An apparatus 100 and method provide relative oscillatory motion between a membrane 107, defined by a plurality of holes 130, and through which a first phase 110 egresses from the membrane into a second phase 111, in a second volume separated from the first phase by the membrane, where the direction of relative oscillatory motion is perpendicular to the direction of egression of the first phase. An emulsion of the first phase dispersed within the second phase results from the use of the relative oscillatory motion between the membrane surface and the second phase.
Fig 1
Fig 4

- D(v,90): 142
- D(v,10): 86
- D(v,50): 115
- Span: 0.49
An apparatus and method for generating emulsions

Embodiments of the present invention relate to an apparatus for generating emulsions or dispersions and a method for making emulsions or dispersions. The emulsions and dispersions may be of two or more immiscible phases.

Dispersions of oil in water, and dispersions of small sized capsules containing solids, or fluids, are of considerable economic importance and are used, by way of example, for creams and lotions, delayed release pharmaceutical products, pesticides, paints and varnishes, spreads and foods. In several instances it is desirable to encase particles in a covering of another phase (microcapsules), to produce a barrier to the ingredient readily dissolving or reacting too quickly in its application. One such example is a delayed release pharmaceutical product.

In many applications it is desirable to employ a consistent drop, or dispersion, size. For example, in the case of a controlled release pharmaceutical product a consistent microcapsule size would result in a predictable release of the encapsulated product. Conversely, a wide drop size distribution would result in rapid release of the product from the fine capsules, which have a high surface area to volume ratio, and a slow release from the larger capsules. Another example is a surface finish, such as paint, lacquer or varnish where a size distributed dispersion would result in a bumpy surface finish.

Current emulsion manufacturing techniques use: stirrers and homogenisers. A two phase dispersion with large drops is forced though valves and nozzles to induce turbulence and thereby to break up the drops into smaller ones. However, it is not possible to control the drop sizes achieved and the size range of drop diameters is usually large. This is a consequence of the fluctuating degree of turbulence found in the systems described and the exposure of the drops to a variable shear field.

In recent years, there has been much research interest in the generation of emulsions using microfilter membranes. Patent Application Number WO 01/45830 A1 describes apparatus for dispersing a first phase in a second phase, comprising a tubular microfilter connecting an interior volume of one liquid phase and an exterior volume of the second immiscible liquid phase. Typically the first phase is provided under pressure to the interior volume of the tubular microfilter and the second phase is circulated through the exterior volume. The method for generation of shear at the surface of the membrane at which the liquid drops egress is by rotation of the tubular membrane. This device has found some application in laboratory studies, but the principle of operation is not one that is easily used in a multiple tube environment for significant commercial application.

It would be desirable to improve further how emulsions are generated in a commercial environment.

According to one aspect of the present invention there is provided an apparatus for dispersing a first phase in a second phase, comprising: a
membrane defining a plurality of through holes that connect a first volume on a first side of the membrane to a second volume on a second different side of the membrane, and through which the first phase egresses from the first volume into the second phase in the second volume; and means for relative oscillating motion of the second phase, or the membrane, in a direction perpendicular to the direction of egression of the first phase.

According to another aspect of the present invention there is provided an apparatus for dispersing a first phase in a second phase, comprising: a membrane defining a plurality of through holes that connect a first volume on a first side of the membrane to a second volume on a second different side of the membrane, and through which the first phase egresses from the first volume into the second phase in the second volume; and means for developing a consistent oscillatory shear field in the second phase at the membrane over the plurality of through holes.

According to another aspect of the present invention there is provided a method for use in dispersing a first phase in a second phase, comprising: providing relative oscillatory motion in a first direction between a membrane, defining a plurality of through holes, and a second phase, while the first phase egresses through the through holes into the second phase in a direction substantially perpendicular to the first direction.

According to another aspect of the present invention there is provided a method for use in dispersing a first phase in a second phase, comprising: providing a consistent oscillatory shear field in a second phase at a membrane over the membrane’s plurality of through holes, while the first phase egresses through the plurality of through holes into the second phase.

For a better understanding of the present invention reference will now be made by way of example only to the accompanying drawings in which:

Fig. 1 illustrates a first embodiment of an apparatus for dispersing a first phase in a second phase;
Fig. 2 illustrates a second embodiment of an apparatus for dispersing a first phase in a second phase.

