to the third environment when the cavities formed by the droplets extend into the film solution to a predefined depth.

10 In a still further embodiment of the invention the film solution is subjected to the third environment when the cavities formed by the droplets are of a predefined size.

Preferably, the third environment is of relative humidity which is adapted to control the vapour-liquid equilibrium adjacent the droplet interface with the third environment for evaporation of the droplets. Advantageously, the relative humidity of the third environment is lower than the relative humidity of the second environment.

15 Preferably, the relative humidity of the third environment does not exceed the relative humidity of the first environment. Advantageously, the relative humidity of the third environment is similar to or lower than the relative humidity of the first environment.

20 In one embodiment of the invention the third environment comprises a gaseous medium of relative humidity lying in the range of 0% to 50%. Preferably, the relative humidity of the gaseous medium of the third environment lies in the range of 0% to 20%. Advantageously, the relative humidity of the gaseous medium of the third environment lies in the range of 0% to 10%.

25 In another embodiment of the invention the gaseous medium of the third environment is passed over the gas/film interface of the film solution as a final gas flow during the period during which the film solution is subjected to the third environment. Preferably, the velocity of the gaseous medium of the final gas flow adjacent the gas/film interface lies in the range of 0 metres per second to 0.4 metres per second. Advantageously, the velocity of the gaseous medium of the final gas flow adjacent the gas/film interface lies in the range of 0.03 metres per second to

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0.29 metres per second. Ideally, the velocity of the gaseous medium of the final gas flow adjacent the gas/film interface is approximately 0.06 metres per second.

5 In one embodiment of the invention the gaseous medium of the third environment comprises nitrogen. Preferably, water vapour is entrained in the gaseous medium of the third environment to produce the third environment to be of the appropriate relative humidity.

10 In one embodiment of the invention the first environment is adapted to control evaporation of the solvent from the film solution to produce a surface temperature at the gas/film interface to facilitate formation of the droplets thereon when the film solution is subjected to the second environment.

15 In another embodiment of the invention the first environment is adapted to control evaporation of the solvent from the film solution to produce a surface temperature at the gas/film interface of the film solution not greater than the dew point temperature of the second environment when the film solution is subjected to the second environment, and preferably, below the dew point temperature of the second environment.

20

In another embodiment of the invention the relative humidity of the first environment is controlled to be below a value at which liquid would condense out of the first environment onto the gas/film interface of the film solution. Preferably, the first environment comprises a gaseous medium of relative humidity lying in the range of 25 0% to 85%. Advantageously, the relative humidity of the gaseous medium of the first environment lies in the range of 0% to 45%. Ideally, the relative humidity of the gaseous medium of the first environment lies in the range of 0% to 5%.

30 In another embodiment of the invention the gaseous medium of the first environment is passed over the gas/film interface of the film solution as an initial gas flow during the period during which the film solution is subjected to the first environment. Preferably, the velocity of the gaseous medium of the initial gas flow adjacent the

gas/film interface of the film solution lies in the range of 0.03 metres per second to 1.14 metres per second. Advantageously, the velocity of the gaseous medium of the initial gas flow adjacent the gas/film interface of the film solution lies in the range of 0.17 metres per second to 0.57 metres per second. Ideally, the velocity of the gaseous medium of the initial gas flow adjacent the gas/film interface of the film solution is approximately 0.29 metres per second.

In one embodiment of the invention at least one of the relative humidity and the velocity of the gaseous medium of the initial gas flow is set to establish an evaporation rate of the solvent from the polymer/solvent solution to produce a surface temperature of the film solution adjacent the gas/film interface not greater than the dew point temperature of the second environment prior to the polymer/solvent solution being subjected to the second environment.

Preferably, at least one of the relative humidity and the velocity of the gaseous medium of the initial gas flow is set to establish an evaporation rate of the solvent from the polymer/solvent solution to produce a surface temperature of the film solution adjacent the gas/film interface below the dew point temperature of the second environment prior to the film solution being subjected to the second environment.

In another embodiment of the invention the gaseous medium of the first environment is nitrogen.

Preferably, water vapour is entrained in the gaseous medium of the first environment to produce the first environment to be of the appropriate relative humidity.

In another embodiment of the invention the relative humidity of the second environment is adapted to control the vapour-liquid equilibrium adjacent the droplet interface with the second environment for controlling the rate of growth of droplets into the film solution.

In another embodiment of the invention the relative humidity of the second environment is controlled for controlling the progression of solvent evaporation from the film solution, and in turn for controlling the polymer concentration gradient in the film solution.

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In another embodiment of the invention the relative humidity of the second environment is greater than the relative humidity of the first environment. In a further embodiment of the invention the relative humidity of the second environment is determined by the depth to which the cavities are required to extend into the polymer/solvent solution and the required transverse cross-section of the cavities. Preferably, the second environment is produced by subjecting the gas/film interface of the film solution to a gaseous medium of relative humidity lying in the range of 15% to 100%. Advantageously, the relative humidity of the gaseous medium of the second environment lies in the range of 40% to 90%. Ideally, the relative humidity of the gaseous medium of the second environment lies in the range of 50% to 85%.

In one embodiment of the invention the gaseous medium of the second environment is passed over the gas/film interface of the film solution as an intermediate gas flow during the period during which the film solution is subjected to the second environment. Preferably, the flow rate of the gaseous medium of the intermediate gas flow over the gas/film interface of the film solution is controlled for controlling the progression of solvent evaporation from the film solution.

In one embodiment of the invention the velocity of the gaseous medium of the intermediate gas flow adjacent the gas/film interface of the film solution lies in the range of zero metres per second to 0.4 metres per second. Preferably, the velocity of the gaseous medium of the intermediate gas flow adjacent the gas/film interface of the film solution lies in the range of 0.03 metres per second to 0.29 metres per second. Advantageously, the velocity of the gaseous medium of the intermediate gas flow adjacent the gas/film interface of the film solution is approximately 0.06 metres per second.

In another embodiment of the invention the duration during which the film solution is subjected to the second environment is determined by the size to which the cavities are to be formed.

- 5 In one embodiment of the invention the polymer/solvent solution is prepared so that the level of solvent in the polymer/solvent solution is such that the level of the solvent in the polymer/solvent solution does not fall below a level which would result in the glass transition temperature of the polymer solution rising above the temperature of the film solution during the period in which the film solution is being
- 10 subjected to the first and second environments, and during the period of the third environment when the film solution is being subjected to the third environment until local polymer flow adjacent the cavities for determining the shape of the cavities is completed.
- 15 The invention also provides a polymer film having an array of cavities therein, the polymer film being formed by a method according to the invention.

The advantages of the method according to the invention are many. A particularly important advantage of the invention is that the latter part of the formation of the

20 cavities is controlled, and is controlled to the extent that the final shape of the cavity can be controlled. In particular, cavities with relatively flat bases, for example, cylindrical cavities with flat bases, can be produced, as well as cavities which are bulbous towards their lower end, and such bulbous cavities may also be produced with relatively flat bases. Thus, the method according to the invention provides more

25 control over the formation of the cavities, and in particular, the method according to the invention provides more control over the latter stages of formation of the cavities.

The invention will be more clearly understood from the following description of some preferred embodiments thereof, which are given by way of example only, with

30 reference to the accompanying drawings, in which:

Fig. 1 is a schematic representation of apparatus for carrying out the method

according to the invention for producing an array of cavities in a polymer film,

Fig. 2 is a transverse cross-sectional side elevational view of a portion of the apparatus of Fig. 1,

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Figs. 3 is a photomicrograph of a portion of a polymer film having cavities formed therein by the method according to the invention,

Figs. 4 is a photomicrograph of a portion of a polymer film having cavities formed therein by the method according to the invention,

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Figs. 5 is a photomicrograph of a portion of a polymer film having cavities formed therein by the method according to the invention,

Figs. 6(a) and (b) are photomicrographs of a portion of a polymer film having cavities formed therein by the method according to the invention,

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Fig. 7 is a graphical representation of the relative humidity of a gaseous medium plotted against time used in the method according to the invention for producing the polymer film of Fig. 3,

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Fig. 8 is a graphical representation of the relative humidity of a gaseous medium plotted against time used in the method according to the invention for producing the polymer film of Fig. 4,

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Fig. 9 is a graphical representation of the relative humidity of a gaseous medium plotted against time used in the method according to the invention for producing the polymer film of Fig. 5,

Fig. 10 is a graphical representation of the relative humidity of a gaseous medium plotted against time used in the method according to the invention for producing the polymer film of Fig. 6,

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Fig. 11 is a graphical representation of the glass transition temperature of the polymer/solvent solution plotted against the concentration of solvent as a percentage of mass in the polymer/solvent solution,

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Fig. 12 illustrates two graphs, one graph being a plot of the concentration of polymer in the polymer/solvent solution against time, and the other being a plot of the glass transition temperature of the polymer/solvent solution against time during the production of a polymer film,

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Fig. 13 is a photomicrograph of a portion of a polymer film having cavities formed therein by the method according to the invention,

Fig. 14 is a photomicrograph of a portion of another polymer film having cavities formed therein by the method according to the invention,

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Figs. 15 and 16 are graphical representations of the relative humidity of a gaseous medium plotted against time used in the method according to the invention for producing the polymer films of Figs. 13 and 14, respectively.

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Referring to the drawings and initially to Figs. 3 to 6, there is illustrated photomicrographs of polymer films according to the invention, which are indicated generally by the reference numerals 1a to 1d. The polymer films 1 are produced by a method according to the invention, which will be described below, and each comprises a plurality of cavities 2 of respective different shapes, but being generally of circular transverse cross-section extending downwardly into the polymer films 1 from a top surface 3 thereof. The cavities 2 in each of the films 1 are arranged in a hexagonally close-packed array. The cavities 2 of each polymer film 1 converge to respective necks 4 adjacent the top surface 3 of each polymer film 1 to define open mouths 7 to the cavities 2.

30

The polymer films 1, as will be described below, are formed from an initial

polymer/solvent solution which is drop-cast onto a substrate 5 as will be described below to form a thin film 6 of the polymer/solvent solution, as will also be described below with reference to Figs. 1 and 2. The film solution 6 on the substrate 5 is subjected sequentially to three environments, namely, first, second and third
5 environments, which are provided by passing a gaseous medium, in this case an inert gas, which in this embodiment of the invention is nitrogen gas entrained with water vapour over a top surface 8 of the film solution 6 on the substrate 5. The top surface 8 of the film solution 6 is the surface which forms the top surface 3 of the polymer film 1 on completion of the formation of the polymer films 1.

10

The first environment is provided by passing an initial gas flow of the nitrogen gas with entrained water vapour over the top surface 8 of the film solution 6. In the initial gas flow the amount of water vapour entrained in the nitrogen is relatively low, so that the relative humidity of the initial gas flow is similarly relatively low. The second
15 environment to which the film solution 6 is subjected is provided by an intermediate gas flow which is passed over the top surface 8 of the film solution 6. The intermediate gas flow comprises the nitrogen gas with entrained water vapour therein in order to produce a gas flow of a relatively high relative humidity, and considerably higher than the relative humidity of the initial gas flow. The third
20 environment to which the film solution 6 is subjected is provided by a final gas flow, which is passed over the top surface 8 of the film solution 6 and comprises nitrogen gas with entrained water vapour. The amount of water vapour entrained in the final gas flow is set so that the relative humidity of the final gas flow is lower than the relative humidity of the intermediate gas flow. The actual values of the relative
25 humidities of the initial, intermediate and final gas flows as well as the velocity of the respective gas flows over each film solution 6 and the durations of the respective gas flows is discussed in detail below.

The initial gas flow is provided to initiate solvent evaporation from the film solution 6
30 in order to reduce the surface temperature at the top surface 8 of the film solution 6 for the purpose of promoting the formation of water droplets on the top surface 8 during the intermediate gas flow. However, the relative humidity and the velocity of

the gas of the initial gas flow over the top surface 8 of the film solution 6 are set such as to minimise, and in general, to eliminate the formation of condensation on the top surface 8 of the film solution 6 during the initial gas flow. The relative humidity and the velocity of the gas of the initial gas flow over the top surface 8 of the film solution 6 are also set to establish a polymer concentration gradient within the film solution 6 in which the polymer concentration decreases downwardly into the film solution 6 from the top surface 8. The polymer concentration gradient in the film solution 6 is established so that the top surface 8 of the film solution 6 is capable of supporting water droplets as they form on the top surface 8 during the intermediate gas flow, and to control the rate of growth of water droplets into the film solution 6 through the top surface 8 to form the cavities 2.

The relative humidity and the velocity of the gas of the intermediate gas flow across the top surface 8 of the film solution 6 are set to control the vapour-liquid equilibrium adjacent the droplet interface with the gaseous medium of the intermediate gas flow in order to promote condensation on the top surface 8 of the film solution 6 to in turn form water droplets arranged in a hexagonally close-packed array. Controlling the vapour-liquid equilibrium adjacent the droplet interface with the gaseous medium of the intermediate gas flow facilitates control of the rate of formation of the droplets, as well as the rate of evaporation of the solvent from the film solution 6 to in turn control the polymer concentration gradient in the film solution 6. Typically, the relative humidity and the velocity of the intermediate gas flow is controlled so that the rate of solvent evaporation from the polymer/solvent solution is sufficient to maintain the temperature at the top surface 8 of the film solution 6 below the dew point temperature of the gaseous medium of the intermediate gas flow. By controlling the growth of the water droplets and the progression of the polymer gradient into the film solution, the rate at which the water droplets grow into the film solution 6 through the top surface 8 is controlled. This, thus, permits control of the length and transverse cross-sectional area of the cavities 2 being formed in the film solution 6 as well as the diameter of open mouths 7 defined by the necks 4. Thus, the relative humidity of the gaseous medium of the intermediate gas flow is significantly higher than the relative humidity of the gaseous medium of the initial gas flow, while the velocity of

the gaseous medium of the intermediate gas flow over the top surface 8 of the film solution 6 is considerably slower than the velocity of the gaseous medium of the initial gas flow over the top surface 8 of the film solution 6. The duration of the intermediate gas flow depends on the length, diameter and the shape of the cavities 2 to be formed.

