There is disclosed a device (1) for generating fine bubbles, comprising a substrate (3) having holes (5) therethrough, each hole comprising a gas inlet (7) and a gas outlet (9), wherein the width of the gas outlet is greater than the width of the gas inlet. A method of manufacturing said device and a method of generating fine bubbles.
Micro-fluidic approach to sparge design

\[ \Delta P_b = \frac{2 \gamma}{r_b} \]

\[ \tau = \mu \frac{dU}{dy} \]

\[ \text{wall shear stress} \]

\[ \tau = \frac{R}{2} \frac{dP}{dx} \]

\[ Q = \frac{\pi d^4}{128 \mu} \left( \frac{\Delta P_p}{l_p} \right) \]

Figure 3.
Figure 5.
Figure 7.
BUBBLES GENERATION DEVICE AND METHOD

[0001] The present invention generally relates to a device for generating bubbles and, more particularly, to a device for generating fine bubbles and various uses thereof. The invention also comprehends a method of manufacturing said device and a method of generating fine bubbles.

[0002] The formation of fine bubbles is a well-studied and reported area of research. Recently, attention has been paid to various methods of utilizing fine bubbles having a diameter of micrometer level, and various apparatus for generating fine bubbles have been proposed.

[0003] Some of the common techniques used to form gas bubbles include: compressed air to dissolve air into a liquid stream, which is then released through nozzles to form bubbles by cavitation; air streams delivered under a liquid surface, where bubbles are broken off mechanically, say by agitation or shear forces; and ultrasonic induced cavitation.

[0004] In a system to generate air bubbles by introducing air into water flow with a shearing force using vanes and an air bubble jet stream, it is often required to employ a higher number of revolutions to generate cavitation. However, problems arise, such as power consumption increase and corrosion of vanes or vibration caused by the generation of cavitation. Further, such a technique does not lend itself to generating large amounts of fine bubbles.

[0005] The desire for small bubbles is that they provide a variety of excellent effects, which have been utilized in many industrial fields including plant cultivation, aquafarming, wastewater treatment and the like. It is effective to reduce the diameter of bubbles to increase their surface area relative to their volumes, thereby enlarging the contact area between the bubbles and the surrounding liquid; thus, a more rapid mass transfer process can take place when the bubble size is reduced.

[0006] In wastewater treatment plants, it is known to aerate effluent, or sludge, as part of the wastewater purification process. Generally, air is introduced near the bottom of an aeration tank containing wastewater and bacterial floc via a system of pipes and/or hoses. As the air rises to the surface as air bubbles, some of the oxygen in the air is transferred to the wastewater and is consumed by the respiring bacteria during digestion which aids in the treatment of sewage. The more oxygen that is supplied to the bacteria, the more efficient the digestion process. It is desirable, therefore, to provide smaller bubbles whereby to enhance further the efficiency of the digestion process.

[0007] A similar requirement exists in bioreactors and fermenters in cases where they are sparged for aeration purposes. Specifically, the yeast manufacturing industry has the requirement where growing and reproducing yeast bacteria need constant oxygen replenishment for respiration purposes.

[0008] However, in an aeration system using a conventional-type fine bubble generating system, for instance a diffusion system based on injection, even when fine pores are provided, when air bubbles are injected under pressure through pores, the volume of each bubble is expanded and the diameter of each bubble is increased to several millimetres due to the surface tension of the air bubbles during injection. Such a method encounters difficulty in generating fine bubbles of small diameter. Another problem associated with such a method is the clogging of the pores, which reduces the efficiency of the system.

[0009] A further application of small bubbles is the extraction of hard-to-lift oil reserves in some fields which either have little oil left, or have the oil locked in sand. Bubbling gas up through such oil-bearing reserves has the effect of lifting the oil as the bubbles rise under gravity and bringing the oil with them. The bubbles are formed in water and pumped into the well or reserve and the oil is carried at the interface between the gas and water of each bubble as it passes through the reserves. Hence, the smaller the bubble, the greater the relative surface area for transport of the oil.

[0010] It is thus desirable to generate fine bubbles in a more convenient and efficient manner than known hitherto.

[0011] The general perception is that in order to reduce the size of a bubble, the solutary requirement is for the pore size through which the bubble is formed be reduced. However, there are a number of reasons why this perception is ill-conceived.