Figs. 1 and 2 schematically illustrates an apparatus 100 for dispersing a first phase 110 in a second phase 111, comprising a membrane 107 defining a plurality of through holes 130 that connect a first volume on a first side of the membrane 107 to a second volume on a second different side of the membrane 107, and through which the first phase 110 egresses from the first volume into the second phase 111 in the second volume; and vibration means 102, 104 for relatively vibrating the second phase 110 and the membrane 107 in a direction perpendicular to the direction of egression of the first phase 110.

In Fig. 1, the apparatus 100 disperses a first liquid phase 110 in a second liquid phase 111. The first liquid 110 is immiscible in the second liquid 111 and is contained in a reservoir 112 from where it is transferred into a tubular membrane 107 by means of a pump 114. The first liquid 110 is consequently
provided to the tubular membrane 107 under pressure. Although in this example the pressure is provided by a pump 114, in other examples it may be provided by other means such as hydrostatic pressure.

The tubular membrane 107 has a plurality of through holes 130, which are completely submerged in the second liquid 111 contained by a vessel 108. The first liquid 110 egresses through the through holes 130 and enters the second liquid 111, while the entire vessel 118 is subject to vertical oscillation 102, typically at a frequency of between 10 to 5000 Hz.

The vertical rectilinear oscillation 102 develops a consistent oscillatory shear field in the second liquid 111 at the surface of the tubular membrane 107. The oscillatory shear field is consistent over the plurality of through holes 130. Thus, the first phase as it emerges through each of the through holes 130 is subject to the same consistent oscillatory shear field perpendicular to the direction of egress. This enables the formation of drops 115 of the first liquid 110 within the second liquid 111 that are of consistent size.

The tubular membrane 130 has a solid base 125 to prevent passage of the first liquid 110 into the second liquid 111 by any means other than the through holes 120.

In this example, only the vessel 108 and its contents 111 and 115 are subject to oscillation and the tubular membrane 130 remains stationary.

The apparatus of Fig. 1 is particularly advantageous in that the membrane 130 does not need to be of a tubular shape or of uniform cross section to ensure a uniform shear at its surface. The membrane 130 may, for example, be formed from rectangular boxes, sheets or discs.

Fig. 2, schematically illustrates, an alternative apparatus for dispersing a first phase 110 in a second phase 112. The apparatus of Fig. 2 is similar to the apparatus of Figure 1 and like reference numerals are used to denote like features.

The apparatus of Fig. 2 differs from the apparatus of Fig. 1 in that the motion of the vessel 108 is provided by the oscillatory rotation of the vessel about an axis that passes through the centre of the tubular membrane 107. The vibration means 104 develops a consistent oscillatory shear field in the second phase at the surface of the membrane 107 over the plurality of through holes 130. The vessel 108 may be oscillated using a simple mechanical arrangement employing a rotating wheel with a cam that pushes the platform on which the vessel rests against a spring.

It should be appreciated that in both embodiments of the described invention, a consistent oscillatory shear field is developed in the second phase at the surface of the membrane 107 over the plurality of through holes 130 in the membrane. In the embodiment of Figure 1, this shear field is produced by rectilinear oscillation of the vessel so that the shear field is substantially perpendicular to the direction of egress of the first liquid 110 into the
second liquid 111. In the second embodiment, the consistent oscillatory shear field is developed by the oscillatory rotational movement of the vessel 108 which develops a consistent uniform shear field in a direction substantially perpendicular to the direction of egression of the first liquid 110 into the second liquid 111.

The membrane 107 may be of any suitable type. It may for example be a ceramic membrane formed by sintering particles together or it may be a microfilter membrane such as described in patent application GB 0202832.2.

Although the invention has been described in relation to "inside-out" embodiments in which the first phase moves from the inside of a membrane 107 to the outside, the invention may also be applied to "outside-in" arrangements in which the first phase moves from the exterior of the membrane into the interior and the dispersion is formed in the interior of the membrane.

It should also be appreciated that the above described embodiments may be used in the formation of double emulsions, whereby an emulsion is produced firstly by injecting a dispersed phase into a continuous phase and then the resulting emulsion is injected into another continuous phase through pores of a large diameter. The above described apparatus may be used with a first type of membrane 107 to inject a first dispersed phase into a continuous phase and then can be used with a different membrane 107 to inject the resulting emulsion into another continuous phase.

Although in the described embodiments, the first and second phases are liquids, it should be appreciated that the first and/or second phase may also contain finely divided solids, for example.

