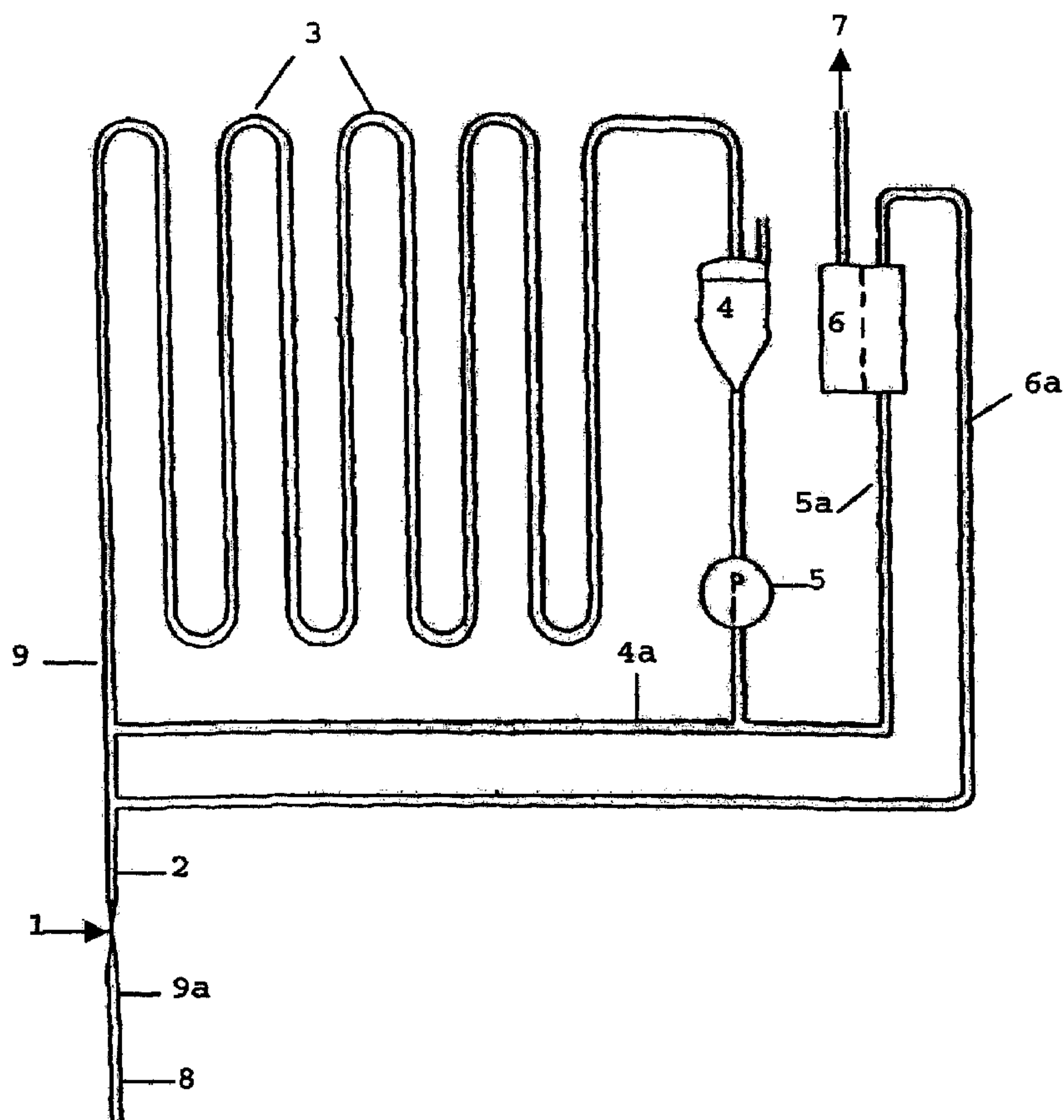




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(54) Titre : PROCÉDE CONTINU D'HYDROGENATION
 (54) Title: CONTINUOUS METHOD OF HYDROGENATION



