US 20020017380A1

(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0017380 A1**
Jonsson et al. (43) **Pub. Date: Feb. 14, 2002**

(54) **CHEMICAL HEAT PUMP USING A SOLID SUBSTANCE**

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(21) Appl. No.: **09/863,406**

(22) Filed: **May 24, 2001**

Related U.S. Application Data

(63) Continuation of application No. PCT/SE99/02187, filed on Nov. 24, 1999.

(30) **Foreign Application Priority Data**

Nov. 24, 1998 (SE) 9804034-8

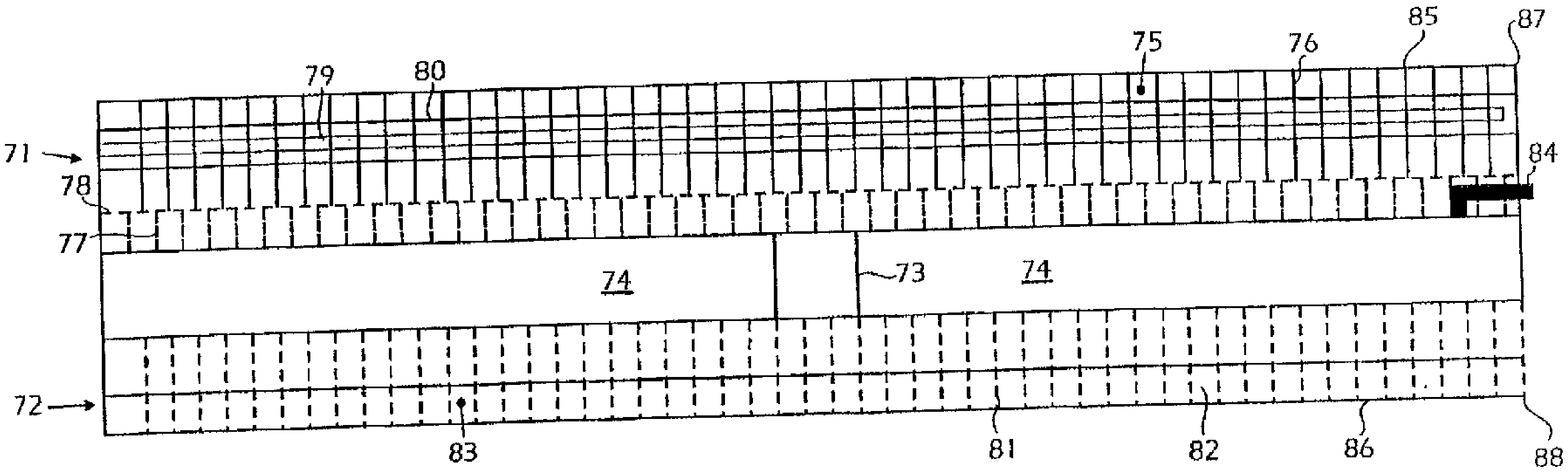
Publication Classification

(51) **Int. Cl.**^{7} **F28D 15/00**; F25B 15/00; F25B 17/08; B21D 51/16

(52) **U.S. Cl.** **165/104.12**; 62/476; 62/480; 29/890.06

(57) **ABSTRACT**

In a chemical heat pump a substance is used which in an efficient way interacts with a volatile liquid such as water. The substance is selected considering among other things the magnitude of its ΔT and its energy content so that the heat pump becomes suited for converting low grade heat energy such as solar energy to cooling for airconditioning and also for a simultaneous production of heat for example for use as hot tap water in houses. The heat pump can also be used in a refrigerating box. Suitable substances comprise barium hydroxide, lithium hydroxide, strontium bromide and cobalt chloride. The substance is applied as a layer (23) on the surface of a heat conducting wall (22) by applying a slurry-like mixture of the substance with the liquid when being vibrated to the wall between heat conducting flanges 25). The mixture is dried under a vacuum and is heated and is simultaneously compressed by applying an exterior pressing force. This gives a solid, well adhering layer of a substance having a high porosity which can resist a large number of cycles without any degradation of the internal structure of the layer and of its adherence to the heat conducting wall and the flanges.



