



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 469 014 B1**

**EUROPEAN PATENT SPECIFICATION**

- (49) Date of publication of patent specification: **17.08.94** (51) Int. Cl.<sup>5</sup>: **B01F 3/08, B01F 5/00**
- (21) Application number: **90906170.7**
- (22) Date of filing: **20.04.90**
- (86) International application number:  
**PCT/EP90/00636**
- (87) International publication number:  
**WO 90/12639 (01.11.90 90/25)**

**EMULGATOR-FREE LIQUID EMULSION AND METHOD AND DEVICE FOR PRODUCING THE EMULSION.**

- (30) Priority: **21.04.89 DE 8905075 U**  
**22.04.89 JP 103268/89**
- (43) Date of publication of application:  
**05.02.92 Bulletin 92/06**
- (45) Publication of the grant of the patent:  
**17.08.94 Bulletin 94/33**
- (84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB IT LI LU NL SE**
- (56) References cited:  
**EP-A- 45 008 EP-A- 263 443**  
**EP-A- 312 642 WO-A-83/01210**  
**AU-B- 541 324 FR-A- 844 009**  
**FR-A- 2 461 515 GB-A- 2 092 025**

- (73) Proprietor: **Tecno-Bio Co., Ltd.**  
**26-2 Nishishinjuku 1-chome**  
**Shinjuku-ku**  
**Tokyo (JP)**
- (72) Inventor: **Ulrich, Armando**  
**Bergstrasse 59**  
**5644 Auw (CH)**  
Inventor: **Ott, Walter H.**  
**deceased (DE)**
- (74) Representative: **Patentanwälte Viering & Jentschura**  
**Postfach 22 14 43**  
**D-80504 München (DE)**

**EP 0 469 014 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

## Description

The present invention relates to a method and a device for producing an emulgator-free liquid emulsion of at least one hydrophobic phase and at least one hydrophilic phase.

GB-A-2 092 025 discloses a method of forming and spraying emulsions of two immiscible liquids by introducing small amounts of a first liquid into a body of a second liquid while electrically charging the first liquid relative to the second liquid to a potential sufficient to cause emulsification therein, and atomising the charged emulsion thereby formed. Atomising the emulsion immediately after mixing results in reducing or eliminating storage time, thereby preventing emulsion break-down.

FR-A-844009 discloses a method for preparing emulsions and colloidal suspensions of vaseline oil, perfume, aromatic essences or the like in water by using ultrasonic in order to obtain very fine emulsions with a particle size of less than 0.4  $\mu\text{m}$ . However, at least traces of stabilizers seem to be necessary for their stability. Also AU-A-541324 discloses a method for preparing emulsions of immiscible fluids, e.g. oil in water, of a particle size from 0.1 to more than 50  $\mu\text{m}$  by passing the mixture through a column packed with steel metal sponge, animal hair or plastic brush or the like in the presence of an emulsifier, e.g. Sapolin.

EP-A-0 263 443 discloses an apparatus for preparing a water-in-oil-emulsion comprising a mixing apparatus according to the introduction portion of claim 3 in a recirculation conduit path. A storage container is connected in the recirculation conduit path behind the mixing apparatus, the emulsion being held in continuous movement in the storage container in order to avoid a decomposition of the mixture.

Various other proposals have heretofore been made on the method and apparatus for mixing a plurality of substances differing in the physical properties. Especially, many methods have been proposed as the means for obtaining mixtures of a hydrophobic liquid and water. However, according to these methods, stable liquid mixtures of water and a hydrophobic liquid are obtained by using an emulsifier.

Use of an emulsifier results in increase of the costs and when the water/hydrophobic liquid is used, for example, for cosmetics or the like, several limitations are imposed in view of influences on the human body.

It is a primary object of the present invention to provide a mixing method for stably mixing hydrophobic and hydrophilic liquids.

Another object of the present invention is to provide a mixing device for use in carrying out this mixing method.

Still another object of the present invention is to provide a stable emulsion of at least one hydrophobic liquid phase and at least one hydrophilic liquid phase and prepared or preparable by this mixing apparatus.

The emulgator-free emulsion, the method and the mixing device in accordance with the present invention have especially the features as described in the claims.

In accordance with the present invention, there is provided a colloidal emulgator-free emulsion comprising a hydrophilic liquid, especially water, and a hydrophobic liquid, wherein fine liquid drops of the disperse liquid phase are homogeneously and stably distributed in the emulsion without the aid of an emulsifier. In the present invention, the preferred composition of the water/hydrophobic liquid mixture is such that the amount of the hydrophobic liquid is up to 20% by volume based on water.

Furthermore, in accordance with the present invention, there is provided a mixture comprising water and a hydrophobic liquid, wherein fine liquid drops of the water are homogeneously and stably distributed in the hydrophobic liquid without the aid of an emulsifier. In the present invention, the preferred composition of the water/hydrophobic liquid mixture is such that the amount of the water is 5-35% by volume based on the hydrophobic liquid.

Moreover, in accordance with the present invention, there is provided a colloidal mixture comprising a hydrophilic liquid and a hydrophobic liquid, wherein fine liquid drops are homogeneously and stably distributed without the aid of an emulsifier. In the present invention, the preferred composition of the hydrophilic liquid and the hydrophobic liquid is such that the amount of the hydrophobic liquid is up to 20% by volume based on the hydrophilic liquid.

The term "colloid" or "colloidal" state means a state in which colloidal particles having a size of about 1,000 nm or less are contained, the existence of the colloidal particles and the occurrence of a Brownian movement are confirmed by an ultramicroscope, and a Tyndall phenomenon is observed.

The present invention will now be described in detail with reference to preferred embodiments illustrated in the accompanying drawings.

Fig. 1 is a diagram illustrating a general layout of a preferred first embodiment of the mixing device comprising a mixing apparatus used in the present invention.

Fig. 2 is an elevation sectional view of the mixing apparatus 1 shown in Fig. 1.

Fig. 3 is a cross sectional view of the top portion of the mixing apparatus 1 shown in Fig. 1.

Fig. 4 is a diagram illustrating a second embodiment of the mixing device used in the present invention.

Fig. 5 is a diagram illustrating a third embodiment of the mixing device used in the present invention .

Fig. 6 is a diagram illustrating the structure of an example of the cylindrical housing defining the hollow interior space of the jet pump 50 of the mixing device shown in Fig. 5.