(57) Abrégé/Abstract:

The invention relates to a continuous method for catalytic hydrogenation, whereby a reaction mixture, containing the substrate for hydrogenation, the hydrogenated product, hydrogen and the hydrogenation catalyst, suspended in the reaction mixture, is fed into

(57) **Abrégé(suite)/Abstract(continued):**

a reactor (3) in a circuit, whereby a part of the hydrogenation product is removed (7) from the reactor and the substrate for hydrogenation and hydrogen (6a) are added to the reaction. The substrate for hydrogenation and the hydrogen (1) are mixed before admission to the reactor. A venturi nozzle is particularly suitable for application as a mixing device. The invention particularly finds application in the method or production of hydrogen peroxide by the anthraquinone method.

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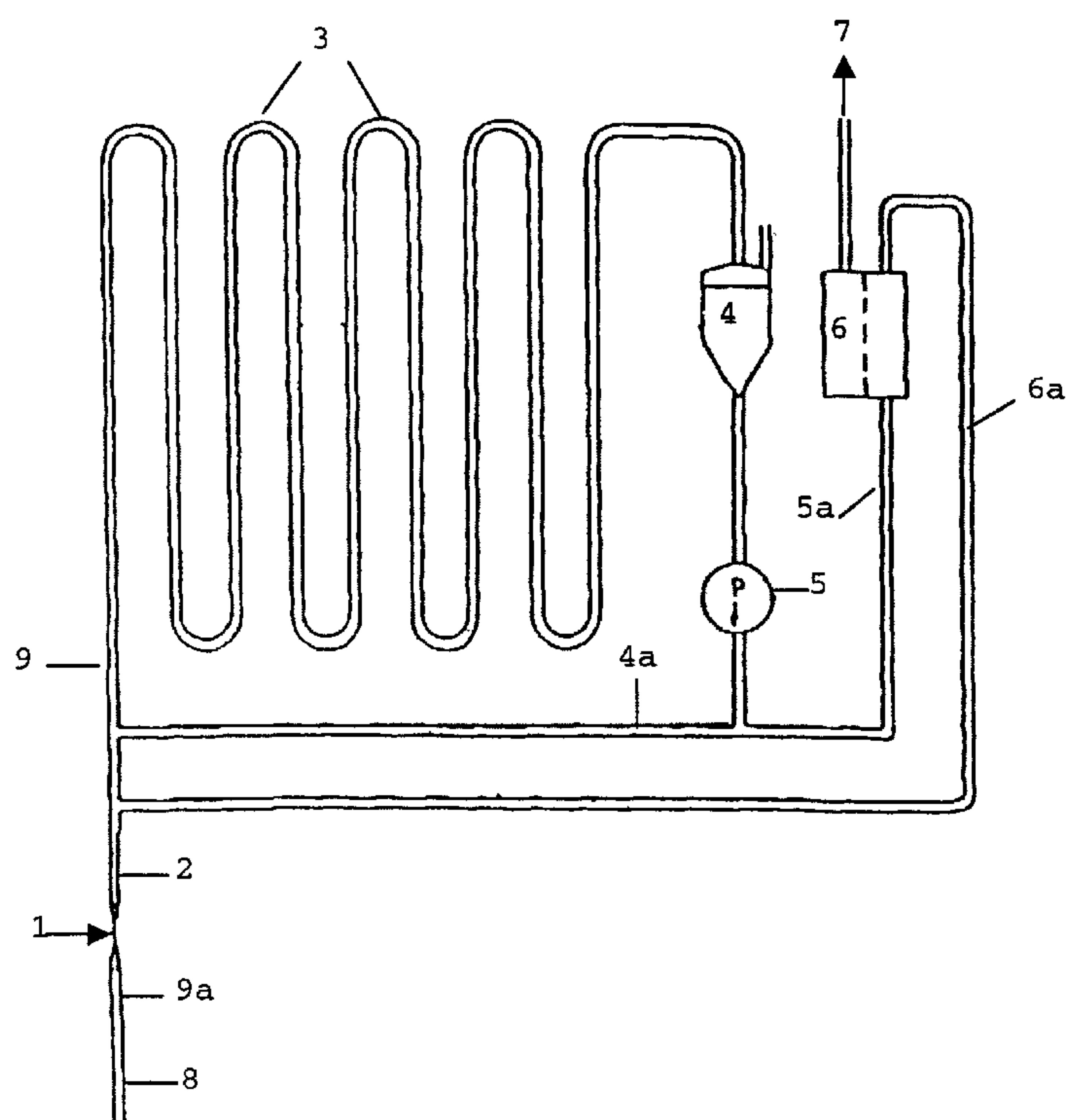
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(54) Title: CONTINUOUS METHOD OF HYDROGENATION