[0012] The first of these reasons is that the bubble is “anchored” to the substrate material through which it is formed, and will continue to inflate until the bubble breaks free by some disruptive force. The forces can, for instance, be buoyancy, inertial or shear forces applied to the bubble as it develops. The interfacial tension controls the force with which the bubble is held by virtue of it being anchored to the surface. In this way, there are three interactions that need be considered:

[0013] the interaction between the liquid and solid substrate, \( \gamma_{ls} \) [mN/m];
[0014] the interaction between the liquid and gas (i.e. air), \( \gamma_{lg} \) [mN/m]; and
[0015] the interaction between the solid substrate and gas (i.e. air), \( \gamma_{sg} \) [mN/m].

[0016] The relative contribution of these forces controls the nature of bubble growth and the ease with which the bubble is able to break away from the surface.

[0017] In addition to the above, the rate of bubble growth,

\[
\frac{dr}{dt}
\]

is independent of the hole size, but can be expressed as:

\[
\frac{dr}{dt} = \frac{F}{4\pi r^2}
\]  \hspace{1cm} \text{Formula (1)}

[0018] Where \( F \) is the flow rate of gas going through the hole, and \( r_b \) is the radius of the bubble. This implies that the smaller the bubble, the faster the rate of growth, and this can clearly be seen from FIG. 1 which shows the rapid growth of a bubble through a single hole of 30 microns diameter.

[0019] It has been observed that bubbles form more or less instantaneously at the surface of a pierced or sintered material. As a gas bubble emerges from a hole into a liquid, the shape of the bubble is assumed to be a spherical cap of radius \( r \), and height \( h \), as seen in FIG. 1. The volume of the bubble is thus given by:

\[
V = \frac{2}{3} \pi h^2 (3r - h)
\]  \hspace{1cm} \text{Formula (2)}
There exists a geometrical relationship between bisecting cords that allows Formula (2) to be transformed to a single variable, \( h \), such that:

\[
V = \pi \left( \frac{r_0 h^2}{2} - \frac{h^3}{6} \right)
\]

Formula (3)

The rate of volumetric growth of a bubble, \( \frac{dV}{dt} \), is equal to the flow rate of gas, \( F \), through the hole, given a constant differential pressure, \( \Delta P \). The differential identity:

\[
\frac{dV}{dt} = \frac{dh}{dt} \frac{dV}{dh}
\]

Formula (4)

Formula (4) can be used to give the linear rate of growth of the bubble:

\[
\frac{dh}{dt} = \frac{2F}{\pi r_0^2 + h^2}
\]

Formula (5)

A numerical solution of Formula (5) gives the rate of growth of the bubble radius, as seen in FIG. 2. The analysis shown in FIG. 2 is consistent with the observation that bubbles form more or less instantaneously at the surface of a pierced or sintered material. The extremely rapid growth of the bubble radius from the initial condition of \( r_0 = 15 \) \( \mu \text{m} \) to a radius of 250 \( \mu \text{m} \) (0.5 mm diameter) in 0.01 seconds can be seen. This is followed by a relatively steady growth rate. The solution of Formula (5) is thus also consistent with the observations.

It is known, from the Young-Laplace equation, that the maximum pressure, \( \Delta P \), within the bubble is achieved when the bubble is at its smallest radius, \( r_0 \):

\[
\Delta P = P_{\text{inside bubble}} - P_{\text{outside bubble}} = \frac{2\gamma}{r_0}
\]

Formula (6)

Where \( \gamma \) is the liquid/gas interfacial tension.

The minimum radius of the bubble occurs when the bubble is a hemisphere of the same radius of the hole through which it passes, which therefore constitutes the point of maximum pressure in the bubble; this is known as the breakthrough pressure.

It is desirable to provide means for removing bubbles from the surface of the substrate and into the liquid before the bubble grows too large. It may be desirable, for instance, to generate fine bubbles having diameters of 100 microns or less, and preferably 50 microns or less.

From the description that is to follow, it will become apparent how the present invention addresses the deficiencies associated with known techniques and provide numerous additional advantages not hitherto contemplated or possible with known constructions.

The inventors postulated that if the flow of air, \( F \), could be stopped on reaching the break-through pressure of the bubble, then the residual pressure in the hole would inflate the bubble to a small size, which subsequently could be cleaved from the surface, before flow was resumed.