During the periods during which the film solution 6 is being subjected to the initial and intermediate gas flows, the rate of solvent evaporation is controlled so that the level of solvent in the polymer/solvent solution of the film solution is such as to maintain the glass transition temperature of the film solution below the temperature of the film solution 6 in order to facilitate the formation of the cavities 2 therein when the film solution 6 is being subjected to the intermediate gas flow.

The final gas flow is commenced when the cavities 2 formed in the film solution 6 during the intermediate gas flow are of a desired predefined length in order to produce the polymer film 1 with the cavities 2 of the desired shape and size. The relative humidity and the velocity of the gaseous medium of the final gas flow over the top surface 8 of the film solution 6 is set for evaporating the water of the water droplets in the cavities 2 formed in the film solution 6. The relative humidity and the velocity of the final gas flow is also set so that when the water of the water droplets has been evaporated to an extent that the water droplets no longer have any influence in determining the shape of the cavities 2, the level of solvent remaining in the polymer/solvent solution of the film solution 6 adjacent the cavities 2 is sufficient to maintain the glass transition temperature of the polymer/solvent solution adjacent the cavities 2 below the temperature of the film solution 6. This thereby permits local polymer flow in the polymer/solvent solution in the vicinity of the cavities 2 for determining the final shape of the cavities 2.

In general, this local polymer flow results in the formation of flat bottomed cavities 2, rather than cavities with a concave base when viewed through the open mouths 7 thereof. To achieve this requirement, the relative humidity of the gaseous medium of the final gas flow is considerably less than the relative humidity of the gaseous

medium of the intermediate gas flow, and is in fact substantially similar to the relative humidity of the gaseous medium of the initial gas flow. The velocity of the gaseous medium of the final gas flow over the top surface 8 of the film solution 6 is, in general, relatively slow in order to adequately control the respective rates of evaporation of the water and the solvent.

Turning now to Figs. 1 and 2, apparatus, indicated generally by the reference numeral 20, for carrying out the method according to the invention on a laboratory bench scale for producing the polymer films 1 with the cavities 2 will now be described. The apparatus 20 comprises a support platform 22 supported on ground engaging legs 24, and defining a planar horizontal upwardly facing top surface 25. A housing 26 supported on the top surface 25 of the support platform 22 comprises a pair of spaced apart elongated longitudinally extending side walls 28 which are joined by a top wall 29. The side walls 28 and the top wall 29 define with the top surface 25 of the support platform 22 a chamber 30 in the form of an elongated tunnel, within which the film solution 6 on the substrate 5 is located during forming of the cavities 2 therein. The chamber 30 extends from an upstream end 31 to a downstream end 32. The upstream end 31 is closed by an upstream end wall 33, within which an input port 34 is located for accommodating the nitrogen gas with entrained water vapour therethrough into the chamber 30 for producing the initial, intermediate and final gas flows through the chamber 30 to which the film solution 6 on the substrate 5 is subjected during forming of the cavities 2 therein. The downstream end 32 of the chamber 30 is open for accommodating the gas flows from the chamber 30.

The substrate 5, which in this embodiment of the invention comprises a borosilicate glass microscope cover slip, is supported on a strain gauge balance 35 on the top surface 25 of the support platform 22 towards the downstream end 32 of the chamber 30. The balance 35 facilitates weighing of the film solution 6 during the initial, intermediate and final gas flows. The substrate 5 defines a smooth planar horizontal upwardly facing top surface 38 for supporting the film solution 6 thereon. A dosing port 39 formed in the top wall 29 of the housing 26 at a location above the

substrate 5 is provided for drop-casting a predefined volume of the polymer/solvent solution onto the top surface 38 of the substrate 5 using a suitable micro-pipette (not shown) to form the film solution 6.

5 Nitrogen gas to produce the initial, intermediate and final gas flows is derived from a nitrogen gas supply 40, and is fed through a first flow control valve 41 to a supply pipe 42, and in turn to a first Y-piece connector 43. A first pipeline 44 is coupled to the supply pipe 42 by the first Y-piece connector 43, and feeds into the inlet port 34 of the housing 26 through a second Y-piece connector 45 for delivering nitrogen gas
10 from the supply pipe 42 into the chamber 30. A second pipeline 46, which is also coupled to the supply pipe 42 through the first Y-piece connector 43 delivers nitrogen gas from the supply pipe 42 into a Dreschel flask 47 wherein water vapour is entrained in the nitrogen gas supplied from the supply pipe 42. A third pipeline 48 couples the Dreschel flask 47 with the first pipeline 44 through the second Y-piece
15 connector 45 for delivering nitrogen gas with water vapour entrained therein from the Dreschel flask 47 for varying the relative humidity of the nitrogen gas being delivered through the first pipeline 44 into the chamber 30.

The Dreschel flask 47 is supported on an electrically powered heater 50 which heats
20 water in the Dreschel flask 47, and maintains the water therein at a suitable temperature to produce a sufficient level of water vapour entrained in the nitrogen gas from the second pipeline 46, so that the relative humidity of the nitrogen gas from the Dreschel flask 47 through the third pipeline 48 is approximately 100%. In this embodiment of the invention the water in the Dreschel flask 47 is de-ionised and
25 filtered.

First and second manually operated isolating valves 52 and 53, respectively, are located in the respective first and second pipelines 44 and 46 for selectively isolating the first and second pipelines 44 and 46 from the supply pipe 42, and also for
30 varying the flow rate of the nitrogen gas through the first and second pipelines 44 and 46.

A second flow control valve 55 located in the first pipeline 44 between the first Y-piece connector 43 and the second Y-piece connector 45 is provided for varying and controlling the flow of nitrogen gas through the first pipeline 44 between the first and second Y-piece connectors 43 and 45 for in turn varying the relative humidity of the nitrogen gas flowing through the first pipeline 44 between the second Y-piece connector 45 and the inlet port 34 for in turn varying the relative humidity of the nitrogen gas flowing through the chamber 30. The first flow control valve 41 facilitates varying the flow rate of nitrogen gas flowing through the chamber 30 for in turn varying the rate of evaporation of the solvent from the film solution 6. The second flow control valve 55 facilitates varying the ratio of nitrogen gas flowing directly from the supply pipe 42 to the chamber 30 to nitrogen gas flowing through the Dreschel flask 47 to the chamber 30, for in turn varying the relative humidity of the nitrogen gas flowing through the chamber 30, for varying the rate of growth of the water droplets on the top surface 8 of the film solution 6 on the substrate 5.

A first flow rate monitor 56 is located on the first pipeline 44 between the first Y-piece connector 43 and the second Y-piece connector 45 for monitoring the flow rate of nitrogen gas through the first pipeline 44 between the first and second Y-piece connector 43 and 45. A second flow rate monitor 57 is located in the third pipeline 48 for monitoring the flow rate of nitrogen gas with entrained water vapour flowing through the third pipeline 48. A third flow rate monitor 58 is located in the first pipeline 44 between the second Y-piece connector 45 and the inlet port 34 of the housing 26 for monitoring the flow rate of nitrogen gas with entrained water vapour being delivered into the chamber 30. Flow rates of nitrogen gas read by the first, second and third flow rate monitors 56, 57 and 58, respectively, are displayed on respective flow rate indicators 59 of the first, second and third flow rate monitors 56 to 58.

A probe 60 of a hygrometer 61, which also includes a temperature sensor 62, extends from the hygrometer 61 into the chamber 30 and terminates at a location adjacent the substrate 5. The probe 60 monitors the relative humidity of the nitrogen gas with the water vapour entrained therein as it passes the film solution 6. The

temperature sensor 62 in the probe 60 monitors the temperature of the nitrogen gas with the entrained water vapour as it passes the film solution 6. The relative humidity of the nitrogen gas flowing through the chamber 30 and the temperature thereof are displayed on a screen 63 of the hygrometer 61. A separate temperature sensor (not shown) located adjacent the top surface 8 of the film solution 6 monitors the temperature of the top surface 8 of the film solution 6. The temperature of the top surface 8 monitored by the separate temperature sensor (not shown) is displayed on a separate screen (also not shown).

10 The first and second flow control valves 41 and 55 in this embodiment of the invention are manually operated for controlling the flow rate and the relative humidity of the nitrogen gas flowing through the chamber 30 by an operator in response to the values of the flow rates, the relative humidity and the temperature displayed by the first, second and third flow rate monitors 56 to 58, and the hygrometer 61, respectively. However, it will be readily apparent to those skilled in the art that a microprocessor or a programmable logic controller may be provided coupled to the hygrometer 61, the temperature sensor 62 and the first, second and third flow rate monitors 56 to 58 which would produce appropriate signals to be read by the microprocessor or the programmable logic controller. The microprocessor or programmable logic controller would then control the operation of the first and second flow control valves 41 and 55 via suitable servomotors in response to the signals from the first, second and third flow rate monitors 56 to 58, the temperature sensor 62 and the hygrometer 61 for in turn controlling the flow rate and the relative humidity of the nitrogen gas flowing through the chamber 30.

25 With the apparatus 20 set up as described, and with the substrate 5 placed on the support platform 22 and the housing 26 also placed on the support platform 22 to form the chamber 30 with the substrate 25 located within the chamber 30 towards the downstream end 32 thereof and beneath the dosing port 39, the apparatus 20 is ready for use.

30 In order to facilitate an understanding of the method according to the invention for

producing the polymer films 1 with the cavities 2 and to facilitate an understanding of the operation of the apparatus 20, the method and apparatus 20 will now be described for producing the polymer film 1a illustrated in Fig. 3.

5 Referring now to Figs. 1 to 3 and 7, the first flow control valve 41 is set to produce the initial gas flow through the chamber 30 at a flow rate of approximately 5 litres of nitrogen gas and entrained water vapour per minute. The second flow control valve 55 in conjunction with the second isolating valve 53 are set in order to produce a relatively dry initial gas flow of nitrogen of relative humidity, which is maintained at
10 approximately 3%, through the chamber 30.

Once the initial gas flow of relative humidity of approximately 3% and at a flow rate of 5 litres per minute is established in the chamber 30, an appropriate volume, which in this embodiment of the invention is 60 micro-litres of the polymer/solvent solution
15 is drop-cast through the dosing port 39 in the housing 26 onto the top surface 38 of the substrate 5 to form the film solution 6. Needless to say, the volume of polymer/solvent solution which is drop-cast onto the substrate 5 may be of any suitable volume, and will be dependent on the desired product output. Drop-casting of the polymer/solvent solution is carried out using a suitable micro-pipette (not
20 shown). The depth t to which the film solution 6 of polymer/solvent solution settles on the top surface 38 of the substrate 5 depends on the polymer and solvent of the polymer/solvent solution and the proportions thereof in the solution, as well as other parameters such as surface tension, the smoothness of the top surface 38 of the substrate 5, the temperature of the polymer/solvent solution and the temperature
25 and pressure within the chamber 30.

In this embodiment of the invention the polymer is α , ω -Dicarboxy Terminated Polystyrene of number average molecular weight of 93,800gms/mol, and the solvent is chloroform. The starting proportion of the polymer to the solvent by mass is 3.5%
30 polymer to 96.5% solvent. The method is carried out at room temperature, which is approximately 21°C, and pressure, and on being drop-cast onto the top surface 38 of the substrate 5, the polymer/solvent solution is at room temperature. The

temperature and pressure within the chamber 30 during the carrying out of the method is substantially room temperature and pressure. Under these conditions the depth t to which the film solution 6 settles on the top surface 38 of the substrate 5 in a central area of the film solution 6 where the depth t is substantially constant and is
5 in the order of 550 microns.

The top surface 8 of the polymer/solvent film solution 6 forms an upwardly facing exposed gas/film interface surface over which the initial, intermediate and final gas flows pass, and forms the top surface 3 of the polymer film 1 when the cavities 2
10 have been formed therein.

By selecting the starting proportions of the polymer and solvent of the polymer/solvent solution as described above, with this particular type of polymer and solvent, it has been found that the level of solvent in the polymer/solvent solution
15 remains at a level which is sufficient for maintaining the glass transition temperature of the polymer/solvent solution below the temperature of the film solution 6 during the initial and intermediate gas flows, and also during the final gas flow until local polymer flow in the film solution adjacent the cavities has been completed in order to form the cavities 2 of the desired shape. However, it will be appreciated that the
20 starting proportions of the polymer and solvent in the polymer/solvent solution in order to maintain the glass transition temperature of the polymer/solvent solution below the temperature of the film solution until local polymer flow in the film solution adjacent the cavities has been completed will depend on the types of polymers and solvents which are selected to form the polymer/solvent solution.

25 The maximum feasible concentration as a percentage of mass of the polymer of the polymer/solvent solution for any polymer/solvent solution is achieved when the vapour pressure of the polymer solution induces exactly enough evaporative cooling so that the polymer surface is reduced to the dew point temperature of the system.
30 With any further increase in polymer concentration, the dew point temperature will not be reached, and so no condensation or minimum condensation of water on the surface of the polymer/solvent solution will occur.

Taking account of the transverse cross-sectional area of the chamber 30, the flow rate of the initial gas flow of 5 litres per minute through the chamber 30 equates to a velocity of the gas of the initial gas flow over the top surface 8 of the film solution of approximately 0.29 metres per second. The film solution 6 is subjected to the initial gas flow for a first time period of approximately 45 seconds, see Fig. 7, in order to produce a polymer concentration gradient extending from the top surface 8 into the film solution 6 with the polymer concentration decreasing from the top surface 8 in a direction into the film solution 6. Additionally, by providing the initial gas flow to flow over the top surface 8 of the film solution 6 at a velocity of 0.29 metres per second and at a relative humidity of approximately 3%, the evaporation of the solvent from the film solution 6 reduces the surface temperature of the top surface 8 of the film solution 6 to a temperature of the order of 0°C to 5°C at the end of the first period of 45 seconds. This temperature range is well below the dew point temperature of the intermediate gas flow, and on the film solution being subjected to the intermediate gas flow, water droplets immediately commence to form on the top surface 8 of the film solution 6. However, during the first time period while the film solution 6 is being subjected to the initial gas flow, condensing of water vapour from the initial gas flow onto the top surface 8 of the film solution 6 is minimal, and in general, does not occur.