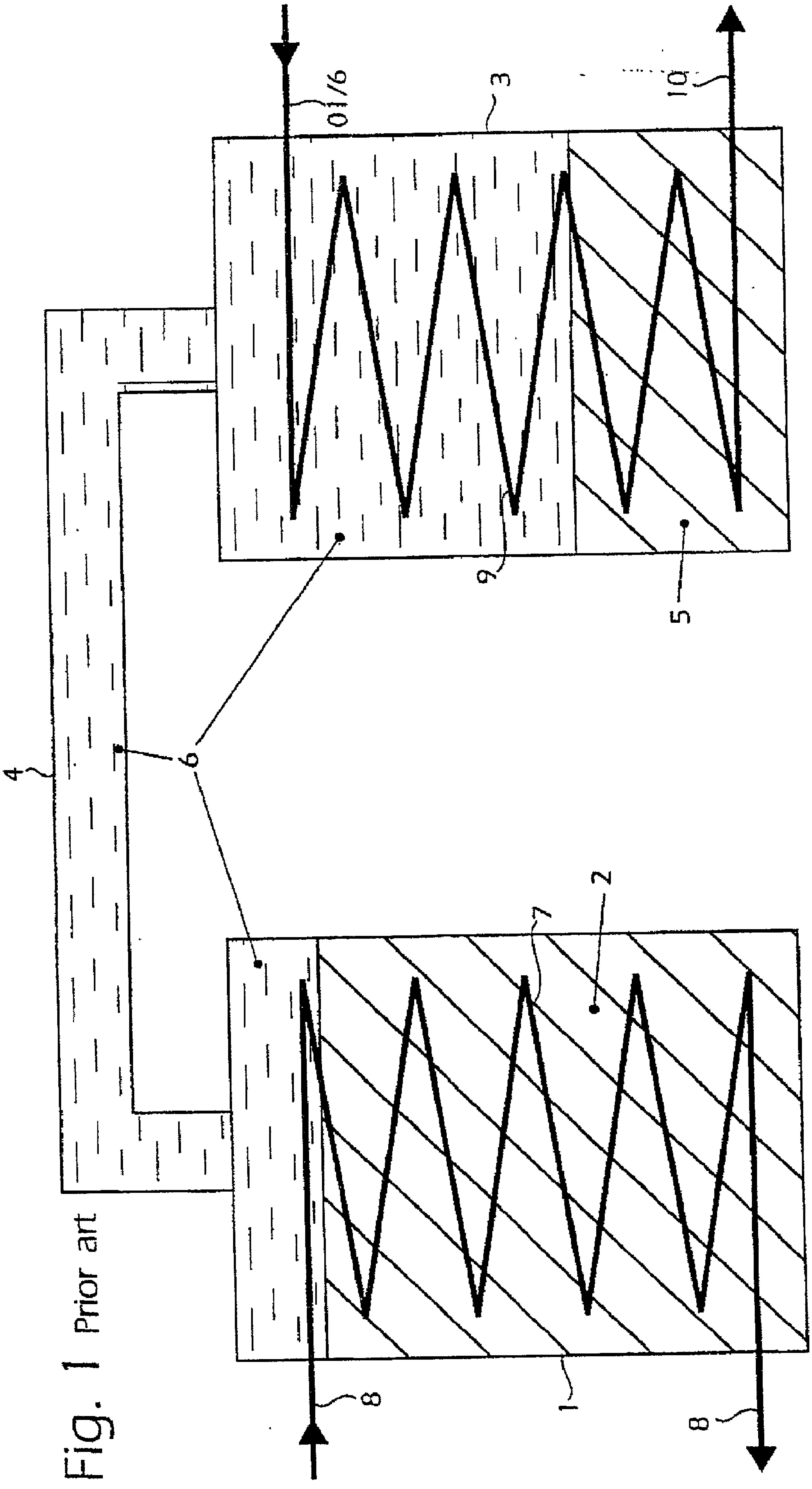


Fig. 1 Prior art

Fig. 2a

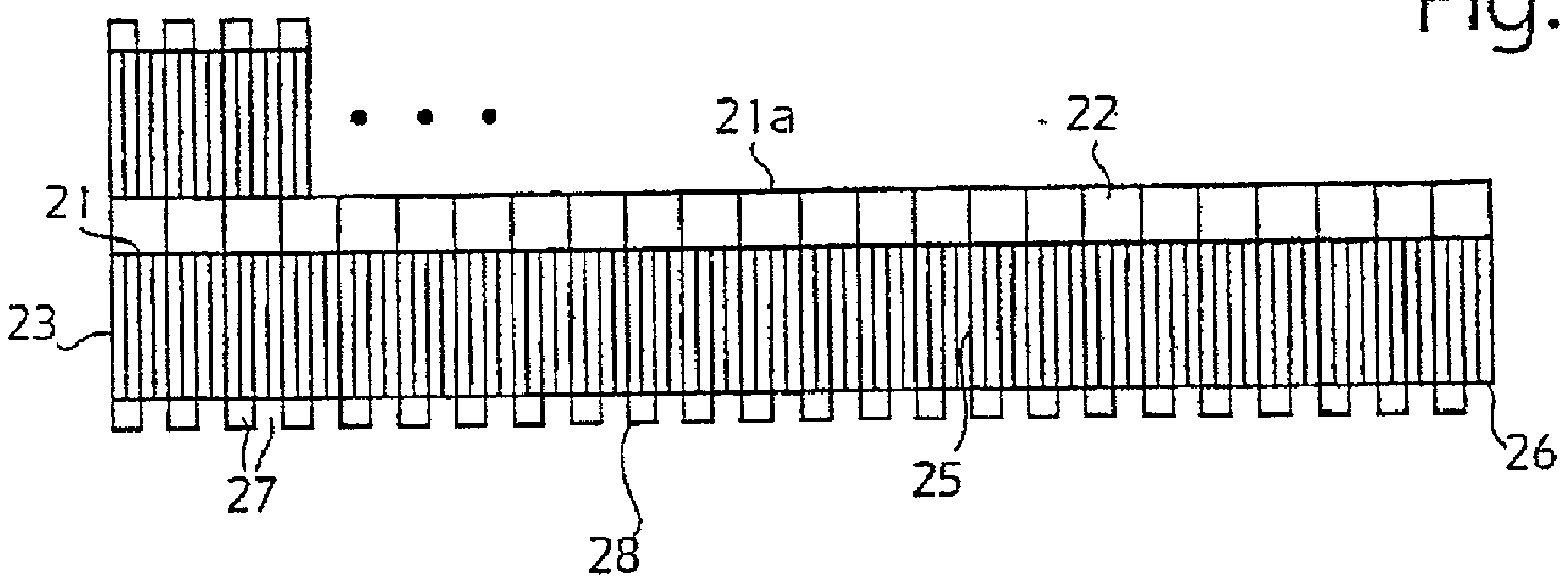


Fig. 2b