A reservoir of air would be formed in the pore that feeds the bubble, which is of depth \( \delta \), and radius \( r_0 \). From Boyle’s law, the initial state and bubble break-through, subscript “0”, can be related to the final state, subscript “1”:

\[
\rho_0 V_0 = \rho_1 V_1
\]

Formula (7)

The volumes at the initial and final states are given by:

\[
V_0 = 2\pi r_0^2 \delta + \frac{2}{3} \pi r_0^3
\]

Formula (8)

\[
V_1 = 2\pi r_1^2 \delta + \frac{4}{3} \pi r_1^3
\]

Formula (8)

The potential bubble size can be determined by combining Formulas (6), (7) and (8), and simplifying gives the relationship in the form of depressed cubic expression:

\[
2r_1^3 - (3\rho_0 r_0^2 \delta + \rho_1 r_1^2) r_1 + 3\rho_0 \rho_1 r_1^2 = 0
\]

Formula (9)

Where \( \delta \) is the length/depth of the hole (i.e., thickness of substrate), \( r_0 \) is the radius of the hole through which the bubble is formed, and \( r_1 \) is the final bubble size.

The solutions to Formula (9) are clearly dependent on the values of \( r_0 \) and \( \delta \). For typical values of \( r_0 = 15 \) \( \mu \text{m} \) and \( \delta = 70 \mu \text{m} \), the solution to Formula (9) gives, \( r_1 = 30 \mu \text{m} \), a bubble twice the size of the hole, but within the desired range. Table 1 gives a range of solutions for which a bubble will form when equilibrium is reached. These final values are all of a size which would provide good mass transfer if formed in large quantities.

### Table 1

<table>
<thead>
<tr>
<th>Hole radius [( \mu \text{m} )]</th>
<th>Plate thickness [( \mu \text{m} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>22</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>23</td>
<td>35</td>
</tr>
</tbody>
</table>

The inventors considered means for stopping the gas flow at the point of break-through of the bubble. As there are tens of thousands of holes in a typical porous element, individually stopping flow in each hole would seem prohibitively complex.

A number of alternative routes were considered which included:

- oscillatory or pulsed gas flow;
- using a sonic frequency actuator, such as a speaker, to cause pressure peaks and troughs;
- a flexible membrane that would open and close the rear of the holes as gas flowed; and
- use of orifice plates to restrict flow during the expansion phase of growth.

Thus, according to a first aspect of the present invention, there is provided a device for generating fine bubbles, comprising a substrate having holes therethrough, each hole comprising a gas inlet and a gas outlet, wherein the width of the gas outlet is greater than the width of the gas inlet; wherein
the average gas inlet width ranges from about 2 to 10 microns; and/or wherein the average gas outlet width ranges from about 5 to 100 microns; and/or wherein the inlet diameter is \( \tfrac{3}{16} \) to \( \tfrac{3}{4} \) of the outlet diameter.

**0042** It was found that use of an orifice having an outlet size greater than the inlet size for the purpose of restricting flow would deliver the sought-after properties. As the bubble expands beyond the break-through pressure, air supply would be limited by the restriction of the orifice, and so the flow term, \( F \) in Formula (1) is reduced and consequently the rate of growth of the bubble is accelerated. In this way, there is provided a way in which to minimise the bubble size while retaining the capability of generating large amounts of fine bubbles. The complexity of the device is far less than that of known devices, such as those that employ cavitation as the predominant technique for generating fine bubbles.

**0043** With regard to the device, the cross-sectional shape of each hole may be one selected from circular, triangular, square, rectangular, pentagonal, hexagonal, heptagonal, octagonal, nonagonal and decagonal. Of course, it will be appreciated that other geometric shapes may be equally as effective in achieving the function of the present invention. A circular cross-section may in some embodiments be particularly effective in generating fine bubbles.

**0044** The device may be a porous member or may be regarded as such. The porous member may be utilised in applications such as redox fuel cells, particularly regeneration systems for such cells.

**0045** The width of the gas outlet may be an order of magnitude greater than the width of the gas inlet. Typically, the outlet diameter may be less that half the diameter of the desired bubble diameter. The inlet diameter should be small enough to choke the gas flow. This effect is particularly seen when the inlet diameter is \( \tfrac{3}{16}(0.1) \) to \( \tfrac{3}{4}(0.2) \) of the outlet hole diameter. Gas inlet widths in the range of 2 microns to 10 microns and gas outlet widths in the range from 20 microns to 50 microns in diameter are particularly effective. Consistency on geometry across the perforated surface may be critical to the effective performance of the devices; thus, a variation of no more than 10% is preferred; more particularly a variation of less that 1% may be desirable.