It has been found that with the relative humidity and the velocity of the initial gas flow over the top surface 8 of the film solution 6 as set out above, the initial gas flow can be terminated after approximately 45 seconds, and the intermediate gas flow can be immediately commenced, see Fig. 7. After approximately 45 seconds of the initial gas flow, it has been found that sufficient solvent has been evaporated from the film solution 6 to establish the polymer concentration gradient down through the film solution 6 from the top surface 8 thereof whereby the concentration of the polymer decreases downwardly into the film solution 6 from the top surface 8. The polymer concentration gradient controls the rate at which the water droplets which form on the top surface of the film solution 6 grow downwardly through the top surface 8 into the film solution 6 to form the cavities 2.

Once the film solution 6 has been subjected to the initial gas flow for the first time period of 45 seconds, the relative humidity of the gas flow is immediately increased to reach a target value of approximately 85% by appropriately setting the second flow control valve 55 to produce the intermediate gas flow, see Fig. 7. However, the manually operated isolating valves 52 and 53 may also be used for controlling the relative humidity of the initial, the intermediate and the final gas flows. The first flow control valve 41 is operated to reduce the flow rate of the intermediate gas flow to a steady state flow rate of approximately 1.0 litres per minute. The flow rate of 1.0 litres per minute equates to a velocity of the gas of the intermediate gas flow over the top surface 8 of the film solution 6 of approximately 0.06 metres per second. The target relative humidity is reached after approximately 110 seconds after the commencement of the intermediate gas flow, and the intermediate gas flow is continued for a further 10 seconds thus, giving a total second time period for the intermediate gas flow of approximately 120 seconds, see Fig. 7. At that stage the intermediate gas flow is terminated, and the final gas flow is commenced. During the intermediate gas flow, the average relative humidity of the gas is approximately 69%. It has been found that by maintaining the intermediate gas flow for the second time period of 120 seconds under the conditions set out above, cavities 2 of a predefined size and shape are formed, which result in the cavities 2 of the polymer film 1a of Fig. 3 being formed after the film solution 6 has been subjected to the final gas flow.

Immediately on termination of the intermediate gas flow, the first flow control valve 41 and the second flow control valve 55 are operated to reduce the relative humidity of the gas flow to approximately 11% in order to establish the final gas flow to which the film solution 6 is now subjected. During the final gas flow the flow rate of the gas is maintained substantially similar to the flow rate during the intermediate gas flow so that the velocity of the final gas flow over the top surface 8 of the film solution 6 is maintained at approximately 0.06 meters per second. As can be seen from the graph of Fig. 7 the relative humidity of the final gas flow drops off relatively rapidly over a period of 60 seconds to approximately 11%.

As the final gas flow continues, water of the water droplets in the cavities 2 is evaporated until eventually the water remaining in the cavities has substantially no influence or no over-riding influence on the shape and size of the cavities 2. At that stage, there is still sufficient solvent remaining in the film solution 6 to maintain the glass transition temperature of the polymer/solvent solution below the temperature of the film solution 6 adjacent the cavities 2. This permits local flow of the polymer adjacent the cavities 2, and in particular, adjacent the base 10 of the cavities 2 to permit final shaping of the cavities 2. Local polymer flow occurs at the bases 10 of the respective cavities 2, which after evaporation of all or most of the water therefrom are of a concave configuration when viewed downwardly through the respective open mouths, to form relatively flat bases in the cavities 2.

The final gas flow may also be controlled to permit local polymer flow adjacent the side walls of the cavities 2, which generally results in a decrease in the diameter of the cavities 2, and it is possible to control the diameter of the cavities to begin to approach the diameter of the respective open mouths 7 defined by the necks 4 of the cavities 2. This shaping of the side walls of the cavities 2 may also result in an increase in the spacing between adjacent cavities 2.

Thereafter the final gas flow is continued until substantially all of the solvent has been evaporated from the film solution 6 to produce the polymer film 1 as an entangled polymer film, in which the polymer can no longer flow. As the final gas flow progresses, the relative humidity of the final gas flow is allowed to fall off to a value of approximately 4%, see Fig. 7.

In general, it has been found that the total time during which the film solution should be subjected to the intermediate and final gas flows is approximately eight minutes. Thus, in cases where the film solution 6 is subjected to the intermediate gas flow for relatively long time periods, the duration during which the film solution 6 is subjected to the final gas flow will be relatively shorter than cases where the film solution is subjected to the intermediate gas flow for relatively shorter periods. It will be

appreciated that the total time period during which the film solution is subjected to the intermediate and final gas flows may be greater or less than eight minutes, depending on the size of the cavities required, and indeed, it is envisaged that a shorter time period than eight minutes may be sufficient for the formation of cavities of relatively small size.

As mentioned above, the relative humidity and the flow rate of the initial gas flow are set so that the polymer gradient of the polymer in the film solution 6 is appropriately set in order to support condensing water from the intermediate gas flow as the water droplets are formed on the top surface 8 of the film solution 6, while at the same time the viscosity of the film solution 6 adjacent the top surface 8 thereof is such as to permit penetration into the film solution 6 through the top surface 8 thereof of the water droplets in order to form the cavities 2. Additionally, as mentioned above, the rate of evaporation of the solvent from the film solution 6 during the initial gas flow is such as to reduce the surface temperature of the top surface 8 of the film solution 6 to be well below the dew point temperature of the intermediate gas flow.

The flow rate and the relative humidity of the intermediate gas flow is such that water droplets condense out of the intermediate gas flow onto the top surface 8 of the film solution 6 in the form of a hexagonally close-packed array. During the intermediate gas flow, solvent continues to evaporate from the film solution 6, although at a reduced evaporation rate due to the slower velocity of the intermediate gas flow over the top surface 8 of the film solution 6. This reduction in the evaporation rate of the solvent during the intermediate gas flow results in a gradual increase in the temperature of the top surface 8 of the film solution 6, although it has been found that this gradual increase in the temperature of the top surface 8 of the film solution 6 does not to any great extent hinder the formation of the water droplets in the hexagonally close-packed array of the film solution 6.

Additionally, during the intermediate gas flow the polymer gradient progressively increases downwardly into the film solution 6 from the top surface 8 thereof. This, thus, controls the growth of the water droplets downwardly from the top surface 8

into the film solution 6. Thus, the relative humidity and the flow rate of the intermediate gas flow is also set to control the progression of the polymer concentration gradient downwardly through the film solution 6 during the period during which the film solution 6 is subjected to the intermediate gas flow.

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The duration of the intermediate gas flow will vary depending on the size and shape of the cavities required. However, in order to produce the polymer film 1 with the cavities 2 with a flat base, it is important that the second time period during which the film solution 6 is subjected to the intermediate gas flow is terminated prior to
10 evaporation of all of the solvent from the film solution 6, so that sufficient solvent remains in the film solution 6 during the final gas flow when the water droplets have been evaporated from the cavities 2 to the extent that the remaining water in the cavities 2 has little or no influence on the formation of the cavities 2, to maintain the glass transition temperature of the polymer/solvent solution below the temperature of
15 the film solution 6, in order to permit local polymer flow adjacent the bases 10 of the cavities 2 so that the cavities 2 are produced with flat bases 10.

The relative humidity and the flow rate of the final gas flow and the duration of the final gas flow will also vary depending on the size and shape of the cavities required.
20 However, when it is desired to form the polymer film 1 with cavities 2 with flat bases 10, it is important that the relative humidity and flow rate of the final gas flow should be set so that water of the droplets in the cavities 2 is evaporated to the extent that the amount of water remaining in the cavities 2 no longer has an over-riding influence on the size and shape of the cavities while there is still sufficient solvent
25 remaining in the film solution 6 to permit local polymer flow adjacent the cavities, and in particular, adjacent the base 10 of the cavities 2.

The local polymer flow adjacent the base of the cavities 2 results in the formation of the cavities 2 with flat bases 10. This requirement may also require adjustment of
30 the relative humidities and flow rates of the initial and intermediate gas flows, to ensure that when the cavities 2 are of the predefined size, depth and diameter at the end of the intermediate flow to produce the cavities 2 in the polymer film 1 of the

desired size and shape, sufficient solvent remains in the film solution 6 so that during the period while the film solution 6 is being subjected to the final gas flow, sufficient solvent remains in the film solution after the water of the water droplets has been evaporated from the cavities 2 to the extent that the water in the cavities no longer has an over-riding influence on the size and shape of the cavities to maintain the glass transition temperature of the polymer/solvent solution below the temperature of the film solution 6 in order to facilitate local polymer flow adjacent the relevant portions of the cavities 2 which are to be shaped in order to produce cavities 2 in the polymer film 1 of the desired size and shape.

10

In general, it is envisaged that the relative humidity of the initial gas flow will lie in the range of 0% to 45%, while the flow rate will in general lie in the range of 0.5 litres per minute to 20 litres per minute in order to produce a velocity of the initial gas flow over the top surface 8 of the film solution 6 in the range of 0.03 metres per second to 1.14 metres per second.

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In general, it is envisaged that the relative humidity of the intermediate gas flow will lie in the range of 10% to 100%, depending on the size and dimensions of the cavities 2 to be formed in the polymer film 1. The flow rate of the intermediate gas flow will in general lie in the range of zero litres per minute to 7 litres per minute in order to produce a velocity of the intermediate gas flow over the top surface 8 of the film solution 6 in the range of zero metres per second to 0.4 metres per second.

20

In general, it is envisaged that the relative humidity of the final gas flow will lie in the range of 0% to 50%, while the flow rate will in general lie in the range of zero litres per minute to 7 litres per minute in order to produce a velocity of the final gas flow over the top surface 8 of the film solution 6 in the range of zero metres per second to 0.4 metres per second.

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By altering the relative humidity and the flow rate of the intermediate gas flow, the size and shape of the cavities 2 can be altered. For example, flat based cavities, spherical cavities, bulbous cavities with narrow necks 4 and conical flask-like cavities

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can be formed in the film solution 6. It is believed that by increasing the flow rate of the intermediate gas flow, the evaporation rate of the solvent from the film solution 6 can be accelerated, and this results in an increase in the polymer concentration at lower depths in the film solution 12, thereby slowing down the downward growth of the water droplets in the film solution 6. Thus, by appropriately simultaneously altering the flow rate and the relative humidity of the intermediate gas flow, the size and shape of the cavities formed in the film solution may be altered. Flat base cavities, as discussed above, are achieved by ensuring that at the stage in the final gas flow when the water has been evaporated to a stage when the remaining water in the cavities no longer has an over-riding influence on the shape and size of the cavities, sufficient solvent remains in the film solution 6 to maintain the glass transition temperature of the polymer/solvent solution below the temperature of the film solution. This, thus, permits local polymer flow adjacent the cavities in order to determine the final shape of the cavities 2 in the polymer film 1.

15

In general, the relative humidity of the initial gas flow should be below or close to the critical humidity level required to initiate water condensation onto the top surface 8 of the film solution 6 as the solvent is evaporating. The term critical humidity level is used in this specification to mean the borderline humidity below which condensation of water onto the surface 8 of the film solution is not favoured. The initial gas flow is chosen to set the minimum feasible surface temperature of the top surface 8 of the film solution by controlling the rate of evaporation while minimising water condensation. Accordingly, the initial gas flow for a given solution dictates the temperature and concentration gradient within the film solution 6.

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The flow rate and the relative humidity of the intermediate gas flow is set in conjunction with the surface temperature induced from the initial gas flow to allow control of the vapour-liquid equilibrium of water adjacent the top surface 8 of the film solution 6, and hence, the drive to condense water vapour from the intermediate gas flow to form water droplets on the gas/film interface 8 of the film solution 6 during the intermediate gas flow. This drive to condense the water vapour from the intermediate gas flow is modified to induce the required amount of droplet growth on

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the top surface 8 of the film solution 6, and in turn the droplet growth into the film solution to form the cavities. The intermediate gas flow also controls the progression of the solvent evaporation and the polymer concentration gradient in the film solution 6, thereby allowing and controlling the growth rate of the droplets into the solution.

5

It is believed that it is important to control the time at which the top surface 8 of the film solution reaches a high enough viscosity to be stable and fixed, while still ensuring the lower parts of the film solution 6 are not so viscous as to inhibit droplet growth into the film solution 6.

10

By providing the final gas flow to be of low humidity results in a change of the vapour-liquid equilibrium of the droplets, and thereby ensures their rapid evaporation before complete evaporation of the solvent from the film solution 6. By ensuring that the intermediate flow rate is terminated prior to completion of evaporation of the polymer solution, and setting the relative humidity of the final gas flow at a relatively low level, the vapour-liquid equilibrium adjacent the droplet interface with the gas of the final gas flow favours the evaporation of water droplets from the cavities, however, due to the presence of solvent in the film solution 6, the film solution 6 is sufficiently viscous to allow local polymer flow adjacent the base of the cavities to form flat bottomed cavities.

20

Shallow cavities can also be formed by significantly decreasing the relative humidity of the intermediate gas flow until it is just above the critical humidity level at which condensation would form on the top surface 8 of the film solution 6 and terminating the intermediate gas flow when the cavities 2 have been formed to a predefined depth, which would result in the cavities 2 in the polymer film 1 being formed to the desired shallow depth. However, it is important that the intermediate gas flow should be terminated prior to all of the solvent being evaporated from the film solution 6, and this may require increasing the relative humidity of the intermediate gas flow and decreasing the duration during which the film solution 6 is subjected to the intermediate gas flow.

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In general, the size and depth of the cavities are determined by the relative humidity of the intermediate gas flow and the duration during which the film solution 6 is subjected to the second gas flow.

5 It has been found that in general while the vapour-liquid equilibrium adjacent the droplet interface with the gas of the intermediate gas flow initially favours condensation of water vapour from the intermediate gas flow on the top surface 8 of the film solution 6, a gradual decrease in the evaporation rate of the solvent during the intermediate gas flow is detected, which is believed to result from the increase in
10 the polymer concentration adjacent the top surface 8 and the build-up of droplets on the top surface 8, which in turn leads to an increase in the temperature adjacent the gas/film interface 8 of the film solution 6, which in turn leads to the temperature at the gas/film interface 8 of the film solution 6 approaching the dew point of the intermediate gas flow. However, if the relative humidity of the intermediate gas flow
15 remains constant, the vapour-liquid equilibrium adjacent the droplet interface with the gas of the intermediate gas flow will in due course favour water droplet evaporation.