(54) Bezeichnung: KONTINUIERLICHES VERFAHREN ZUR HYDRIERUNG



(57) Abstract: The invention relates to a continuous method for catalytic hydrogenation, whereby a reaction mixture, containing the substrate for hydrogenation, the hydrogenated product, hydrogen and the hydrogenation catalyst, suspended in the reaction mixture, is fed into a reactor (3) in a circuit, whereby a part of the hydrogenation product is removed (7) from the reactor and the substrate for hydrogenation and hydrogen (6a) are added to the reaction. The substrate for hydrogenation and the hydrogen (1) are mixed before admission to the reactor. A venturi nozzle is particularly suitable for application as a mixing device. The invention particularly finds application in the method or production of hydrogen peroxide by the anthraquinone method.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein kontinuierliches Verfahren zur katalytischen Hydrierung, bei der ein Reaktionsgemisch, das die zu hydrierende Substanz, das Hydrierungsprodukt, Wasserstoff und den im Reaktionsgemisch suspendierten Hydrierkatalysator enthält, in einem Reaktor (3) im Kreislauf geführt wird, ein Teil des Hydrierungsproduktes dem Reaktor entnommen wird (7), und die zu hydrierende Substanz und Wasserstoff (6a) der Reaktion zugeführt wird. Dabei wird die zu hydrierende Substanz und der Wasserstoff (1) vor dem Eintritt in den Reaktor vermischt. Als Mischorgan eignet sich besonders eine Venturi-Düse. Die Anmeldung findet besonders Anwendung im Verfahren zur Herstellung von Wasserstoffperoxid nach dem Anthrachinonverfahren.

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Continuous method of hydrogenation

The present invention relates to a continuous catalytic hydrogenation process, in which the hydrogenation catalyst suspended in the reaction mixture is recirculated. This
5 process is particularly suitable for the hydrogenation step in the anthraquinone process for the production of hydrogen peroxide.

In known hydrogenation processes the catalyst is generally used as a fixed bed, as a supported or as a suspended
10 catalyst.

In the fixed bed reactor the catalyst is applied to a support. A great disadvantage of this type of reactor is the slow transfer of the gaseous hydrogen into the solution and on to the catalyst surface.

15 Various ways of bringing the hydrogen into solution more rapidly have been suggested. US patent 2 837 411 describes the saturation of the solution with hydrogen before hydrogenation in a separate tank. Considerable investment costs and the fact that only a fraction of the hydrogen
20 required in the reaction can be brought into solution make this route unattractive.

Even the pre-mixing of the hydrogen with solution to be hydrogenated by means of a static mixer, as described in US
25 patent 4 428 922, leads only to a slight improvement, since the hydrogen bubbles coalesce on contact with the inserts in the reactor.

When using a supported or suspended catalyst, as described in EP-A-111 133, these disadvantages do not occur.

In EP-A-111 133 it is shown that in a continuous co-current
30 catalytic hydrogenation process for the production of hydrogen peroxide by the so-called anthraquinone process, the efficiency of the hydrogenation can be increased if

this is carried out in a loop reactor at flow velocities of more than 3 m/s, preferably 4 - 7 m/s. The flow velocity is selected such that the gas/liquid interface remains as produced at the beginning of the reactor. In this way it is guaranteed that the hydrogen can react completely along the reaction zone and no separations occur between the gas and the liquid phase.