The technological method of generating drops is now described below together with a comparison with existing methods to generate emulsions using membrane systems. In a 1997 publication, WO9736674, crossflow of one liquid phase over the surface of a microfilter with varying internal diameter is used, and in the paper 'preparation of monodisperse microspheres using the Shirasu porous glass emulsification technique' by Sinzo Omi, Colloids and Surfaces A; 109, 1996, pp 97-107, crossflow over a sintered glass tube is used. In both of these cases, great effort is made to maintain uniform shear of the liquid phase flowing over the surface of the microfilter so that the immiscible liquid emerging from the pores of the microfilter experiences a uniform shear field, resulting in a uniform force on the emerging liquid and, therefore, a near uniform drop size. The drop will break away from the surface of the microfilter when the shear is sufficient to overcome the surface tension force holding the emerging liquid together, in the pore of the filter, and any adhesion force between the emerging liquid and the solid surface of the filter.

In the system described by Figs 1 and 2, a uniform shear field does not exist. Instead, the shear field is oscillating in a sinusoidal manner; between zero shear and high shear in one direction and then high shear in the reverse direction. However, the shear at the membrane surface is varying in this
manner consistently over the full surface of the microfilter. Thus, when moved in accordance with Fig 1, the shear varies in a ‘consistent linear oscillation’. When moved in accordance with Fig 2, the shear varies in a ‘consistent rotational oscillation’ at all positions on the surface of a tubular microfilter, with circular cross-section. Clearly, the consistent linear oscillation does not demand a particular geometry in order to function: the filter could be a flat plate, tube, rectangular box, etc.

A consistent oscillation will generate a uniform emulsion, or dispersion, so long as the rate of oscillation is sufficiently high enough such that the emerging liquid drop, from a microfilter pore, experiences a number of oscillations. At the peak shear during an oscillation, where the gradient on the sinusoidal curve is the greatest, the drop will break free from the surface because the shear force is sufficient to overcome the surface tension force and any adhesion force between the emerging liquid and the solid surface of the filter. This surface shear is a function of both the frequency and the amplitude of oscillation. Hence, there are two independent means of controlling the peak shear at the surface, providing a system that has a high degree of control over the surface shear and, hence, the formed drop size.

This method of generating emulsions, or drops, is different from the commonly employed technique of vibrating a tube, orifice (see US2002054912 for an example), or plate behind an orifice for two main reasons. Firstly, in the case of emulsions, and dispersions, a membrane with a multitude of pores is used – rather than a single orifice. Secondly, the vibration employed in these other systems is normal to the orifice, or hole, whereas the invention here relies on oscillation perpendicular to the membrane pores. It would not be possible to generate a uniform emulsion by providing a system with a multitude of pores using a normal vibratory source, as the shear field would vary in an inconsistent fashion over the surface of all the pores; as the shear would depend on the distance from the normal vibratory source. Whereas in this invention the shear field varies, but in a highly consistent fashion over all the pores. Thus, in the prior art, it is shown that it is possible to generate uniform drops from a single orifice with normal vibration, but the technique is both different to that described here and generates only single drops at a time, whereas the invention describes a technique whereby a multitude of uniform drops may be generated simultaneously over the surface of the microfilter. There are many similar patents where vibration normal, or perpendicular, to the membrane surface has been employed, see US 4793714 and FR 2699091 A1 for two further examples. This mode of oscillation is well known and is completely different to the method of linear oscillatory vibration of the membrane surface parallel to that surface, as illustrated in Fig 1 and Fig 2.

Embodiments of the invention will now be described, by way of example only, with reference to Fig 3 and Fig 4, which illustrate the uniformity of the emulsion resulting from the process.

A tubular microfilter, as prepared according to patent application GB 0202832.2, was mounted vertically inside a beaker with the lower end blocked off. The beaker was filled with water containing a 1% w/w solution of Tween
20, a commercially available surfactant for stabilising dispersions, and a pipe was connected to the top of the tube so that sunflower oil could be pumped to the inside of the microfilter tube. The beaker was mounted on the centre of a laboratory sieve shaker, that oscillated the beaker, and its contents, at a frequency of 75 Hz and an amplitude of 0.5 mm. Careful positioning on the sieve shaker at its centre was required to ensure that the oscillation was linear, rather than simple vibratory motion. The apparatus is adequately illustrated by reference to Fig 1. The resulting dispersion was evaluated using a microscope and a captured image is provided in Fig 3. The uniform nature of the drops is apparent in this picture, with drop sizes between 110 and 140 microns and a median size of 125 microns.