Table 1 sets out the conditions and durations of the initial, intermediate and final gas
20 flows used in the formation of the polymer films 1b to 1d of Figs. 4 to 6. In all the examples the polymer and solvent and the starting proportions thereof of the film solutions are similar to those of the example of the polymer film described above, and the polymer/solvent film solutions of Examples 1 to 3 are formed on the substrate 5 to a similar depth t of 550 microns as that of the film solution 6. The
25 graphs of Figs. 8 to 10 show the relative humidity of the initial, intermediate and final gas flows during the respective initial, intermediate and final gas flows plotted against time during the formation of the polymer films 1b to 1d of Figs. 4 to 6, respectively.

30 As can be seen from a comparison of the cavities of the polymer films 1a and 1b of Figs. 3 and 4, the depth of the cavities 2 in the polymer film 1b is less than the depth of the cavities 2 in the polymer film 1a. This has resulted from the fact that firstly, the

average relative humidity of the intermediate gas flow at 65.2% of Example 1 was less than the average relative humidity of the intermediate gas flow which produced the polymer film 1a of Fig. 3, and secondly, as can be seen from a comparison of the graphs of Figs. 7 and 8 the duration of the intermediate gas flow was shorter at approximately 90 seconds than the duration of the intermediate gas flow of 120 seconds which produced the polymer film 1a of Fig. 3.

Table 1

	Sample	Example 3	Example 2	Example 1
Initial gas flow	Target relative humidity	Dry	Dry	Dry
	Average relative humidity	3	3.9	3.5
	Velocity of gas flow (metres per second)	0.29	0.29	0.29
	Duration of initial gas flow (seconds)	45	45	45
Intermediate	Target relative humidity	60	80	85
	Average relative humidity	39.9	56.2	65.2
	Velocity of gas flow (metres per second)	0.06	0.06	0.06
	Duration of intermediate gas flow (seconds)	30	60	90
Final	Target relative humidity	Dry	Dry	Dry
	Average relative humidity	7.3	11.1	9.4
	Velocity of gas flow (metres per second)	0.06	0.06	0.06
	Duration of final gas flow (seconds)	450	420	390

10

A further comparison of the polymer films 1a, 1b and 1c of Figs. 3, 4 and 5 shows that the depth of the cavities 2 in the polymer film 1c is less than the depth of the cavities in the polymer film 1b which in turn is less than the depth of the cavities 2 of

the polymer film 1a. The further reduction in the depth of the cavities 2 of the polymer film 1c of Fig. 5 can be explained by virtue of the fact that the average relative humidity of the intermediate gas flow at 56.2% of Example 2 which produced the polymer film 1c of Fig. 5 was less than the relative humidity of 65.2% and 69% of the intermediate gas flows which produced the polymer films 1b and 1a, of Figs. 4 and 3, respectively. Additionally, as can be seen from the graph of Fig. 9 the duration of the intermediate gas flow of Example 2 which produced the polymer film 1c of Fig. 5 at 60 seconds approximately was less than the 90 second duration of the intermediate gas flow which produced the polymer film 1b of Fig. 4 and the 120 second intermediate gas flow which produced the polymer film 1a of Fig. 3.

A further comparison of the polymer film 1d of Figs. 6a and b with the polymer films 1c, 1b and 1a of Figs. 5, 4 and 3, respectively, shows that the depth of the cavities 2 of the polymer film 1d is less than the depth of the cavities 2 of the polymer film 1c of Fig. 5 which in turn is less than the depth of the cavities of the polymer film 1b of Fig. 4, which in turn is less than the depth of the cavities 2 of the polymer film 1a of Fig. 3. The lesser depth of the cavities 2 of the polymer film 1d of Figs. 6a and b can be explained by the fact that the average relative humidity of the intermediate gas flow at 39.3% of Example 3 which produced the polymer film 1d is less than the average relative humidity of the intermediate gas flow of 56.2% of Example 2 which produced the polymer film 1c of Fig. 5 which in turn is less than the average relative humidity of the intermediate gas flow at 65.2 of Example 1 which produced the polymer film 1b of Fig. 4, which in turn is less than the average relative humidity of the intermediate gas flow at 69% which produced the polymer film 1a of Fig. 3. Additionally, the duration of the intermediate gas flow of Example 3 which produced the polymer film 1d of Figs. 6a and b at 30 seconds is less than the intermediate gas flow at 60 seconds which produced the polymer film 1c of Fig. 5 which in turn is less than the 90 second intermediate gas flow which produce the polymer film 1b of Fig. 4, which itself is less than the 120 second intermediate gas flow which produced the polymer film 1a of Fig. 3. Thus, it can be seen that by reducing the average relative humidity of the intermediate gas flows and the duration thereof, the depth of the cavities 2 can be reduced.

It can be seen from all the polymer films 1a to 1d of Figs. 3 to 6a and b that the cavities formed in the polymer films 1a to 1d each have a substantially flat base, which results from local flow of the polymer in the film solution 6, while there is still
5 sufficient solvent remaining in the film solution 6 after the water of the water droplets in the cavities 2 has been evaporated to an extent that the water in the cavities no longer has an over-riding influence on the shape and size of the cavities.

Additionally, it can be seen that in all the polymer films 1a to 1d the cavities 2 extend
10 downwardly into the polymer film from the neck 4 which is of smaller diameter to the diameter of the cavities beneath the neck. This enlargement of the diameter of the cavities beneath the neck is believed may also result from local flow of the polymer in the film solution 6 while the amount of solvent in the film solution 6 is sufficient to accommodate local polymer flow adjacent the cavities 2 after the water of the water
15 droplets in the cavities 2 has been evaporated to an extent that the remaining water in the cavities 2 no longer influences the size and shape of the cavities. It has also been found that this local polymer flow may increase the spacing between adjacent cavities.

20 It can also be seen from Figs. 6a and 6b that cavities failed to form in some areas of the polymer film 1d and in other areas cavities did not fully form. Additionally, in some areas of the polymer film 1d the water droplets resulted in the formation of shallow indents into the top surface of the polymer film 1d. Why cavities failed to be formed and shallow indents were formed is not fully understood. However, it is
25 believed that the failure of cavity formation may be as a result of the fact that the areas in which cavities did not form, or where the water droplets merely resulted in shallow indents, were exposed to the intermediate gas flow for such a short time that sufficient quantities of solvent remained in the film solution 6 to allow almost complete recovery of the film solution 6 in those areas.

30

Referring now to Figs. 11 and 12, an experiment to track the percentage concentration by mass of the polymer in the polymer/solvent solution as the film

solution is subjected to the initial and intermediate gas flows will now be described. A film solution identical to the film solution 6 of similar depth and comprising a similar polymer/solvent solution was placed on the substrate 5 in the chamber 30 of the apparatus 20 of Fig. 1. The film solution was subjected to an initial gas flow of 5 litres per minute of dry nitrogen for a first time period of 45 seconds. At the end of the first time period of 45 seconds, the film solution was subjected to an intermediate gas flow at a rate of 1 litre per minute of humid nitrogen until all the solvent was evaporated. In this case the film solution was not subjected to a final gas flow, rather, the intermediate gas flow was continued until all solvent had been evaporated from the film solution. However, the graph of Fig. 12 may be used to indicate where the second time period of the intermediate gas flow would end and the third time period of the final gas flow could commence as will be described below.

Fig. 11 illustrates a plot of the glass transition temperature in degrees centigrade, which is plotted on the vertical Y-axis against the concentration of solvent as a percentage of the mass of the polymer/solvent solution, which is plotted on the horizontal Y-axis. This plot has been prepared from the Beuche equation.

Fig. 12 illustrates two graphs, namely Graph A, which illustrates a plot of the concentration of polymer as a percentage of the mass of the polymer/solvent solution plotted against time as the film solution is being subjected to the first and second gas flows described above. The concentration of polymer as a percentage of the mass of the polymer/solvent solution is plotted on the left-hand vertical Y-axis, and time in seconds is plotted on the horizontal X-axis. Graph B of Fig. 12 is a plot of the glass transition temperature in degrees centigrade plotted against time as the film solution is being subjected to the first and second gas flows. The glass transition temperature in degrees centigrade is plotted on the right-hand vertical Y-axis, and time, as discussed above, is plotted on the horizontal X-axis. However, in this case the plot of the glass transition temperature against time has been derived empirically from the Beuche equation and the graph of Fig. 11.

The film solution was subjected to the first and second gas flows at room

temperature, namely, approximately 21°C, and room pressure, and thus, the film solution would have been maintained at a temperature of approximately 21°C. As can be seen from Graph A of Fig. 12, while the concentration of polymer in the polymer/solvent solution of the film solution did not rise above 66%, the glass transition temperature of the polymer/solvent solution remained below 0°C at -27°C, which is well below the room temperature of 21°C.

Ideally, from Graphs A and B of Fig. 12, the evaporation of the solvent from the polymer/solvent solution commences to accelerate at approximately 100 seconds into the experiment, and this, thus, leads to an acceleration of the increase in the glass transition temperature of the polymer/solvent solution. In general, it is desirable that the second time period during which the polymer/solvent solution is subjected to the intermediate gas flow should terminate prior to the time at which the concentration of the polymer in the film solution commences to increase more rapidly. Thus, in the present case it is clear from the graphs A and B of Fig. 12, and in particular, Graph A of Fig. 12, that the second time period should terminate between 30 and 60 seconds after the commencement thereof, or in other words, between 80 seconds and 100 seconds from the commencement of the experiment, and at that stage, the polymer/solvent solution should be subjected to the third gas flow.

Referring now to Figs. 13 to 16, Figs. 13 and 14 illustrate three further examples of polymer film 1(e), 1(f) and 1(g) prepared in three further examples of the method according to the invention, namely, Examples 4 and 5. The conditions under which Examples 4 and 5 have been carried out are set out in Table 2. Graphs of the relative humidity of the gas flows during the initial, intermediate and final gas flows to which the polymer films 1(e) and 1(f) of Figs. 13 and 14 were subjected in Examples 4 and 5 are illustrated in Figs. 15 and 16, respectively. The polymer/solvent solution of the film solution of Examples 4 and 5 are similar to the polymer/solvent solution of the film solution 6 described above, and the film solution was formed to a depth of 550 microns on the substrate 5, which in turn was placed in the chamber 30 of the apparatus 20.

Table 2

	Sample	Example 4	Example 5
Initial gas flow	Target relative humidity	Dry	Dry
	Average relative humidity (%)	1.9	2.0
	Velocity of gas flow (metres per second)	0.29	0.29
	Duration of initial gas flow (seconds)	45	45
Intermediate	Target relative humidity	80	85
	Average relative humidity (%)	57.0	59.3
	Maximum relative humidity (%)	82.2	84.9
	Velocity of gas flow (metres per second)	0.06	0.06
	Duration of intermediate gas flow (seconds)	60	90
Final	Target relative humidity	Dry	Dry
	Average relative humidity (%)	7.4	9.3
	Velocity of gas flow (metres per second)	0.06	0.06
	Duration of final gas flow (seconds)	420	390

5

In Example 4 the first time period during which the polymer/solvent solution was subjected to the first gas flow was approximately 50 seconds, see Fig. 15. In Example 4 the relative humidity of the intermediate gas flow was raised rapidly to approximately 82%. The third gas flow commenced in Example 4 at 160 seconds approximately from the commencement of the initial gas flow.

10

In Example 5 the polymer/solvent solution was subjected to the initial gas flow for approximately 60 seconds, and to the intermediate gas flow for approximately 140 seconds, see Fig. 16. During the intermediate gas flow the relative humidity was raised rapidly to approximately 80% and subsequently to 84%. The third gas flow
5 commenced at approximately 200 seconds from the commencement of the initial gas flow.

In the polymer film 1e of Fig. 13 prepared in the method of Example 4 relatively shallow cavities have been formed, however, the cavities are substantially
10 cylindrical, with a relatively flat base 10.

In the polymer film 1f of Fig. 14 prepared by the method of Example 5 the cavities 2 which have been formed in the polymer film 1f are of circular transverse cross-section in plan view with a relatively flat base 10 but rather bulbous above the base
15 10 and below the neck 4.

While the polymer/solvent solution has been described as comprising specific constituents of specific starting proportions, it will be readily apparent to those skilled in the art that the polymer/solvent solution may be provided with the constituents in
20 other suitable starting proportions. Needless to say, the polymer solvent solution may comprise constituents other than those described, and/or may comprise additional constituents as well as those described.

While the method according to the invention requires subjecting the film solution to
25 an initial gas flow, an intermediate gas flow and a final gas flow, it is envisaged that in certain cases instead of relatively abruptly switching from one gas flow to the next, the method could be carried out by gradually transitioning from one gas flow to the next.

30 It will also be appreciated that while specific values of relative humidity, velocity of the gas flows over the top surface of the film solution have been described, other relative humidities and velocities may be adopted without departing from the scope

of the invention.

It is also envisaged that other suitable means of forming the film solution on the substrate besides drop casting may be used, and indeed, it is envisaged in certain cases that the film solution instead of being formed on the top surface of a substrate which is horizontally oriented, the film solution may be formed on an inclined surface of a substrate. Indeed, in certain cases, it is envisaged that the surface of the substrate may be a vertical surface, and in other cases, it is envisaged that the film solution may be formed on an underneath surface of a horizontal or inclined substrate.

While a specific polymer and a specific solvent have been described from which the film solution is prepared, the film solution may be prepared from any other suitable polymer and/or solvent, and the starting proportions of the polymer and the solvent of the solution will be largely determined by the types of polymer and the types of solvent.

While the initial, intermediate and final gas flows have been described as comprising a humid gaseous medium which comprises nitrogen with entrained water vapour, any other suitable gaseous medium may be used, for example, air, and the gaseous medium may be entrained with any suitable liquid besides water.

While the film solutions have been described as being subjected to first, second and third environments which are provided by initial, intermediate and final gas flows, in certain cases, it is envisaged that other forms of first, second and third environments may be provided. For example, it is envisaged in certain cases that the film solution may be subjected to static first, second and third environments. For example, the three environments could be established in a three-stage process, where the film solution on the substrate could be moved sequentially through the three stages of the process. Indeed, in each stage of such a three-stage process, the environments could be static or could be provided as gas flows.

