July 20, 1971 D. SPAHRBIER 3,594,232

DEVICE FOR THE AUTOMATIC ADJUSTMENT OF THE SUPPLY OF LIQUIDS

Filed July 12, 1968 7 Sheets-Sheet 1

Fig. 1.

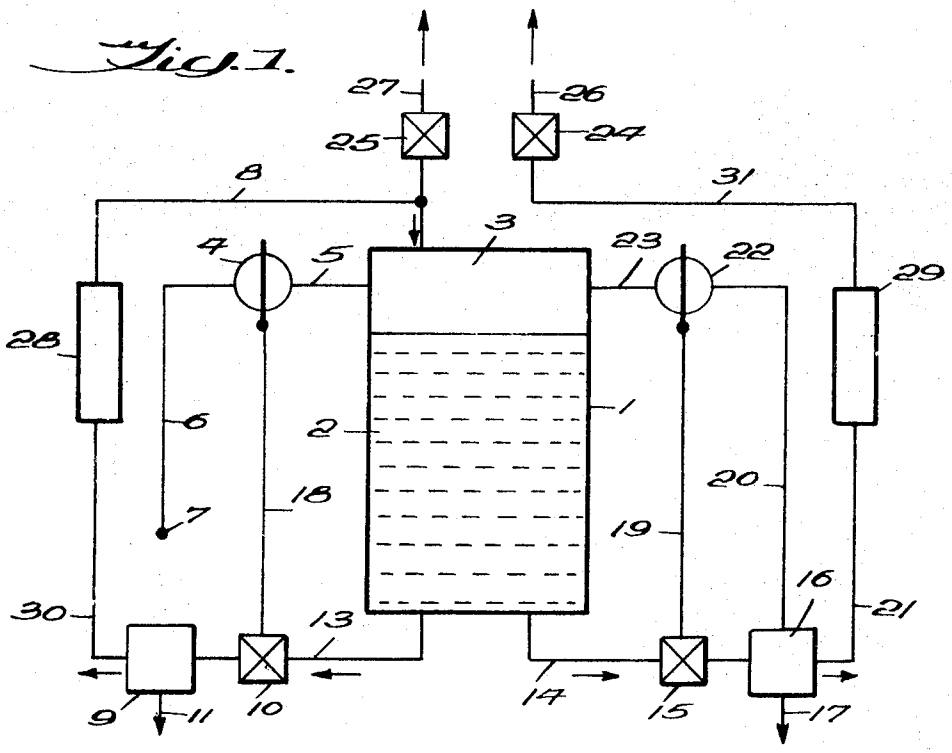
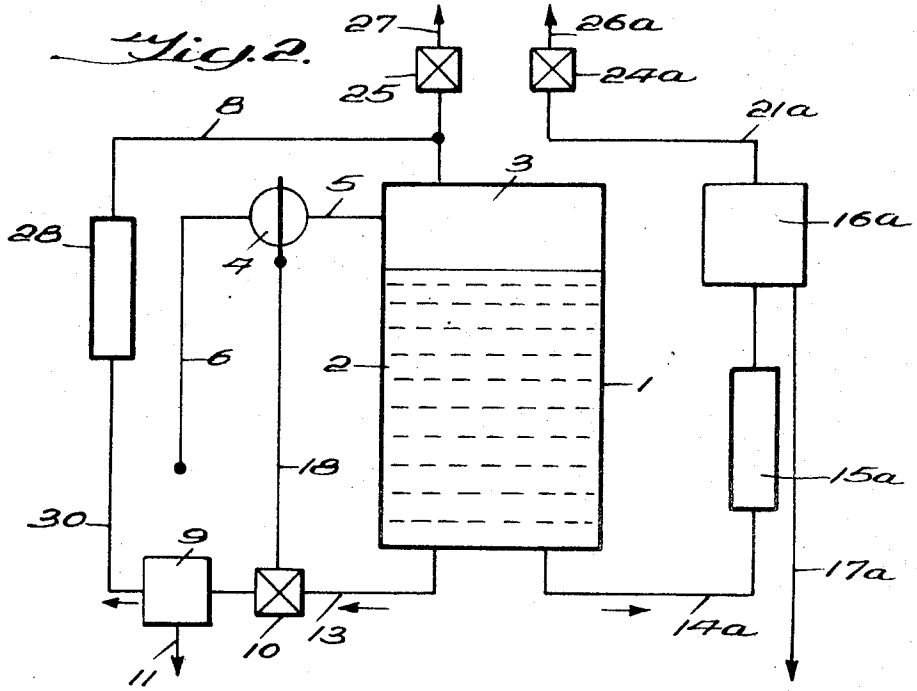


Fig. 2.



INVENTOR

DIETER SPAHRBIER,

BY Stephens, Huettig and O'Connell

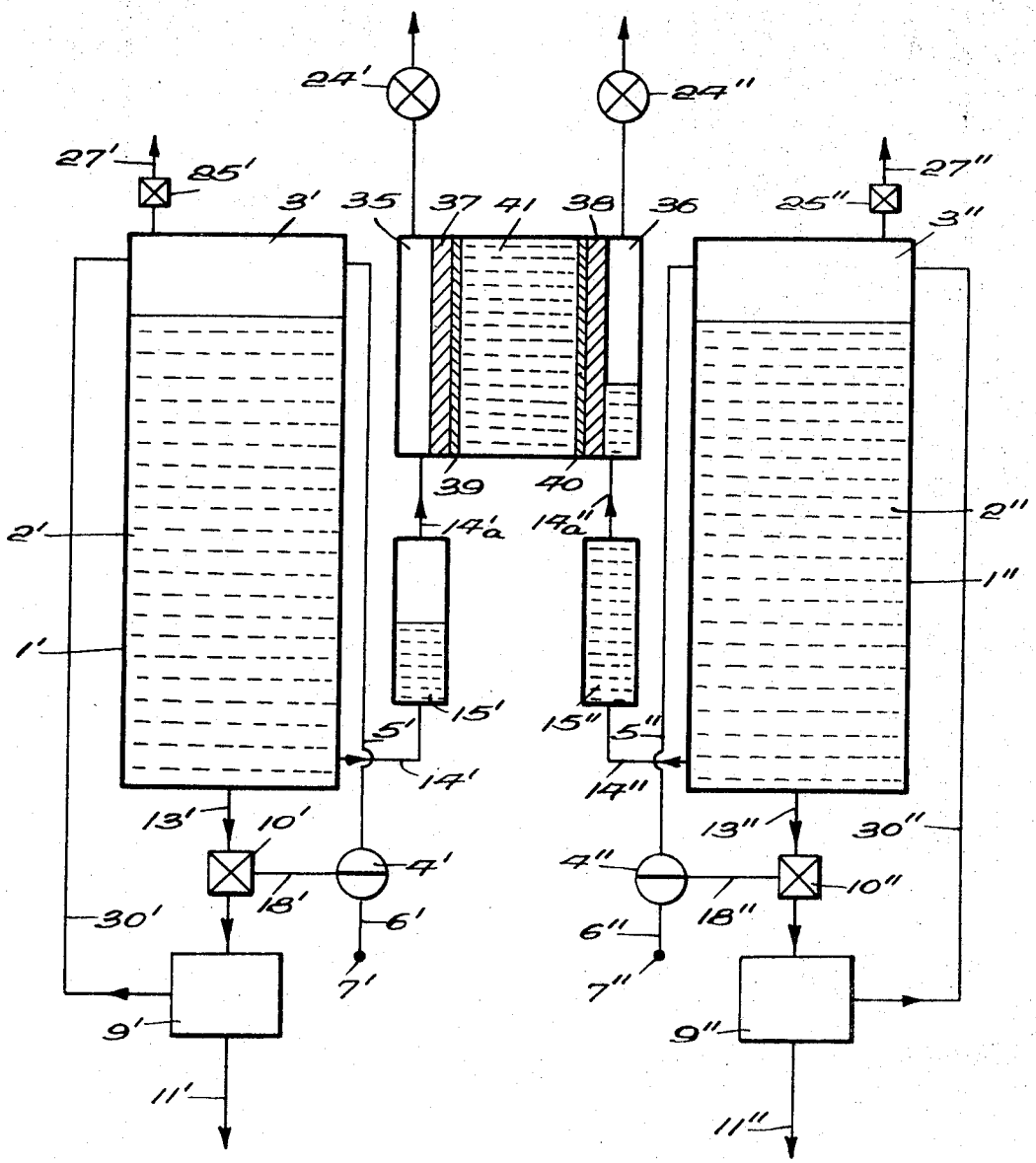
ATTORNEYS

July 20, 1971 D. SPAHRBIER 3,594,232

DEVICE FOR THE AUTOMATIC ADJUSTMENT OF THE SUPPLY OF LIQUIDS

Filed July 12, 1968 7 Sheets-Sheet 2

Fig. 3.



