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(54) Device for generating and handling nanobubbles

(57) The present invention discloses an apparatus for generating microbubbles, nanobubbles and ultra-nanobubbles, and a methodology for collecting said bubbles. The devise is consisted of three generators (G_1,G_2,G_3); the two of them (G_2,G_3) have a rotating porous plug head (201,301). For the production of ultra-nanobubbles, the corresponding generator has a piston (306) which oscillates the liquid back and forth over a fractal porous medium (301) (fractal pump) (Fig. 1 301). Nanobubbles have many potential industrial applications including many biological ones. They can be collected by using fine powders. In specific, by using dietary powders such as medicinal charcoal, zeolite, etc, nanobubbles become ready for human ingestion.

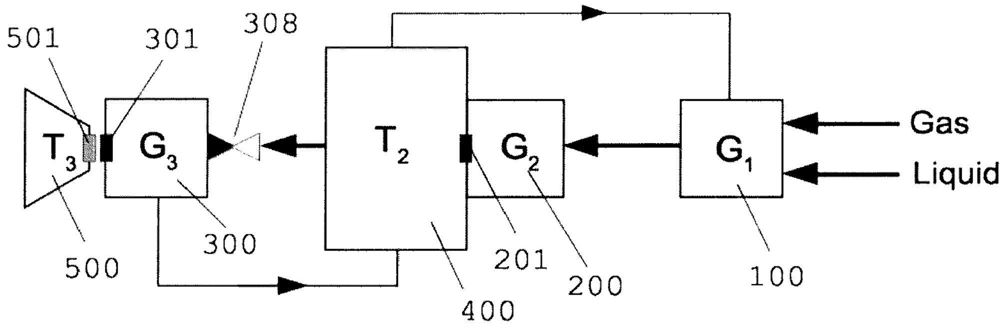

FIG. 1

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a device for generating and handling nanobubbles and, more particularly, to a device for generating microbubbles, nanobubbles and ultra-nanobubbles of desired sizes and a method of handling them in bulk solution.

BACKGROUND ART

[0002] Nanobubbles (NB) are recognized as those gaseous cavities with diameters between 1μm and 100nm. Ultra-nanobubbles (UNB) are gaseous cavities with diameters below 100nm. When we refer to microbubbles (MB), we are discussing bubbles with diameters 1-50μm.

[0003] There has arisen in recent years great scientific curiosity in the area of NB. At the same time, many industrial applications for such bubbles have also been suggested; especially in the combining case of micro-nanobubbles (MNB). One reason is that MB alone have been found to exhibit short-term stability in bulk; they shrink towards the NB range and then collapse. On the other hand, NB have been found to exist many orders of magnitude longer, both at the air-liquid interface and in bulk. The wide variety of MNB application has attracted significant industrial attention, especially in Japan and the US, with many patents existing for industrial cleaning, wastewater treatment, environmental-protection, sterilization and disinfection, home-use, etc.

[0004] In Patent Document 1 a method of forming NB, of size between 1μm and 200nm is described, by applying physical irritation to MB contained in a liquid with electrical conductivity of 300μS/cm, so that the MB contract abruptly to form NB. Patent Document 2 details a method for forming MNB, of size 10μm-300nm, from an impregnated nano-particle. Patent Document 3 describes a method for generating and dissolving NB, of size from 50μm to a few hundred nanometers, by applying a gas to the inside of a bamboo filter. In Patent Document 4 a method for producing NB, of size of 10^2 nm, by mixing different amounts of water on different temperatures, is described. In Patent Document 5, a NB generator device is detailed, which can produce a fluid stream of bubbles with the aid of an oscillating wave feed pump. Microporous beads are used in a porous sleeve, and air and liquid are introduced into the sleeve. Nanobubbles are formed in the voids between the porous beads, and are then introduced into a liquid flowing parallel to the major axis of the porous sleeve. A low cost and quickly made generator to produce a NB-containing liquid is described in Patent Document 6. A fine-bubble-containing liquid is produced by introducing a gas into the MB generator and finer bubbles are produced by shearing the liquid and gas with an impeller in a second tank. Nanobubbles are prepared in such a way from the MB liquid passed into a third tank.