It is disadvantageous in this process described in EP-A-111 133 that the mixing devices for the substance to be hydrogenated and the hydrogen lead to large pressure drops, particularly when tubular reactors are to be operated at the high circulating flows and circulation rates specified, and therefore a higher input of energy is necessary.

The object of the present invention was therefore to increase the efficiency of a hydrogenation process in which a reaction mixture containing the substance to be hydrogenated, the hydrogenation product, hydrogen and the catalyst suspended in the reaction mixture, is recirculated, part of the hydrogenation product is removed from the reactor and the substance to be hydrogenated and hydrogen are fed into the reaction.

The object is achieved in that the substance to be hydrogenated, the hydrogenation product, hydrogen and the hydrogenation catalyst suspended in the reaction mixture are recirculated in a reactor, part of the hydrogenation product is removed from the reactor and the substance to be hydrogenated and the hydrogen are fed into the reactor, the substance to be hydrogenated and the hydrogen being mixed before entering the reactor.

As a result, the pressure drop in the hydrogenation reactor is reduced quite substantially, which leads to a reduction in the energy costs. Alternatively, the total circulating quantity can be increased at a constant speed of the

circulating pump, which leads to a higher velocity and space-time yield and thus, ultimately, to an increase in capacity.

This result was surprising for the hydrogenation reactor described above, in which the majority of the reaction mixture is recirculated and only a small part is removed from the reactor, and accordingly the quantity of substance to be hydrogenated and of hydrogen being fed into the reactor is small in comparison with the quantity of the reaction mixture being recirculated.

As set forth in EP-A-111 133, the conversion in the type of reactor described above is greatest when the gas/liquid interface produced is maintained along the reaction zone. This is the case when the mixing of gas and liquid phase takes place at flow velocities of at least 3 m/s. Outside the hydrogenation reactor, the flow velocities are clearly lower than 3 m/s. In consequence, it should be expected that no transfer of the dispersion into the reactor should take place, accompanied by a reduced conversion. However, it has now been shown that, even when the gas and liquid phase are premixed upstream of the hydrogenation reactor, the conversion is not reduced.

According to an embodiment of the present invention, there is provided a continuous catalytic hydrogenation process, comprising recirculating a reaction mixture containing a substance to be hydrogenated, a hydrogenation product, hydrogen and a hydrogenation catalyst suspended in the reaction mixture in a reactor, removing part of the hydrogenation product from the reactor and feeding the substance to be hydrogenated and hydrogen into the reactor, wherein a catalyst-free liquid phase containing

3a

the substance to be hydrogenated is mixed with hydrogen before entering the reactor and this mixture is fed into the catalyst-containing reaction mixture.

5 According to another embodiment of the present invention, there is provided a process for the production of hydrogen peroxide by an anthraquinone cyclic process, comprising a catalytic hydrogenation of a working solution, an oxidation of hydrogenated working solution
10 with oxygen or an oxygen-containing gas, wherein hydrogen peroxide and substituted anthraquinone or a mixture containing its ring-hydrogenated tetrahydro-anthraquinone is obtained, and an extraction of the hydrogen peroxide from the mixture obtained after the oxidation, wherein
15 the hydrogenation is performed according to claim 9 or 10.

The process according to the invention for the mixing of substance to be hydrogenated and hydrogen can preferably be
20 carried out in that the gas bubbles produced in the mixing device have a maximum diameter of 2.5 mm, particularly preferably less than 1.5 mm, to allow a rapid transfer into the liquid phase.

Possible mixing devices with which this size of gas bubbles
25 can be achieved are e.g. perforated plates, frits, nozzles or static mixers.

Particularly suitable for the process according to the invention is a venturi nozzle. This known device has a
30 small pressure drop compared with other mixing devices, and

is largely maintenance-free. As a function of the energy input and the volume flow, the nominal width of the channel is adjusted so that the maximum gas bubble diameter does not exceed 2.5 mm.