In a similar experiment to that described above, but with a linear oscillatory amplitude of 0.7 mm, a slightly finer dispersion was produced. The median size was 115 microns, as illustrated in Fig 4 which is the complete particle size distribution measured by a Malvern Mastersizer. It is common practice to evaluate the uniformity of emulsions and dispersions with reference to the 'span'. This is defined as the particle diameter below which 90% of the distribution occurs, D(v,90), minus the particle diameter below which 10% of the distribution occurs, D(v,10), all divided by the median diameter, D(v,50). These calculations are based on a volume distribution. The dispersion from this experiment has a span of 0.49. Uniform dispersions are commonly deemed to be ones with spans of 0.9, or less, and it is usually more difficult to produce narrow spans with larger drops, ones with sizes over ten microns.

In another example crosslinked Poly Vinyl Alcohol (PVA) particles were produced by first dispersing an aqueous solution of 15% PVA into a continuous phase of kerosene containing the surfactant Span 80 through a single tubular membrane containing an array of pores 20 microns in diameter. The tube dimensions were: 14 mm outside diameter and 50 mm length. The arrangement was similar to Fig 1, except that the membrane was mounted on an electrically driven oscillator and the liquid surrounding the membrane was not oscillated. It was found that the median drop size of the aqueous PVA drops within the kerosene was controllable within the range of 40 to 80 microns, depending on the frequency and amplitude of oscillation used. A frequency of 20 Hz and amplitude of 2 mm provided a median size of 80 microns and a frequency of 70 Hz and amplitude of 5 mm provided a median drop size of 40 microns. The PVA drops were then crosslinked by addition of glutaraldehyde to the kerosene liquid and the mixture was left to gently stir for ten hours to form the solidified PVA particles from the aqueous phase drops. By thus controlling the frequency and amplitude of linear oscillation of the membrane it was possible to produce solid particles that had 90% of their size distribution between 40 and 70 microns, as measured by a Coulter Multisizer model II. These beads are of a sufficiently uniform quality for use in chromatography applications for blood diagnostic tests.

In another example a tubular microfilter, with an internal diameter of 14 mm and slot width of 5 micrometres and slot length of 400 micrometres, prepared according to patent application GB 0202832.2, was mounted vertically and connected to a linear oscillator. The tube contained slotted pores which were
arranged perpendicular to the direction of the shear field, which was generated by the linear oscillation of the tubular membrane within melted cocoa butter. A pectin solution to be used for the egression was prepared by placing a mass of 494 g of water in a two litre beaker with a suspended magnetic stirrer and heated up to 80°C. The inner bar could rotate freely from the supports and it was stirred at a rate sufficient to provide an air vortex. A mass of 6 g of pectin was weighed out and very slowly added to the stirred water – in the air core, but away from the top of the suspended stirrer. To cool, the solution was left stirring with the heater turned off. The stock pectin solution was left overnight to swell the hydro-colloid. A second solution of: Gum Arabic, sugar and calcium chloride was prepared by placing a mass of 59.5 g water in a beaker and a magnetic stirrer added. The water was heated to no more than 80°C. A mass of 0.4 g of Gum Arabic was added slowly whilst stirring rapidly. When the Gum Arabic had dissolved 10 g of polydextrose and 0.033 g of calcium chloride was added.

The two solutions were to form the aqueous phase to become the egression liquid into a melted liquid of cocoa butter oil. The mass of cocoa butter used was 93 g, to which 7 g of the well-known chocolate surfactant polyglycerol polyricinoleate (PGPR) was added. The mass of pectin solution used was 30 g and the mass of gum, sugar and calcium solution was 70 g. The two aqueous solutions were heated to 80°C in separate containers and agitated by magnetic stirrers. When at temperature, the gum, sugar and calcium solution was poured into the pectin solution whilst stirring vigorously. Gelling immediately started. After further mixing for 5 minutes the temperature dropped to 45 to 50°C and the gel was of an acceptable consistency for injection into the cocoa butter. Egression of the gel in to the cocoa butter continuous phase, which had been heated to 40°C, was performed. The temperature of the dispersed phase was maintained at 80°C during injection and the temperature of the two-phase mixture was maintained at between 40 and 45°C during the process. A linear oscillation frequency of 50 Hz and 2 mm amplitude was used.