INVENTOR
DIETER SPAHRBIER,

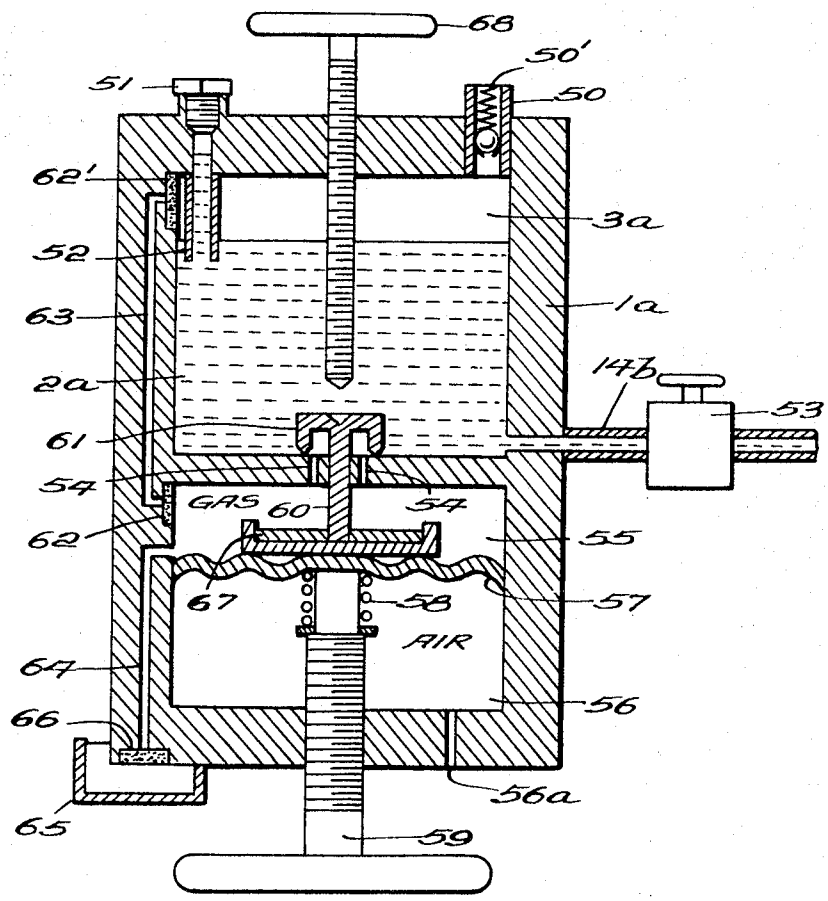
BY Stephens, Huelleg and McConnell
ATTORNEYS

July 20, 1971 D. SPAHRBIER 3,594,232

DEVICE FOR THE AUTOMATIC ADJUSTMENT OF THE SUPPLY OF LIQUIDS

Filed July 12, 1968 7 Sheets-Sheet 3

Fig. 4.



INVENTOR
DIETER SPAHRBIER,

BY Stephens, Huellig and O'Connell.

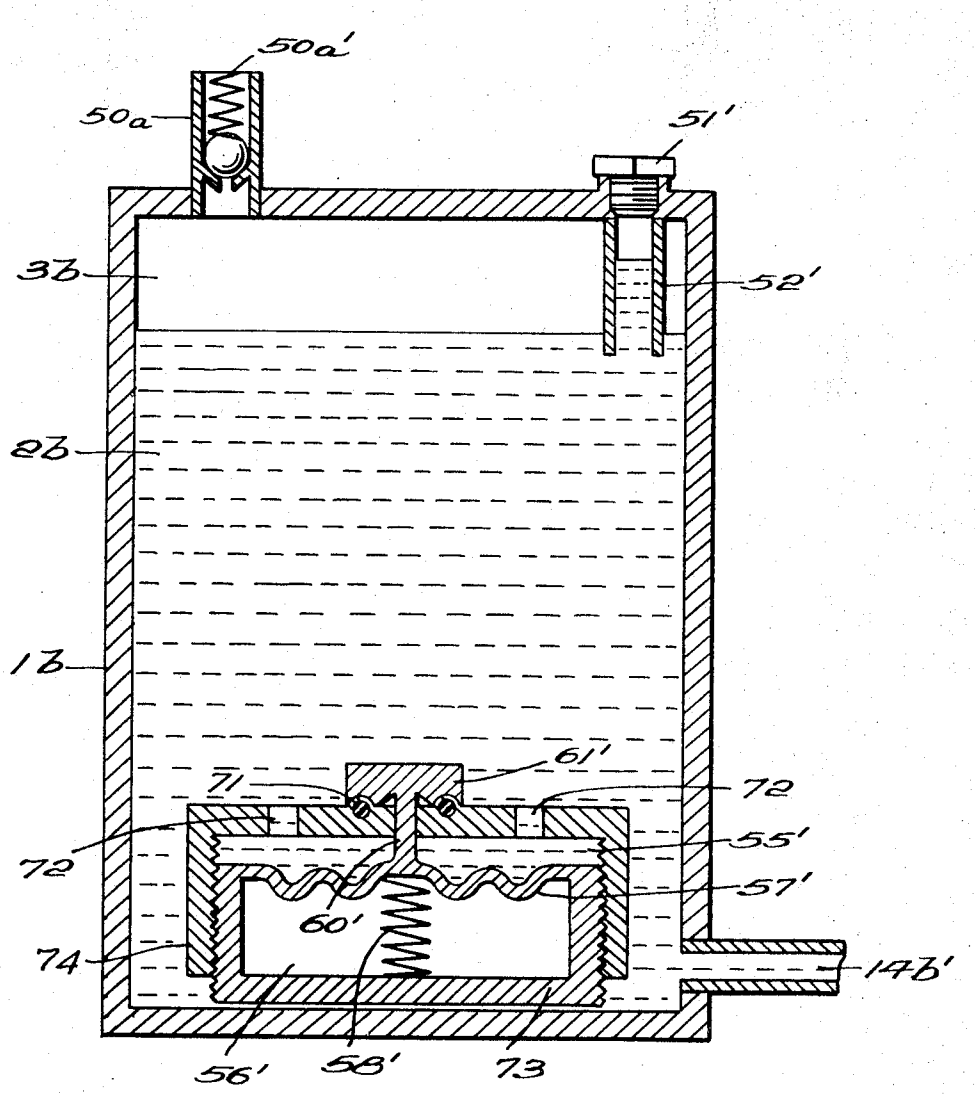
ATTORNEYS

July 20, 1971 D. SPAHRBIER 3,594,232

DEVICE FOR THE AUTOMATIC ADJUSTMENT OF THE SUPPLY OF LIQUIDS

Filed July 12, 1968 7 Sheets-Sheet 4

Fig. 5.