A general device according to the first embodiment of the device for use in carrying out the present invention is shown in Fig. 1. The elevation of a mixing apparatus 1 is shown in Fig. 2 and the top section of the mixing apparatus 1 in the plane of a hole of the mixing apparatus 1 is shown in Fig. 3. At first, the mixing apparatus 1 is described with reference to Figs. 2 and 3.

The mixing apparatus 1 comprises a cylindrical wall which is opened at one end 10 and closed at the opposite end 11. Within this cylinder, there is defined a hollow element 13 comprising a first portion 14 having a circular rim 12 connected to the central part thereof and a second portion 17. The first portion 14 of this element 13 has a shape of a substantially hollow parabolic surface arranged in a closed chamber formed between the rim 12 and the closed end 11 of the mixing apparatus 1. The first portion 14 has a shape of a completely hollow parabolic surface. A certain number of holes 15 are formed through wall of the element 13 at the height (about 1/3 in the embodiment) of the upper position of the first portion 14. The holes 15 are formed in the tangential direction. A duct 16 is extended from the closed end 11 of the mixing apparatus 1 slightly inclinedly with respect to the axis of the mixing apparatus. The element 13 includes the second portion 17 communicating with the first portion 14 at the plane of the rim 12, and this portion has a substantially tapered shape which is continuous as a short cylindrical duct 18. The portion 17 has a shape of a complete hyperbola. The mixing apparatus 1 is formed of glass. A fluid component is caused to flow to the first portion 14 through the inclined duct 16 while being rotated, and in the first portion 14, the majority of the fluid component introduced into the holes 15 is caused to flow along the inner wall of the first portion 14 toward the top (downward in Fig. 2) while being further rotated. At the top, the flow is reflected and the flow speed is gradually increased, and a vortex state is formed on the central axis toward the second portion. Different substances are mixed by this vortex state.

In use a liquid mixture of a hydrophobic liquid phase and an hydrophilic liquid phase is introduced through the inlet duct 16. Owing to the off-axis and oblique arrangement of the inlet duct 16 the in-

flowing fluid will rotate around the central axis of the mixing apparatus 1 and the rotating fluid enters in through the tangential openings 15 in the wall 14 of the first chamber portion. In the first chamber portion which has a rotational paraboloid shape of nth grade, a focal line is formed where pressure is at minimum, and along the axis the pressure decreases in axial direction towards the outlet opening. This means that pressure is decreasing gradually both in radial and axial direction, and the fluid rotates around the axis and flows in axial direction.

In the second chamber portion, in the tapering section 17, the speed of flow and the velocity of rotation increases gradually toward the outlet duct portion 18 and in radial direction the pressure decreases towards the axis and a minimum is experienced along the axis. It is preferred if the rotational hyperboloid function has the same grade as the paraboloid function of the first chamber portion has.

The flow will have a structure which can be visualized in such a way as if the fluid mass consisted of an infinitely high numbers of annular hollow tubes having a form substantially following that of the tapering section 17, and the speed of rotation was different in case of each tube so that the elementary tubes were sliding on each other during their rotational movements. Moreover, the elementary tubes slide with respect to each other not only due to their differing speeds of rotation but they are moving and sliding in axial direction as well.

From this flow picture it will be clear that the imaginary contacting surface of phase boundaries will be extremely large and owing to the imaginary shearing effects between the elementary tubes, very effective contacts will be formed between differing components of the mixture. While the pressure minimum lies in the central axis, the components with lower specific mass will tend to collect at the axis in the vicinity of which the speed is at maximum. This ensures that tiny particles cannot escape from getting in the active zones.

The flow rate should be adjusted in such a way that phase transition (i.e. vaporization of any component) do not take place, nevertheless the minimum pressure should be just above the vapour pressure of the liquid mixture. As several liquid components are present, this condition should relate to the one which has the highest vapor pressure at the given temperature. This condition is equivalent to the statement that cavitation cannot occur in the flow. The mixing apparatus being preferably of glass, said condition can be adjusted by increasing the flow velocity up to a measure at which fine gas bubbles appear in the duct portion 18, and then lowering the flow velocity by a small amount just until the gas bubbles disappear again.

The first embodiment will now be described with reference to Fig. 1. In the mixing apparatus 1, a closed circulation passage comprising a pump 2 and a vessel 3, which are connected to each other through conduits 4, 5, 6 and 7, is formed. Reference numeral 8 represents a withdrawal opening for the withdrawal of a mixture, which has a cock. The opening is always closed except at the time of the withdrawal of the mixture. The vessel 3 has a cock-provided duct 31 and a cock-provided duct 32 for charging starting materials to be formed into a mixture. The fluid flows as indicated by arrows.

How a stable water/hydrophobic liquid mixture is prepared by introducing a hydrophobic liquid into water without the aid of an emulsifier by using the device shown in Figs. 1 through 3 will now be described.

At first, the cock of the duct 31 is opened and 9 l of distilled water is filled in the vessel 3. Then, the cock of the duct 32 is opened and 1 l of a vitamin A oil as the starting oil is filled in the vessel 3 and the cocks of the ducts 31 and 32 are closed. Incidentally, the vessel 3 is fully filled with water and vitamin A oil, or the upper portion of the vessel 3 may be vacant.

In this arrangement, the pump 2 is started. This pump has a flow quantity of 25 l/min. The inner diameters of the conduits 4, 5, 6 and 7 are equally about 14 mm. The flow direction is indicated by arrows in Fig. 1. Water and vitamin A oil are introduced into the mixing apparatus 1, and in the mixing apparatus 1, water and vitamin A oil flow into the interior of the cylindrical wall from the inclined duct 16 while being rotated and flow in the first portion 14 through the tangential holes 15 to form a vortex in the hollow element 13. This will now be described in detail. The majority of the rotating fluid component first flows to the closed top of the paraboloid and is reflected forward therefrom, and because of the exponentially tapered shape of the second portion 17 of the hollow element 13, the fluid component is promptly rotated together with the other component and the fluid component is advanced in the conduit 5 toward the vessel 3. Thus, the fluid component is circulated in the closed system until the pump 2 is turned off. After the flow of the mixture of water and vitamin A oil stops, the cock is opened and the water/vitamin A oil mixture is withdrawn from the withdrawal opening 8.

An example in which a hydrophilic liquid is mixed with a hydrophobic liquid by using the mixing device of the embodiment shown in Fig. 1 will now be described. The cock of the duct 31 is opened, and the vessel 3 is filled with 9 l of ethyl alcohol, and then the cock of the duct 32 is opened and 1 l of a vitamin oil is filled in the vessel 3. The subsequent procedures are the same as de-

scribed above. Furthermore, a mixture of 9 l of a vitamin A oil and 1 l of ethyl alcohol is similarly prepared according to the above-mentioned method. The obtained mixture formed by mixing ethyl alcohol and vitamin A oil without the aid of an emulsifier according to the above-mentioned method can be widely used for cosmetic lotions and cosmetic creams.