**0046** The hole may taper regularly from the gas inlet towards the gas outlet. Depending on the liquid-solid interfacial tension, the shape of the hole may prevent ingress of liquid into the holes. For example, a hydrophobic substrate with an open conical structure may desirably prevent liquid ingress.

**0047** The hole may taper irregularly from the gas inlet towards the gas outlet.

**0048** The hole density on the substrate may range from 400 to 10000 holes/cm\(^2\). The hole density is a balance between pressure drop and coalescence of the bubbles. The higher frequency of bubble generation, the more likely they are to coalesce when the hole packing density is high. Hole density of 1,000 to 2,500 holes/cm\(^2\) may be particularly favourable when using a square pitch. Staggered pitches have also been used to maximise bubble separation. Hexagonal and other pitches have been effective. Of course, it will be appreciated that other geometric pitches may be equally as effective in achieving the function of the present invention.

**0049** The thickness of the substrate may range from 20 to 1,000 microns; the thickness will impact the final bubble diameter as the reservoir of air increases. The preferred range may be 50 to 100 microns. Of course, it will be understood that other thicknesses of the substrate may be more suitable in different applications of the invention.

**0050** The gas outlet width may be about half the width of the desired bubble size, wherein the desired bubble size may range from 50 to 100 microns.

**0051** The substrate may have an active surface towards the gas outlets of the holes. The active surface is the surface in contact with the liquid phase in which the bubbles are to be dispersed. Having an active surface that attracts the liquid phase, for example a hydrophilic surface in the case as an aqueous liquid, is advantageous in producing small bubbles as the liquid favourably flows under the forming bubble and lifts the bubble from the surface, thereby enhancing fine bubble generation.

**0052** The wetting of the surface at which the bubbles form can be significant. To this end, at least a portion of the active surface may be formed of or coated with a hydrophilic material. A hydrophilic surface allows the liquid to “get under” the bubble as it grows, so as to lift it off and thus generate smaller bubbles.

**0053** It may be that at least a portion of the surface towards the gas inlet of the holes is formed of or coated with a hydrophilic material. Additionally, or alternatively, at least a portion of the interior of the holes may be coated with a hydrophobic material. A hydrophobic material does not wet and so the ingress of liquid into the holes or across to the gas side when the device is not active, under gas pressure, is prevented and allows rapid start-up with minimal breakthrough pressure requirements.

**0054** The substrate may be an elongate member. An elongate member may be particularly suitable for applications such as regeneration of catholyte solutions in redox fuel cells.

**0055** The gas outlet may comprise a lip projecting away from the active surface. The lip may act to lift the exiting-bubble higher in the laminar boundary layer of liquid flow, and to increase shear stresses to detach the bubble from the solid substrate. Of course, the substrate may be flexible which may improve its bubble-detachment capabilities.

**0056** The device may comprise one or more of sintered glass or metal powders, plastics, porous membranes, meshes and drilled or punctured sheets.

**0057** In some embodiments, it may be preferred that the device comprises stainless steel foils and/or polyimide films. These materials may be readily formed as thin sheets/substrates, which ability/property lends itself to the intended function of the invention.

**0058** In some embodiments, it may be that the angle of taper from the gas inlet towards the gas outlet is relative to the longitudinal axis of each hole and ranges from about 6° to 26°, and preferably from about 10° to 15°. Such angles, combined with the orifice diameter, provide superior control over the bubble size formation by limiting the reservoir of gas available for bubble formation.

**0059** It may be particularly advantageous that each hole is a frusto-conical shape.

**0060** In a second aspect, the present invention comprehends a method of manufacturing a device for generating fine bubbles, comprising the steps of:

- **0061** providing a substrate; and
- **0062** perforating the substrate at predetermined locations with holes of predetermined widths.

**0063** Selecting the locations of the holes in the substrate may be significant to prevent coalescence of the bubble at the substrate surface. A well designed pattern of distribution will
allow bubbles to form and be released into the liquid without other bubbles impacting during the formation process. A random distribution of holes may not necessarily allow this level of engineered control.

[0064] The step of perforating the substrate may involve using a laser. A laser provides an accurate way in which to perforate the substrate in term of location and size of the holes. This may be by way of forming a master template using laser machining and then mass producing sparge elements by electroplating or electro deposition.