INVENTOR
DIETER SPAHRBIER,

BY Stephens, Hueltig and O'Connell

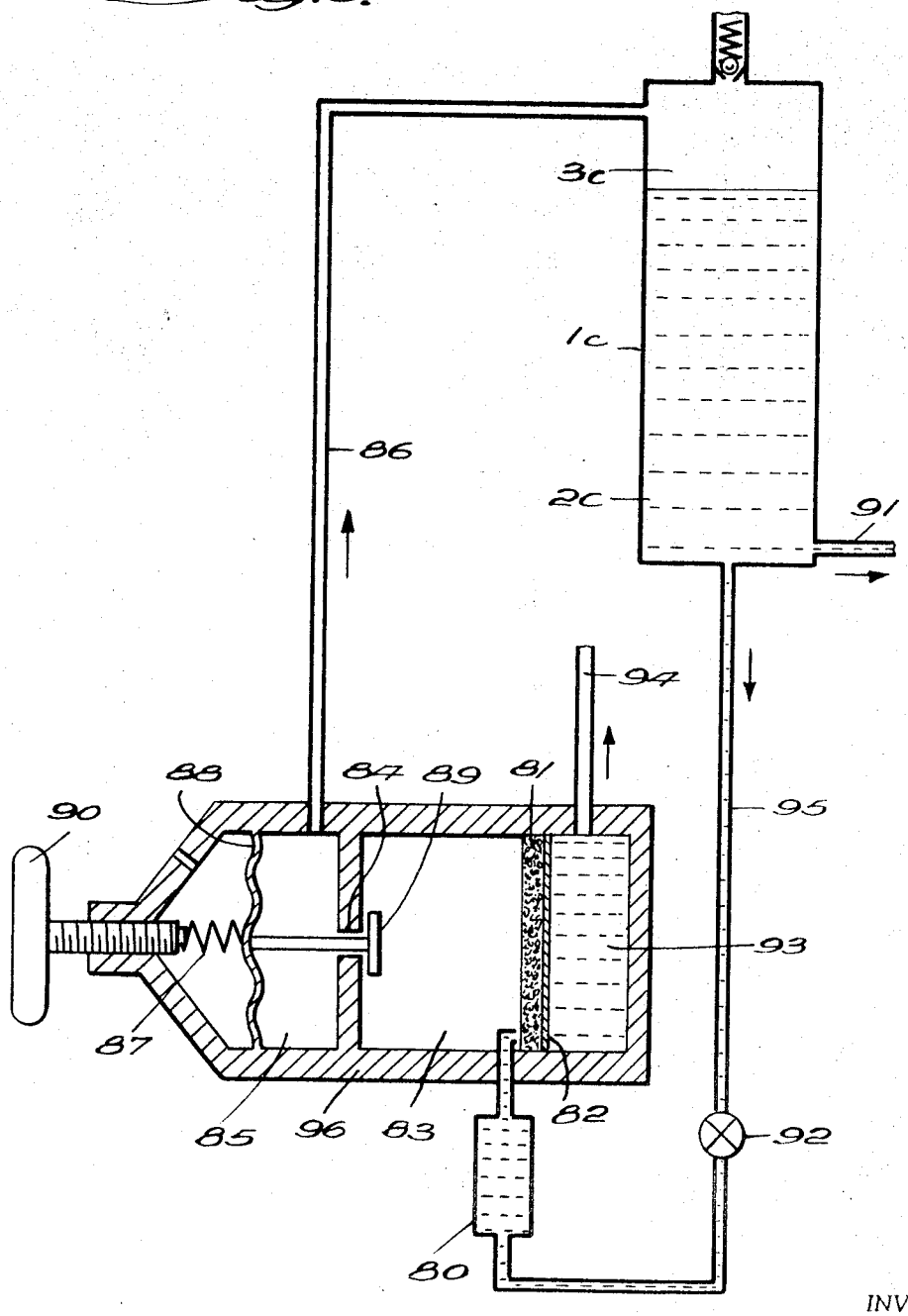
ATTORNEYS

July 20, 1971 D. SPAHRBIER 3,594,232

DEVICE FOR THE AUTOMATIC ADJUSTMENT OF THE SUPPLY OF LIQUIDS

Filed July 12, 1968 7 Sheets-Sheet 5

Fig. 6.



INVENTOR
DIETER SPAHRBIER,

BY Stephens, Huellig and O'Connell

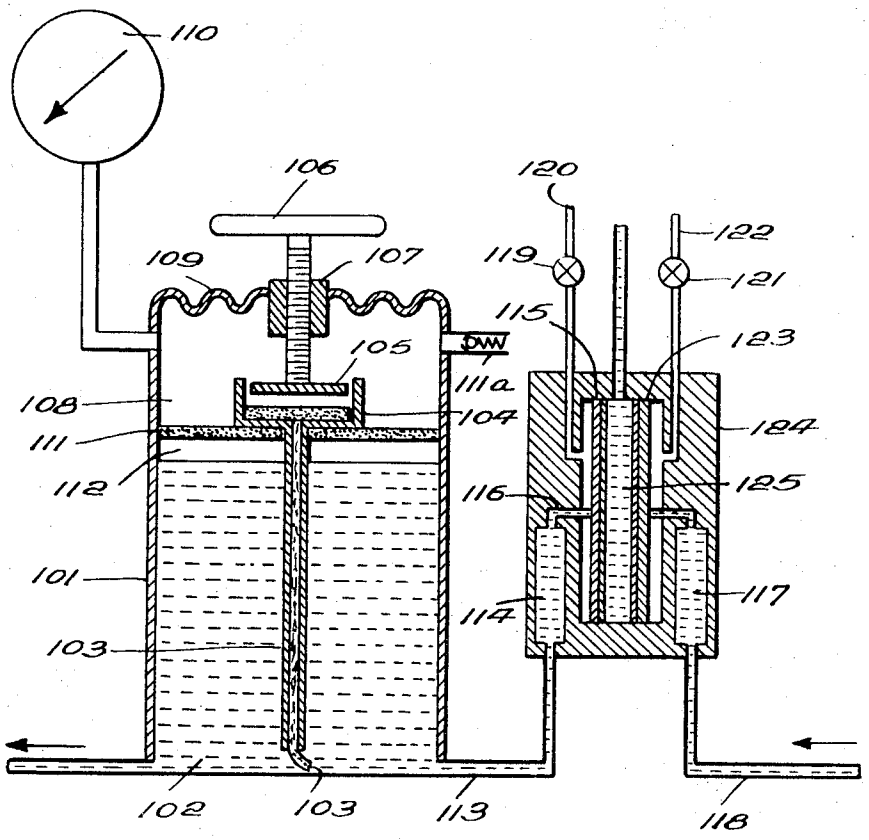
ATTORNEYS

July 20, 1971 D. SPAHRBIER 3,594,232

DEVICE FOR THE AUTOMATIC ADJUSTMENT OF THE SUPPLY OF LIQUIDS

Filed July 12, 1968 7 Sheets-Sheet 6

Fig. 7.