- 5 In addition to the bubble size, the stability of the bubbles is also significant. The bubbles should be prevented from coalescing, which would result in inadequate distribution of the hydrogen in the liquid phase.

A particularly preferred embodiment of the process according to the invention is therefore to carry out the hydrogenation in a coalescence-inhibited system. Coalescence-inhibited systems are to be understood as those gas/liquid systems in which the gas bubbles retain their size if no external influence is present. Interface-
10 influencing values of the liquid, such as viscosity and specific surface tension, are responsible for this,
15 together with the nature of the gas.

As described in EP-A-221 931, the working solutions used in the AO process for the production of hydrogen peroxide as
20 the liquid phase fulfil the conditions for a coalescence-inhibited system when the sum quotient of all interfacial surface tensions of the components involved reaches at least 16 mN/m, preferably 17 to 25 mN/m.

In EP-A-221 931, oxygen or an oxygen/nitrogen mixture is
25 described as the gas phase. It can also be shown, by a simple test, that working solutions and hydrogen or a hydrogen-containing gas form a coalescence-inhibited system when the above-mentioned condition for the sum quotient of all interfacial surface tensions of the components involved
30 is fulfilled. Thus, it can be ensured by an appropriate choice of the components of the reaction system and their relative quantities that, when hydrogen and working solution are pre-mixed, a coalescence-inhibited system is formed and enters the hydrogenation reactor as such.

In order to achieve a quantitative hydrogenation as far as possible, the gas portion of the premix of hydrogen and substance to be hydrogenated should be over 30 vol.%, preferably over 40 vol.%. The range is particularly preferably between 60 and 80 vol.%.

The maintenance of a coalescence-inhibited system during the course of the reaction is favoured by hydrogenation reactors that are free from inserts which, according to experience, lead to coalescence of the gas bubbles.

10 Particularly suitable types of reactors, the reaction chamber of which is free from inserts with a gas-splitting function, apart from the distributing device, are in particular stirred vessels, gas-lift reactors, fluidised-bed reactors or loop reactors for hydrogenation by the AO

15 process for the production of hydrogen peroxide.

The process according to the invention is particularly suitable in the above-mentioned process for the catalytic hydrogenation of

20 substituted anthraquinones or mixtures of substituted anthraquinones,

the partially ring-hydrogenated alpha- and beta-tetrahydro derivatives thereof and

mixtures of a) and b)

to the corresponding anthrahydroquinones and tetrahydro-

25 anthrahydroquinones.

In particular, 2-alkyl-substituted anthraquinones, the alkyl residue of which can contain 1 to 8 C atoms and can be linear or branched, are used. Examples of these are 2-ethyl, 2-amyl und 2-tert.-butyl anthraquinone and their

30 tetrahydro derivatives.

Other compounds that can be advantageously hydrogenated by the process according to the invention are olefins, aromatic and heteroaromatic rings, carbonyl compounds and nitriles.

- 5 The substance to be hydrogenated can be introduced as such or in solution. Anthraquinones are preferably dissolved in a mixture of solvents containing a quinone solvent and a hydroquinone solvent.

10 Known quinone solvents are benzene, tert.-butylbenzene, tert.-butyltoluene, trimethylbenzene, polyalkylated benzenes and methylnaphthalene.

15 Known hydroquinone solvents are alkyl phosphates, alkyl phosphonates, nonyl alcohols, alkylcyclohexanol esters, N,N-dialkyl carbonamides, tetraalkyl ureas, N-alkyl-2-pyrrolidones.

The premixing of hydrogen and liquid phase according to the invention is preferably performed in the catalytic hydrogenation of substituted anthraquinones by the AO process in the insert-free type of reactor described. In
20 this process, the substance to be hydrogenated, the hydrogenation product, hydrogen and the catalyst suspended in the reaction mixture are recirculated, part of the hydrogenation product is removed from the reactor and the substance to be hydrogenated and hydrogen are fed into the
25 reaction.