An example of the second embodiment of the present invention will now be described in detail with reference to Fig. 4. The same members as in the first embodiment are indicated by the same reference numerals. The second embodiment is different from the first embodiment mainly in that a vessel 9 for forming a second vortex is used instead of the mixing apparatus 3. The vessel 9 has a substantially spherical upper part 91, a lower part 93 tapered downwardly and an intermediate part 92 connected smoothly to the spherical upper part 91 and the lower part 93. The upper part 91 and intermediate part 92 have a convex face and the lower part 93 has a concave face. Thus, an inflection face is formed between the intermediate part 92 and the lower part 93. In a preferred embodiment, the vessel 9 is formed of glass so that the process occurring in the vessel 9 can be observed. Three ducts 95, 96 and 97 are formed on the top wall of the upper part 91 and they are sealed. The vessel 9 is filled with starting substances.

The vessel 9 further has two openings. At a substantial height where the vessel has a maximum diameter, a duct 98 extends obliquely from the upper portion of the intermediate 92. The duct 98 forms an acute angle to each of equator and tangent planes of the vessel 9 and the axis of the duct 98 is slightly inclined inwardly and upwardly in the interior direction of the vessel 9. In general, these angles are smaller than 30°. The second opening is the end of the open bottom of the lower part 93 of the vessel 9. A circulation passage comprising the pump 2, the mixing apparatus 1 and four conduits 4, 5, 6' and 7 is arranged between the lower part 93 and the inclined duct 98.

The second embodiment will now be described with reference to Fig. 4. In the mixing apparatus 1, a closed circulation passage is formed through the pump 2, the vessel 9, withdrawal opening 8 and the conduits 4, 5, 6' and 7.

How a water/hydrophobic liquid can be prepared without the aid of an emulsifier by using the device shown in Fig. 4 is described. At first, 9.5 l of distilled water is filled in the vessel 9 through the duct 97. Then, 0.5 l of squalane is filled in the vessel 9 through the duct 95. The ducts 95 and 97 are sealed. Incidentally, the vessel 9 may be completely filled with water and squalane, or the upper part of the vessel 9 may be left vacant. In this arrangement, the pump 2 is started. The flow direc-

tion is indicated by arrows in Fig. 4. When water and squalane are introduced into the mixing apparatus 1, they flow through the tangential holes 15 to form a first vortex in the hollow element 13, and this first vortex is formed in the same manner as described above. Thus, water and squalane flow into the vessel 9 in the tangential direction through the inclined inlet duct 98.

Water and squalane which have been quiet in the vessel 9 begin to turn, and a second vortex is formed. A certain time (about 1 to about 2 minutes) is necessary for attaining a stationary state in the vortex. The rotation number of the vortex at the topmost part and maximum diameter part is about 50 r.p.m., and the rotation number increases substantially exponentially toward the lower part. Thus, the mixture of water and squalane is circulated in the closed system until the pump 2 is turned off. After the flow of the mixture stops, the cock is opened and the water/squalane mixture is withdrawn from the withdrawal opening 8.

An example of the first embodiment of the present invention will now be described with reference to Figs. 5 and 6. The same members as in the first embodiment are represented by the same reference numerals. The third embodiment is different from the first embodiment mainly in that a jet pump 50 connected to the mixing apparatus 1 is arranged in the closed system.

In this embodiment, a vessel 30 comprising a cover and ducts 31 and 32 is used. The vessel 30 is filled with starting substances. The vessel 30 is connected to the pump 2 through the conduit 6', withdrawal opening 8 and conduit 7 located at the lower portion of the vessel 30. The flowout conduit 4 is connected to the inlet of the jet pump 50. The internal structure of the jet pump 50 is shown in Fig. 6. An inlet duct 54 of the jet pump 50 communicates with the vessel 30 through a duct 51. The jet pump 50 exerts a function of promoting the mixing of two different liquids. The jet pump 50 has a substantially cylindrical housing 52 having a hollow internal space, as shown in Fig. 6. A nozzle 53 is inserted in the hollow internal space of the housing 52 and the top end of the nozzle 52 is connected to the duct 4. A cylindrical space is formed in the vicinity of the top end of the nozzle 53 and an inlet duct 54 is inserted in the wall of the housing 52, and as the result, the hollow internal space of the inlet duct 54 communicates with the cylindrical space in the vicinity of the top end of the nozzle 53. In this example, the water jet pump is used, but there may be adopted a method in which a branched pipe is used instead of the water jet pump and the outlet side of this tube is connected to the inlet side of the mixing apparatus 1.

It will now be described how a stable hydrophilic liquid/hydrophobic mixture is prepared by

introducing a hydrophobic liquid into a hydrophilic liquid without the aid of emulsifier by using the device shown in Figs. 5 and 6.

At first, the cock of the duct 31 is opened and the vessel 31 is filled with 9.5 l of ethyl alcohol. Then, the cock of the duct 32 is opened and 0.5 l of squalane as the starting oil is filled in the vessel 30. The cock of the ducts 31 and 32 are closed. When the pump 2 is started, a squalane-rich liquid in the vessel 30 is sucked into the pump 2 and is caused to flow in the vessel 30 through the conduit 4, jet pump 50, mixing apparatus 1 and conduit 5. Thus, a closed system is formed. Furthermore, an alcohol-rich liquid in the vessel 30 is injected into the jet pump 50 through the conduit 51. In this closed system, ethyl alcohol and squalane are mixed by the circulation. In this manner, a mixture of ethyl alcohol and squalane is formed.

If the mixing apparatus 1 is used, at least two kinds of liquids can be stably and homogeneously mixed.