INVENTOR
DIETER SPAHRBIER,

BY Stephens, Huettig and O'Connell

ATTORNEYS

July 20, 1971 D. SPAHRBIER 3,594,232

DEVICE FOR THE AUTOMATIC ADJUSTMENT OF THE SUPPLY OF LIQUIDS

Filed July 12, 1968 7 Sheets-Sheet 7

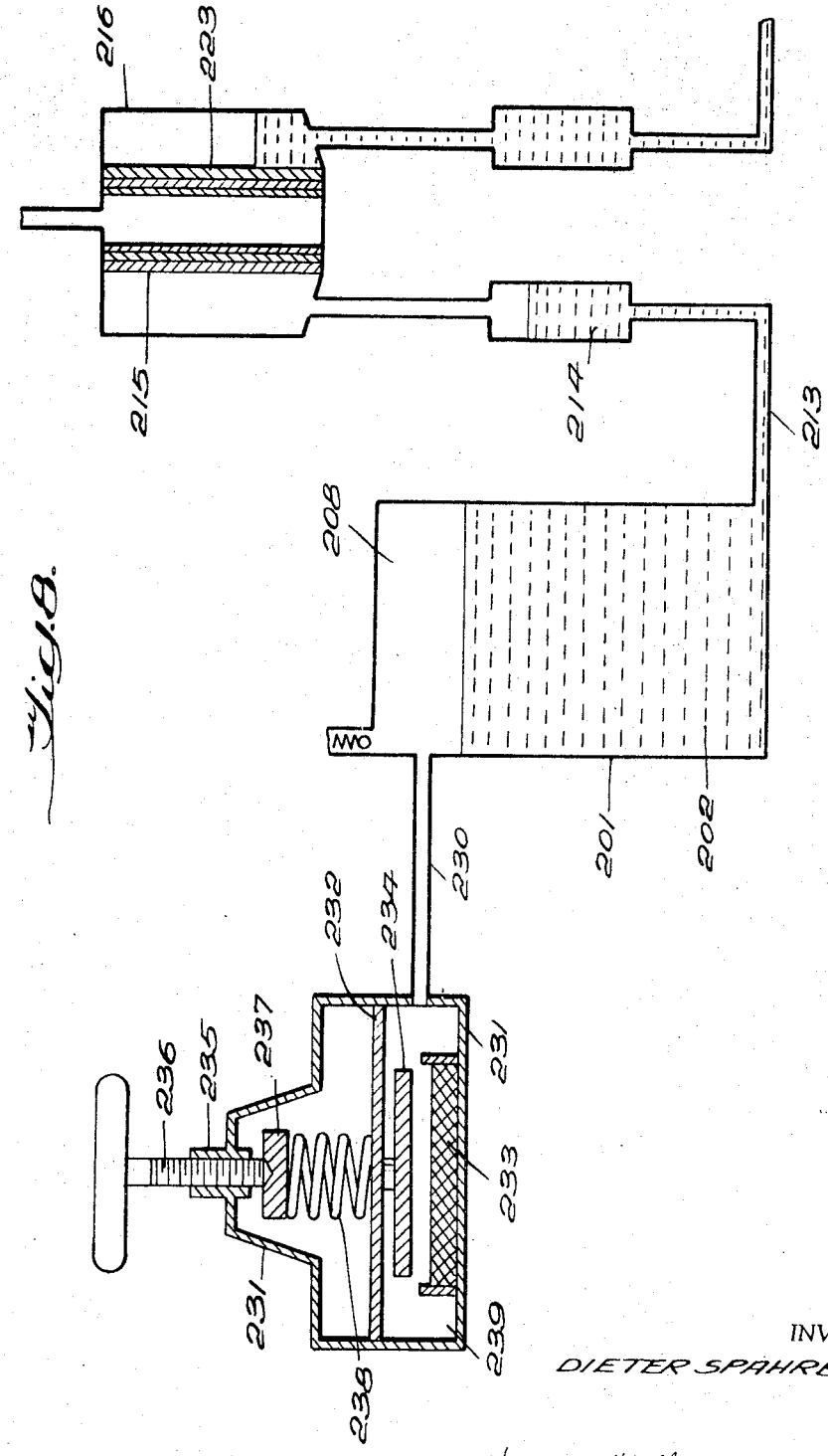


Fig. 8.

INVENTOR
DIETER SPAHRBIER,

BY Stephens, Huettig and O'Connell

ATTORNEYS

United States Patent Office 3,594,232 Patented July 20, 1971

3,594,232

DEVICE FOR THE AUTOMATIC ADJUSTMENT OF THE SUPPLY OF LIQUIDS

Dieter Spahrbier, Frankfurt am Main, Germany, assignor to Varta Aktiengesellschaft, Frankfurt am Main, Germany

Filed July 12, 1968, Ser. No. 744,357
Claims priority, application Germany, July 19, 1967, V 34,103; Mar. 13, 1968, P 16 67 346.4
Int. Cl. B01j 7/02; F04f 1/14; H01m 27/14
U.S. Cl. 136—86C 18 Claims

ABSTRACT OF THE DISCLOSURE

The supply of liquid, which may be catalytically decomposed with the evolution of gas, to a main decomposing catalyst body, is regulated by the pressure of gas generated from such liquid on an auxiliary catalyst body. The main catalyst body may be in a gas diffusion electrode.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The invention relates to the field of supplying catalytically decomposable liquids or dissolved materials to a catalyst on which such liquids or materials may be decomposed with the attendant formation of gas. The catalyst may be located in a gas diffusion electrode of a fuel cell element.

(2) Description of the prior art

German Pat. 1,180,438 discloses that one can operate hydrogen diffusion electrodes in fuel cell elements by supplying the electrode with liquid electrolyte which contains sodium borohydride. The sodium borohydride is decomposed at the catalyst material of the hydrogen diffusion electrode with evolution of hydrogen.

British Pat. 963,254 discloses a fuel cell element in which a solution of hydrogen peroxide is forced through the porous oxygen electrode and the excess liquid electrolyte is removed from the space between the two electrodes.

It is possible, by using appropriate conveyors and suitable control systems to supply liquid electrolyte or a liquid which contains hydrogen or oxygen yielding substances to diffusion electrodes in amounts corresponding to the amount of electrical power withdrawn from the fuel cell element. Pumps may be used for this purpose but the electrical power used by the pumps decreases the electrical power output of the fuel cell system. The use of pumps also increases the possibility of failure of the installation. One can also supply liquids to the electrodes by gas pressure instead of other conveyor means.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process and suitable devices for the automatic adjustment of the flow of liquids or dissolved substances, which may be decomposed on a catalyst with the evolution of gas, from a storage container for such liquid to a decomposer which contains catalyst which may be used for the decomposition of such liquids or substances with the evolution of gas.

Another object of the present invention is to provide such a process and devices whereby liquids which are decomposable upon contact with catalysts with the attendant evolution of gas may be supplied to the catalyst bed of a decomposer under constant pressure without using a pump.

A further object of the present invention is to provide

such a process and devices which are adaptable for supplying such catalytically decomposable liquids to catalytically active layers of gas diffusion electrodes in fuel cell elements in the simplest manner possible.

The essence of the present invention resides in employing an auxiliary catalyst body on which a relatively small portion of liquid may be decomposed so as to thereby provide a pressurized supply of gas with a predetermined pressure which may be used, in turn, to regulate the main supply of decomposable liquid to the main liquid decomposing catalyst body.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an embodiment of the devices of the present invention wherein an auxiliary decomposer is employed.

FIG. 2 shows a modification of the device of FIG. 1.

FIGS. 3, 7 and 8 show embodiments of the devices of the present invention which are adapted for use with the gas diffusion electrodes of fuel cell elements.

FIGS. 4, 5 and 6 show embodiments of the devices of the present invention in which the auxiliary decomposer is either directly connected to, or located inside of, or arranged outside of, the storage container for the decomposable liquid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The problems facing the present inventor were solved by means of the devices and process of the present invention which may be employed for the automatic adjustment of the supply of liquids or dissolved substances, which may be decomposed on a catalyst with the evolution of gas, from a storage container for such liquids or substances to a decomposer container catalyst material under a predetermined feed pressure. The characteristic feature of the devices of the present invention is that the storage container is in liquid supply communication with an auxiliary decomposer which contains catalyst material by way of a valve for liquids, and the operation of the valve is controlled by the gas pressure above the level of the liquid in the storage container. The valve for the liquids is adjusted in such a way that the supply of liquid to the catalyst bed of the auxiliary decomposer is released if the gas pressure above the level of the liquid in the storage container falls below a certain predetermined value.

In an advantageous embodiment of the devices of the present invention the auxiliary decomposer is arranged immediately inside the liquid storage container above the level of the liquid therein. The liquid supply communication between the liquid and the catalyst bed of the auxiliary decomposer is formed by a wick. The valve for the liquid is a device for severing the liquid supply communication between the wick and the catalyst bed. The valve can take the form, for example, of a membrane subjected to tension by the pressure of a spring, to which membrane the catalyst bed is attached. When the gas pressure above the level of the liquid decreases, which pressure acts upon the membrane, the tension of the spring prevails and moves the catalyst bed against the wick. The liquid absorbed by the wick is decomposed as it contacts the catalyst bed. When the gas pressure above the level of the liquid again reaches a predetermined value due to the pressure of the gas which is liberated by the catalytic decomposition, then the gas pressure is stronger than the tension of the spring and the membrane is deflected and the liquid supply communication between the catalyst bed and the wick is thereby broken.

In another advantageous embodiment of the devices of the present invention it is not necessary to fixedly arrange the auxiliary decomposer inside the liquid storage

container above the level of the liquid. In this arrangement the auxiliary decomposer is arranged in the liquid inside the storage container and the valve for the liquid is rigidly connected to a movable shutter cover over the catalyst bed of the auxiliary decomposer. The valve for the liquid can also contain in this instance a pressure bellows having a membrane tensioned by the pressure of a spring.

It is particularly advantageous in the devices of the present invention to also connect the storage container to the catalyst bed of the main decomposer by means of a pressure controlled valve for the liquid. It is thereby provided by this procedure that an approximately constant gas pressure is continuously afforded to the gas consumer. The pressure control of the valve for the liquid can be accomplished, for example, by measuring the pressure differential between the gas pressure in the gas consumer and the gas pressure above the level of the liquid and by allowing for the opening of the valve for the liquid when this pressure differential attains a certain predetermined value. In a preferable embodiment of the devices of the present invention the storage container for the liquid is placed in liquid supply communication by means of a valve for the liquid with the catalyst material containing working layer of one of the two gas diffusion electrodes of a fuel cell element, which electrode is the main gas decomposer. The valve for the liquid is operated by a predetermined pressure differential between the gas pressure above the level of the liquid in the liquid storage container and the gas pressure in the gas chamber of the gas diffusion electrodes. As a result of the supply of liquid to the catalyst bed of the main gas decomposer the volume of liquid in the liquid storage container is lowered and the volume of the gas space above the level of the liquid in the storage container is increased. The gas pressure in this gas space is lowered, therefore, correspondingly to the volume of liquid supplied to the catalyst bed of the main decomposer. The auxiliary decomposer must produce a corresponding amount of gas in order to maintain the gas pressure above the level of the liquid in the storage container at a constant value. In general the increase of the volume with the decomposition of the liquid and the generation of gas in the main decomposer results in a volume amplification factor of the order of magnitude of 100, so that a simple construction and operation of the control system formed by the devices of the present invention is thus made possible.