Samples of the dispersion were taken for microscope analysis during the egression. The liquid cocoa oil was mixed with kerosene to dilute the drops sufficiently to observe them under the microscope. The largest aqueous drop size obtained was 15 micrometres and there is a substantial amount of drops with diameters less than 8 micrometres. During the egression process the pressure required to inject the egression liquid was monitored, to check for membrane blockage, and the pressure remained constant at only a few inches of water gauge. Hence, the injection pressure was minimal and stable, a consequence of the use of slotted through holes as the membrane material. The injection rate was 1.5 ml per minute per cm length of membrane. The resulting emulsion of pectin gel in cocoa butter oil was suitable for further processing into a useful product, such as the production of a lower fat chocolate product using conventional, or only slightly modified, chocolate processing technology.
These experiments show that the invention is successful at producing closely sized emulsions, or dispersions, and that the system is highly controllable by varying the amplitude of motion. Another possible way to control the size of drop formed is to control the frequency of linear oscillation. Thus, the invention provides a system that can be easily tuned to the desired product drop size.

Although embodiments of the present invention have been described in the preceding paragraphs with reference to various examples, it should be appreciated that modifications to the examples given can be made without departing from the scope of the invention as claimed.

Whilst endeavouring in the foregoing specification to draw attention to those features of the invention believed to be of particular importance it should be understood that the Applicant claims protection in respect of any patentable feature or combination of features hereinbefore referred to and/or shown in the drawings whether or not particular emphasis has been placed thereon.
Claims

1. An apparatus for dispersing a first phase in a second phase, comprising: a membrane defining a plurality of through holes that connect a first volume on a first side of the membrane to a second volume on a second different side of the membrane, and through which the first phase egresses from the first volume into the second phase in the second volume; and means for relative shear in a first direction between a membrane and a second phase formed by relative oscillatory motion of the second phase and the membrane in a direction perpendicular to the direction of egression of the first phase.

2. An apparatus for dispersing a first phase in a second phase, comprising: a membrane defining a plurality of inter-connected holes, as provided by a sintered type of membrane, that connect a first volume on a first side of the membrane to a second volume on a second different side of the membrane, and through which the first phase egresses from the first volume into the second phase in the second volume; and means for relative shear in a first direction between a membrane and a second phase formed by relative oscillatory motion of the second phase and the membrane in a direction perpendicular to the direction of egression of the first phase.

3. An apparatus as claimed in claims 1 or 2, wherein the direction of oscillation is substantially perpendicular to the direction of egression of the first phase.

4. An apparatus as claimed in claims 1 to 3, wherein the membrane is oscillated perpendicular to the direction of egression of the first phase.

5. An apparatus as claimed in any preceding claim, further comprising a vessel for providing the second volume, wherein the vessel is oscillated perpendicular to the direction of egression of the first phase.

6. An apparatus as claimed in any preceding claim wherein the membrane has a vertically extending surface and the relative motion involves substantially oscillatory rectilinear motion in the vertical direction.

7. An apparatus as claimed in anyone of claims 1 to 5, wherein the membrane is substantially tubular with an axis, and the relative motion involves substantially oscillatory rotation of the membrane about the axis.

8. An apparatus as claimed in any preceding claim, further comprising means for providing the first phase to the first volume under pressure.

9. An apparatus for dispersing a first phase in a second phase, comprising: a membrane defining a plurality of through holes that connect a first volume on a first side of the membrane to a second volume on a second different side of the membrane, and through which the first phase egresses from the first volume into the second phase in the second volume; and
means for developing a consistent oscillatory shear field in the second phase at the membrane over the plurality of through holes.

10. An apparatus as claimed in claim 9, wherein the shear field is in a direction substantially perpendicular to the direction of egression of the first phase.

11. A method for use in dispersing a first phase in a second phase, comprising:
relative shear in a first direction between a membrane and a second phase formed by providing relative oscillatory motion in a first direction between a membrane, defining a plurality of through holes, and a second phase, while the first phase egresses through the through holes into the second phase in a direction substantially perpendicular to the first direction.

12. A method for use in dispersing a first phase in a second phase, comprising: providing a consistent oscillatory shear field in a second phase at a membrane over the membrane's plurality of through holes, while the first phase egresses through the plurality of through holes into the second phase.

13. An apparatus or method substantially as hereinbefore described with reference to and/or as shown in the drawings.

14. Any novel subject matter or combination including novel subject matter disclosed, whether or not within the scope of or relating to the same invention as the preceding claims.
Application No: GB0623510.5  
Examiner: Heather Webber  
Claims searched: 1-8, 11 & 13  
Date of search: 23 March 2007

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

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