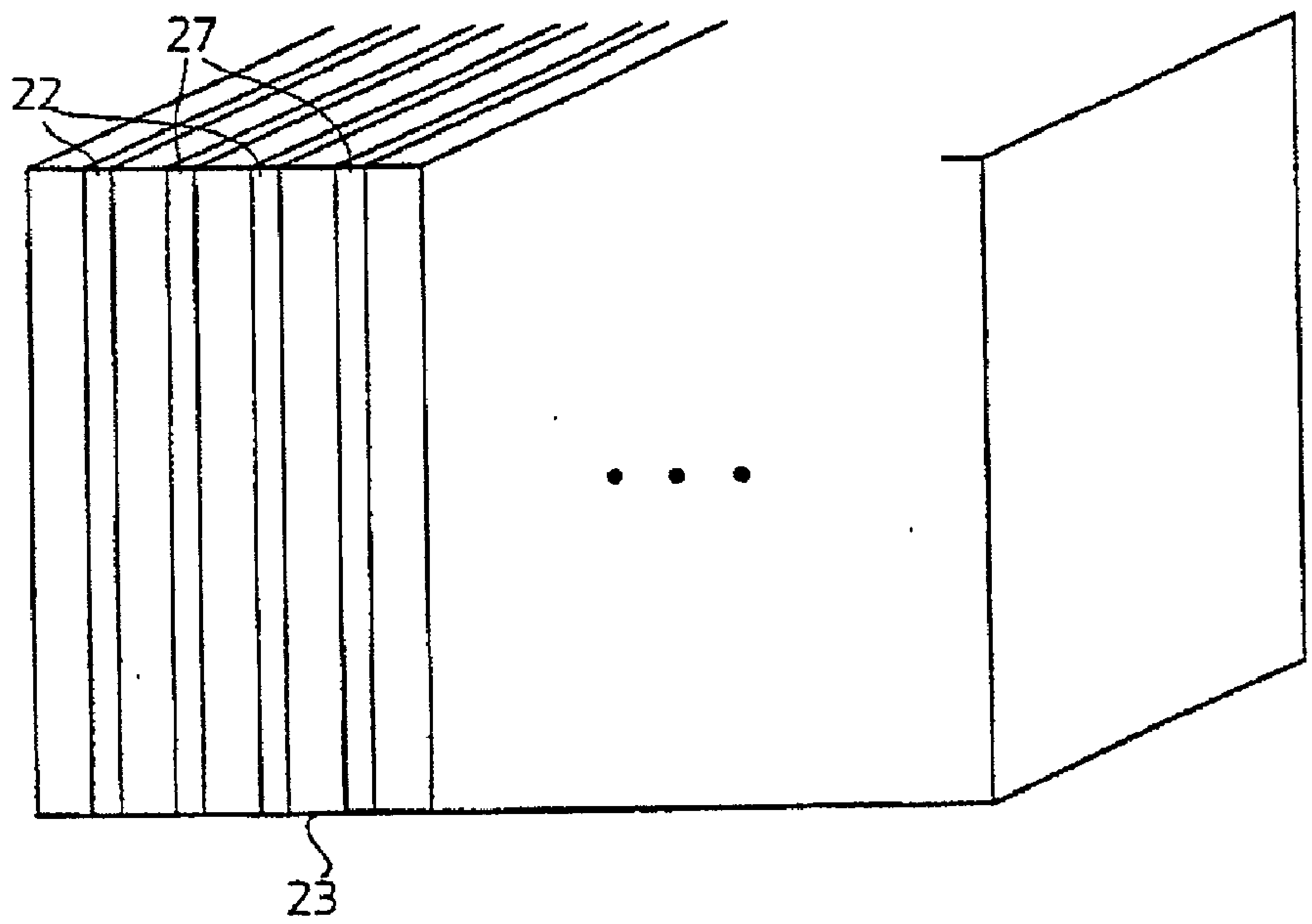


Fig. 3a

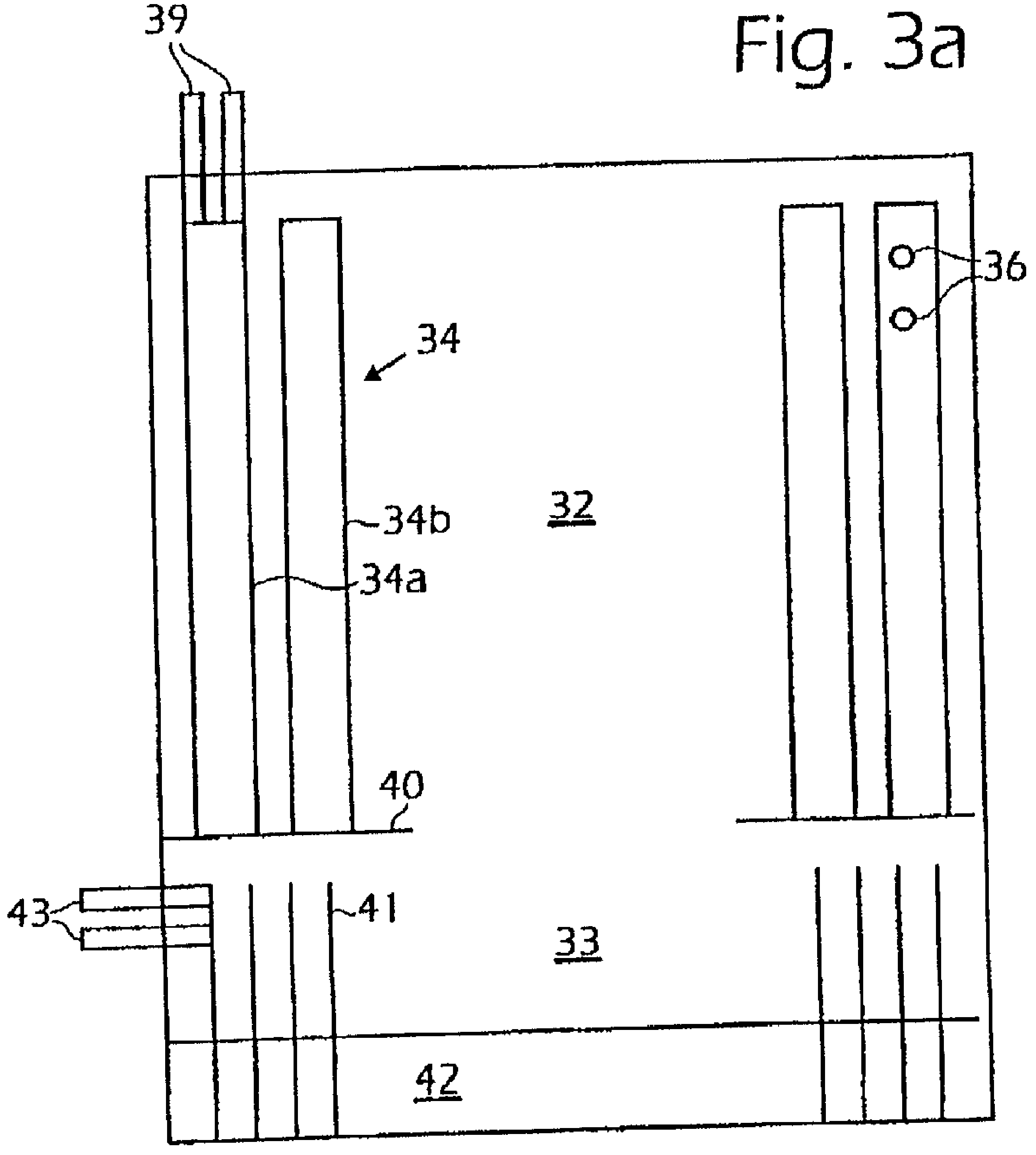


Fig. 3c

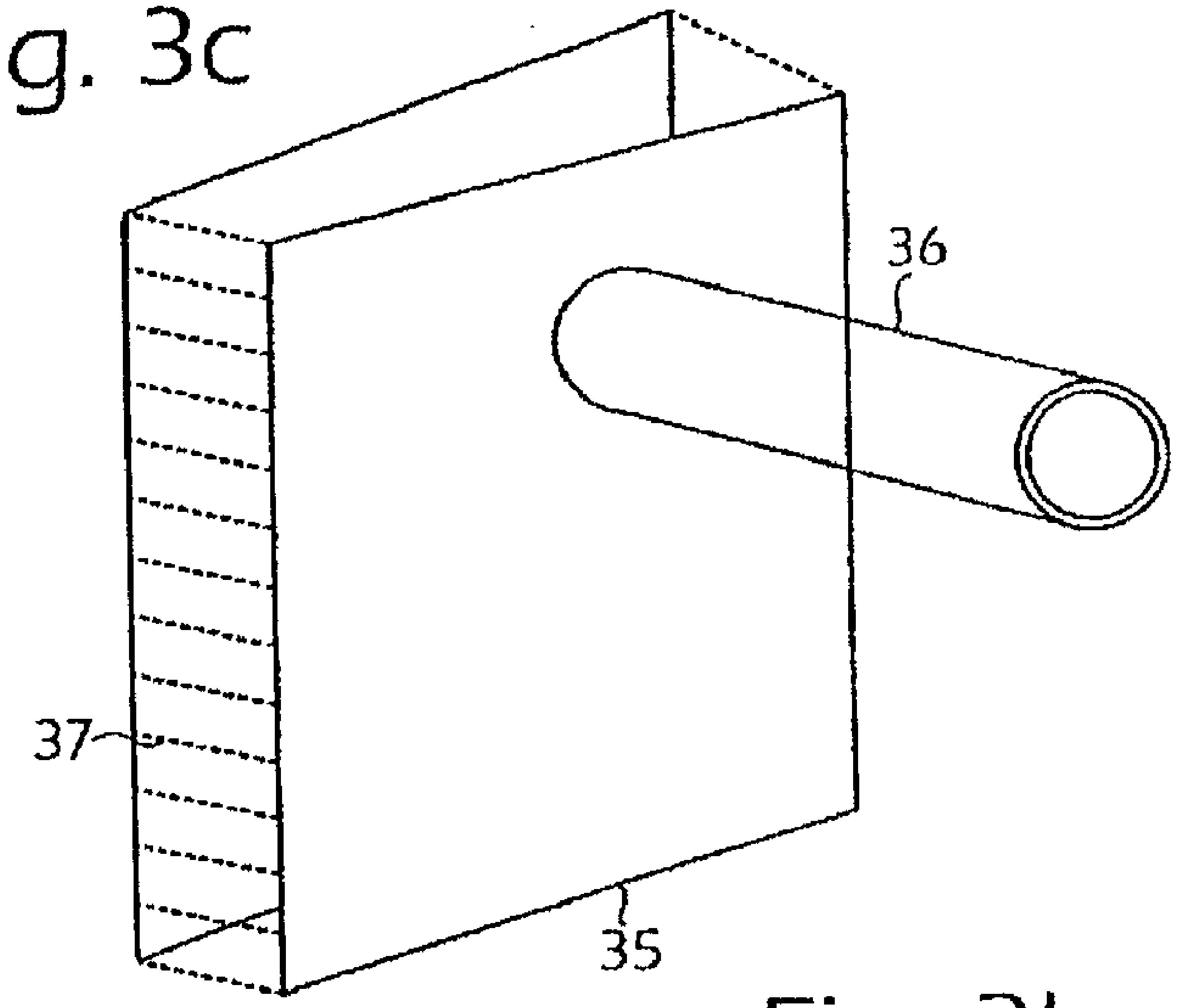


Fig. 3b