The physical states of water/hydrophobic liquid mixtures and hydrophilic liquid/hydrophobic liquid mixtures obtained according to the above-mentioned first through third embodiments were tested. One drop of the water/vitamin A oil obtained according to the first embodiment was collected from each of the upper and lower portions of the vessel 30 by a syringe and dropped on a preparation. The water/vitamin A oil mixture on the preparation was photographed (600 magnifications) at a photographic sensitivity of ASA1000 by Nikon F.2 supplied by Nippon Kogakusha, which was attached to an optical microscope (M-862 supplied by Carton Co.), and it was confirmed that the vitamin A oil was homogeneously distributed in the form of droplets having a size of about 500 nm. In order to confirm the stability of the water/vitamin A oil mixture, the mixture was stored in the sealed state in a thermostat tank maintained at 50°C for 13 days, and the mixture was observed by a microscope photo in the same manner as described above. The state was not substantially different from the state just after the mixing. Thereafter, about 4 ml of the mixture of water and vitamin A was placed in a cubic cell and, after setting a slit (width = 0.1mm), to a laser beam from a laser beam source unit (i.e., GL-803N, manufactured by Nakamura Rika Kō o K.K.), the cubic cell was irradiated with a laser beam. As a result, Tyndall phenomenon was confirmed. Then, the cubic cell was set on a microscope (BH-2 manufactured by Olympus optical co., Ltd.) and a ultramicroscope was composed, together with the above-mentioned laser beam source unit. Thus, the cubic cell was irradiated with a laser beam via the above-mentioned slit from the laser beam source unit. As a result, the existence of oil drops was confirmed and the occurrence of a

Brownian movement was also confirmed. As a comparative sample, a mixture of 10 ml of vitamin A oil and 90 ml of water was placed in a vessel and was stirred for a long time in a ultrasonic cleaner (i.e., "SONO CLEANER" CA=2480 manufactured by Kaijyo Denki K.K.). The resultant mixture was allowed to stand at room temperature for one day under a tightly sealed condition. As a result, it was confirmed that the water and the vitamin A oil in the vessel were separated and the underpositioned water was transparent and was not turbid. On the other hand, when one drop each of the upperpositioned vitamin A oil and the underpositioned water placed on a separate preparation was observed by the above-mentioned optical microscope, it was confirmed that neither the water drops nor the oil drops were a mixture of water and oil. Furthermore, neither oil in the water drops nor water in the oil drops were observed by the above-mentioned ultramicroscope.

It also was confirmed that as the circulation time in the embodiment of Fig. 1 was long, the droplet size became finer. The water/vitamin A oil mixture on the preparation was warmed to evaporate water, and adhesion of the oily substance onto the preparation was confirmed. When the water/squalane mixture was similarly tested, the same results as described above were obtained.

Similarly, the physical conditions of mixtures of water and gas oil obtained from 1 liter of water and 9 liters of gas oil (i.e., hydrophobic oil) in the above-mentioned first, second and third embodiments of the present invention were examined. As a result, it was confirmed by the optical microscope that the water drops having approximately the same size of about 500 nm were uniformly distributed in the oil liquid. Furthermore, similarly as mentioned above, the occurrence of the Tyndall phenomenon, the existence of the water drops by the ultramicroscope, and the occurrence of the Brownian movement of the water drops were confirmed. Furthermore, when the mixtures were allowed to stand for a long time, it was observed that the upper oil-in-water portion and the lower water-in-oil portion are stably existed as a colloidal condition. In addition, when the resultant mixtures were centrifugally separated for 5 minutes at 3,000 rpm, it was confirmed by the above-mentioned optical microscope that the occurrence of the Tyndall phenomenon was confirmed in the resultant centrifugally separated portion although the present of the water drops was not observed. Furthermore, when the centrifugally separated portion was observed by a ultramicroscope, the existence of the water drops and the occurrence of the Brownian movement were confirmed. Accordingly, the size of the water drops was estimated to be about 100 nm.

Moreover, when the mixtures was prepared by the above-mentioned ultrasonic cleaner, the resultant mixtures were separated after allowing to stand at room temperature for one hour, into water and gas oil and the lower water phase was transparent.

When the ethyl alcohol/vitamin A oil mixture prepared according to the first embodiment as the hydrophilic liquid/hydrophobic mixture was photographed by the microscope according to the above-mentioned method, it was confirmed that the droplet size of the vitamin A oil in ethyl alcohol was about 500 nm. No substantial change of the state was observed with respect to the distribution of ethyl alcohol and vitamin A oil between the mixture just after the mixing and the mixture which had been stored in a thermostat tank maintained at 50°C for 20 days. When the ethyl alcohol/vitamin A oil mixture on the preparation was warmed to evaporate water, adhesion of the oily substance onto the preparation was confirmed.

When the ethyl alcohol/squalane mixture was similarly tested, the same results as described above were obtained.

A plurality of mixing apparatus 1 can be arranged in series or in parallel in one closed flow passage, and other substance can be supplied linearly or in the reversely rotated state in a vortex formed within the mixing apparatus. Furthermore, the mixing method, mixing device and mixture are not limited to those specifically disclosed in the examples.

As is apparent from the foregoing illustration, by using the mixing device and mixing method of the present invention, a plurality of substances different in the physical properties can be mixed. By the term "hydrophobic liquid" are meant oily materials such as carnauba wax and liquid paraffin and fossil fuels such as benzene, decane, and gas oil, vegetable oils such as sesame oil, and by the term "hydrophilic liquid" are meant various alcohols such as monohydric and dihydric alcohols.

The obtained mixture is advantageous in the cost because an emulsifier need not be used, and hence, the limitations by the use of the emulsifier or the like are eliminated and the mixture can be widely used.

## Claims

1. Emulgator-free liquid emulsion comprising at least one hydrophobic liquid phase selected from the group consisting of Vitamin A, squalane, octane, carnauba wax, liquid paraffin, fossil fuels, benzene, decane and vegetable oils and at least one hydrophilic liquid phase selected from the group consisting of water and monohydric alcohols, one of said phases being a disperse phase of the emulsion, and

said emulsion being in a stable colloidal state with a particle size of the disperse phase of 1,000 nm or less.

2. A method for producing a emulgator-free liquid emulsion being in a stable colloidal state and being of at least one hydrophobic liquid phase and at least one hydrophilic liquid phase with a particle size of the dispersed phase of 1000 nm or less, wherein the liquid phases are repeatedly recirculated in the form of their mixture through a mixing chamber which is composed of a first portion and of a second portion and which has an axially symmetrical shape and in which the mixture is brought into a rotational flow about the axis with a flow component parallel to the axis and in which the flow pressure of the mixture is reduced in flow direction by gradually increasing the flow velocity of the mixture up to the coaxial discharge of the rotating mixture out of the second portion of the mixing chamber, the first portion of the mixing chamber being connected to the second portion and having a top opposite to the second portion, characterized in that the flow pressure up to the discharge of the mixture from the mixing chamber is reduced to a minimum pressure being near to the vapor pressure of the mixture without reaching or falling below the vapor pressure, and the majority of the mixture in the form of a fluid introduced into the first portion of the mixing chamber is caused to flow along the inner wall of the first portion toward the top, while being further rotated, whereby the flow, at the top, is reflected and the flow speed is gradually increased and a vortex state is formed on the central axis of the mixing chamber toward the second portion.
3. A device for carrying out the method according to claim 2, comprising a recirculation conduit path and a mixing apparatus connected in said loop, the mixing apparatus (1) comprising a mixing chamber of a rotational symmetrical shape in a hollow element (14) with a plurality of tangential inlet openings (15) opening into a first chamber portion connected to a second chamber portion having a tapering section in flow direction and an axial outlet being coaxial with the axis of the mixing chamber, characterized in that the first chamber portion has a rotational paraboloid form of nth grade and said second chamber portion has a rotational inverse hyperboloid form of nth grade, said axial outlet being a cylindrical duct portion (18), the parabolic wall (14) of said first chamber portion defining a focal line falling in the