The removed part, which contains the hydrogenated product, is oxidised in a downstream reaction step, wherein hydrogen peroxide is formed, and the substance to be hydrogenated is re-formed. The hydrogen peroxide is then extracted and the
30 substance to be hydrogenated is fed back into the hydrogenation again.

A possible embodiment of a hydrogenation reactor with premixing of the hydrogen is shown in fig. 1.

The three-phase mixture 9, containing a solution with the substance to be hydrogenated and already hydrogenated, hydrogen and the suspended hydrogenation catalyst, is circulated, starting from a pump receiver 4, via the line 4a, by means of a circulating pump 5, through the loop reactor 3. A partial stream of this solution is passed via the line 5a through a filter device 6. This stream is again divided at this point: catalyst-containing solution is fed back via the line 6a to the loop reactor 3, while the catalyst-free product stream 7 is removed from the circulation and made up with fresh catalyst-free solution 9a, containing the substance to be hydrogenated, at the inlet point 8.

In the process according to the invention, the hydrogen 1 is dispersed in the catalyst-free liquid phase 9a in the gas inlet point 2 preferably designed as a venturi nozzle, and only then combined with the catalyst-containing partial streams 4a and 6a.

Operating tests in a full-scale AO plant have shown that the pressure drop of a hydrogenation reactor could be substantially reduced or, at a constant speed of the circulating pump, the total circulating quantity could be increased by approx. 30%. As a result of the increased circulating quantity, a higher catalyst concentration profile was therefore established, so that it was possible to increase the reactor capacity by approx. 15%.

Alternatively, by reducing the speed of the circulating pump, if no increase in capacity is intended, an energy saving of approx. 40% can be calculated.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A continuous catalytic hydrogenation process, comprising recirculating a reaction mixture containing a substance to be hydrogenated, a hydrogenation product, hydrogen and a hydrogenation catalyst suspended in the reaction mixture in a reactor, removing part of the hydrogenation product from the reactor and feeding the substance to be hydrogenated and hydrogen into the reactor, wherein a catalyst-free liquid phase containing the substance to be hydrogenated is mixed with hydrogen before entering the reactor and this mixture is fed into the catalyst-containing reaction mixture.
2. The process according to claim 1, wherein the mixing of the substance to be hydrogenated and hydrogen produces gas bubbles having a diameter of no more than 2.5 mm.
3. The process according to claim 1 or 2, wherein a venturi nozzle, a perforated plate or frit is used as the mixing device.
4. The process according to any one of claims 1 to 3, wherein a system containing the substance to be hydrogenated and hydrogen is coalescence-inhibited.
5. The process according to claim 4, wherein the system is a system having a sum quotient of all specific interfacial surface tensions of the components involved in the system which reaches a value of at least 16 mN/m.

6. The process according to any one of claims 1 to 5, wherein the mixture of hydrogen and the substance to be hydrogenated possesses a gas proportion of 40 vol.% to 80 vol.%.

7. The process according to according to any one of claims 1 to 6, wherein the reactor is free from inserts.

8. The process according to according to any one of claims 1 to 7, wherein a stirred vessel, a gas-lift reactor, a fluidised-bed reactor or a loop reactor are used as the reactor.

9. The process according to any one of claims 1 to 8, wherein the substance to be hydrogenated is:

a) a substituted anthraquinone or a mixture of substituted anthraquinones,

b) a ring-hydrogenated tetrahydro derivative of a substituted anthraquinone or a mixture of substituted anthraquinones, or

c) a mixture of a) and b).

10. The process according to any one of claims 1 to 9, wherein the substance to be hydrogenated is introduced as such or in solution.

11. A process for the production of hydrogen peroxide by an anthraquinone cyclic process, comprising a catalytic hydrogenation of a working solution, an oxidation of hydrogenated working solution with oxygen or an oxygen-containing gas, wherein hydrogen peroxide and substituted anthraquinone or a mixture containing its ring-hydrogenated tetrahydro-anthraquinone is obtained, and an extraction of

the hydrogen peroxide from the mixture obtained after the oxidation, wherein the hydrogenation is performed according to claim 9 or 10.