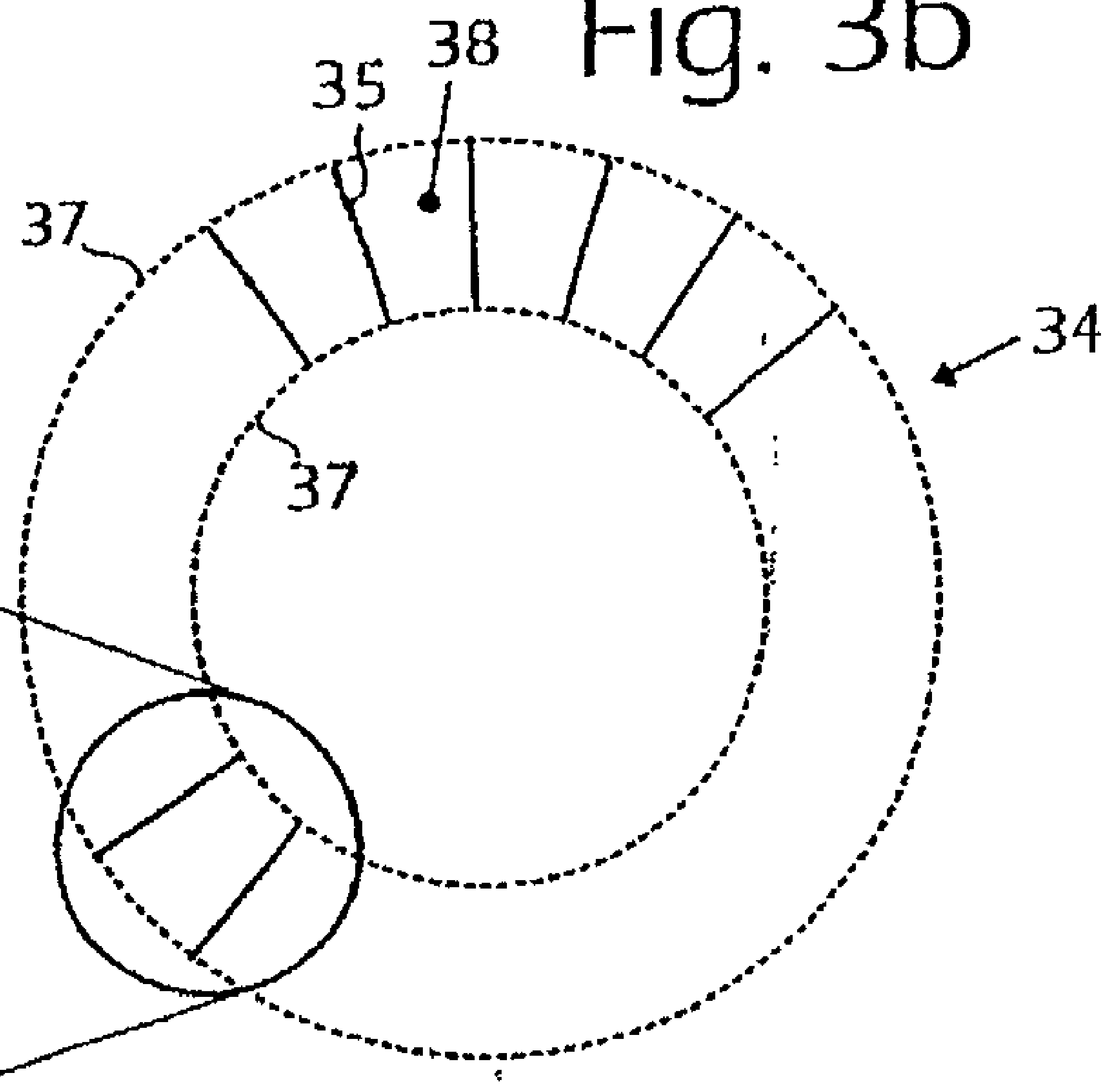


Fig. 3d

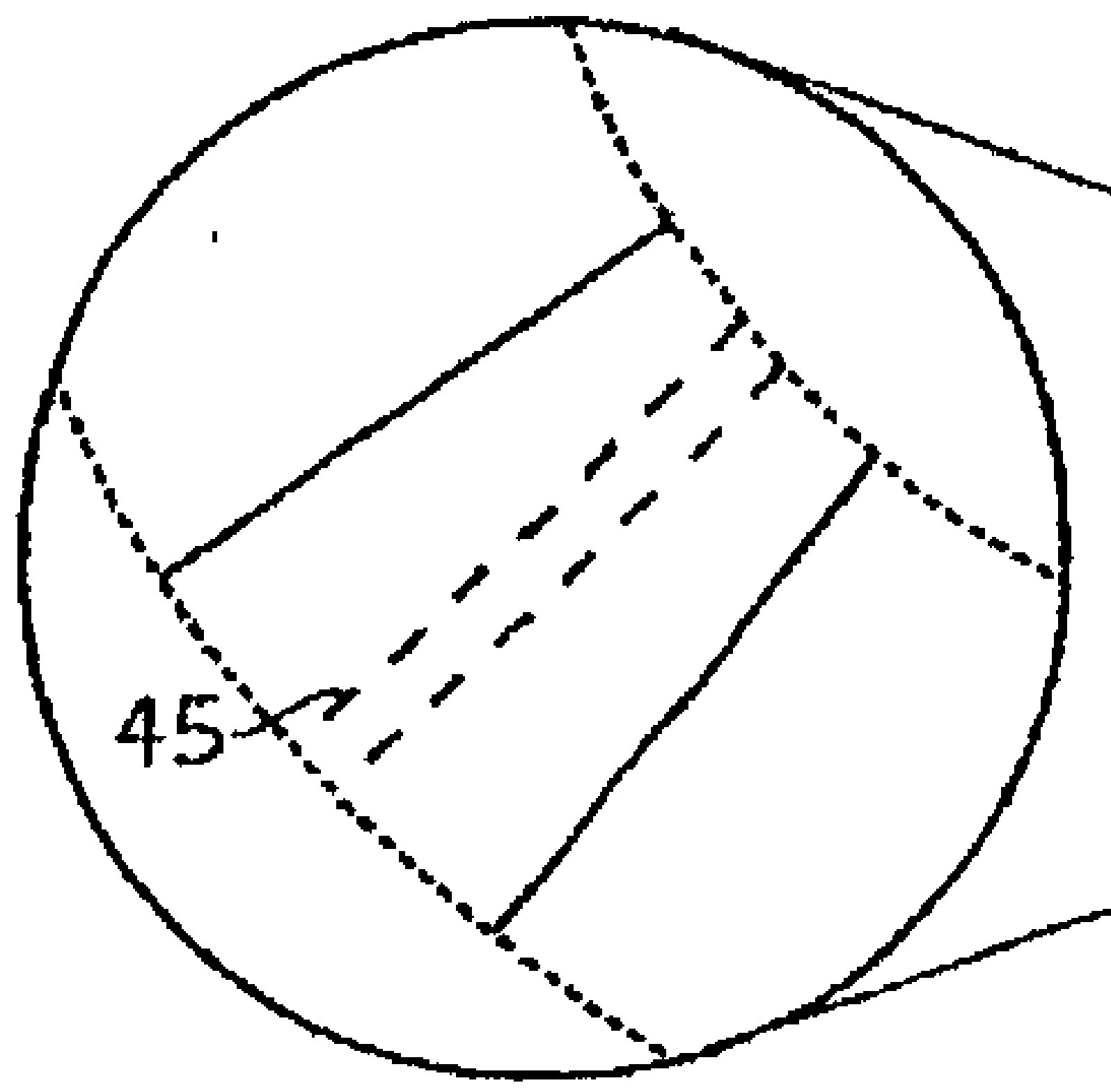
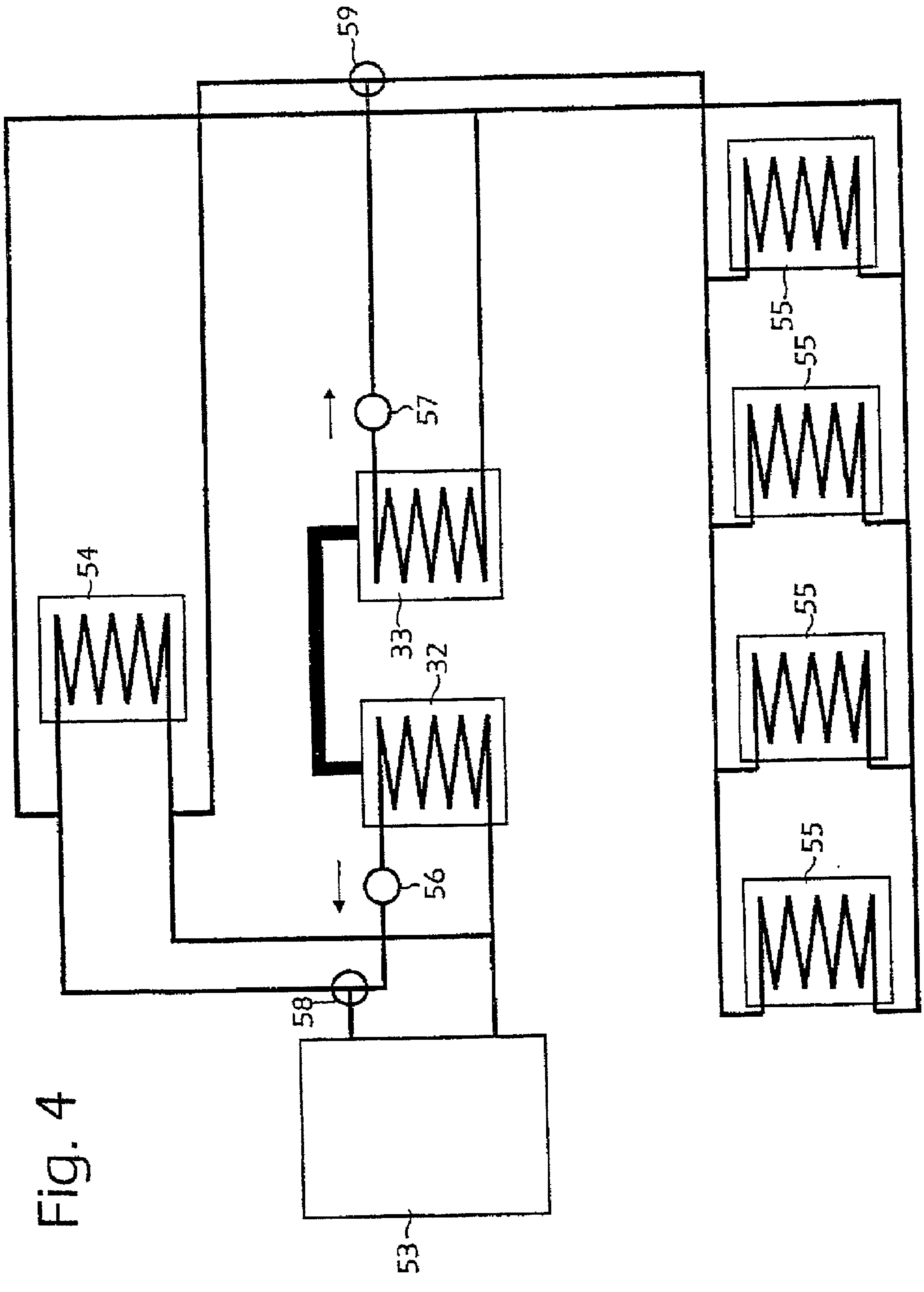