Particularly advantageous is a preferred embodiment of the devices of the present invention wherein the auxiliary decomposer is arranged outside the liquid storage container. The storage container is placed in liquid supply communication with one surface of the catalytically active layer of the porous catalyst body of the auxiliary decomposer by means of a rising main or pressure pipe. The other surface of the porous catalyst body is in intimate contact with a fine pored layer which is filled with liquid. To the catalyst body there is attached a gas chamber which is in liquid supply communication with the gas space above the level of the liquid of the storage container via a valve controlled by gas pressure. This embodiment of the devices of the present invention makes possible a particularly reliable and effective regulation of the supply of liquid to the main decomposer.

Various embodiments of the devices of the present invention may be further explained by references to the drawings. The manner of operating one embodiment of the devices of the present invention may be explained by the following, with reference to FIG. 1. In storage container **1** there is placed liquid **2** which is catalytically decomposable with the attendant formation of gas. Gas chamber or area **3** above the level of liquid **3** is connected with a pressure difference sensing regulator **4** via line **5**, which sensing regulator, together with control line **18**, effects the control of liquid valve **10**. The atmospheric pressure also acts on pressure difference regulator **4** over line **6**. When the difference between the gas pressure in gas space **3** and the atmospheric pressure at point **7** is less than the pressure to which the pressure difference regulator **4** is adjusted then liquid valve **10** is closed by means of control line **18**.

If the level of liquid **2** in storage container **1** falls because of the supplying of liquid to the main decomposer **16**, then the pressure difference to which the pressure difference sensing regulator **4** is adjusted becomes greater than the difference in pressure between the pressure in gas space **3** and the atmospheric pressure at point **7** and liquid valve **10** is opened by control line **18**. The liquid **2** flows over connecting line **13** into auxiliary decomposer **9** and is decomposed on the catalyst bed in such decomposer. The gas that is thus set free flows over line **30** and **8**, and through buffer volume **28** inserted between such lines, into gas space **3** and valve **10** is closed when the pressure differential between the pressure in gas space **3** and the atmospheric pressure at point **7** reaches the pressure to which pressure sensing regulator **4** is adjusted. Buffer volume **28** inserted in lines **8** and **30** allows for the delay of the decomposition of the liquid in auxiliary decomposer **9**. It has the function in this regard of a surge tank as is customarily employed in discontinuously operating gas pumps (piston pumps). Buffer volume **28** is not needed, however, if the volume of gas area **3** is sufficiently large.

Storage container **1** and main decomposer **16** are also part of a second control system, which supplies operating gas over line **26** to the gas consumer. In this second control system a pressure difference regulator **22** also controls the supply of liquid from storage container **1** over line **14** to main gas decomposer **16** by means of valve **15**. The gas pressures in gas space **3** and in main gas decomposer **16** act on pressure difference regulator **22** over lines **23** and **20**, respectively. Valve **15** is opened by control line **19** as soon as the pressure difference exceeds the pressure to which pressure difference regulator is adjusted. This is the case when valve **24** is opened and the gas which is set free in main decomposer **16** is supplied to the gas user over lines **21** and **31** and buffer volume **29**. When valve **24** is closed, the pressure in main decomposer **16** rises. The pressure differential then becomes greater than the pressure at which pressure difference regulator **22** is standardized and valve **15** is closed. If the decomposition of liquid in main decomposer **16** is not spontaneous, but takes place with a certain delay, then fluctuations in pressure arise which are intercepted by buffer volume **29** and are smoothed out. The fluctuations in pressure are very small if the pressure in main decomposer **16** is made large in comparison to the pressure at which pressure difference regulator **22** is standardized. The constructive configuration of the devices of the present invention is dependent upon the type and concentration of the catalytically decomposable substances employed in the liquids which are supplied to the catalysts in the decomposers. For a trouble free functioning of the devices of the present invention the following conditions, therefore, must be fulfilled:

(1) The auxiliary decomposer must be able to produce a larger volume of gas per unit of time, than that corresponding to the maximum volume of liquid that is supplied to the main decomposer in the same period of time.

(2) The maximum volume of gas, which can be produced in a given unit of time in the main decomposer, must be greater than the volume of liquid supplid in the same unit of time to the main decomposer multiplied by the gas amplification factor. This factor specifies how large the volume of gas is which comes into being upon the decomposition of a specific volume of liquid.

Lines **11** and **17** in the device of FIG. 1 serve as outlet lines for residual liquid.

FIG. 2 shows a particularly advantageous embodiment of the devices of the present invention which is a modifica-

tion of the device shown in FIG. 1. Elements **1–11, 13, 25, 27** and **30** are the same in FIG. 2, and perform in the same manner, as the correspondingly numbered elements of FIG. 1. The control system which contains main decomposer **16***a* of the device of FIG. 2 has a particularly simple construction. A rising main **15***a* which is inserted in line **14***a* forms the valve for the liquid. In addition, rising main **15***a* also assumes the function of buffer volume **29** and pressure difference regulator **22** of FIG. 1. Elements **17***a*, **21***a*, **24***a* and **26***a* are the same, and function in the same manner, as elements **17, 21, 24** and **26**, respectively, of FIG. 1.

FIG. 3 shows an example of an embodiment of the devices of the present invention which contains two main liquid decomposers which are each catalyst layers of gas diffusion electrodes of a fuel cell element. Elements **1'** to **7', 9'** to **11', 13', 18', 25', 27'** and **30'**, as well as elements **1''** to **7'', 9''** to **11'', 13'', 18'', 25'', 27''** and **30''** of FIG. 3, correspond to elements **1** to **7, 9** to **11, 12, 18, 25, 27** and **30**, respectively, of FIG. 1. Storage containers **1'** and **1''** are in liquid supply communication with rising mains **15'** and **15''** over lines **14'** and **14''** which rising mains simultaneously assume the function in the main control system of the pressure difference regulator and the valve for the liquid. The rising mains **15'** and **15''** are connected over liquid supply line **14***a'* and **14***a''* to gas chambers **35** and **36** of gas diffusion electrodes. Working layer **37** of the porous hydrogen diffusion electrode contains carbonyl nickel and, as a catalyst, Raney-nickel and the fine pored cover layer **39** of the electrode consists of carbonyl nickel. In container **1'** there is a 16% by weight solution **2'** of sodium borohydride in 6 N KOH, which solution decomposes on working layer **37** with the evolution of hydrogen gas. At room temperature around 0.5 normal liters of hydrogen gas are produced per hour per cm.^{2} of electrode surface and at 60° C. about 1 normal liter of gas is produced. The hydrogen gas is electrochemically reacted in the electrode and residual liquid electrolyte is forced through the pores of working layer **37** and cover layer **39** out into electrolyte chamber **41** which is filled with a 6 *n* aqueous solution of sodium hydroxide by the gas pressure in gas chamber **35**. Rising main **15'** simultaneously acts as a pressure difference regulator and as a valve for the liquid from container **2'**. If the gas pressure in gas chamber **35** is higher than the gas pressure in gas area **3'** and the hydrostatic pressure of the column of liquid lying between gas chambers **35** and **3'**, then the liquid is forced out of gas chamber **35** into rising main **15'** and rising main **15'** becomes partially filled with gas. In this way the supply of liquid **2'** to gas chamber **35** and working layer **37** is prevented when the predetermined pressure differential is exceeded and rising main **15'** acts as a pressure difference regulator and as a liquid valve. If, because of the consumption of gas in the electrode, the gas pressure in gas chamber **35** decreases, then, because of the gas pressure in gas area **3'**, liquid is supplied through rising main **15'** to working layer **37** of the electrode.

The oxygen for the oxygen electrode of the fuel cell element which contains silver as a catalyst in working layer **38** and whose fine pored cover layer **40** is made of carbonyl nickel is produced in a manner similar to that described above for the generation of hydrogen gas by the decomposition of liquid **2''** which is supplied by a device in accordance with the present invention from storage container **1''** over rising main **15''** and into the gas chamber **36** of the oxygen electrode. The liquid **2''** in storage container **1''** is in the form of a 30% by weight solution of hydrogen peroxide in water. Valves **24'** and **24''** allow for the venting of excess gas.