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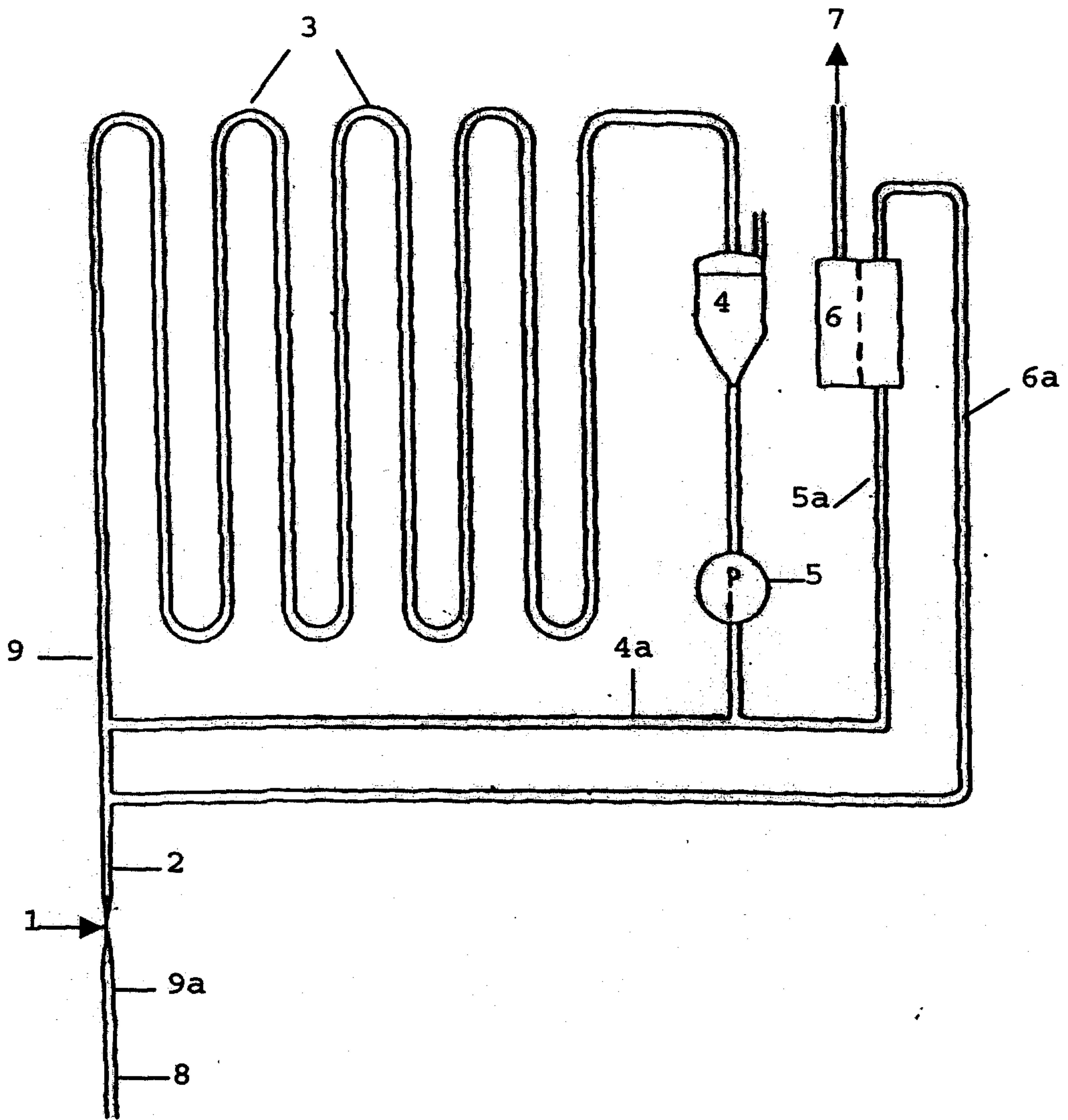


Figure 1

Marks & Clerk