Fig. 4



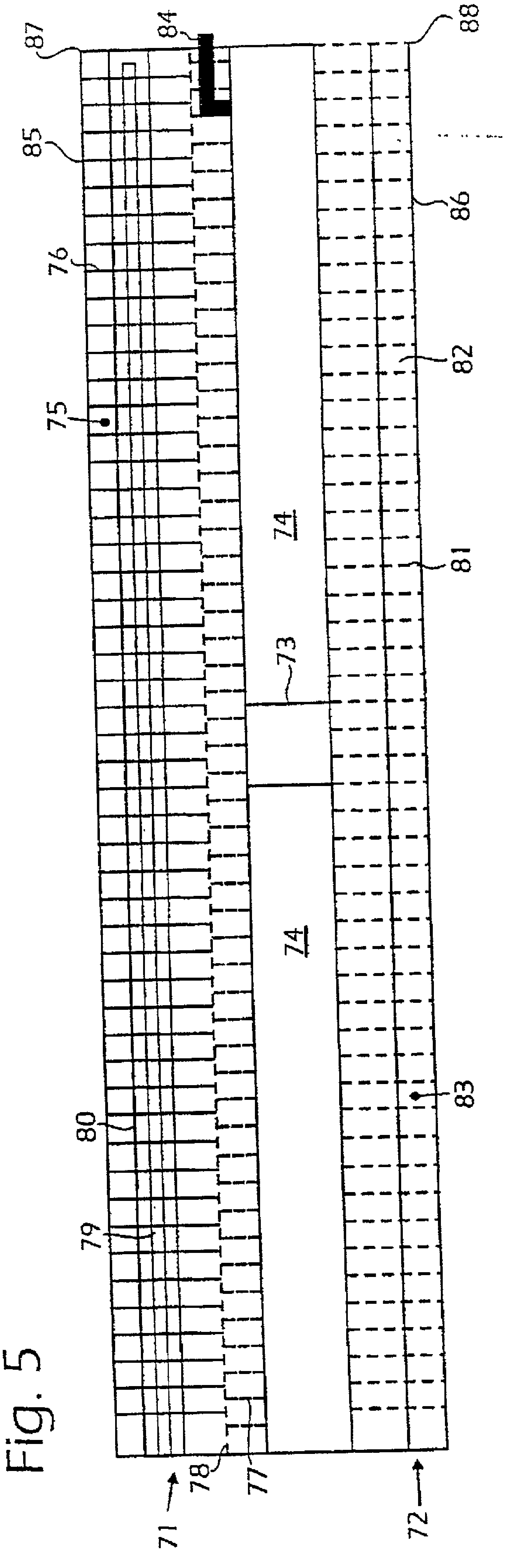
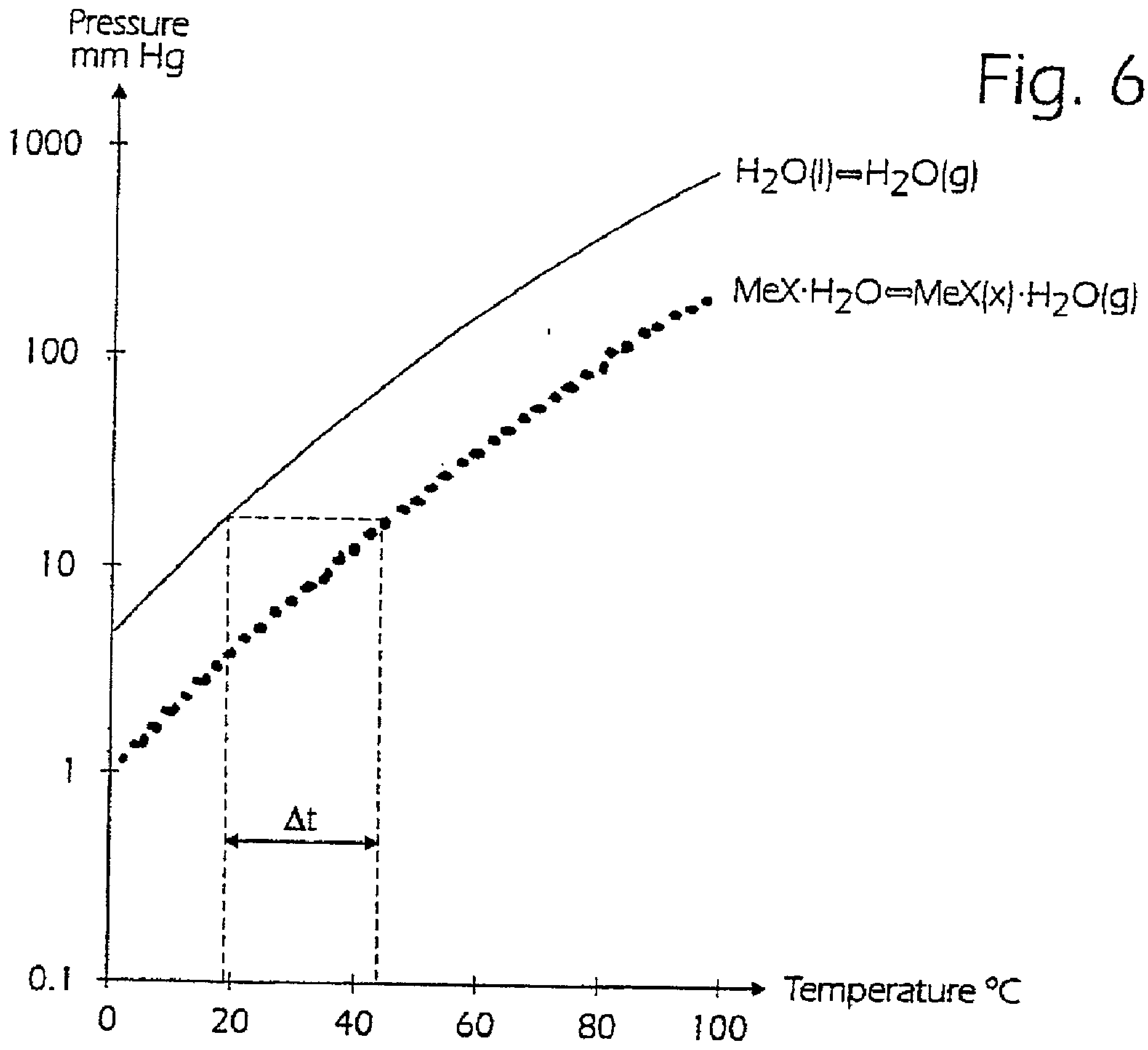


Fig. 5

Fig. 6


Pressure mm Hg
1000
100
10
1
0.1
$H_2O(l) \rightleftharpoons H_2O(g)$
$MeX \cdot H_2O \rightleftharpoons MeX(x) \cdot H_2O(g)$
Δt
0
20
40
60
80
100
Temperature °C

CHEMICAL HEAT PUMP USING A SOLID SUBSTANCE

TECHNICAL FIELD

[0001] The present invention relates to a chemical heat pump, a method of the manufacture thereof, and systems constructed including such a chemical heat pump.,

BACKGROUND OF THE INVENTION

[0002] The principle of operation of the chemical heat pump is well-known, see for example U.S. Pat. Nos. 5,440, 889, 5,056,591, 4,993,239, 4,754,805 and the published International patent application WO 94/21973. A complicated heat pump apparatus is disclosed in U.S. Pat. No. 5,360,057. The reason why practical solutions cannot be easily found and commercial products cannot easily be produced resides both in the nature of the chemical process in a chemical heat pump and the technical structure in which the chemical process is to take place. There is a difficulty of finding suitable substances where this difficulty can be compared to corresponding conditions for electrochemical cells (for producing electric power). Moreover, there exists a great analogy between a chemical heat pump (=a chemical heat battery) and an electrochemical cell. Furthermore, the mechanical design and its interaction with the substance is an important factor in the chemical process in a heat pump in order to make the process in the heat pump operating in the intended way. Further, in order that the chemical process is to operate satisfactorily for a very long time, a system is required which is very tight or leak-proof. Extremely small amounts of unwanted gases can completely stop the process in a system used as a chemical heat pump. This is particularly important in a case where a liquid having a low vapour pressure such as e.g. water is used. The requirement on tightness of a completely closed system corresponds to the requirements which are set in high vacuum technology. Thus, all the components in a system used as a chemical heat pump have to be tested for leaks using helium to a tightness of 10^{-10} mbarl/s.