axis of rotation, said inlet openings (15) being arranged at a wide cross-section of the first chamber portion which is connected to the second chamber portion at the widest cross-section thereof, the sum of the cross-sections of the inlet openings (15) substantially corresponds to the cross-section of said duct portion (18) and the difference between these cross-sections is at most 1:3, and a pressure equalizing chamber (11) is provided around said first chamber portion, into which fluid mixture is circulated and passed through said tangential inlet openings (15), and which has a cylindrical shape and is coaxial with said axis of rotation and comprises a bottom wall upstream of said first chamber portion, an inlet duct (16) defining an acute angle with said axis is opening into the pressure equalization chamber (11) at the center of said bottom wall.

4. The device as claimed in claims 3, characterized in that the grade of the hyperboloid function defining said tapering section substantially corresponds to the grade of the paraboloid defining the first chamber portion.
5. The device as claimed in claim 3, comprising a pump means in said recirculation path for passing said fluid through said mixing chamber and for recirculating it through said recirculation path with a flow rate at which the minimum pressure provided at the central axis is still somewhat higher than the highest vapor pressure of the liquid components to be mixed.

#### Patentansprüche

1. Emulgatorfreie Flüssigkeitsemulsion mit wenigstens einer hydrophoben Flüssigkeitsphase aus Vitamin-A-, Squalan-, Benzol-, Dekan- oder Pflanzenöl und wenigstens einer hydrophilen Flüssigkeitsphase aus Wasser oder monohydratischem Alkohol, wobei eine dieser Phasen in der Emulsion als disperse Phase vorliegt und die Emulsion sich in stabilem kolloidalen Zustand mit einer Teilchengröße der dispersen Phase von 1000 nm oder weniger befindet.
2. Verfahren zur Herstellung einer emulgatorfreien Flüssigkeitsemulsion, die in einem stabilen kolloidalen Zustand vorliegt und aus wenigstens einer hydrophoben Flüssigkeitsphase und wenigstens einer hydrophilen Flüssigkeitsphase bei einer Teilchengröße der dispersen Phase von 1000 nm oder weniger ist, bei welchem die Flüssigkeitsphasen wiederholt in Form ihres Gemisches durch eine Mischkam-

mer rezirkuliert werden, welche aus einem ersten Abschnitt und einem zweiten Abschnitt aufgebaut ist und eine rotationssymmetrische Gestalt hat und in welcher das Gemisch in eine Rotationsströmung um die Achse mit einer Strömungskomponente parallel zu der Achse versetzt wird und in welcher der Strömungsdruck in dem Gemisch in Strömungsrichtung durch allmähliches Erhöhen der Strömungsgeschwindigkeit des Gemisches bis zu dem koaxialen Austreten des rotierenden Gemisches aus dem zweiten Abschnitt der Mischkammer abgesenkt wird, wobei der erste Abschnitt der Mischkammer an den zweiten Abschnitt angeschlossen ist und einen dem zweiten Abschnitt entgegengesetzten Scheitel aufweist, dadurch gekennzeichnet, daß der Strömungsdruck bis zu dem Austreten des Gemisches aus der Mischkammer bis auf einen Minimalwert nahe des Dampfdrucks des Gemisches ohne Erreichen oder Unterschreiten des Dampfdruckes abgesenkt wird, und daß der Hauptteil des in den ersten Abschnitt der Mischkammer eingeführten Gemisches in Form eines Strömungsmediums dazu gebracht wird, entlang der Innenwandung des ersten Abschnittes zu dem Scheitel hin zu strömen, während er weiter gedreht wird, wobei der Strom an dem Scheitel reflektiert wird und die Strömungsgeschwindigkeit allmählich gesteigert wird und ein Wirbelzustand an der Mittelachse der Mischkammer zu dem zweiten Abschnitt hin gebildet wird.

3. Einrichtung zum Durchführen des Verfahrens nach Anspruch 2, mit einem Rezirkulationsleitungsweg und einer in den Kreis eingeschalteten Mischvorrichtung, wobei die Mischvorrichtung (1) eine Mischkammer (13) rotationssymmetrischer Gestalt in einem Hohlelement (14) mit einer Mehrzahl von tangentialen Einlaßöffnungen (15) aufweist, die in einen ersten Kammerabschnitt münden, der an einen zweiten Kammerabschnitt (17) mit sich in Strömungsrichtung verjüngendem Querschnitt angeschlossen ist, und ein axialer Auslaß koaxial zu der Achse der Mischkammer ist, dadurch gekennzeichnet, daß der erste Kammerabschnitt eine rotationsparabolische Form n-ten Grades hat und der zweite Mischkammerabschnitt (17) die Form eines inversen Rotationshyperboloids n-ten Grades hat, wobei der axiale Auslaß ein zylindrischer Stutzenabschnitt (18) ist, die parabolische Begrenzungswand (14) des ersten Kammerabschnittes (14) eine in die Rotationsachse fallende Fokallinie definiert, die Einlaßöffnungen (15) an einem weiten Querschnitt des ersten Kammerabschnittes angeordnet

sind, welcher an den zweiten Kammerabschnitt (17) an seinem weitesten Querschnitt angeschlossen ist, die Summe der Querschnitte der Einlaßöffnungen (15) im wesentlichen dem Querschnitt des Stutzenabschnitts (18) entspricht und die Differenz zwischen diesen Querschnitten höchstens 1:3 beträgt, und eine Druckausgleichskammer (11) rings des ersten Kammerabschnitts vorgesehen ist, in welche Flüssigkeitsgemisch rezirkuliert und durch die tangentialen Einlaßöffnungen (15) geführt wird und welche eine zylindrische Form hat und koaxial zu der Drehachse ist und stromaufwärts des ersten Kammerabschnitts eine Bodenwand aufweist, wobei ein Einlaßstutzen (16), der mit der Achse einen spitzen Winkel bildet, in die Druckausgleichskammer (11) in der Mitte der Bodenwand mündet.