While the method and apparatus for carrying out the method according to the invention for producing the polymer films have been described as essentially being carried out on laboratory bench scale apparatus, it will be readily apparent to those skilled in the art that the method according to the invention can be scaled up into an industrial process, and the scaling up of the method will be readily apparent to those skilled in the art.

It is envisaged that the polymer films formed according to the invention will have many uses, for example, in drug delivery devices, such as micro-needle and other micro devices for delivering drugs to a subject over relatively lengthy treatment periods, for example, over seven to fourteen days, and indeed longer. The polymer films are also suitable for use in photonic applications, whereby the cavities may be used as time delay elements, filter elements and for other photonic applications.

In particular, the polymer films produced according to the invention are relatively lightweight, strong and mechanically robust structures with tuneable strength such as crush strength, yield points and the like.

It is also envisaged that the polymer films according to the invention may be used as cell scaffolding to grow cells, such as skin and tissue cells. It is envisaged that nutrients to grow cells may be included in the cavities formed in the polymer film which would enhance cell growth.

It is also envisaged that the method according to the invention may be carried out at any suitable temperature or pressure, other than room temperature and pressure as has been described. Indeed, it is envisaged that the method could be carried out in a completely enclosed environment whereby as well as controlling the relative humidity of the first, second and third environments, the temperatures and pressures of the first, second and third environments could also be controlled. In which case, the method could be carried out as a three-stage process with the film solution on the substrate being moved sequentially through the three stages of the process.

Claims

1. A method for producing a polymer film with an array of cavities therein, the method comprising forming a film of a polymer/solvent solution on a substrate, subjecting the film solution to a first environment adjacent a gas/film interface of the film solution, the first environment being adapted to accelerate solvent evaporation from the film solution through the gas/film interface of the film solution to establish a polymer concentration gradient in the film solution with the polymer concentration decreasing in a direction into the film solution from the gas/film interface so that the polymer concentration gradient is suitable for facilitating growth of liquid droplets into the film solution through the gas/film interface, subjecting the film solution to a second environment adjacent the gas/film interface thereof on establishment of the polymer concentration gradient, the second environment being adapted to condense a liquid on the gas/film interface surface to form droplets of the liquid thereon with the droplets growing into the film solution through the gas/film interface to form the cavities, and subjecting the film solution adjacent the gas/film interface thereof to a third environment adapted to inhibit further droplet growth and to evaporate the droplets from the cavities, the third environment being further adapted to control the rate of evaporation of the solvent from the polymer/solvent solution, so that when the liquid of the droplets is evaporated to an extent that the droplets no longer solely determine the shape and size of the cavities, the level of the solvent remaining in the polymer/solvent solution is sufficient to maintain the glass transition temperature of the film solution at a level below the temperature of the film solution adjacent the cavities to permit local polymer flow adjacent the cavities for determining the shape of the cavities.

25

2. A method as claimed in Claim 1 in which the rate of evaporation of the solvent from the film solution is controlled by the third environment so that when the droplets no longer solely determine the shape and size of the cavities, the level of the solvent remaining in the film solution is sufficient to maintain the glass transition temperature of the film solution adjacent the bases of the cavities below the actual temperature of the film solution adjacent the bases of the cavities.

30

3. A method as claimed in Claim 1 or 2 in which the film solution is subjected to the third environment until substantially all of the solvent is evaporated from the polymer/solvent solution of the film solution.
- 5 4. A method as claimed in any preceding claim in which the film solution is subjected to the third environment when the cavities formed by the droplets extend into the film solution to a predefined depth.
5. A method as claimed in any preceding claim in which the film solution is
10 subjected to the third environment when the cavities formed by the droplets are of a predefined size.
6. A method as claimed in any preceding claim in which the third environment is of relative humidity which is adapted to control the vapour-liquid equilibrium adjacent
15 the droplet interface with the third environment for evaporation of the droplets.
7. A method as claimed in Claim 6 in which the relative humidity of the third environment is lower than the relative humidity of the second environment.
- 20 8. A method as claimed in Claim 6 or 7 in which the relative humidity of the third environment does not exceed the relative humidity of the first environment.
9. A method as claimed in any of Claims 6 to 8 in which the relative humidity of the third environment is one of similar to and lower than the relative humidity of the
25 first environment.
10. A method as claimed in any of Claims 6 to 9 in which the third environment comprises a gaseous medium of relative humidity lying in the range of 0% to 50%.
- 30 11. A method as claimed in Claim 10 in which the relative humidity of the gaseous medium of the third environment lies in the range of 0% to 20%.

12. A method as claimed in Claim 11 in which the relative humidity of the gaseous medium of the third environment lies in the range of 0% to 10%.
13. A method as claimed in any of Claims 10 to 12 in which the gaseous medium of the third environment is passed over the gas/film interface of the film solution as a final gas flow during the period during which the film solution is subjected to the third environment.
14. A method as claimed in Claim 13 in which the velocity of the gaseous medium of the final gas flow adjacent the gas/film interface lies in the range of 0 metres per second to 0.4 metres per second.
15. A method as claimed in Claim 14 in which the velocity of the gaseous medium of the final gas flow adjacent the gas/film interface lies in the range of 0.03 metres per second to 0.29 metres per second.
16. A method as claimed in Claim 15 in which the velocity of the gaseous medium of the final gas flow adjacent the gas/film interface is approximately 0.06 metres per second.
17. A method as claimed in any of Claims 10 to 16 in which the gaseous medium of the third environment comprises nitrogen.
18. A method as claimed in any of Claims 10 to 17 in which water vapour is entrained in the gaseous medium of the third environment to produce the third environment to be of the appropriate relative humidity.
19. A method as claimed in any preceding claim in which the first environment is adapted to control evaporation of the solvent from the film solution to produce a surface temperature at the gas/film interface to facilitate formation of the droplets thereon when the film solution is subjected to the second environment.

20. A method as claimed in any preceding claim in which the first environment is adapted to control evaporation of the solvent from the film solution to produce a surface temperature at the gas/film interface of the film solution not greater than the dew point temperature of the second environment.
- 5
21. A method as claimed in any preceding claim in which the first environment is adapted to control the evaporation of the solvent from the film solution to produce a surface temperature at the gas/film interface of the film solution below the dew point temperature of the second environment.
- 10
22. A method as claimed in any of Claims 19 to 21 in which the relative humidity of the first environment is controlled to be below a value at which liquid would condense out of the first environment onto the gas/film interface of the film solution.
- 15
23. A method as claimed in Claim 22 in which the first environment comprises a gaseous medium of relative humidity lying in the range of 0% to 85%.
24. A method as claimed in Claim 23 in which the relative humidity of the gaseous medium of the first environment lies in the range of 0% to 45%.
- 20
25. A method as claimed in Claim 24 in which the relative humidity of the gaseous medium of the first environment lies in the range of 0% to 5%.
26. A method as claimed in any of Claims 23 to 25 in which the gaseous medium of the first environment is passed over the gas/film interface of the film solution as an initial gas flow during the period during which the film solution is subjected to the first environment.
- 25
27. A method as claimed in Claim 26 in which the velocity of the gaseous medium of the initial gas flow adjacent the gas/film interface of the film solution lies in the range of 0.03 metres per second to 1.14 metres per second.
- 30

28. A method as claimed in Claim 27 in which the velocity of the gaseous medium of the initial gas flow adjacent the gas/film interface of the film solution lies in the range of 0.17 metres per second to 0.57 metres per second.
- 5 29. A method as claimed in Claim 28 in which the velocity of the gaseous medium of the initial gas flow adjacent the gas/film interface of the film solution is approximately 0.29 metres per second.
30. A method as claimed in any of Claims 27 to 29 in which at least one of the
10 relative humidity and the velocity of the gaseous medium of the initial gas flow is set to establish an evaporation rate of the solvent from the polymer/solvent solution to produce a surface temperature of the film solution adjacent the gas/film interface not greater than the dew point temperature of the second environment prior to the film solution being subjected to the second environment.
- 15 31. A method as claimed in any of Claims 27 to 30 in which at least one of the relative humidity and the velocity of the gaseous medium of the initial gas flow is set to establish an evaporation rate of the solvent from the polymer/solvent solution to produce a surface temperature of the film solution adjacent the gas/film interface
20 below the dew point temperature of the second environment prior to the film solution being subjected to the second environment.
32. A method as claimed in any of Claims 23 to 31 in which the gaseous medium of the first environment is nitrogen.
- 25 33. A method as claimed in any of Claims 23 to 32 in which water vapour is entrained in the gaseous medium of the first environment to produce the first environment to be of the appropriate relative humidity.
- 30 34. A method as claimed in any preceding claim in which the relative humidity of the second environment is adapted to control the vapour-liquid equilibrium adjacent the droplet interface with the second environment for controlling the rate of growth of

droplets into the film solution.

35. A method as claimed in any preceding claim in which the relative humidity of the second environment is controlled for controlling the progression of solvent
5 evaporation from the film solution, and in turn for controlling the polymer concentration gradient in the film solution.

36. A method as claimed in any of Claims 34 or 35 in which the relative humidity of the second environment is greater than the relative humidity of the first
10 environment.

37. A method as claimed in any of Claims 34 to 36 in which the relative humidity of the second environment is determined by the depth to which the cavities are required to extend into the polymer/solvent solution and the required transverse
15 cross-section of the cavities.

38. A method as claimed in any of Claims 34 to 37 in which the second environment comprises a gaseous medium of relative humidity lying in the range of 15% to 100%.
20

39. A method as claimed in Claim 38 in which the relative humidity of the gaseous medium of the second environment lies in the range of 40% to 90%.

40. A method as claimed in Claim 39 in which the relative humidity of the gaseous medium of the second environment lies in the range of 50% to 85%.
25

41. A method as claimed in any of Claims 38 to 40 in which the gaseous medium of the second environment is passed over the gas/film interface of the film solution as an intermediate gas flow during the period during which the film solution is
30 subjected to the second environment.

42. A method as claimed in Claim 41 in which the flow rate of the gaseous

medium of the intermediate gas flow over the gas/film interface of the film solution is controlled for controlling the progression of solvent evaporation from the film solution.

5 43. A method as claimed in Claim 42 in which the velocity of the gaseous medium of the intermediate gas flow adjacent the gas/film interface of the film solution lies in the range of zero metres per second to 0.4 metres per second.

10 44. A method as claimed in Claim 43 in which the velocity of the gaseous medium of the intermediate gas flow adjacent the gas/film interface of the film solution lies in the range of 0.03 metres per second to 0.29 metres per second.

15 45. A method as claimed in Claim 44 in which the velocity of the gaseous medium of the intermediate gas flow adjacent the gas/film interface of the film solution is approximately 0.06 metres per second.

46. A method as claimed in any preceding claim in which the duration during which the film solution is subjected to the second environment is determined by the size to which the cavities are to be formed.

20 47. A method as claimed in any preceding claim in which the polymer/solvent solution is prepared so that the level of solvent in the polymer/solvent solution is such that the level of the solvent in the polymer/solvent solution does not fall below a level which would result in the glass transition temperature of the polymer solution rising above the temperature of the film solution during the period in which the film solution is being subjected to the first and second environments, and during the period of the third environment when the film solution is being subjected to the third environment until local polymer flow adjacent the cavities for determining the shape of the cavities is completed.

30 48. A polymer film having an array of cavities therein, the polymer film being formed by a method as claimed in any preceding claim.