[0003] Thus, in a chemical heat pump an active substance is provided which executes the very process of the heat pump and which works together with a volatile medium, usually being a dipolar liquid, in most cases water. A multitude of such active substances has been proposed to be used together with water, see for example the patents and the patent application cited above. Typical substances include for example calcium chloride, magnesium chloride, lithium chloride and sodium sulphide. The cooling power in a cooling system comprising a chemical heat pump is determined by the physical design of the system. The transfer of energy between the substance and the heat exchanger included in such a system is in a system using a solid substance reduced to a considerable extent compared to the case in which the substance is a liquid. The cooling power is primarily determined by the thickness of a layer of the substance located on the surfaces of the heat exchanger and by the availability of gas in relation to the substance surfaces, i.e. how well the volatile liquid can leave the active substance and how well it can in a vaporised state be absorbed by the active substance.

[0004] The internal operation of a chemical heat pump is determined by a complex interaction between kinetics of the chemical reaction between active substance and volatile liquid, the diffusion of the volatile liquid in the active substance and the transport of heat in the reactor part accomodating the solid substance, which factors are also dependent on the geometrical design and the mechanical construction of the heat pump. In particular the interaction between diffusion and heat conduction has a great importance to make-the-reactor operate at high power rates without causing that an unbalance leading to a stop of the reaction, a selfchoking, will appear in the discharging process, i.e. when the active substance absorbs vapour of the volatile liquid.

[0005] In U.S. Pat. No. 5,440,899 for De Beijer et al. cited above a heat pump is disclosed having a heat accumulator designed as a cylindrical chamber and a space placed therebelow for an evaporator/condenser separated by a partition wall. In the accumulator part, in one embodiment, a surface magnifying and heat conducting structure is provided designed as a rectangular helical winding of metal wire. In the accumulator part and in the evaporator/condenser heat exchangers are provided. At the interior side of the evaporator/condenser part support elements are provided covered with capillary sucking web. In the accumulator part, in the space between the parts of the helical flange, a fibrous material is arranged, in the preferred case a mixture of cellulose and graphite, which then is made to absorb sodium sulphide. In the mixture the graphite is provided in order to improve the heat conduction characteristics. Artificial resin plates can also be arranged in the accumulator part, which are removed after introducing the mixture, so that cavities for the expansion of the mixture are formed. The sodium sulphide is generally arranged at elevated temperature in its most hydrated shape such as $Na_2S \cdot 9H_2O$, i.e. in a melted shape, and is absorbed by the mixture and sodium sulphide crystals are then formed by cooling. These crystals are by the fibrous material attached to the flange in the accumulator.

[0006] When using sodium sulphide in an accumulator according to the prior art there is firstly an important problem associated with the adhesion of the sodium sulphide to the heat exchanging surfaces, so that, if not using a fibre reinforcement according to the description above, after a number of cycles small slits can be created between the layer of sodium sulphide and the surface, to which heat is provided and from which heat is transported away. In addition, there is a second problem associated with the fact that, considered in a long term perspective, other gases can be formed, so called residual gas, see the discussion hereinbelow.

SUMMARY OF THE INVENTION

[0007] It is an object of the invention to provide a chemical heat pump which can be used to be driven by solar energy.

[0008] It is another object of the invention to provide a chemical heat pump which is capable of performing a large number of cycles including charging and discharging without a degradation of its performance.

[0009] It is another object of the invention to provide heat exchanger elements for a chemical heat pump which have an efficient transfer of heat between heat conducting parts of the elements and an active substance and which allow that the active substance can be attached to heat conducting parts in such a way that the substance can efficiently interact with the gaseous phase of a volatile liquid.

[0010] In order that a chemical heat pump will operate practically the active substance, which executes the very process in the heat pump, i.e. absorbing and desorbing (emitting) a sorbate, must fulfil at least the following criteria:

[0011] 1. The substance must have a suitable ΔT, where ΔT is the temperature difference which for a pressure equilibrium exists between the substance and the volatile, dipolar liquid in the condenser/evaporator. A suitable ΔT for systems comprising water/water vapour is in the range of 20-40° C., see the discussion hereinafter.

[0012] 2. The substance should preferably react with the gas, i.e. the vapour phase of the volatile liquid, at one single phase transition having a constant ΔT or at least for phase transitions having closely located ΔT.

[0013] 3. The substance must at all instances during the process remain in a solid state, i.e. it must have a suitable melting point in relation to the process temperatures.

[0014] 4. The substance is not allowed to sublimate.

[0015] 5. The substance must be chemically stable and stand long term operation.

[0016] 6. The substance is not allowed to produce other gaseous by-products than the volatile liquid in a gaseous form.

[0017] 7. The substance must be mechanically stable and is not allowed to change its structure in time or have significant changes of the outer physical shape thereof when it absorbs and emits gas.

[0018] 8. The substance must have a high reaction capacity with the gaseous phase of the volatile liquid and maintain the high reaction capacity for as many cycles as possible.

[0019] 9. The substance must have a high energy content counted as energy of evaporation on the condenser/evaporator side per unit volume of the substance.

[0020] 10. The substance must be capable of being applied to surfaces of heat exchangers and must not be apt to be detached therefrom, i.e. it must be rigidly attached to the surfaces. This can be achieved if substance can be made to form a slurry in water, see the discussion hereinafter.

[0021] 11. The substance should not be corrosive, inflammable or otherwise be a problem to for example the environment or to an operator.

[0022] 12. It should not be too costly to initially buy, obtain or produce the substance.

[0023] The definition of the quantity ΔT mentioned under point **1**. is illustrated by the diagram of **FIG. 6**. There the vapour pressure as a function of temperature for pure water and for a typical salt MeX containing water of crystallization is illustrated. According to the discussion above the temperature difference ΔT is the difference between the temperature of a quantity of salt and the temperature of a quantity of water when an adiabatic process comprising that the salt quantity absorbs water vapour proceeds. As appears from the diagram, AT is rather constant for pressures around the atmospheric pressure.

[0024] The criterion **1** is particularly decisive when constructing a chemical heat pump intended for solar driven air conditioning. In the charging phase, which occurs at daytime, the outdoor temperature can be very high. Since the condenser/evaporator will be preferably cooled by a flow of liquid from an air heat exchanger connected to the air conditioning system, the current outdoor temperature will limit the condensing temperature. Thus, for an imaginary charging temperature of the substance having a maximum of about 90° C. also the possible AT value of the substance is limited.

[0025] Considering that totally about 10° C. must be reserved as a power driving temperature difference on the substance side and the condenser/evaporator side, for an outdoor temperature of 40° C. only 30° C. is left to the ΔT of the substance. The selected substances should thus be restricted to only include substances having a ΔT between 20° C. and 40° C. The criterion **1** must as well be satisfied for the actual conditions existing when discharging the system. In a discharging process which for the application comprising solar driven airconditioning is preferably intended to occur at night, the lowest cooling temperature generated by the system is limited by the temperature of the substance in the discharging process, which as well is determined by the liquid flow from the air heat exchanger of the air-conditioning system. If this temperature for example is 30° C. and 5° C. must be reserved totall on the substance side and the condenser/evaporator side as a power driving temperature difference (the power in discharging is lower because of a longer time cycle) and the cooling water to the room coolers are to hold 10° C., it is required, that the substance has a ΔT of 30° C. However, some substances such as LiOH and $Ba(OH)_2$ have a large advantage in that their ΔT is reduced for increased temperatures and thereby the charging at high temperatures of the condenser is facilitated.

[0026] Also the criterion **3** must be carefully observed. Many substances have a sufficiently high melting point for the phase transition or transitions used but obtain a significantly low melting point for a following phase transition. If the vapour pressure for the substance in a saturated solution is sufficiently low to fulfil the transition to this phase anywhere in the system the substance will partially be transformed to a liquid phase. This is particularly risky close to the heat exchanger surfaces for a large draw of power, since if melting occurs the substance can be detached from the heat exchanger surfaces.