4. Einrichtung nach Anspruch 3, dadurch gekennzeichnet, daß der Grad der hyperbolischen Funktion, von welcher der sich verjüngende erste Kammerabschnitt definiert wird, im wesentlichen dem Grad der Paraboloidfunktion entspricht, die den ersten Kammerabschnitt (14) definiert.
5. Einrichtung nach Anspruch 3, mit einer Pumpeneinrichtung in dem Rezirkulationskreis zum Hindurchführen der Flüssigkeit durch die Mischkammer und zum Rezirkulieren derselben durch den Rezirkulationskreis mit einer Strömungsrate, bei welcher der Minimaldruck an der Mittelachse noch etwas höher als der höchste Dampfdruck der zu mischenden Flüssigkeitskomponenten ist.

#### Revendications

1. Emulsion liquide exempte d'émulsifiant, comprenant au moins une phase de liquide hydrophobe choisi parmi le groupe composé de vitamine A, squalane, octane, cire carnauba, paraffine liquide, carburants fossiles, benzène, décane et huiles végétales et au moins une phase de liquide hydrophile choisi parmi le groupe composé d'eau et alcools monovalents, l'une desdites phases étant une phase dispersée de l'émulsion et ladite émulsion étant à l'état colloïdal stable, avec une grosseur de particules de la phase dispersée de 1.000 nm ou moins.
2. Un procédé de production d'une émulsion liquide exempte d'émulsifiant à l'état colloïdal stable et composée d'au moins une phase de liquide hydrophobe et d'au moins une phase de liquide hydrophile à grosseur de particules

de la phase dispersée de 1.000 nm ou moins, dans lequel les phases liquides sont circulées de manière répétée sous forme de leur mélange dans une chambre de mélange qui se compose d'une première partie et d'une seconde partie et qui est de forme axialement symétrique et dans laquelle le mélange est amené en circulation rotative autour de l'axe avec une composante de circulation parallèle à l'axe et dans laquelle la pression de circulation du mélange est réduite dans le sens de la circulation en élevant progressivement la vitesse de circulation du mélange jusqu'à la décharge coaxiale du mélange en rotation hors de la seconde partie de la chambre de mélange, la première partie de la chambre de mélange étant reliée à la seconde partie et présentant une partie supérieure opposée à la seconde partie, caractérisé en ce que la pression de circulation jusqu'à la décharge du mélange de la chambre de mélange est réduite à une pression minimale proche de la pression de vapeur du mélange, sans atteindre ou tomber au-dessous de la pression de vapeur, et que l'on fait circuler la majeure partie du mélange sous forme de fluide introduit dans la première partie de la chambre de mélange le long de la paroi intérieure de la première partie vers la partie supérieure, tout en continuant à être tourné, la circulation étant réfléchiée à la partie supérieure et que la vitesse de circulation est progressivement élevée et qu'un état de vortex est formé sur l'axe central de la chambre de mélange vers la seconde partie.

3. Un dispositif pour la mise en oeuvre du procédé suivant la revendication 2, comprenant un circuit de circulation et un mélangeur raccordé dans ladite boucle, le mélangeur (1) comprenant une chambre de mélange de forme symétrique en rotation dans un élément creux (14), avec une pluralité d'ouvertures d'entrée tangentielles (15) donnant dans une première partie de chambre reliée à une seconde partie de chambre de section conique dans le sens de la circulation et une sortie axiale étant coaxiale à l'axe de la chambre de mélange, caractérisé en ce que la première partie de chambre est en forme de paraboloïde rotatif du n-ième degré et que ladite seconde partie de chambre est en forme d'hyperboloïde inversé rotatif du n-ième degré, ladite sortie axiale étant une partie de conduit cylindrique (18), la paroi parabolique (14) de ladite première partie de chambre définissant une ligne focale tombant dans l'axe de rotation, lesdites ouvertures d'entrée (15) étant disposées sur une section large de la première partie de chambre qui est

reliée à la seconde partie de chambre, à sa section la plus large, la somme des sections des ouvertures d'entrée (15) correspondant sensiblement à la section de ladite partie de conduit (18) et la différence entre ces sections étant de maximum 1:3, et qu'une chambre d'égalisation de pression (11) est prévue autour de ladite première partie de chambre, dans laquelle le mélange de fluides circule et passe par lesdites ouvertures d'entrée tangentielles (15) et qui est de forme cylindrique et coaxiale audit axe de rotation et comprend une paroi inférieure en amont de ladite première partie de chambre, un conduit d'entrée (16) définissant un angle aigu avec ledit axe donnant dans la chambre d'égalisation de pression (11) au centre de ladite paroi inférieure.

4. Le dispositif suivant la revendication 3, caractérisé en ce que le degré de la fonction d'hyperboloïde définissant ledit segment conique correspond sensiblement au degré du paraboloïde définissant la première partie de chambre.
5. Le dispositif suivant la revendication 3, comprenant un moyen de pompe dans ledit circuit de circulation, destiné à faire passer ledit fluide dans ladite chambre de mélange et à le faire circuler dans ledit circuit de circulation à un débit auquel la pression minimale créée à l'axe central est encore quelque peu supérieure à la pression de vapeur la plus élevée des éléments liquides à mélanger.