[Patent Document 1] US patent number 20070189972A1
[Patent Document 2] US patent number 20100080759A1
[Patent Document 3] US patent number 20120086137A1
[Patent Document 4] Chinese patent number 101804309 B
[Patent Document 5] US patent number US 8,678,354 B2
[Patent Document 6] US patent number 8317165 B2

DISCLOSURE OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0005] In accordance with the NB described in the above patents, the previously generated NB have been restricted to sizes between 1μm and 100nm; or to MNB range (100nm-50μm). The smallest claimed size in open literature is 50nm. Besides, there is not a method for handling NB in bulk; NB adhere to adjacent surfaces of the NB reservoir instead of remaining in the bulk. In a recent experiment, described in EXAMPLE 1, it has been discovered that under certain circumstances drainage of a liquid from a porous medium is forced by UNB (<10nm) that are formed by utilizing the energy difference between Baxter-Cassie and Wenzel wetting states. Based on the aforementioned observation, the present invention produces NB that may also have dimensions smaller than 50nm; that is UNB. Because of their astonishing small size, UNB have potential for use in many industrial applications as well as in biological ones. For the latter case (e.g. human health), it is important that the NB be ingested.

MEANS TO SOLVE THE PROBLEM

[0006] In accordance with the present invention, there is provided a device for producing bubbles in three stages at three different dimensions (MB, NB, UNB) by using three different generators. In the first stage, in generator 1 (G1), a liquid is mixed with pressurized oxygen or other gas to generate bubbles in the liquid. The bubbles produced at this stage progressively decay in G1 to the MB size range. Said MB liquid is then passed through generator 2 (G2) where NB are generated by passing the liquid through a macro-porous material. In the third stage UNB are generated either statically or through rotational and/or vibrational forces; the NB produced in G2 are introduced into generator 3 (G3) which is a fractal pump. Said pump consists of a porous plug with a fractal roughness on the pore walls, and an oscillating piston. This pump works by utilizing the energy differences between Baxter-Cassie and Wenzel wetting states to produce UNB under high pressure. The porous plugs can rotate for more effective production of NB or UNB in the liquid, and the material from which they are made can be of various composition and pore size (e.g. porous glasses, porous gold, etc).

[0007] This production process is complimented by a NB capture device, in the best form of dietary powders such as: zeolite, medicinal activated charcoal, etc. This is achieved through the introduction, agitation and sedimentation of the powders in the stage-two NB reservoir. The NB will preferentially adsorb on the particle walls. The NB-attached powder is then removed from the NB generation tank and provided for storage, handling, transport or even human consumption.

EFFECT OF THE INVENTION

[0008] As a result of the herein described NB generator, NB of specific size can be produced by design for the first time. The novel methodology for capturing and extracting the NB described herein implies that said NB can be ingested by humans in a human-friendly and beneficial means.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

Fig. 1: A schematic diagram of the NB generating device.
Fig. 2: Generator 1.
Fig. 3: Generator 2.
Fig. 4: Generator 3 (fractal pump).
Fig. 5: NB-tank with NB-capturing system.
Fig. 6: Small-angle x-ray scattering spectra of water and NB-water.

BEST METHOD OF CARRYING OUT THE INVENTION

DESCRIPTION OF THE NANOBUBBLE GENERATING DEVICE

[0010] Fig. 1 is a schematic illustrating the main components of the Nanobubble Generating Device, and their interconnection. The system consists of three generators connected in series. Gas and a liquid are introduced to G1 [100] to produce a MB-containing liquid. The liquid is fed to G2 [200] where it passes through a porous material [201], generating MNB. These are stored in G2-Tank [400] and can be collected for various applications, even for human ingestion by introducing a dietary powder into G2-Tank [400]. The MNB-containing liquid from this tank can be circulated back to G1 or pumped to G3 [300]. In G3 the liquid is compressed at 150bar and oscillated back and forth through a fractal porous material [301] to generate an UNB-containing liquid. This can be collected in Tank 3 [500], or deposited on a hydrophobic surface such as Highly Ordered Pyrolytic Graphite (HOPG) [501].