[0065] In a third aspect, the present invention envisages a method of generating fine bubbles, comprising the steps of:

[0066] providing a device according to any of claims 1 to 25 (or as defined herein);

[0067] supplying the holes with a liquid; and

[0068] feeding a gas through the holes via the gas inlet of each hole.

[0069] In some embodiments, it may be preferred that the liquid is supplied across the holes to induce flow of the liquid. This may significantly reduce the resultant bubble size. The viscous drag on the forming bubble provided by liquid flow is a significantly larger force than buoyancy between the gas and the liquid. The viscous drag overcomes the adhesion force interfacial tension more rapidly and so smaller bubbles are formed.

[0070] While the device for generating bubbles described herebefore has various applications, a particularly effective application is use of the device in a catholyte regeneration system for a redox fuel cell, for example.

[0071] In an indirect or redox fuel cell, the oxidant (and/or fuel in some cases) is not reacted directly at the electrode but instead reacts with the reduced form (oxidized form for fuel) of a redox couple to oxidise it, and this oxidised species is fed to the cathode.

[0072] There are a number of constraints on this step of oxidising the redox couple. Oxidation of the redox couple should occur as rapidly as possible as a reduction in flow rate of the catholyte through the cathode will reduce the rate of energy production. The rate of energy production will also be reduced if oxidation of the redox couple is not as complete as possible, i.e. if a significant proportion of the redox couple remains unoxidised. The provision of apparatus which rapidly and completely oxidises redox couples present in catholyte solutions is made challenging by the need to ensure that the energy consumed when the oxidation step is taken is relatively low, otherwise the overall power generation performance of the fuel cell will be reduced. Additionally, the apparatus used to oxidise the redox couple should be as compact as possible, especially when the fuel cell is intended for use in portable or automotive applications.

[0073] The need to balance these conflicting requirements gives rise to inefficiencies in cell performance, particularly in automotive applications and in combined heat and power.

[0074] The device for generating fine bubbles may be taken to be a porous member.

[0075] In operation of a redox fuel cell, the catholyte may be provided flowing in fluid communication with the cathode through the cathode region of the cell. The redox mediator couple is at least partially reduced at the cathode in operation of the cell, and at least partially re-generated by reaction with the oxidant after such reduction at the cathode. The at least partial regeneration of the redox mediator couple is effected in the regeneration zone. Specifically, the interfacial area of oxidant passing through the active surface of the porous member and the catholyte flowing towards or adjacent to the porous member is large. Regeneration of the redox mediator couple begins at this point and continues as the catholyte, with oxidant entrained therein, passes through the reoxidation zone.

[0076] In a preferred arrangement, at least a portion of the channel wall may be open to expose the interior of the catholyte channel to at least a portion of the active surface of the porous member.

[0077] The porous member may be formed of any porous material that permits the throughput of the oxidant in sufficient volumes to enable the at least partially reduced redox couple to be at least partially re-generated, i.e. oxidised.

[0078] Thus, according to fourth aspect, the present invention contemplates a catholyte regeneration system for a redox fuel cell, comprising: a chamber; a first inlet port for receiving into the chamber reduced redox mediator couple from the cathode region of the cell; a first outlet port for supplying oxidised redox mediator couple to the cathode region of the cell; a second inlet port for receiving a supply of oxidant; and a second outlet port for venting gas, water vapour and/or heat from the chamber, a catholyte channel in fluid communication with the first inlet port, a device according to any of claims 1 to 25 (or as defined herein) having an active surface, and the catholyte channel being arranged to direct a flow of catholyte adjacent to or towards the active surface.

[0079] The device may comprise holes having an average diameter of 5 to 100 microns, preferably 20 to 50 microns.

[0080] By “cathode region” is meant that part of the cell bounded on one side by the cathode side of the membrane electrode assembly. Alternatively, or as well, the “cathode region” may be thought of as that part of the cell in which at least a part of the catholyte flowing therethrough in operation of the cell contacts the cathode side of the membrane electrode assembly.

[0081] Likewise, by “anode region” is meant that part of the cell bounded on one side by the anode side of the membrane electrode assembly.

[0082] To enhance the performance of the fine-bubble generating device (porous member), it may be formed or modified specifically to maximise the surface area of the oxidant passing therethrough. For example, the location and size of the pores (holes) may be controlled to encourage the release of small fine gas bubbles. Further, the flow of catholyte liquid towards or past the porous member will encourage the release of small bubbles before they have time to grow. The rapid removal of bubbles is advantageous as it allows fresh catholyte liquid to contact the active surface of the porous member.