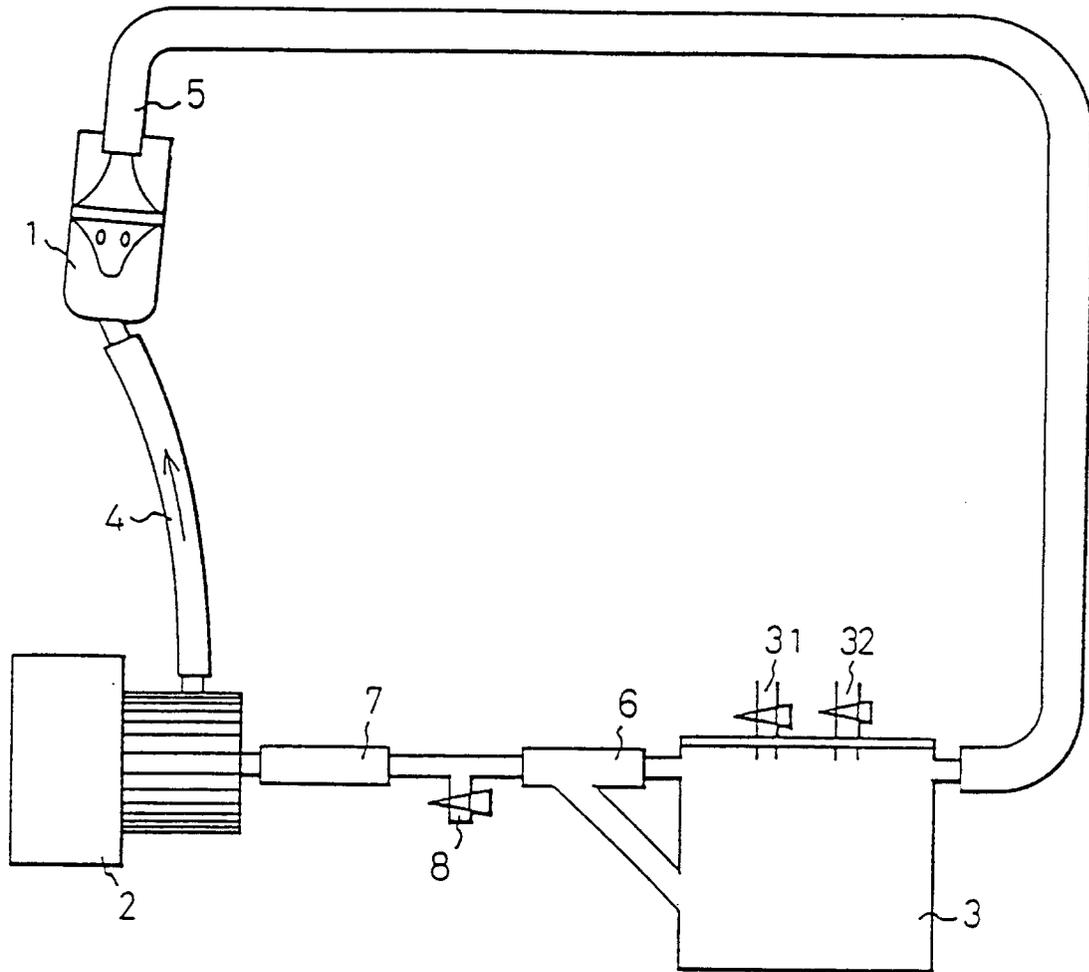


Fig. 1

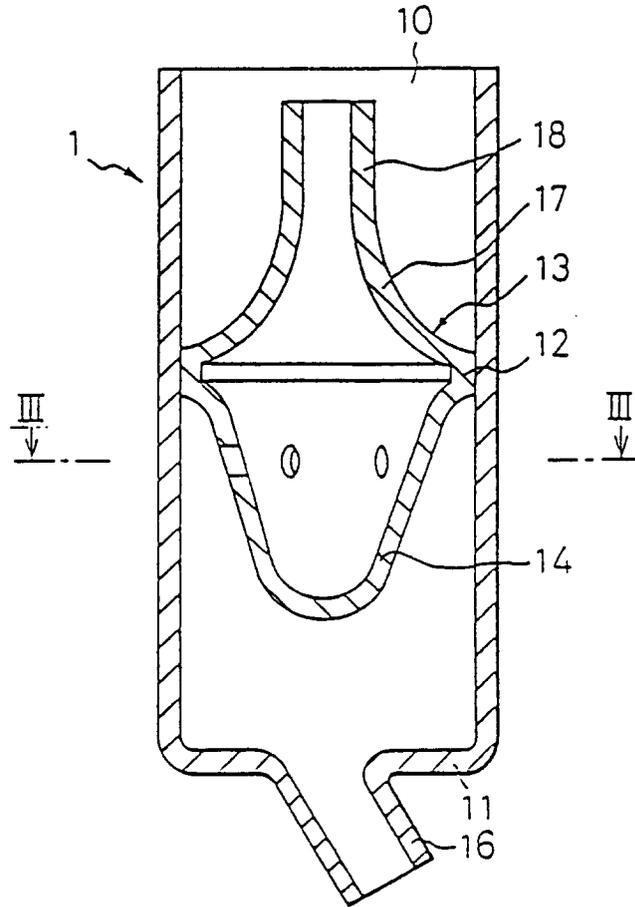


Fig. 2

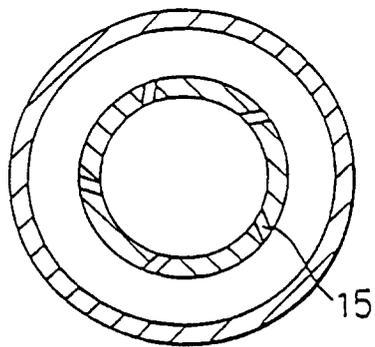


Fig. 3