[0011] In specific, in Fig. 2, G1 [100] consists of rotary pump 1 [101] and rotary pump 2 [102] connected in series. Gas and a liquid enter a mixer [103] through a capillary tube [104] from a gas tank. Two check valves [105] ensure the flow is one directional. The MB-containing liquid passes through pump 1 and then pump 2, then into G2 [200] pre chamber [202] shown in Fig.3. Said generator contains a diaphragm assembly [203] for compressing the MB-containing liquid and a fan [204] for stirring the MB-containing liquid. In this step, the pre chamber [202] is pressurized at 30 to 40bar to ensure permeability of the MB-containing liquid through the porous material [201]. Said porous material can be rotated by switching on the DC motor [205], which in turn rotates the two rollers [207], [208], a belt [206] and the porous material. The MNB are generated as the liquid passes through the porous material and are collected in G2-Tank [400] shown in detail in Fig. 5. A bypass system can be used to return the MNB-containing liquid back to G1 [100].

[0012] Alternatively, said MNB-containing liquid can be pumped into G3 [300] shown in detail in Fig. 4. Once full, the high-pressure chamber [307] in G3 is sealed and pressurized to 150bar via a piston [306] which oscillates back and forth in both directions to pump and pull the MNB-containing liquid through the fractal porous material [301]. On the reverse movement of the piston [306], suction from G2-Tank [400] occurs to fill the high-pressure chamber, while on the forward movement the liquid is extruded at his pressure through the fractal porous material [301]. During the extrusion phase, a check valve [308] prevents the liquid from returning back to G2. The movement of the piston is achieved either by mechanical cam or by automatic hydraulic system. The porous material can be rotated by a motor [302], two rollers [303], [304] and a belt [305]. The generated UNB-containing liquid is collected in G3-Tank [500]

DESCRIPTION OF THE CAPTURING SYSTEM

[0013] The MNB produced by G2 accumulates in G2-Tank [400] which is shown in detail in Fig 5. A dietary powder, such as natural zeolite of high purity, medicinal activated charcoal, etc., is inserted through a funnel [401] in the reservoir. The mixture of MNB-containing liquid and powder is stirred by a rotating stirrer [403] driven by a DC motor [402]. The MNB or NB attach onto the surface of the powder. After a short time, the stirring is stopped, and the mixture is allowed to settle. The sediment can be collected from G2-Tank [400]. It is also possible to capture UNB generated by G3 [300] in a G3-Tank [500] or onto a hydrophobic surface such as Highly Ordered Pyrolythic Graphite (HOPG) surface [501] positioned above said tank.

EXAMPLE 1: X-RAY SPECTRUM OF NANOBUBBLES

[0014] Fig.6 shows a small-angle X-ray scattering spectrum of a sample containing oxygen NB in water. For comparison, a blank water sample is presented too.

From the produced X-rays the most intense of the characteristic lines Ka was selected as the experimental wavelength; λ=1.54Å. The detector was a 2D X-ray imaging system based on a gas-filled multi-wire proportional counter coupled to an artificial delay line. Capillary tubes of diameter equal to 1mm are used as liquid sample holders. The scattered intensity I(Q) was recorded in a range of $0.05Å^{-1}<Q<0.3Å^{-1}$, where Q is the scattering vector; $Q=4\pi\sin\theta/\lambda$ with 2θ the scattering angle. Pure water spectrum is in a higher I(Q) than water with NB because 02-filled NB are of much lower density than water.

Claims

1. An apparatus with three in-line generators for the production of microbubbles, nanobubbles, and ultra-nanobubbles having sizes: 50μm-1μm; 1μm-100nm; and 100nm-10nm or less, respectively.

2. An apparatus according to claim 1, which can be used to generate microbubbles, nanobubbles and ultra-nanobubbles containing any single gas or gas mixture or vapors.

3. An apparatus according to claim 1, which can be used to generate microbubbles, nanobubbles and ultra-nanobubbles in any liquid.

4. An apparatus according to claim 1, where the generators can have porous plug heads of various material composition and pore size (e.g. silica and non silica of macro- meso- or micro-porous materials).

5. An apparatus according to claim 1 which further comprises of rotating porous plugs heads.

6. An apparatus according to claim 1 which further comprises a vibrational system for liquid-bubble agitation.

7. An apparatus according to claim 1, which can be used to generate ultra-nanobubbles through the use of a generation system where the liquid can be moved forward and backward through a porous material having a fractal (or rough) internal surface via an hydraulically operated piston (fractal pump).

8. An apparatus according to claim 1, which can be used to collect ultra-nanobubbles on a hydrophobic surface.

9. An apparatus according to claim 1, with a sedimentation tank into which any insoluble adsorbing material can be used to adsorb and collect nanobubbles or ultra-nanobubbles.