FIG. 4 shows a storage container **1***a* in a device of the present invention to which there are directly connected a combined pressure difference regulator, a liquid valve and an auxiliary decomposer. In storage container **1***a* there is located gas chamber or area **3***a* above the level of liquid **2***a* and gas chamber **3***a* is closed by an orifice **50** having an excess pressure valve **50^1** therein. Liquid **2***a* is charged into container **1***a* through tube **52** after twisting out filling screw **51**. Valve **53** is arranged in line **14***b* which leads to the main decomposer. At the base of storage container **1***a*, the device is sealed by connecting tubes **54** which simultaneously act as pressure difference regulator, liquid valve and auxiliary decomposer. Chamber **55** is filled with gas and chamber **56** beneath membrane **57** is filled with air under atmospheric pressure by reason of air vent **56***a*. Compression spring **58** can be regulated by means of thumbscrew **59**, and it is used to provide membrane **57** with the desired tension, when membrane **55** is displaced, valve cap **61** is actuated by connecting rod **60**, which cap in its closed position prevents the passage of liquid **2***a* from storage container **1***a* into chamber **55**. Chamber **55** is subjected to the gas pressure existing in chamber **3***a*, which latter chamber is in gas supply communication with chamber **55** through porous hydrophobic plates **62** and **62^1** and gas line **63**. Hydrophobic plates **62** and **62^1** prevent the passage of liquid through line **63** due to the capillary depression of these plates. A discharge line **64** is provided for undecomposed liquid from chamber **55**, and line **64** opens at its lower end into drain vessel **65**. At the mouth of the lower end of line **64** there is a porous hydrophilic plate **66** inserted and the capillary pressure in the pores of porous plate **66** is so high that the passage of gas formed in chamber **55** through such plate is prevented. Normally, the connection between chamber **55** and storage container **1***a* is interrupted by valve cap **61**. When the gas pressure in chamber **3***a* falls and, as a result, also the gas pressure in chamber **55**, the pressure of spring **58** on membrane **55** preponderates. The membrane is then deflected upwards and valve cap **61** is lifted off connecting tube **54** and fresh gas carrier fluid, laden with dissolved decomposable gas yielding substances, passes from storage container **1***a* through tubes **54** and onto catalyst bed **67**. Gas is generated by the decomposition of the liquid on bed **67**. The gas thus generated can then proceed into gas chamber **3***a* through hydrophobic plates **62** and **62^1** and gas supply line **63**. The increased gas pressure in chamber **55** causes membrane **57** to be forced down into its original position and connecting tubes **54** are sealed again as rod **60** pulls down cap **61**.

Thumbscrew **68** serves the purpose, during the filling of liquid into storage container **1** through filling tube **52**, of blocking valve cap **61** so that cap **61** is not raised by tensed spring **58** and thus allow liquid to enter catalyst bed **67** during the filling of the liquid into container **1***a*. The generation of gas on bed **67** during the filling operation would disturb such operation. Screw **68** is used to limit the extent to which valve cap **61** may be raised.

FIG. 5 shows an embodiment of the pressure difference regulator, liquid valve and auxiliary decomposer of the devices of the present invention in which the function of these three elements is undertaken by a single device. This device can be directly inserted in the liquid **2***b* in storage container **1***b*. In this way, it is to be observed, the device is so arranged that the liquid has access to catalyst bed **71** when valve cap **61^1** is raised. The device consists of a pressure bellows **73**, which has a membrane **57^1** on one of its surfaces, and a lid **74** which, together with membrane **57^1**, encloses chamber **55^1** which is filled with electrolyte. By means of tubes **72** chamber **55^1** is placed in continuous liquid supply communication with the volume of liquid **2***b* and thus chamber **55^1** is under the same pressure as is the volume of liquid in container **1***b*. Chamber **56^1** which is inside pressure bellows **73** is filled with air or another gas or with another good compressible substance and it also contains compression spring **58^1** which so acts that membrane **57^1** continuously maintains a desired tension. If desired, a known regulating device can also be attached to compression spring **58^1** in order to change the tension of compression spring **58^1**. Connecting rod **60^1** is affixed to membrane **57^1** and this rod moves valve cap **61** off and onto catalyst bed **71**. When the gas

pressure in gas chamber 3*b* decreases then the corresponding pressure in chamber 55^1 decreases and membrane 57^1 is so deflected by the tension of compression spring 58^1 that valve cap **61** is raised off catalyst bed **71** and fresh liquid 2*b* flows onto the catalyst. The gas thus formed by the catalytic decomposition of the liquid on bed **71** flows from the open space beneath cap 61^1 and collects in gas chamber 3*b*. The pressure in gas chamber 3*b* thereby continues to increase until the pressure of the liquid on membrane 57^1 in chamber 55^1 neutralizes the tension of spring 58^1 and the total pressure in pressure bellows 56^1. Elements 14^1b, 50*a*, $50a^1$, 51^1 and 52^1 are the same, and serve the function, as elements 14*b*, **50**, 50^1, **51** and **52**, respectively, of FIG. 4.

FIG. 6 shows an embodiment of the device of the present invention in which the auxiliary decomposer is arranged outside of storage container 1*c*. Liquid 2*c* is supplied over liquid supply line **95** and through rising main **80** into auxiliary decomposer **96**. The catalyst bed of the auxiliary decomposer consists of a porous catalyst containing body **81**. Adjacent to this body **81** there is a fine pored layer **82** filled with liquid. Liquid 2*c* is decomposed upon coming in contact with the catalyst in porous body **81** and the gas which is thus generated collects in gas chamber **83** and from there it passes into gas chamber 3*c* above the level of liquid 2*c* in container 1*c* by way of connecting gas line **84**, valve chamber **85** and gas line **86**. Gas is generated by the decomposition of liquid 2*c* on the catalyst of body **81** up to the point where the spring pressure of spring **87** is overcome by the pressure of the gas being exerted on membrane **88** and then the valve opening between chambers **83** and **85** is closed by valve plate **89**. The gas pressure in chamber 3*c* then ceases to rise any further. With the further decomposition of liquid on bed **81**, the gas that is formed, therefore, only then raises the pressure in chamber **83** and under the effect of this rising gas pressure in chamber **83** the liquid is forced back into rising main **80** and the supply of liquid 2*c* to porous body **81** is interrupted until the pressure in chamber 3*c* subsides again and thus alows valve **89** to open again. By means of thumb screw **90** the pressure of spring **87** can be regulated. In this way the gas pressure in chamber **83** and in chamber 3*c* can be regulated. If a main decomposer is supplied with liquid 2*c* over liquid supply line **91** then the standardized and regulated gas pressure in chamber 3*c* which is used for operating the auxiliary decomposer remains constant in spite of the outflow of a volume of liquid for this purpose. In order to assure a trouble-free operation of auxiliary decomposer **96** it is expedient to insert a device **92** with a suitable resistance to the flow of liquid in connecting line **95**. With the selection of a properly dimensioned current resistance **92** it is possible to supply only as much liquid 2*c* to layer **81** as can be optimally decomposed on the catalyst layer in a given unit of time. The undecomposable residual liquid passes through porous layer **82** into chamber **93** and from there it passes out through drain line **94**. Porous layer **83** can be formed as a fine pored diaphragm completely filling chamber **93**. The diaphragm then has a smaller average pore diameter than the pores of porous body **81** and liquid 2*c* is, in this way, retained in layer **82**.

The capillary pressure of the liquid in layer **82** prevents the passage of gas from chamber **83** into chamber **93**. Fine pored layer **82** can also be fixedly combined with porous body **81** by sintering or by other ways. It is also possible to fill chamber **92** completely with a porous layer **82**.

The device of the present invention have a series of advantages. These devices, in particular, do not have any movable parts such as supply pumps and the power units that are used with such pumps. In this way the life and reliability of the devices are considerably increased.

The supply of liquid to the catalyst bed of the main decomposer takes place automatically without the need for any outside source of energy in this regard. The supply pressure thus remains constant.

The regulating process can be initiated with a pressure difference of a few millimeters of a water column between the desired and the existing supply pressure.

In comparison to installations in which supply pumps are used the flow resistance for the liquid gas carrier is small in the control system. Therefore one has a high speed control together with a good constant holding of the supply pressure. The supply pressure can be easily adjusted.

The devices of the present invention can be used for different fields for use. For example, they can be used for the generation of operating gases such as hydrogen and oxygen for fuel cell batteries. Also they can be used for the production of the purest hydrogen and oxygen gases for different purposes or for the production of the gases, hydrogen and nitrogen, that may be split from hydrazine. These devices can also be used for the production of oxygen gas for breathing devices. In these instances it is of particular advantage that the liquids which have to be transported for a certain amount of gas represent significantly less weight than has been the case with the devices employed up to this time since such latter devices employ steel flasks of considerable weight which are filled with pressurized gas.