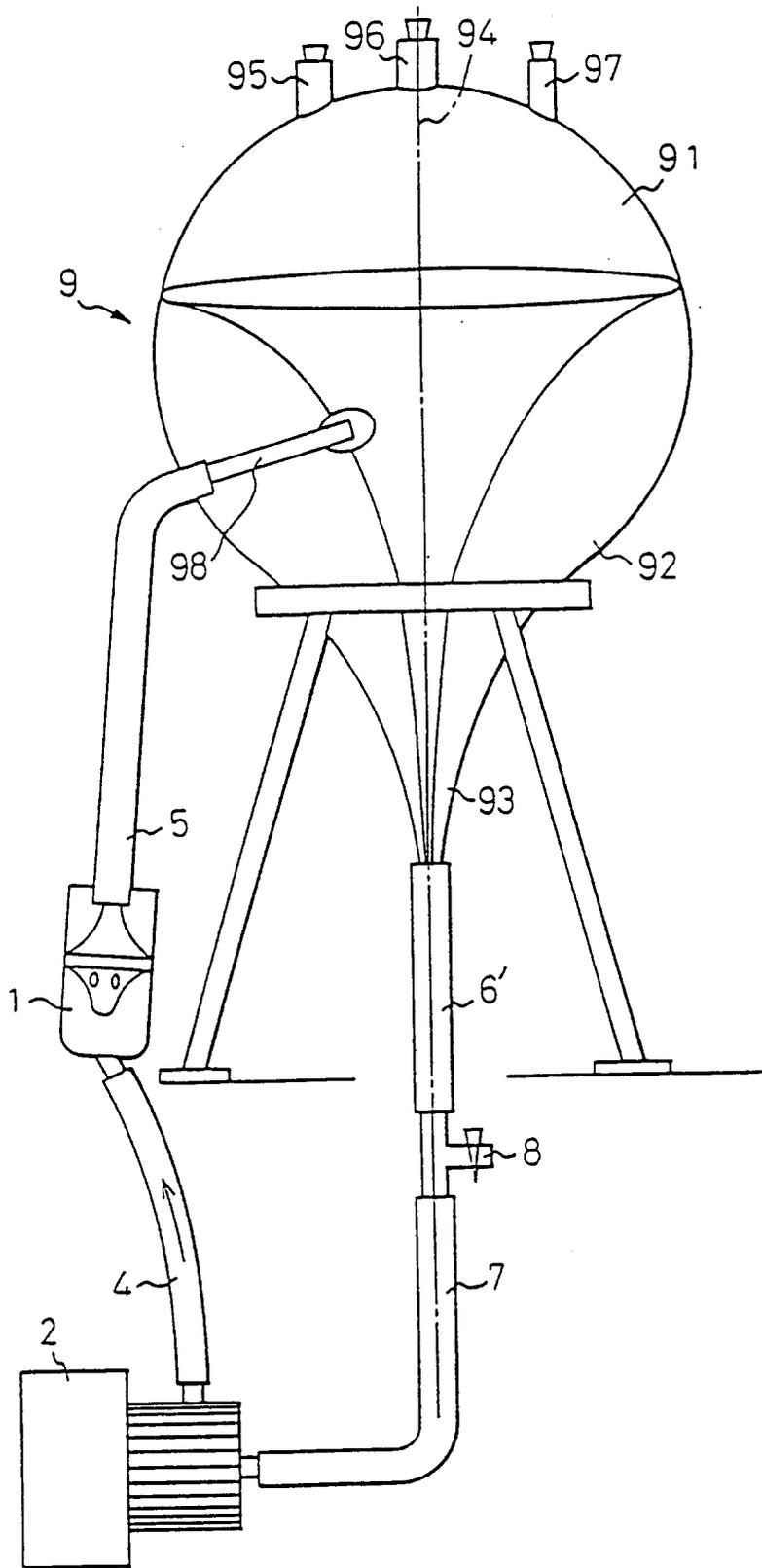


Fig. 4

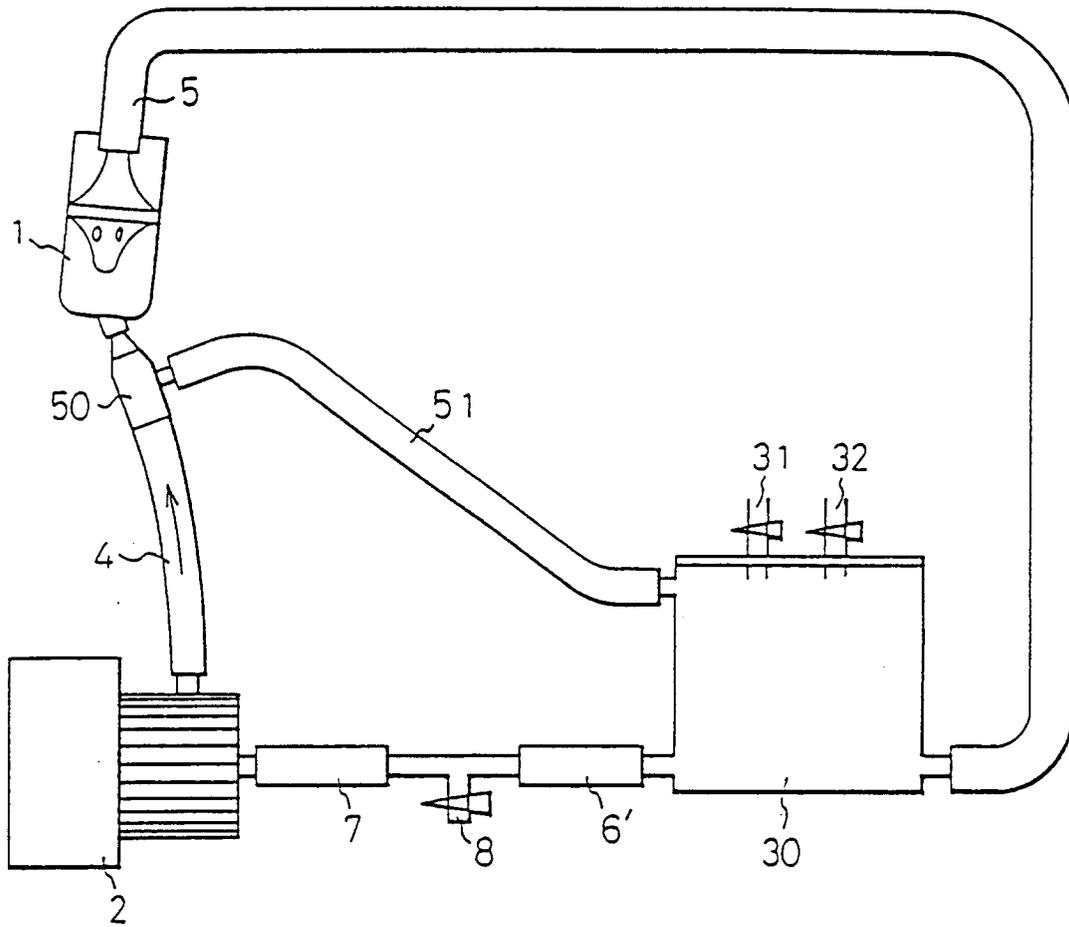


Fig. -5

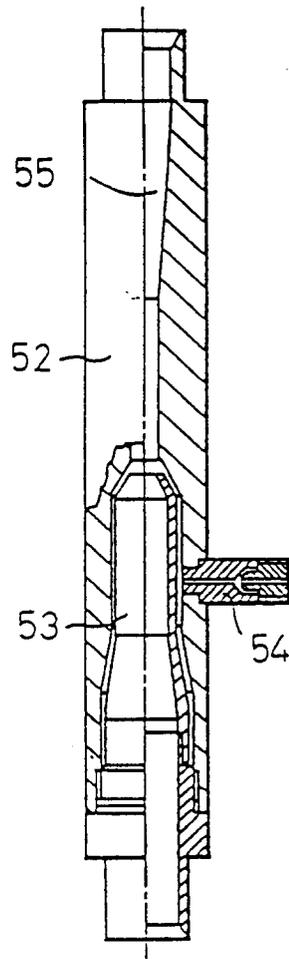


Fig. 6