10. A method for capturing the produced nanobubbles according to claim 9 where the adsorbing material can be a dietary powder (e.g. medicinal charcoal, zeolite of high purity, etc).

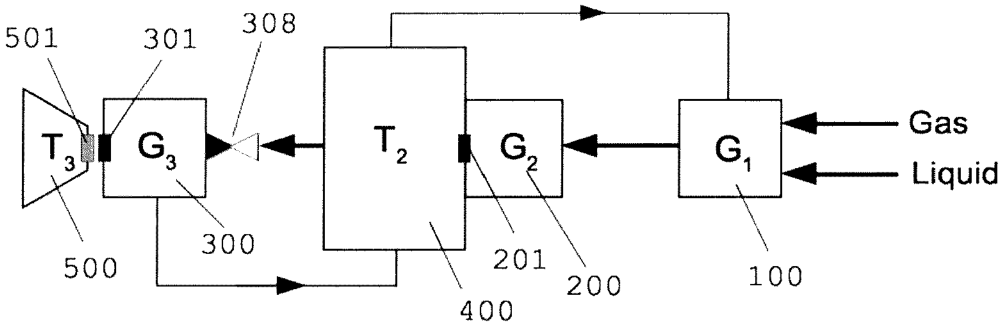
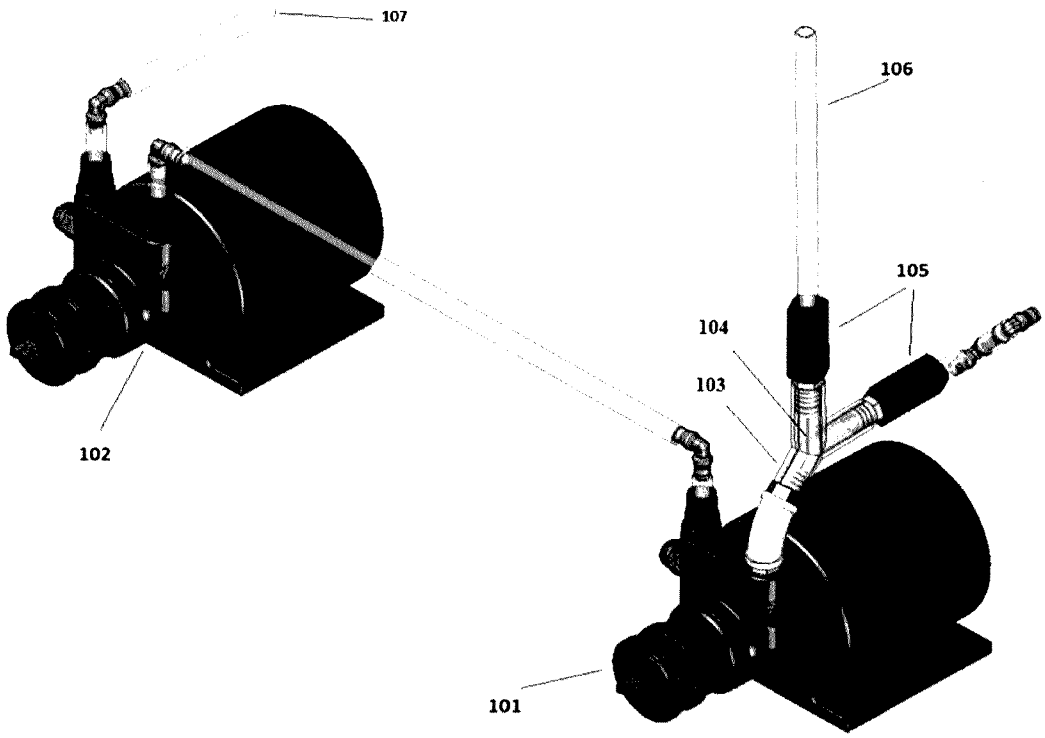