[0027] The criterion **4** also sorts some possible substances away. Thus, oxalic acid $(COOH)0\text{-}2H_2O$ has a ΔT of 30° C. and a relatively large energy content but it sublimates in the temperature range within which a solar driven heat pump is driven. Sublimation means that the vapour pressure of the substance is so low that the substance is volatilized without first being melted. When used in a chemical heat pump for the current temperatures and pressures this acid is transferred as a finely dispersed power to the condenser. Thereby there will eventually be no substance left in the reactor. Also boron acid BOOH, which otherwise is a good substance suited for storing heat but which has a too high ΔT to be capable of being used for the application intended here for air-conditioning, sublimates in charging.

[**0028**] In the criterion **9** the term energy content means the energy of vaporisation which is consumed for the vaporisation when a unit volume of the substance absorbs the gaseous phase of the volatile liquid. A high energy content is here at least 0.15 kWh/l, preferably at least 0.2 kWh/l and most preferably at least 0.3 kWh/l.

[**0029**] A plurality of substances which correspond to the criteria set has been produced and tested during realistic conditions. All of the substances are primarily intended for converting heat energy to refrigeration but heat can in some cases be obtained at the same time as refrigeration is generated. The substances are suited for solar driven air-conditioning installations and for refrigerators and refrigerating bags which can be charged by being heated by electrical resistance elements or some other energy source selected at will.

[**0030**] All of the substances are intended to be used with water as the working medium. Water has a high energy of vaporisation, is non-costly and non-dangerous and gives in the intended applications a suitable temperature on the cooling side.

[**0031**] Primarily selected substances include

[**0032**] 1. $CoCl_2$ (Cobalt chloride) in the phase transition 1-2 H_2O having ΔT=42° C. and the phase transition 2-6 H_2O having ΔT=20° C.

[**0033**] 2. $Ba(OH)_2$ (Barium hydroxide) in the phase transition 1.5-6.5 H_2O having ΔT20° C.

[**0034**] 3. LiOH (Lithium hydroxide) in the phase transition 0-0.65 H_2O and ΔT25° C.

[**0035**] 4. $SrBr_2$ (Strontium bromide) in the phase transition 1-6 H_2O and ΔT=**35° C.**

[**0036**] All these substances are very well suited as an active chemical compound in a chemical heat pump intended for cooling. $SrBr_2$ has a sufficiently high ΔT to be capable of also producing heat at the same time as cooling or refrigeration is produced, at a temperature level which for example allows production of hot tap water to be used in houses. The substances are very reactive with water vapour and have no difficulties neither in discharging or charging. No demonstratable retardations of the reaction speed arise with time due to formed gaseous decomposition products. No structural changes have been observed for a large number of cyclings. The substances have high energy contents counted as cooling energy per volume substance. The energy content is for all these substances except LiOH about 0.2 kWh/l for dry packing and about 0.3 kWh/l for drying using the slurry method, see the discussion hereinafter. Lithium hydroxide has an energy content of about 0.15 kWh/l for dry packing and about 0.17 kWh/l for slurry packing.

[**0037**] The cooling power is determined by the construction of the system. The energy transfer between the substance and the heat exchanger is in a system having a solid substance significantly reduced compared to the case having a substance in liquid form. The power is primarily determined by the thickness of the substance layers on the heat exchanger surfaces and by the gas availability of the substance surfaces. However, it is possible to significantly increase the power if thin and most preferably very thin layers are used, such as layers having a thickness of at most about 10 mm. Thereby a significantly larger flexibility can be achieved in the adaption of substance and technical design to the applications which are practically useful.

[**0038**] In a reactor for a chemical heat pump in which the operatiorn has-been optimized aiming at rapid charging, long discharge time periods and a high power ratio, both heat conduction and the diffusion in the solid substance should occur in the same direction within the substance. The term reactor herein means the vessel in which the active substance is arranged and in which the reaction of the substance with the gaseous phase of the volatile liquid occurs. An improvement of the heat conduction of the substance by integrating a grating, a net, wires or a folded band made of metal or of other suitable material directed in the correct direction should thus be supported by other means which improve the diffusion in microchannels of the substance.

[**0039**] In the reactor a heat exchanger unit is provided which transfers heat between the active substance and an external medium. The chemical substance can be integrated with the heat exchanger unit to form a compact unit in which a heat transport improving structure, also called heat conducting reinforcement, attached to heat exchanging surfaces in the heat exchanger unit, mechanically stabilizes the substance to form a combined heat exchanger/substance unit in which a maximum adhesion between the substance and the surface of the heat exchanger is obtained, compare the discussion hereinabove of U.S. Pat. No. 5,440,899 for De Beijer et at. In order to obtain such a combined unit the chemical substance is made to form a slurry in an adapted amount of water which constitutes a certain excess above the most hydrated state of the substance of working molar concentrations. The chemical substance has before that obtained an adapted granular size distribution by screening and the substance will then when silted up in water to form a desired slurry-like mixture. When being stirred or most preferably vibrated this mixture is applied to heat exchanging surfaces provided with heat conducting reinforcement in the heat exchanger unit.

[**0040**] During a gradual reduction of the atmospheric pressure around the region including the slurry-like substance applied to the heat exchanger surfaces at the same time as a gradual increase of the temperature of this region is produced, the substance is dried to adopt a state which approaches its working molar concentration, i.e. water is made to be released or emitted from the unit. This vacuum drying process preferably occurs at the same time as a gradually increasing force compresses this region and thereby the substance to a homogenous thin layer. Thereby an improvement of the diffusion in the micro-channels of the substance is produced. The method of applying the substance in which it is most preferably vibrated and of performing a final formation by at the same time gradually drying and also compressing the substance maximizes the packing density and thereby the energy density in the substance applied to the heat exchanger structure.

[**0041**] In a preferred geometric layout of the heat exchanger unit and the surfaces thereof for retaining the substance, which layout herein is called the flat self-supporting reactor, this final formation can be made in siru in the very reactor during the final stage in the manufacture. The pressing operation of the final formation is produced from the atmospheric pressure acting on an outer enclosure of the substance, so that the walls of the outer enclosure owing to the self-supporting structure compress all substance layers in the reactor.

[**0042**] In circular or cylindrical reactors having radially arranged heat exchanger surfaces, which thus are located in planes extending through an axis of a reactor, it can be difficult to use substance layers which are sufficiently thin over all of their extension, even though such a geometry has apparent constructional advantages. An alternative could be to have the heat exchanger surface mainly located in radial planes, i.e. in planes perpendicular to the axis of the cylindric shape, such as illustrated by the helical surfaces in U.S. patent **5,440,899** for De Beijer et al. discussed above.

BRIEF DESCRIPTION OF THE DRAWINGS

[**0043**] The invention will now be described by way of non-limiting embodiments with reference to the accompanying drawings in which

[**0044**] **FIG. 1** is a schematic picture of a chemical heat pump,

[**0045**] **FIG. 2***a* is a cross-sectional view of an integrated heat exchanger/substance unit,

[**0046**] **FIG. 2***b* is a perspective view of a self-supporting accumulator having a plurality of heat exchanger/substance units,

[**0047**] **FIG. 3***a* is a schematic cross-sectional view of a chemical heat pump having an accumulator and an evaporator/condenser in the same circular enclosure or housing,

[**0048**] **FIG. 3***b* is a schematic cross-sectional view of a circular substance unit,

[**0049**] **FIG. 3***c* is a perspective view of a portion of a circular substance unit,

[**0050**] **FIG. 3***d* is a view of a detail of a circular substance unit,

[**0051**] **FIG. 4** is a schematic picture of a chemical heat pump as part of an air-conditioning system,

[**0052**] **FIG. 5** is a cross-sectional view of a chemical heat pump used as a cooling element in a refrigerating box, and

[**0053**] **FIG. 6** is a diagram showing vapour pressures of water and of a metal salt as functions of temperature.

DETAILED DESCRIPTION

[**0054**] In **FIG. 1 a** chemical heat pump for producing cooling (refrigeration) or heating is schematically illustrated. The chemical heat pump as illustrated is a closed system and consists of a first container **1** or accumulator containing a substance **2** which can exothermally absorb and endothernally desorb a sorbate, usually water. The first container **1** is coupled to a second container **3**, also called condenser/evaporator, through a fixed gas conduit **4** designed as a pipe connected at its ends to the top sides of the containers. The interior spaces of the containers **1, 4** and the conduit form a closed, leak-proof system. The second container **3** acts as a condenser for condensing a gaseous sorbate **6** to liquid sorbate **5** under endothermal desorption from the solid substance **2** in the first container **1** and as an evaporator of liquid sorbate **5** to gaseous sorbate **6** under exothermal absorption of sorbate in the solid substance **2** in the first container **1**.