The devices of the present invention, and the process in which they are employed are particularly suited for use in regulating the supply of decomposable liquid to the catalytically active layers of gas diffusion electrodes in fuel cell elements and batteries. A particularly advantageous embodiment of a fuel cell element or fuel cell battery with which the process of the present invention may be employed is characterized in that the storage container for the decomposable liquid is in liquid supply communication over a liquid supply line or liquid supply line system with the surface of the catalytically active layer of the corresponding electrode and the storage container is in gas supply communication with a gas chamber. In such gas chamber there is located a movable catalyst body which contains a catalyst which is adapted for decomposing the liquid and liberating gas therefrom for use in the electrodes. The catalyst body is connected to a movable membrane which is moved by the gas pressure existing over the liquid in the storage container, and a wick or absorbent body is positioned in the direction of movement of the movable catalyst body, which wick body is filled with the decomposable liquid. A device of the present invention of this type is shown in FIG. 7, together with a fuel cell element. In storage container **101** there is located liquid reactant **102**, for example, a 7% by weight solution of hydrogen peroxide in water. Into this liquid **102** there is dipped a wick body **103** so that porous plate **104** which is arranged above the level of liquid **102**, is saturated with such liquid. Above porous plate **104** there is located catalyst body **105** which can be brought into contact with porous plate **104** by means of thumb screw **106** and gas tight threaded collar **105**. As soon as such contact takes place the solution of peroxide which is present in porous plate **104** decomposes into water and oxygen gas. The oxygen which evolves causes a rise in gas pressure in chamber **108**. With the rise in gas pressure in chamber **108** flexible membrane or diaphragm **109** is forced outward and catalyst body **105** is thereby raised off porous plate **104** so that further decomposition of the liquid is interrupted. The gas pressure thus created in chamber **108** can be vented to manometer **110**. If such gas pressure does not yet correspond to a desired supply pressure then catalyst body **5** is brought into contact with porous plate **104** again by turning thumb screw **106**. The liquid present in plate **104** is then decomposed with the formation of oxygen gas and the gas pressure in chamber **108** rises further. By repeating this process the desired supply pressure can be created in chamber **108**. The catalyst body **105** is then lifted off porous plate **104** by the

deflection of flexible membrane **109** by the gas pressure in chamber **108**.

The gas pressure in chamber **108** also prevails in chamber **112** above the level of liquid **102** since porous hydrophobic plate **111** allows for the passage of gas into chamber **112**. The capillary depression in porous hydrophobic plate **111** makes it possible to tip storage container **101** over more than 90° without having liquid **102** flow directly onto catalyst layer **105**. For venting excess gas pressure from chamber **108** a safety valve **111***a* can be placed in the wall of the chamber.

Due to the gas pressure in chamber **112**, liquid **102** is supplied over supply line **113**, rising main **114** and capillary **116** to the working layer of the oxygen electrode **115** of a fuel cell element **124**. As the level of the liquid in storage container **101** falls then so falls the gas pressure in chambers **112** and **108**. As a result of this decrease in gas pressure flexible membrane **109** is so deflected as to cause catalyst body **105** to fall again and come in contact with porous plate **104** and a generation of gas is initiated again which will persist until the original gas pressure is generated again so as to again deflect membrane **109** outwards and thus cause catalyst body **105** and porous plate **104** to be separated again. The deflection of flexible membrane **109** is determined by the difference in pressure between the pressure inside chambers **108** and **112** and the atmospheric pressure outside membrane **109**.

It is, however, also possible to provide an embodiment of the devices of the present invention which operates independently of the outside atmospheric pressure. Thus, one can replace the atmospheric air pressure which acts on the outside of membrane or diaphragm **109** by a spring, the pressure of which is as high as that of the atmospheric air. Thumb screw **106** is, in this instance, replaced by another thumb screw which is adapted to adjust the pressure of the spring on the membrane.

As soon as liquid reactant **102** reaches electrode **115** the decomposition reaction proceeds on the catalyst of the electrode after a certain delay, which reaction causes the formation of oxygen gas whereby the liquid reactant present in capillary **116** is forced back by the resulting gas. In this way the decomposition reaction at the electrode is interrupted. If the pressure of the resulting cushion of gas at electrode **115** is designated as p_g, and the gas pressure in gas chambers **108** and **112** of container **101** is designated as p_v, and the hydrostatic pressure of the liquid reactant is designated as p_h, then the following holds true:

$$p_g = p_v + p_h$$

(as long as no consumption of gas occurs).

Electrode **115** functions when pressure p_g corresponds to the operating pressure of the electrode. If the fuel cell is subjected to an electrical load, then pressure p_g falls due to the consumption of gas and liquid reactant **102** is caused to flow in the direction of electrode **115**. As soon as the volume of gas which is between liquid reactant **102** and electrode **115** is consumed then liquid reactant **102** begins to moisten the catalytically active layer of the electrode. Since the decomposition reaction does not take place spontaneously and, on the other hand, since the velocity of the flow of the liquid reactant to the electrode continues as a result of the continuous flow of the electric load even after the initial wetting of the electrode, more liquid reactant flows and therefore more gas is steadily evolved until the point is reached where more gas is being evolved by the decomposition of the liquid at the electrode than is being consumed by the electrical load. Under these conditions an excess of gas arises which leads to an increase in gas pressure. In order to avoid the situation wherein under a constant consumption of gas the pressure of the entire system continues to increase in the manner described above, rising mains **114** and **117**, which are provided in the device of FIG. 7, have been found necessary. The liquid coreactant, which is supplied from container **101**, must be continuously supplied through rising main **114** from the bottom thereof to the top. The same holds true for liquid reactant supplied over line **118** to rising main **117**, such as a solution of sodium borohydride for decomposition on hydrogen gas diffusion electrode **123** with the attendant evolution of hydrogen gas. The rising mains are so dimensioned that they can completely absorb any excess volume of gas arising during the decomposition of the decomposable gas yielding liquids on the respective electrodes under the prevailing electrical load conditions. In this way the rise in pressure which is created by such decomposition is caused to regress since the resulting excess volume of gas is used first before the decomposable liquid coreactant can again wet the electrode, whereupon the above described liquid supply and gas generation process is repeated again. A completely analogous regulation of the supply of liquid takes place if the fuel cell element **124** shown in FIG. 7 is operated as a gas generator. If, for example, a solution of hydrogen peroxide is supplied over line **113** and a sodium borohydride solution is supplied over line **118** then oxygen that is generated on catalytically active layer **115** can be supplied over gas line **120** by opening valve **119** and hydrogen that is generated on catalytically active layer **123** can be supplied over line **122** by opening valve **121**. Electrolyte **125** is used in the electrochemical reactions.

FIG. 8 shows another embodiment of the devices of the present invention for the automatic supply of liquid **202** from storage container **201** to the decomposition catalyst in layer **215** of fuel cell element **216** over supply line **213** and rising main **214**. The device of the present invention is connected by by gas line **230** to open gas area **208** which is above the level of liquid **202** in container **201**. The sealed pressure chamber **239** is formed by the lower part of container **231** and by gas impermeable elastic membrane or diaphragm **232** which cats to form and seal the upper portion of chamber **239**. Porous absorbent body or wick **233** is located in sealed chamber **239** and above this absorbent body or wick **233** there is positioned a catalyst body **234** which is fixedly connected to movable membrane **232**. In the upper portion of container **231** there is located an internally threaded shaft **235**, threaded bolt **236** and a pressure plate **237** and by means of turning nut **236** and forcing down plate **237** tension is applied to spring **238** and, in turn, to membrane **232**, which tension corresponds to the desired pressure for the delivery gas in chamber **239**. If the pressure of the delivery gas lies below the desired delivery pressure then catalyst body **234** is pressed down on porous body **233**. Porous body **233** is filled with decomposable gas yielding liquid before initiating the operation of the device through an orifice which is not shown. As a catalyst there can be used a sintered nickel body, for example, for the decomposition of a 16% by weight solution of sodium borohydride in 6 N aqueous sodium hydroxide for the generation of hydrogen gas. If the liquid **202** which is to be supplied to electrode **215** is also a 16% by weight solution of sodium borohydride in 6 N aqueous sodium hydroxide then sucking body **233** can also be filled from the liquid in container **201** by tipping the device so as to allow liquid **202** to flow through line **230** onto sucking body **233**.