501
301
308
T3
G3
T2
G2
G1
Gas
Liquid
500
300
201
200
100
400

FIG. 1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101

FIG. 2

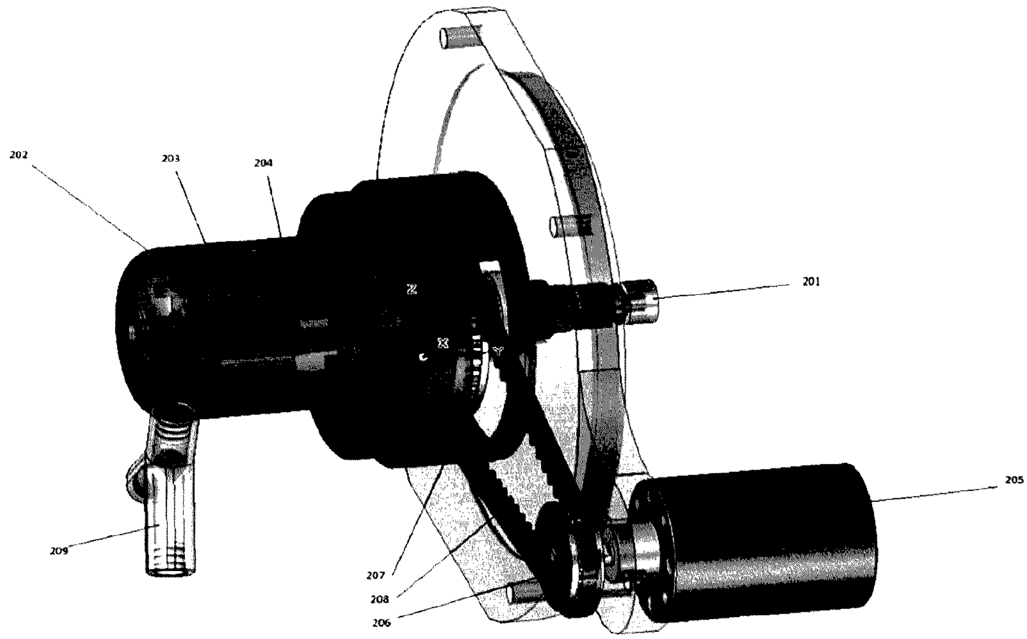

FIG. 3

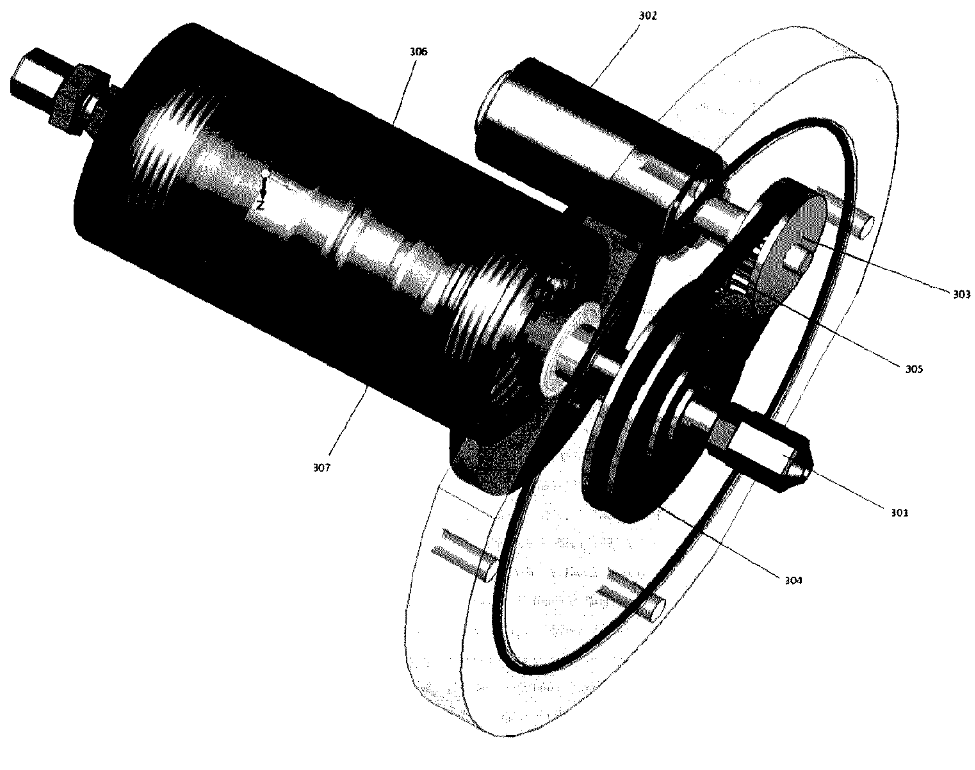

FIG. 4

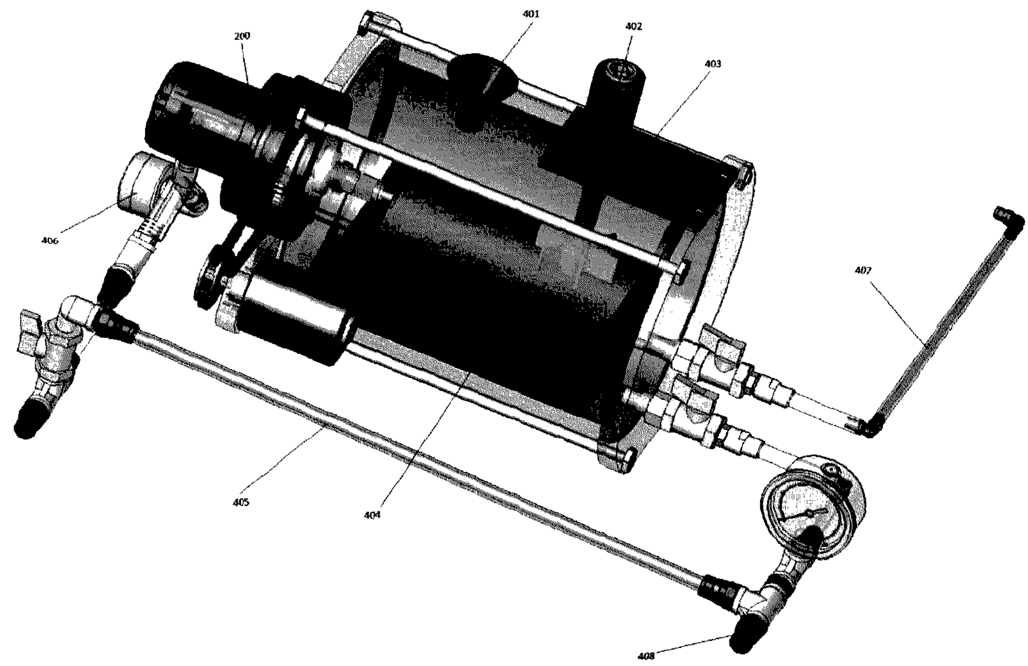
200
401
402
403
404
405
406
407
408

FIG. 5

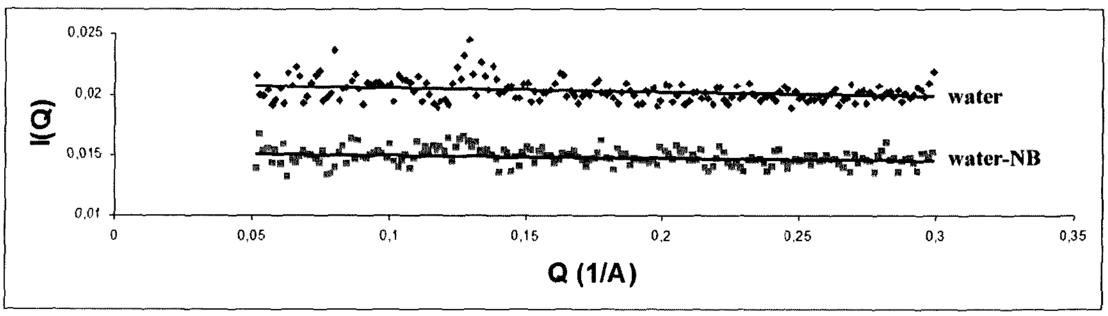
I(Q)
0,025
0,02
0,015
0,01
0
0,05
0,1
0,15
0,2
0,25
0,3
0,35
Q (1/A)
water
water-NB

FIG. 6

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EUROPEAN SEARCH REPORT

Application Number
EP 14 38 6022

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	28 August 2015	Voltz, Eric

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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EUROPEAN SEARCH REPORT

Application Number
EP 14 38 6022

DOCUMENTS CONSIDERED TO BE RELEVANT			
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			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	28 August 2015	Voltz, Eric

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Application Number
EP 14 38 6022

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION SHEET B

Application Number

EP 14 38 6022

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-7

   An apparatus with three in-line generators.

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2. claims: 1, 8-10

   An apparatus and a method for capturing nano-bubbles.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 14 38 6022

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