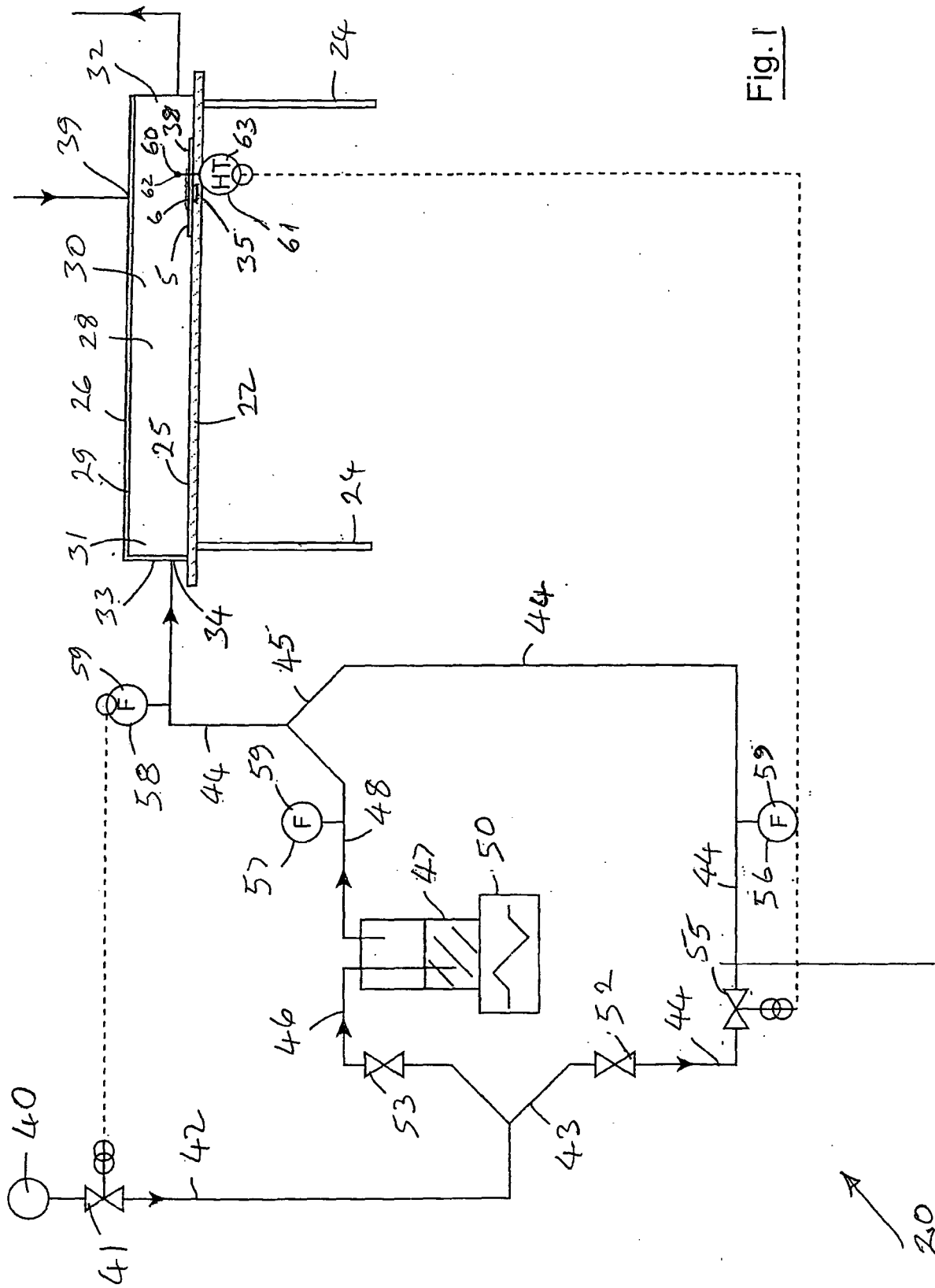


Fig. 1

20

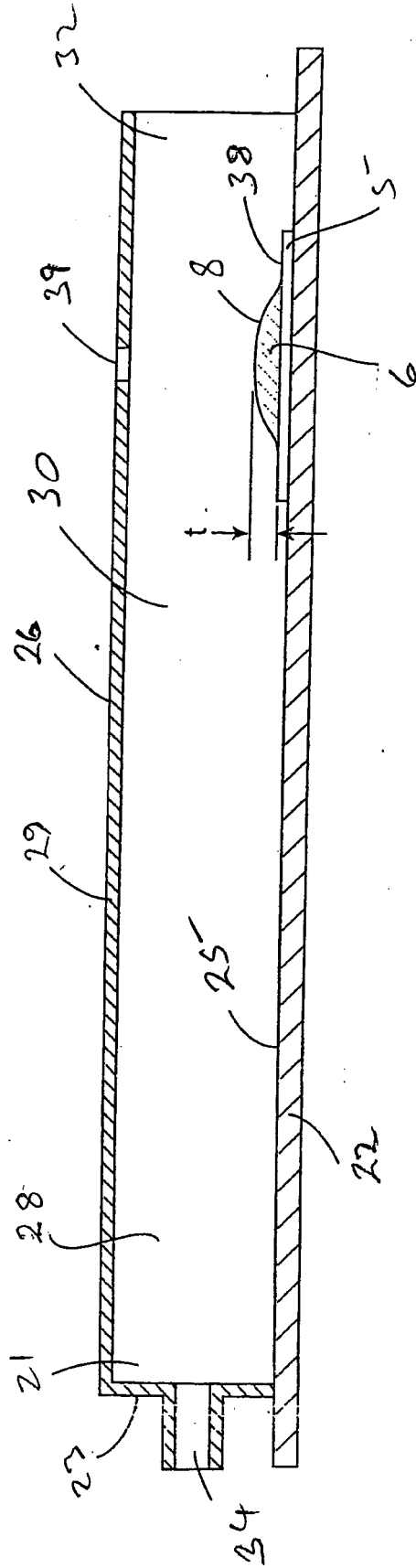
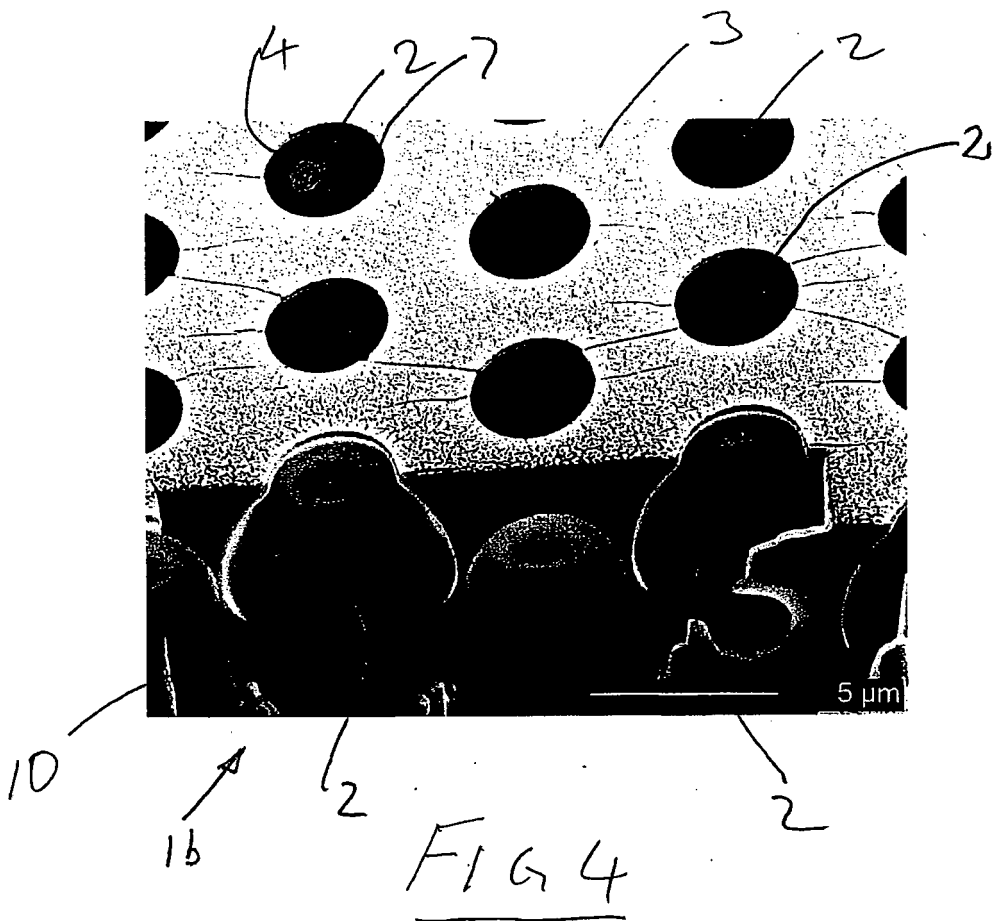
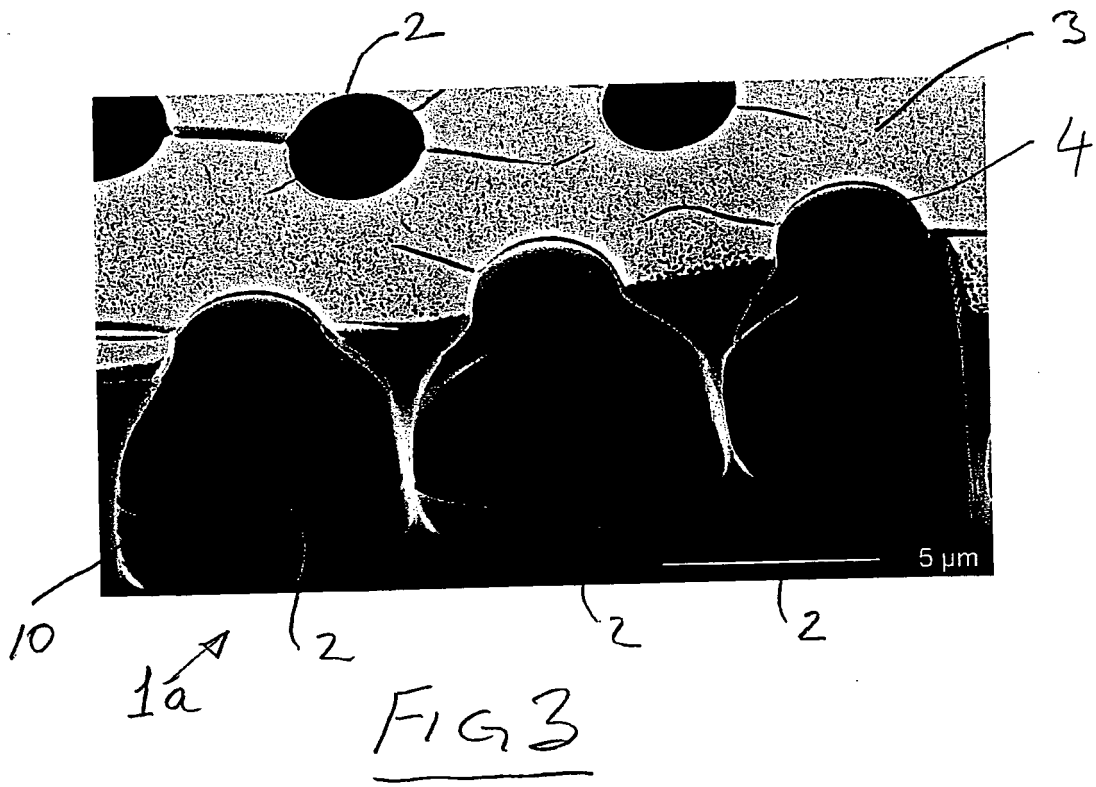
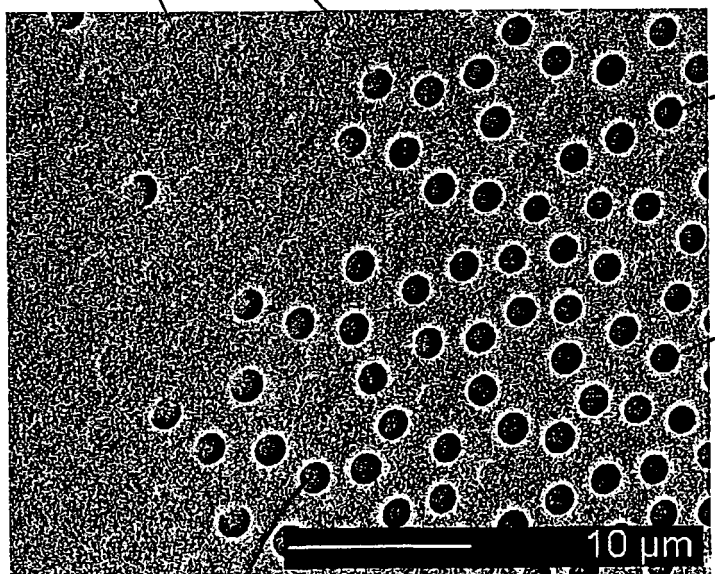
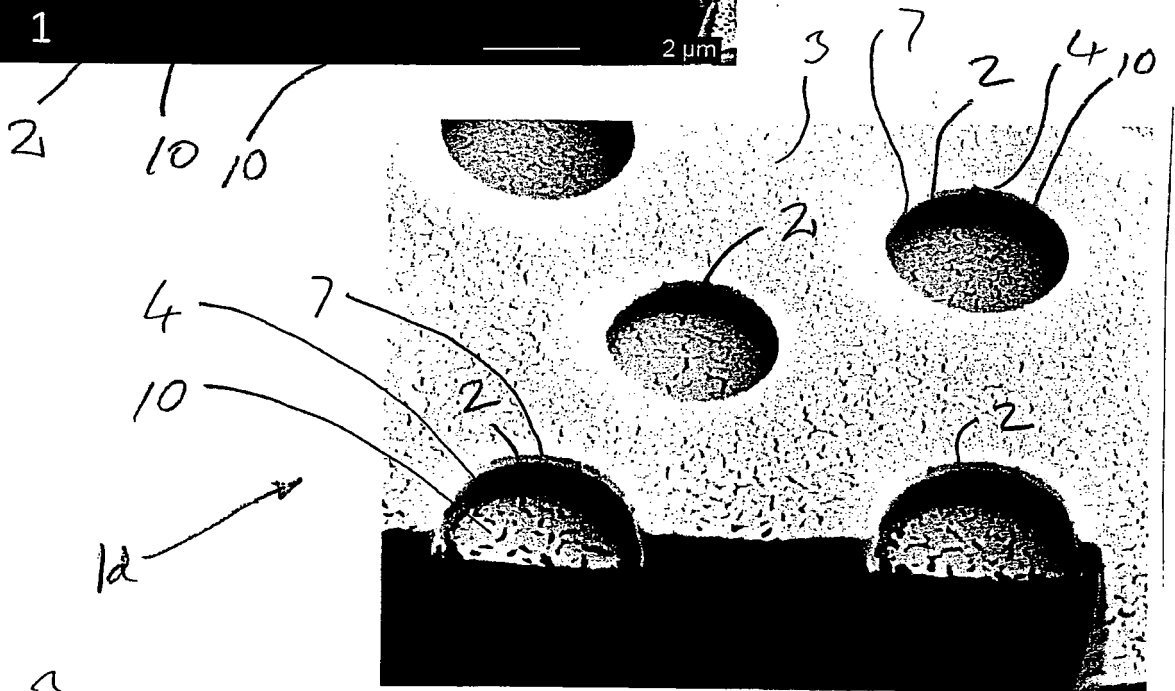
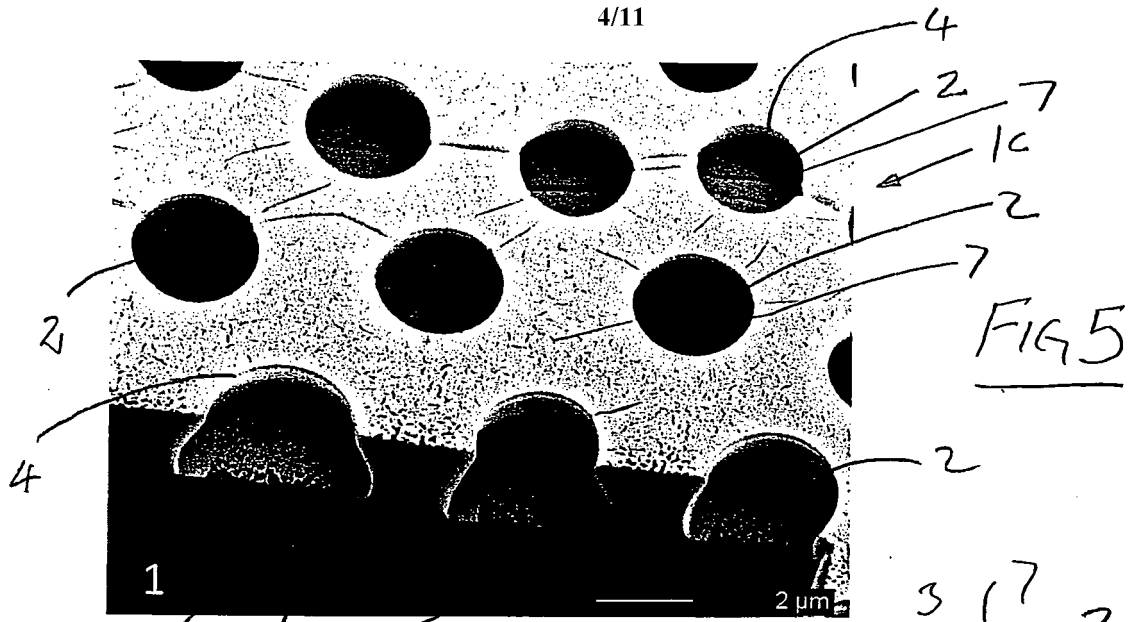