[0083] Typically, average bubble size diameters are in the range of 1 to 1000 microns. Preferably, the formed bubble size is smaller, for example 150 microns in diameter or less, 1 to 100 microns, or most preferably, 25 to 50 microns in diameter. To achieve a flow of bubbles having average diameters falling within these preferred ranges, pores should be provided having a diameter which is smaller than the target bubble diameter by a factor of 3 to 10 times.

[0084] The rapid removal of bubbles can also be encouraged by rendering the surface of the porous member hydrophilic, either by coating it with a hydrophilic material, or by forming the active surface of the porous member from a hydrophilic material. The presence of a hydrophilic material on the active surface of the porous member will cause formed bubbles to be more easily released than from a hydrophobic.
surface. Preferably, such materials will have a surface energy of greater than 46 dynes/cm² and/or may include hydrophilic groups, such as hydroxyl groups. An example of such a material is acetate rayon. Additionally, or alternatively, acceptable hydrophilic properties can be achieved by treating metal surfaces. Such treated metal surfaces include annealed austenitic stainless steel, laser or plasma coated stainless steel or oxide or nitride modified surface coatings.

In a further arrangement, the regeneration zone may comprise generally planar porous members which define one or more walls of a chamber. An open end of the catholyte channel is provided to ensure that the stream of catholyte exiting the catholyte channel is directed toward and flows past at least a portion of the active surface of the porous member. This may be achieved by locating the open end of the catholyte channel substantially adjacent to the planar porous member or a slight distance away from, but pointed toward the porous member.

The flow rate of the catholyte through the regeneration zone is preferably relatively high. In a preferred embodiment, the flow rate of the catholyte, as it contacts or passes adjacent to the active surface of the porous member is at least about 0.2 m/s. In an especially preferred embodiment, the flow rate of the catholyte as it contacts or passes adjacent to the active surface of the porous member is about 0.5 to about 1.5 m/s.

According to a fifth aspect, the present invention provides a use of the device according to any of claims 1 to 25 in generating fine bubbles.

According to a sixth aspect, the present invention comprehends a use of the device according to any of claims 1 to 25 in a catholyte regeneration system of a redox fuel cell.

According to a seventh aspect, the present invention contemplates a use of the device according to any of claims 1 to 25 in treating sewage water with small oxygen bubbles.

According to an eighth aspect, the present invention envisages a use of the device according to any of claims 1 to 25 in growing and reproducing yeast bacteria with small oxygen bubbles.

According to a ninth aspect, the present invention provides a use of the device according to any of claims 1 to 25 in carbonisation of beverages with small carbon dioxide bubbles.

According to a tenth aspect, the present invention comprehends a use of the device according to any of claims 1 to 25 in removing oil from oil-bearing reserves such that oil is carried at the interface between the gas and liquid of each small bubble as it bubbles therethrough.

Various embodiments of the present invention will now be more particularly described by way of example only, with reference to, and as shown in the accompanying drawings, in which:

**FIG. 1:** is a schematic diagram of a gas bubble as it emerges from a traditionally-shaped hole (PRIOR ART);  
**FIG. 2:** is a graph of bubble growth for a fixed feed flow (7 μl/s) and hole size of 30 μm diameter;  
**FIG. 3:** is an embodiment of the present invention in the form of a schematic diagram (side view) and descriptive Formulae for bubble formation through a conical hole;  
**FIG. 4:** is a plan view of a device formed in accordance with an embodiment of the present invention;  
**FIG. 5:** is a plan view of a hole formed in a substrate shown from the laser entry (gas outlet);
FIG. 6: is a plan view of a hole formed in a substrate shown from the laser exit (gas inlet);

FIG. 7: is a photograph of fine-bubble formation by induced liquid; and

FIG. 8: is a photograph of fine-bubble formation in static water;

FIG. 9: is a photograph of bubble formation in Polyoxometalate using current invention.