Obviously the device of FIG. 8 can also be so constructed that absorbent body **233** is made movable and catalyst body **234** is permanently positioned.

As a result of the supplying of liquid **202** from storage container **201** to electrode **215** the volume of open gas chamber **208** above the level of liquid **202** is increased and the gas pressure, therefore, in the entire area encompassing gas chambers **208** and **239** and gas line **230** is correspondingly decreased so that membrane **232**, which had been raised while the desired gas pressure was in chamber **239**, and catalyst body **234** are again pushed down against body **233** by spring **238**. By a choice of a suitable dimensioning of the volume of gas that is to be employed in areas **239** and **208** it is possible to continuously provide in the devices of the present invention

that only relatively slight fluctuations of the delivery gas pressure occur.

A continuously regulatable gas or electric current supply under constant pressure is possible as long as the velocity of the decomposition of the liquid coreactants on catalytically active gas diffusion electrodes **215** and **223**, as well as the possible speed of supply of the liquid to the electrodes, is greater than the corresponding consumption of gas and electric current.

I claim:

1. In a gas generating installation comprising:

a container to contain a supply of gas yielding decomposable liquid,

a gas space above the level of said liquid,

a main decomposer having a catalyst adapted to catalytically decompose said liquid and thus provide for the generation of gas therefrom,

a first liquid supply passage means adapted to supply said liquid from said container to said main decomposer,

an auxiliary decomposer having a catalyst adapted to catalytically decompose said liquid to provide for generation of gas pressure,

a first gas supply passage means adapted to convey gas from said auxiliary decomposer to said gas space so as to provide a desired supply of gas pressure therein,

second liquid supply passage means adapted to supply liquid from said container to said auxiliary decomposer,

and pressure operated automatic liquid supply control means adapted to control the supply of liquid to said auxiliary decomposer to limit the generation of gas in said auxiliary decomposer.

2. An installation as in claim **1** in which said liquid supply control means includes a first control valve in said second liquid supply passage means, a sensing means to sense the gas pressure in said gas space adapted to operate said control valve according to the gas pressure in said gas space in order to release a supply of said liquid to said auxiliary decomposer when the gas pressure in said gas space falls below a predetermined supply.

3. An installation as in claim **2** in which said pressure difference sensing means adapted to control said first control valve is actuated by a difference in pressure between the gas pressure in said gas space and a reference pressure external of said gas space.

4. An installation as in claim **1** in which said first gas supply passage means further includes a buffer volume means.

5. An installation as in claim **1** in which said first liquid supply passage means comprises a second control valve for said liquid which is adapted to be controlled by the gas pressure in said gas space and to release a supply of said liquid to said main decomposer when the gas pressure in said gas space exceeds a predetermined supply pressure.

6. An installation as in claim **5** further including second gas passage means for conveying gas from said main decomposer to a gas consuming device and said second gas line means comprises buffer volume means.

7. An installation as in claim **1** in which said first liquid supply passage means further comprises rising main means.

8. An installation as in claim **1** in which said main decomposer is a power cell.

9. An installation as in claim **1** in which said liquid supply control means comprises a first valve for said gas in said first gas supply passage means which is adapted to be controlled by the pressure of gas generated by said auxiliary decomposer and thereby control the pressure of gas in said gas space and thus control the supply pressure of said liquid to said auxiliary decomposer.

10. An installation as in claim **9** in which said second liquid supply passage means comprises rising main means.

11. An installation as in claim **10** in which said second liquid supply passage means further comprises means throttling the flow of liquid therethrough.

12. An installation as in claim **1** in which said auxiliary decomposer is positioned within said container above the level of decomposable liquid therein and said second liquid supply passage means comprises a wick adapted to absorb said liquid and supply it to said auxiliary decomposer.

13. An installation as in claim **12** in which said pres surized liquid supply control means comprises a flexible membrane to which said auxiliary decomposer catalyst is rigidly attached and said flexible membrane is adapted to being flexed by variations in gas pressure in said gas space to bring said auxiliary decomposer catalyst into contact with said wick when said flexible membrane is flexed in one direction and to interrupt catalyst contact with said wick within said auxiliary decomposer when said flexible membrane is fixed in the opposite direction.

14. An installation as in claim **1** in which said auxiliary decomposer is positioned outside of, and below the base of said container, and said catalyst is mounted on a movable shaft which is adapted to being raised and lowered through the base of said container, the base of said container having said liquid supply passage means incorporated therein for supplying decomposable liquid to said auxiliary decomposer from said container when said shaft is raised, said shaft having a valve head adapted to seal said liquid supply passage means when said shaft is lowered, and said pressurized liquid supply control means comprising a flexible membrane upon which said auxiliary decomposer rests and said flexible membrane is adapted to be flexed by variations in gas pressure in said gas space and to raise and lower said auxiliary decomposer upon being flexed.

15. An installation as in claim **1** in which said auxiliary decomposer and said pressurized liquid supply control means are positioned within said container and said pressurized liquid supply control means comprises a flexible membrane adapted to be flexed upwards and downwards and a valve head joined by a rigid connecting rod to said membrane, said valve head being adapted to cover and enclose said catalyst and thereby prevent liquid from contacting said catalyst in said auxiliary decomposer when sadi valve head is moved toward said catalyst by flexing of said flexible membrane under an increase in pressure and to uncover said catalyst to thereby allow access of liquid in said container to said catalyst when said valve head is raised by flexing of said flexible membrane under the influence of a decreased pressure, one side of the surface of said flexible membrane being in communication with the liquid in said container and the other side of the surface of said flexible membrane being subject to a predetermined flexing pressure, so that differences in the pressure between the gas pressure in said gas space and said predetermined flexing pressure will cause the flexing of said flexible membrane to cause a raising or lowering of said valve head.

16. An installation as in claim **1** in which said auxiliary decomposer is positioned outside said container and above a supply of decomposable liquid and said pressurized liquid supply control means comprises a movable member adapted to being moved upwards and downwards and to which movable member said auxiliary decomposer catalyst is rigidly attached, one side of said movable member being subjected to a pressure from outside said gas area and the other side of said movable member being subject to the pressure within said gas area whereupon differences in such pressures cause a movement of said movable member and said auxiliary decomposer catalyst upwards and downwards and thus cause an interruptable contact of said auxiliary decomposer catalyst with said supply of decomposable liquid.

17. In combination with a container for a liquid that is decomposable to evolve a gas by contact with a catalyst in which the container is provided with a bottom connection for withdrawing said liquid, the top of said container

defining a gastight space to hold gas under a predetermined pressure so that the liquid may be withdrawn from said bottom connection: an auxiliary decomposer forming a gas supply means to add gas to said top of said container, said auxiliary decomposer including a chamber, a catalyst in said chamber, means to supply decomposable liquid to said chamber, and gas passage means from said chamber to supply gas generated by contact of said liquid with said catalyst to said top of the container; and means operated by a difference of the pressure in said chamber which is connected to the top of said container and a selected other pressure, said means operated by a difference of the pressures being operable to bring said liquid and said catalyst in said chamber into contact with each other to decompose said liquid to generate gas when the pressure in said container and said chamber falls below a predetermined pressure in the top of the container compared with the selected pressure, and preventing contact between said liquid and catalyst when the pressure in said container and said chamber rises to a higher preselected pressure compared to said selected pressure.

18. In combination with a container for a liquid that is decomposable to evolve a gas by contact with a catalyst in which the container is provided with a bottom connection for withdrawing said liquid, the top of said container defining a gastight space to hold gas under a predetermined pressure so that the liquid may be withdrawn from said bottom connection: an auxiliary decomposer forming a gas supply means connected operatively to said container to deliver additional gas to said container when the pressure in said container drops, said auxiliary decomposer comprising a chamber having a wick element providing a source of decomposable liquid, and having a catalyst therein, and incorporating a control means including a diaphragm means operated by the pressure within said chamber on one side, and a selected pressure on the other side to bring said catalyst into contact with said decomposable liquid in said wick element when the pressure in said chamber decreases below said selected pressure and to prevent contact of said catalyst with said wick element and so with said decomposable liquid when said pressure increases.

References Cited

UNITED STATES PATENTS

868,487	10/1907	Rosengarten	103—234
2,258,299	10/1941	Miller	103—240
2,373,006	4/1945	Baker	23—282X
2,658,819	11/1953	Formwalt	23—282X
2,892,416	6/1959	Alexander	103—234

ALLEN B. CURTIS, Primary Examiner

U.S. Cl. X.R.

23—282; 417—65, 118, 120