Fig. 2





(a)
1d
FIG 6
(b)

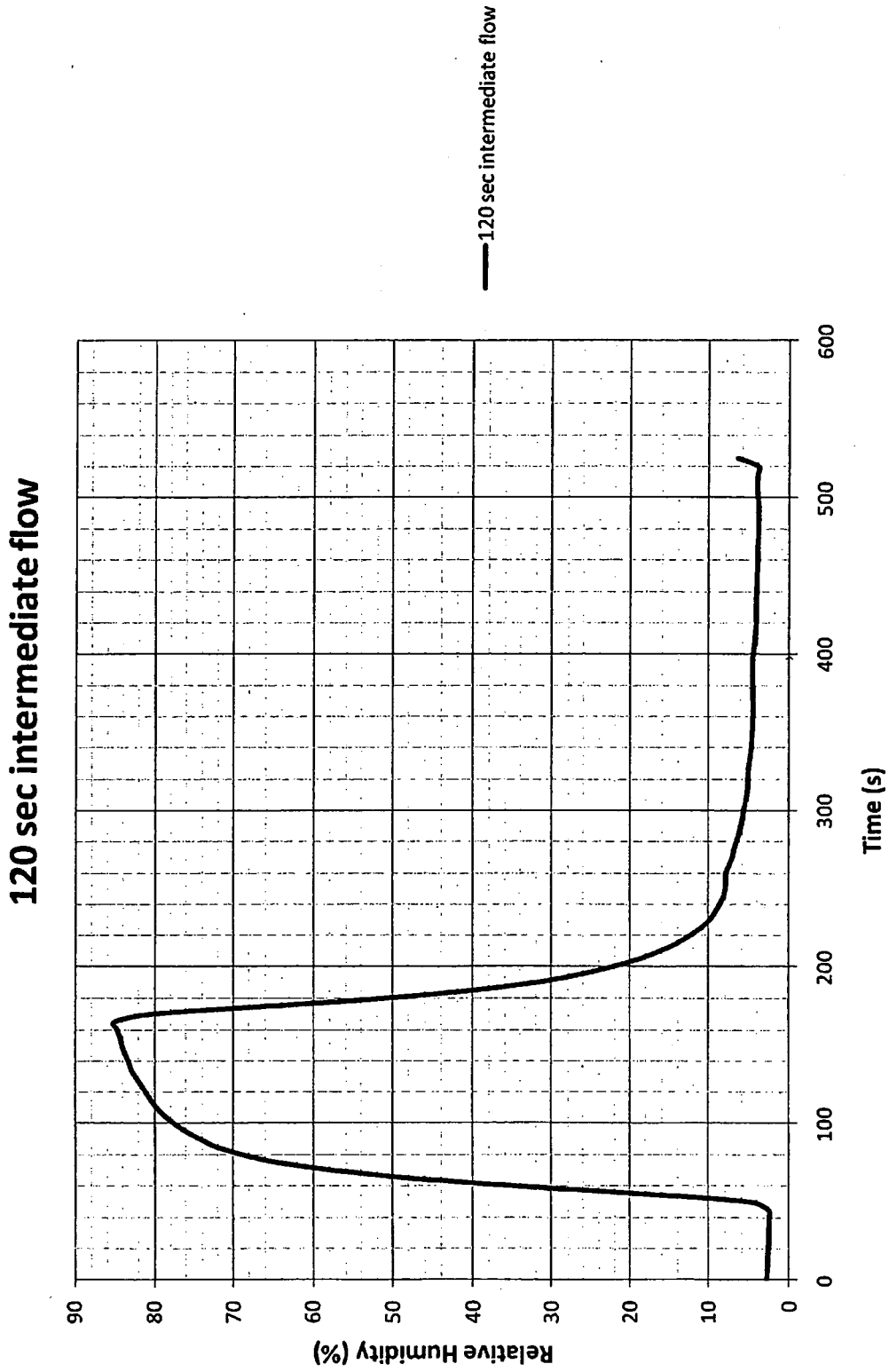


FIG 7

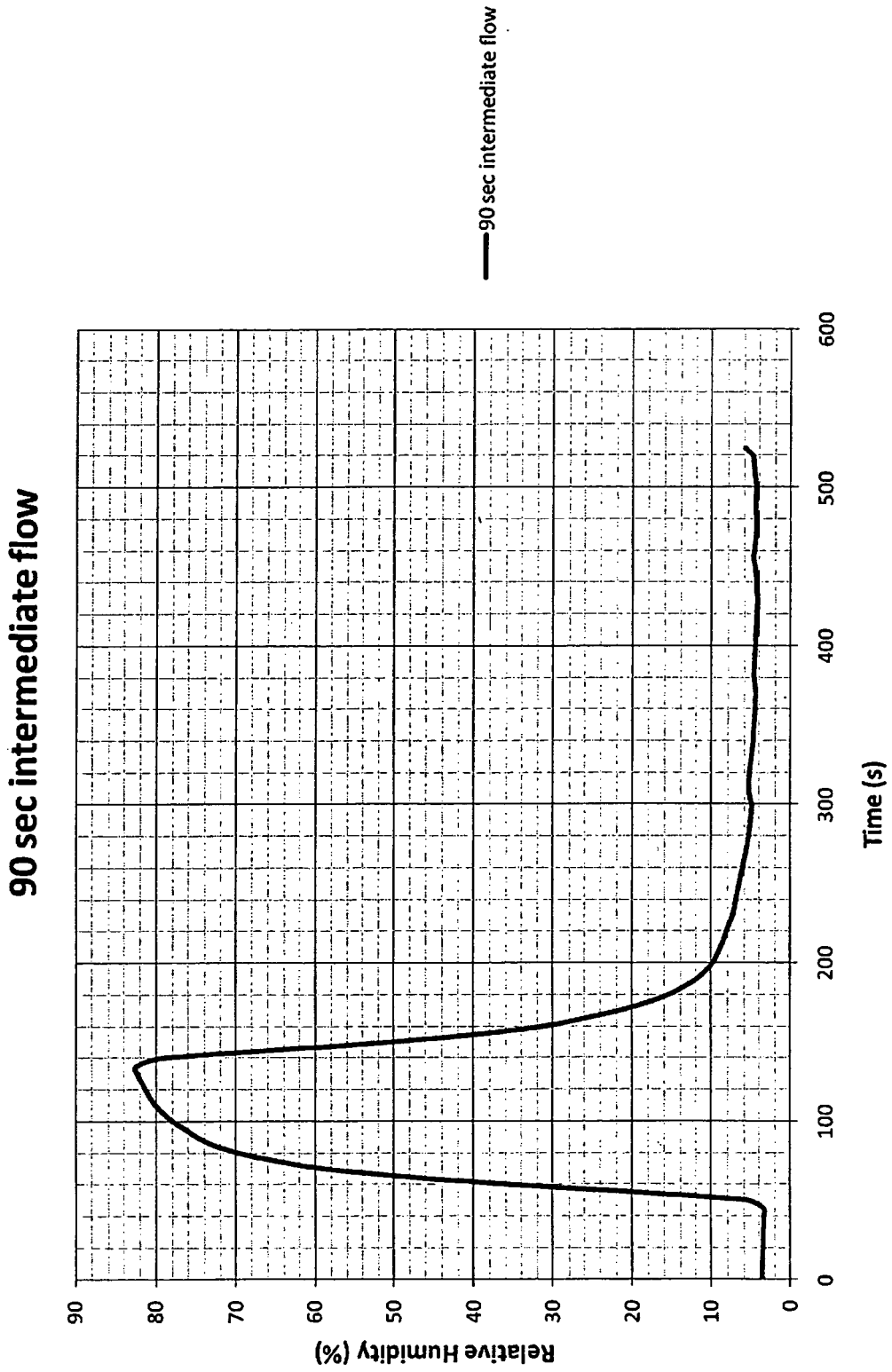


FIG 8

60 sec intermediate flow

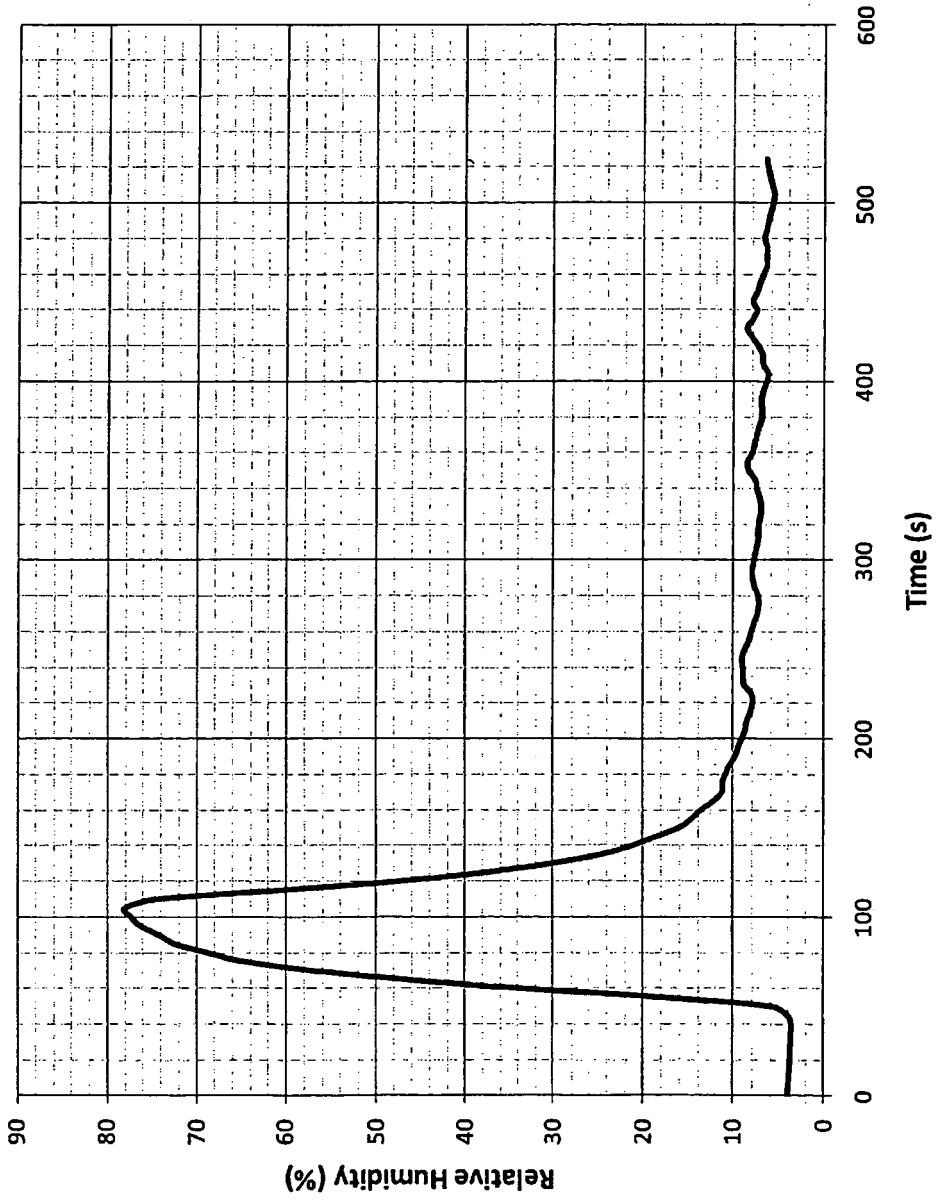


Fig 9

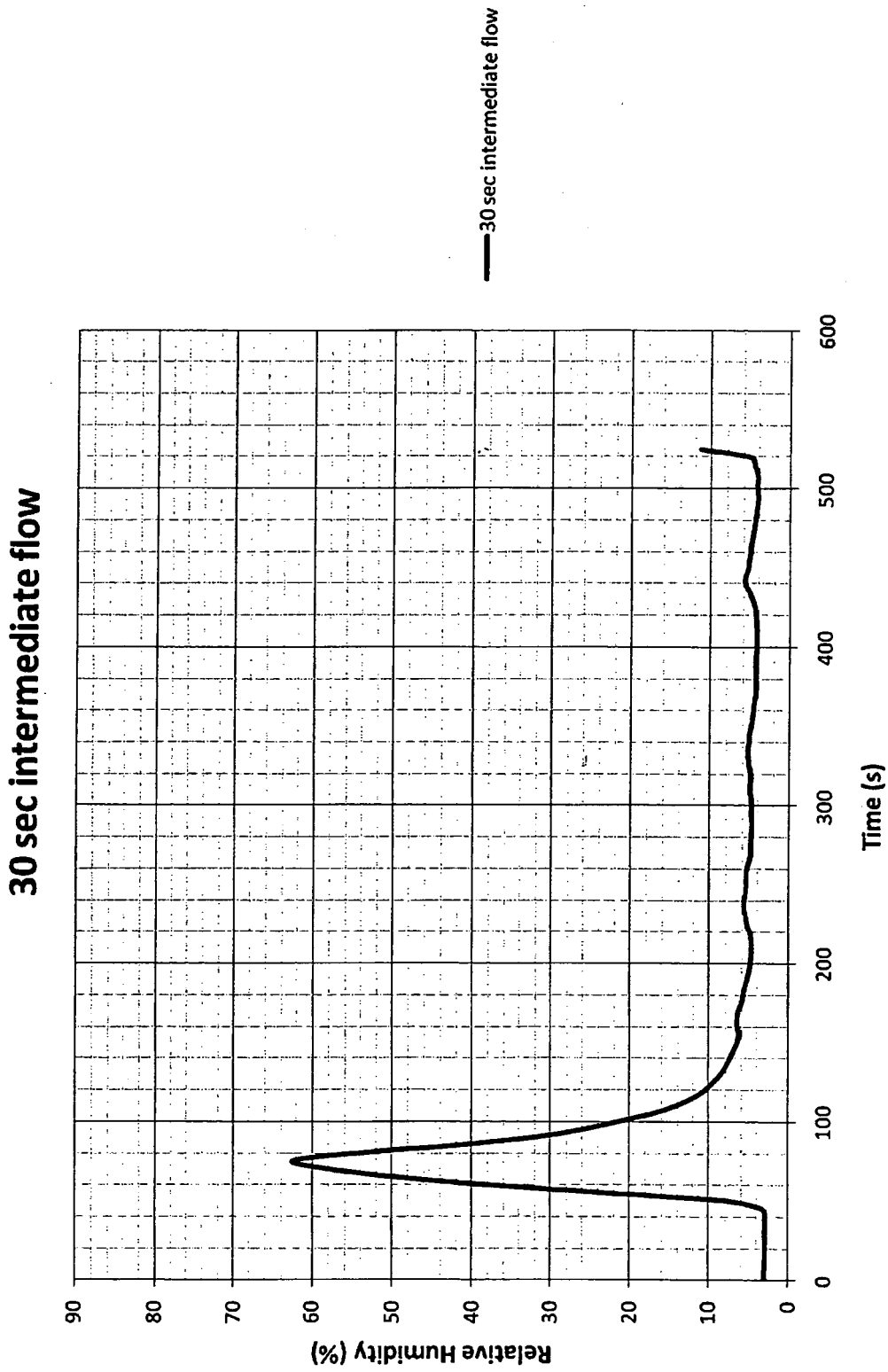


FIG 10

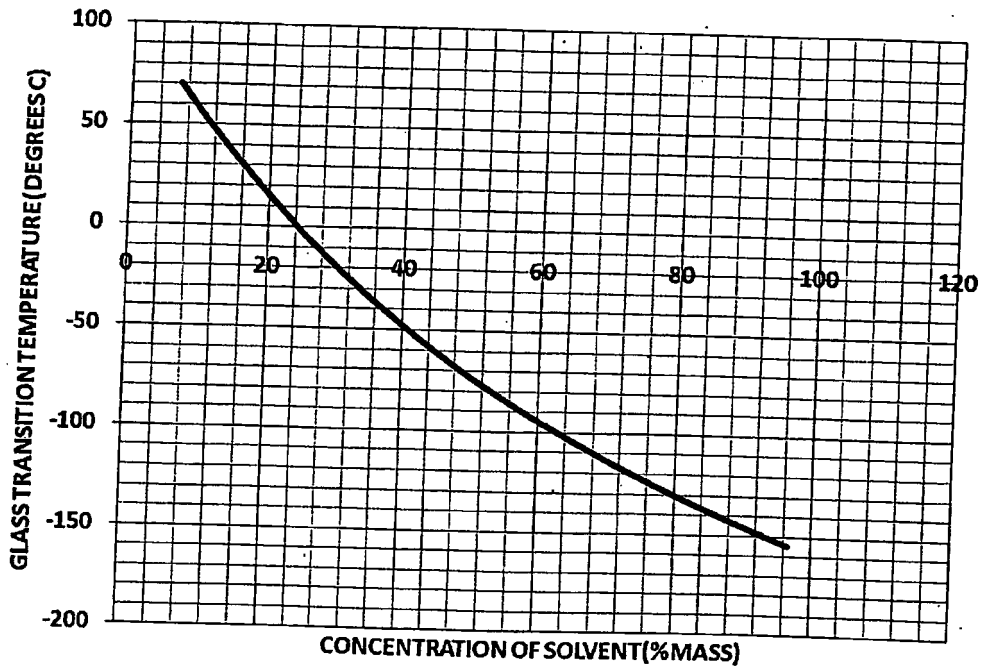


FIG 11

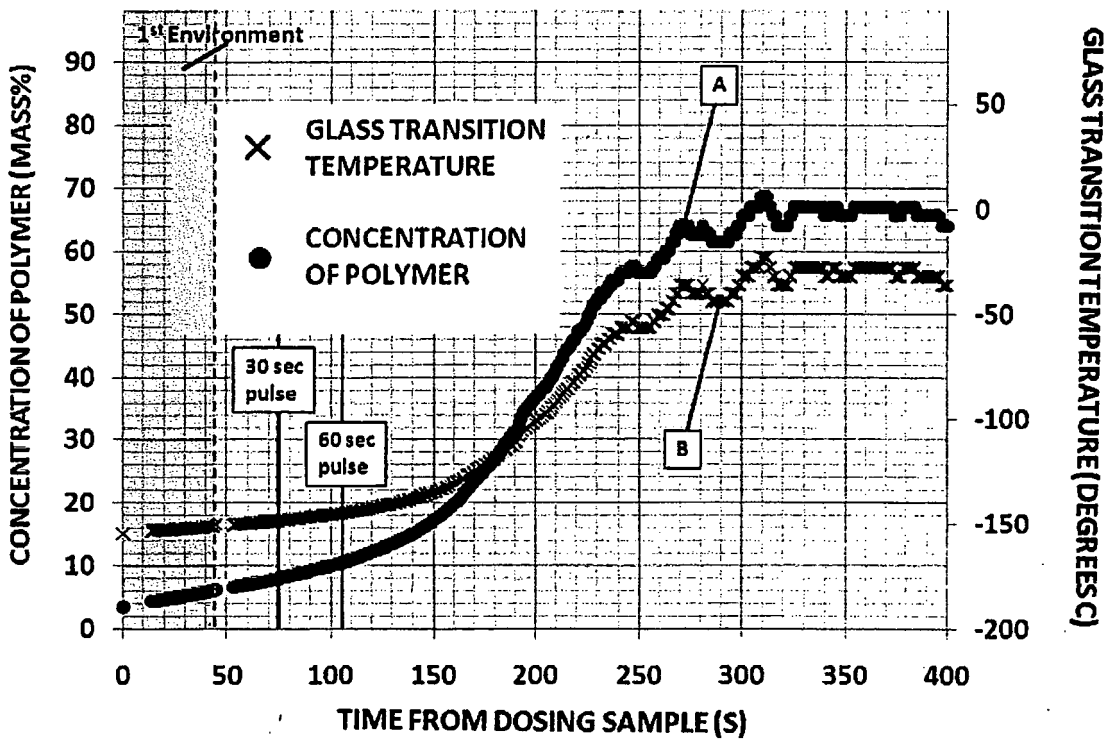


FIG 12

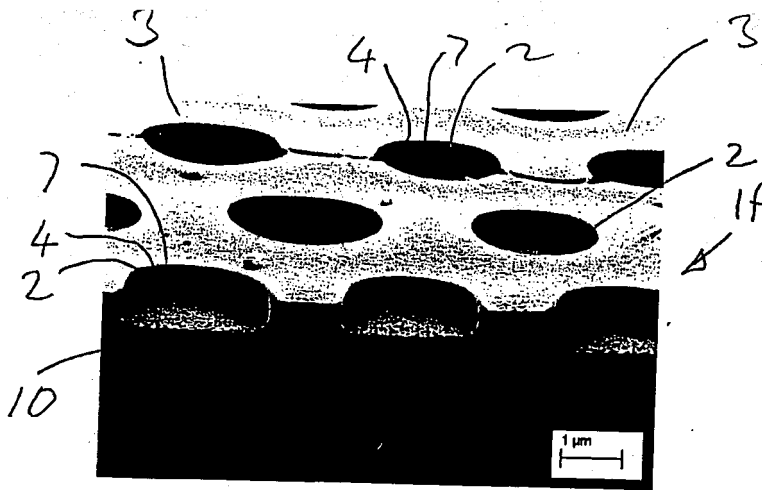


FIG 13

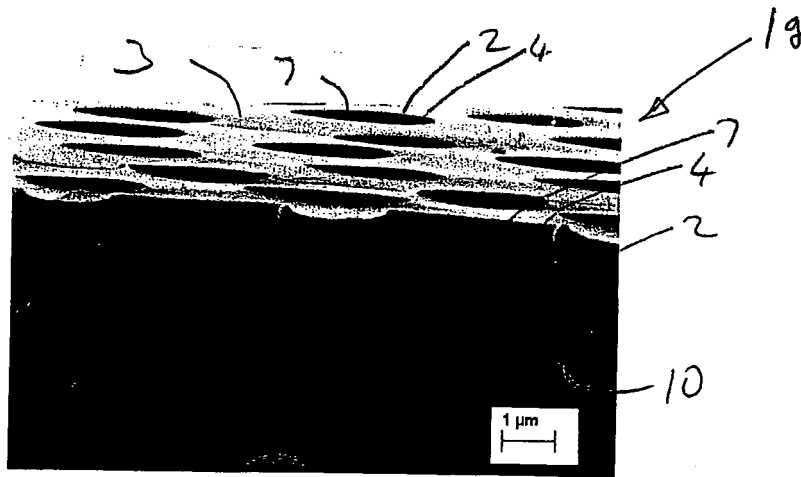


FIG 14

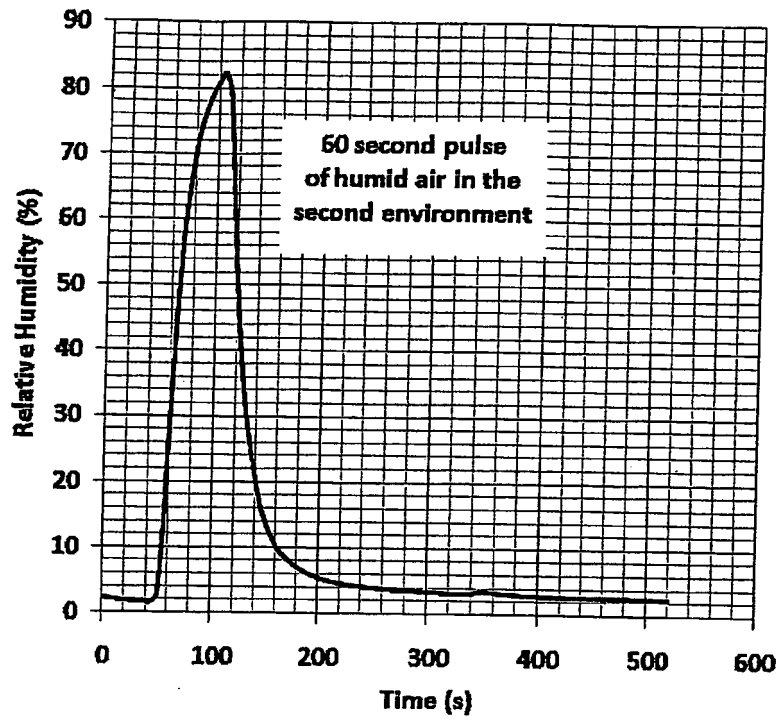


FIG 15

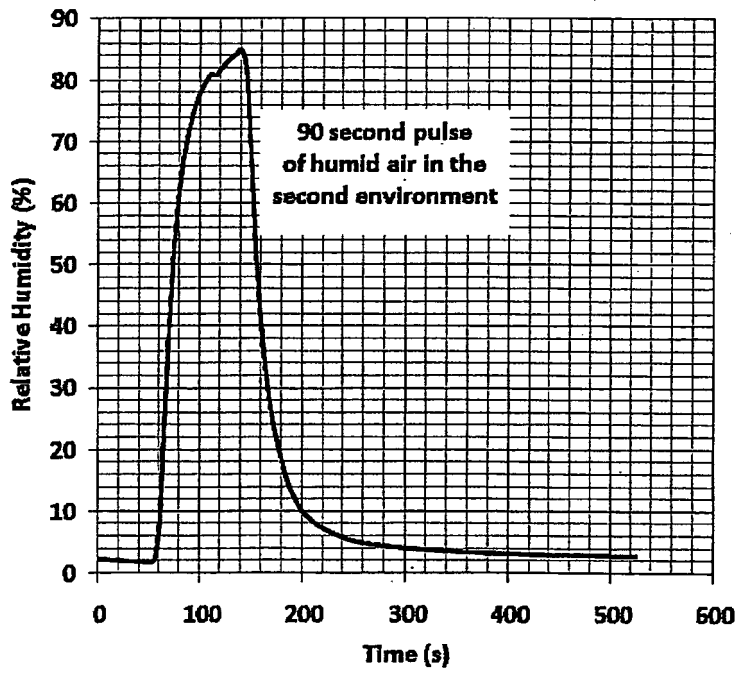


FIG 16

INTERNATIONAL SEARCH REPORT

International application No
PCT/IE2010/000058

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D69/02 B01D67/00 G02B6/122
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
B01D G02B

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	WO 2009/069110 A1 (TRINITY COLLEGE DUBLIN [IE]; DALY RONAN [IE]; BOLAND JOHN [IE]; CONNOL) 4 June 2009 (2009-06-04) cited in the application	48
A	the whole document	1-47
X	DE 10 2006 036863 A1 (UNIV CHEMNITZ TECH [DE]) 14 February 2008 (2008-02-14)	48
A	figures 3,5	1
X,P	US 2010/070026 A1 (ITO KOJU [JP] ET AL) 18 March 2010 (2010-03-18) paragraphs [0079] - [0087]; figures 2-4,10	48

Further documents are listed in the continuation of Box C.

See patent family annex.

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- "P" document published prior to the international filing date but later than the priority date claimed

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- "&" document member of the same patent family

Date of the actual completion of the international search 26 January 2011	Date of mailing of the international search report 03/02/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Goers, Bernd

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IE2010/000058

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009069110	A1	04-06-2009	NONE
DE 102006036863	A1	14-02-2008	NONE
US 2010070026	A1	18-03-2010	JP 2010063768 A 25-03-2010