With reference to FIG. 3, there is shown a schematic diagram (side view) and descriptive Formulae for bubble formation through a conical hole. The inventors found that the use of an orifice to restrict flow by a hole made as a truncated cone would deliver the sought-after properties in accordance with the present invention. As the bubble expands beyond the break-through pressure, air supply would be limited by the restriction of the orifice, and so the flow term, F, in Formula (1) is reduced and the rate of growth is decelerated. A schematic representation of the break-through point is given in FIG. 3, together with the descriptive formulae for the flow rate through the orifice and the rate of bubble growth, in which:

\[ F = \frac{\text{flow rate of gas}}{\text{rate of change of volume in the bubble}} \]

\[ \frac{dV}{dt} \]

\[ r_i = \text{gas inlet hole radius} \]

\[ r_o = \text{radius of bubble} \]

\[ r_h = \text{gas outlet hole radius} \]

\[ P_i = \text{Inlet pressure of gas} \]

\[ P_b = \text{bubble internal pressure} \]

\[ \Delta P = \text{orifice pressure drop} \]

\[ \Delta P_a = \text{pressure drop across bubble=internal pressure} \]

\[ \Delta P_f = \text{liquid flow pressure drop} \]

\[ L = \text{liquid flow characteristic dimension} \]

\[ R = \text{pipe flow radius} \]

\[ d = \text{pipe flow diameter} \]

\[ c_o = \text{orifice discharge coefficient} \]

\[ t = \text{time} \]

\[ \frac{dV}{dt} = \text{liquid rate of strain=velocity profile} \]

\[ A_o = \text{orifice cross sectional area} \]

\[ \rho = \text{gas density} \]

\[ \gamma = \text{interfacial tension} \]

\[ \tau = \text{viscous shear stress} \]

\[ \mu = \text{liquid viscosity} \]

\[ \pi = 3.1415927 \]

To embody this invention into a practical sparage plate (device) the above design formulae were used to calculate the size of entry and exit hole in the truncated cone and resulting flow rate of air. Typical values are shown in Table 2 below.

### Table 2

<table>
<thead>
<tr>
<th>Number of Holes</th>
<th>Inner Radius [( \mu \text{m} )]</th>
<th>Outer Radius [( \mu \text{m} )]</th>
<th>Angle [°]</th>
<th>Flow rate [Litre/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000</td>
<td>0.25</td>
<td>0.25</td>
<td>18</td>
<td>0.5</td>
</tr>
<tr>
<td>10000</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>0.08</td>
</tr>
<tr>
<td>Test Example</td>
<td>1.5</td>
<td>1.5</td>
<td>5</td>
<td>0.01</td>
</tr>
</tbody>
</table>

A test piece to prove the concept was made from 70 \( \mu \text{m} \) 316 stainless steel foil using a laser drilling technique. As part of the drilling technique a lip was formed on the laser entry side, gas outlet side of the hole, of 4 \( \mu \text{m} \). The lip around the gas outlet side is of benefit as it lifts the bubble higher in the laminar boundary layer of liquid flow, and increases shear stress on the bubble from the solid substrate.

FIG. 3 illustrates a side view of a device for generating fine bubble, generally indicated (1), comprising an elongate substrate (3) having at least one hole (5) therethrough, the hole (5) comprising a gas inlet (7) and a gas outlet (9), wherein the width of the gas outlet (9) is greater than the width of the gas inlet (7).

The hole (5) is conical in shape and has inclined walls (11) extending from the gas inlet (7) to the gas outlet (9). The incline (taper of the hole), in this embodiment, is regular. In the schematic representation of FIG. 3, the walls (11) incline at an angle of 15° relative to the longitudinal axis of hole (5).

As air passes through the hole (5), a bubble (13) is formed at the gas outlet (9) side of the hole (5).

With reference to FIG. 4, there is shown a plan view of the device (1) of FIG. 1. The device (1) comprises a substrate (3) formed from 316 stainless steel. The substrate (3) comprises 36 holes (5), each of 50 microns in size. This diagram is not to scale. The holes (5) are arranged in a 6x6 square pattern.

**EXAMPLES**

The practical embodiment of this invention was tested using a 10 mm by 10 mm section of laser drilled stainless steel plate mounted and sealed in an acrylic block with a regulated air supply. The entry and exit holes of the test piece were examined using SEM — see FIGS. 5 and 6. The gas entry (inlet) hole was measured at 3.5 \( \mu \text{m} \) and the gas exit (outlet) hole was measured at 19.1 \( \mu \text{m} \).

The test plate was mounted horizontally. Air pressure of 250 mbar was applied to the feed of the test plate (small holes) and distilled water added to cover the surface. Bubble formation was observed and photographed. Bubbles accumulated and coalesced at the surface. Water flow across the holes was induced using a wash bottle of distilled water; again bubble formation was observed and photographed. Much finer bubbles were observed with the induced water flow.

These experiments were repeated using reduced polyoxometalate (0.3M solution).

From the photographs shown in FIGS. 7 and 8, using relative scaling, the bubbles under induced water flow were estimated to be of the order of 50 \( \mu \text{m} \) diameter. In FIG. 7, water bubbles are breaking at the surface and micro droplets of water can be seen above the surface of the water. In FIG. 8, surface bubbles of 1 mm can also be seen.

From the photograph shown in FIG. 9, the measurements of POM showed larger bubbles, of the order of 75 \( \mu \text{m} \) to 100 \( \mu \text{m} \) diameter. However, due to the opaque nature of POM only surface bubbles could be observed, and these were consistent with those in the water experiment.

1. A device for generating fine bubbles, comprising a substrate having holes therethrough, each hole comprising a gas inlet and a gas outlet, wherein the width of the gas inlet is greater than the width of the gas inlet,

   wherein the average gas inlet width ranges from about 2 to 10 microns; and/or

   wherein the average gas outlet width ranges from about 5 to 100 microns; and/or
wherein the inlet diameter is \( \frac{1}{10} \)th to \( \frac{1}{5} \)th of the outlet diameter.

2. The device of claim 1, wherein the cross-sectional shape of each hole is one selected from circular, triangular, square, rectangular, pentagonal, hexagonal, heptagonal, octagonal, nonagonal and.

3. The device of claim 1, wherein the device is a porous member.

4. The device of claim 1, wherein the width of the gas outlet is an order of magnitude greater than the width of the gas inlet.

5. The device of claim 1, wherein the hole tapers regularly from the gas inlet towards the gas outlet.

6. The device of claim 1, wherein the hole tapers irregularly from the gas inlet towards the gas outlet.

7. The device of claim 1, wherein the hole density on the substrate ranges from 400 to 10000 holes/cm².

8. The device of claim 1, wherein the substrate has a square pitch and the hole density on the substrate ranges from 1000 to 2500 holes/cm².

9. The device of claim 1, wherein the thickness of the substrate ranges from about 20 to 1000 microns.

10. The device of claim 1, wherein the thickness of the substrate ranges from about 50 to 100 microns.

11. The device of any of claim 1, wherein the gas inlet width ranges from about 0.1 to 0.2 gas outlet width.

12. The device of any of claim 1, wherein the average gas outlet width ranges from about 20 to 50 microns.

13. The device of any of claim 1, wherein the variation in the width of the gas outlet and/or gas inlet is no more than 10%.

14. The device of any of claim 1, wherein the gas outlet width is about half the width of the desired bubble size.

15. The device of claim 1, wherein the substrate has an active surface towards the gas outlets of the holes.

16. The device of claim 15, wherein at least a portion of the active surface is formed of or coated with a hydrophilic material.

17. The device of claim 1, wherein at least a portion of the surface towards the gas inlet of the holes is formed of or coated with a hydrophobic material.

18. The device of claim 1, wherein at least a portion of the interior of the holes is coated with a hydrophobic material.

19. The device of claim 1, wherein the substrate is an elongate member.

20. The device of claim 15, wherein the gas outlet comprises a lip projecting away from the active surface.

21. The device of claim 1, comprising one or more of sintered glass or metal powders, plastics, porous membranes, meshes and drilled or punctured sheets.

22. The device of claim 21, comprising stainless steel foil and/or polyimide films.

23. The device of claim 1, wherein the cross-sectional shape of each hole is circular, and the widths of the gas inlet and gas outlet are the diameters of the gas inlet and gas outlet.

24. The device of claim 23, wherein the angle of taper from the gas inlet towards the gas outlet is relative to the longitudinal axis of each hole and ranges from about 6° to 26°.

25. The device of claim 23, wherein each hole is a frustoconical shape.

26. A method of manufacturing a device for generating fine bubbles, comprising the steps of:

   providing a substrate; and
   perforating the substrate at predetermined locations with holes of predetermined widths, optionally wherein the step of perforating the substrate involves using a laser.

27. (canceled)

28. A method of generating fine bubbles, comprising the steps of:

   providing a device according to claim 1;
   supplying the holes with a liquid; and
   feeding a gas through the holes via the gas inlet of each hole,
   optionally wherein the liquid is supplied across the holes to induce flow of the liquid.

29-50. (canceled)

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