[**0055**] The system, i.e. the interior spaces which exist in the first and second containers **1, 3** and the gas conduit **4** and which are in fluid connection with each other, is completely gas tight and is evacuated from all gases other than the gas **6** which is active in the chemical process and which in the preferred case is water vapour. The substance **2** in the accumulator is in a direct contact with the first heat exchanger **7** therein, which in turn through a liquid flow **8** can be supplied with heat from or provide heat to the environment. The liquid **5** in the evaporator/condenser part **3** is in the same way in a direct contact with a second heat exchanger **9** therein, to which heat can be provided from the environment or from which heat can be transported away to the environment through a liquid flow **10**.

[**0056**] In a preferred embodiment of an integrated heat exchanger unit for carrying the active substance which can be suitably used as the heat exchanger **7** in **FIG. 1** and for which unit a cross-sectional view is shown in **FIG. 2***a*, the heat flow and the gas flow are directed perpendicularly to the large exterior surfaces **21** and **21***a* of the heat exchanger. The whole, contiguous parallel surfaces **21, 21***a* which belong to the heat exchanger and are non-permeable to gas and heat exchanger medium and are of for example metal plate are interconnected by a structure such as a crossbar work having channels **22** for an exterior heat exchanger medium through which the heat exchanger medium passes in parallel to the large surfaces. At least on one surface **21** of the heat exchanger a heat transport enhancing structure **25** of metal or other suitable heat conducting material is applied.

[**0057**] The heat conducting structure **25** has "channels" directed perpendicularly to the surface **21** of the heat exchanger, which channels are located in the same direction as the heat and gas transport. The "channels" of this heat transport enhancing structure **25** are flanges which project perpendicularly from the heat transferring surface **21** and are rigidly attached to the surface **21**. If the surface **21** would be made of copper these flanges **25** would be soldered to the surface.

[**0058**] The active solid substance is applied to one surface **21** of the heat exchanger and around the structure **25** enhancing the heat transport, the substance being in the shape of a slurry mixture with water having a larger molar concentration of water than the highest working molar concentration of the substance. By vibrating the thus formed heat exchange/substance unit the mixture is attached to the surface **21** of the heat exchanger and around the structure **25** supporting the heat transport.

[**0059**] The substance layer is at its side opposite the large surface **21** limited by a perforated metal structure such as din perforated metal plate **26** or a metal grating. The gas transport to/from the substance layer **23** occurs through spaces **27** in and at the side of a number of perforated tubular square structures **28** arranged at the exterior surface of the thin perforated plate **26**. In these spaces gas moves mainly in parallel to the large surface **21** of the heat exchanger. The thin perforated plate **26** and the structure **28** at the surface thereof can in some contexts be replaced by metal net structures, not shown, see in addition the discussion hereinafter. Such a net structure can include an interior close-meshed net located directly at the substance and outside it a net having larger or coarser meshes. At the exterior a strong net having a large thickness is arranged which produces transport spaces corresponding to the spaces **27** for transport of gas.

[**0060**] The mixture of substance with water is dried by gradually reducing the pressure around the heat exchanger/substance unit at the same time as the temperature of the substance layer **23** is gradually increased so that extra water and water beyond the highest molar concentration leave the layer and the micro-channel substance in the substance is formed and imnproved. This vacuum drying process is performed at the same time as the substance layer is gradually compressed by a force imparted from the exterior. The dried and compressed substance layer **23** is thereby integrated to a mechanically stable heat exchanger/substance unit which allows a high transport of heat and gas through the layer.

[**0061**] In a preferred embodiment a substance structure **23** and a gas channel structure **27** are arranged on the two opposite large surfaces **21** and **21***a* of the heat exchanger in order to form a double heat exchanger/substance structure having a solid substance at its two large surfaces. Such double heat exchangerlsubstance structures can be placed at each other to form a package, see **FIG. 2***b*, having an exterior tight enclosure of for example thin metal plate, not shown. When the interior of the enclosure is then connected to a vacuum, because of the air pressure the walls of the enclosure will compress the heat exchanger/substance structures located therein, in particular in the x-direction, provided that the heat transport enhancing structure **25** is not completely rigid but can yield a little. It is used in the drying process and the final formation of the substance layer **3**. The accumulator becomes self-supporting in x-, y-and z-directions at the same times as advantageous properties of the transport of heat and gas are obtained by the final formation.

[**0062**] The structure **25** has a depth of about 10 mm in a preferred embodiment suited for room air-conditioning comprising charging at daytime and cooling at night. The flanges or “channels” in these structures **25** are located at a distance of about 5 to 10 mm from each other.

[**0063**] The perforated plate **26** (which as has been mentioned above can be replaced by a o grating) supports, in the drying and pressing processes, the heat transport enhancing structure **25** and distributes the forces between the individual packages so that this structure in each package becomes self-supporting. The term “self-supporting” is herein taken to mean that the whole mechanical structure, without considering the salt or substance, can withstand the forces from the walls of the container when a vacuum is applied. As has been mentioned above the structure yields in the process when the “packages” are pressed to each other and the plates **26** strongly press against the flanges **25** and the substance located therebetween. The substance has in the moulding process, before the packages are subjected to a vacuum for drying, expanded outwards towards the plate **26** in the possible free space existing between the “packages” in this state. Thereby the substance is compressed. The perforated plate or net has so fine or close meshes that crystals or sintered aggregates of crystals of the substance cannot pass the holes therein. Between these crystals or aggregates, in the compressing process, some interspaces are maintained which allow a sufficient transport of gas.

[**0064**] The substances which can be used in a heat exchanger in a chemical heat pump are to react with water to contain water bonded as water of crystallization which can be rather easily emitted from the substance, for moderate increases of the temperature. Such substances typically include various metal salts. Substances which have been mentioned in the literature to be used in chemical heat pumps or which actually have been used in heat pumps include, as has been mentioned above, calcium chloride $CaCl_2$, magnesium chloride $MgCl_2$, lithium chloride LiCl and sodium sulphide Na_2S. In order to work well in a solar driven heat pump using water as a volatile medium a substance must have, within a selected suitable temperature range such as a temperature range of about 0-100° C., where the upper temperature in some cases can be lower, the following characteristics according to the discussion above:

[**0065**] 1. The substance must have a ΔT in the range of about 20-40° C.

[**0066**] 2. The substance is to react with water vapour at phase transitions having ΔT:s close to each other.

[**0067**] 3. The substance must at all instances in the course of the process remain in a solid state, this implying a melting point above 100° C. in the preferred case. In some cases somewhat lower melting points can be allowed.

[**0068**] 4. The substance is not allowed to sublimate.

[**0069**] 5. The substance must be chemically stable in the reaction with water vapour.

[**0070**] 6. The substance is not allowed to emit other gases than water vapour.

[**0071**] 7. The substance must be mechanically stable and is not allowed to change its structure as time passes or have significant changes of its outer shape when it absorbs and emits water vapour.

[**0072**] 8. The substance must have a high reactivity with water vapour, i.e. react rapidly, and maintain the high reactivity as time passes, for as many cycles as possible.

[**0073**] 9. The substance must have an energy content of at least 0.15 kWh/l and preferably more.

[**0074**] 10. The substance must be capable of being rigidly applied to surfaces of heat exchangers and is not allowed ta have, as time passes, an aptitude to be detached therefrom.

[**0075**] Another requirement is that the substance is not allowed to deliquesce. In discharging, generally, a first crystal phase A is transformed to a second phase B. This occurs at a definite vapour pressure. For example, if the substance is maintained at 30° C. and its melting point is 80° C., nothing particular occurs. However, when the discharging process approaches its end and all the substance in the first phase A has been consumed and is transformed to the second phase B it can occur that water still is in the evaporator and that a third phase C, considering the vapour pressure, is allowed to be formed, i.e. the conditions in regard of temperature and pressure for this transition are fulfilled. Furthermore, the third phase C can be liquid at 30° C. instead of solid. Then a risk of deliquescing exists. All of the substance in solid form can now become liquified and melt. Such a risk can exist also in the middle of a discharging process when partially or locally some portion of the substance fulfils the conditions for stransition to the third liquid phase C. When loading the substance by trying to cool it significantly beneath its normal balance in order to achieve as much power as possible, in this case down to 30° C., no such liquid phases are allowed. The condition that the substance is not allowed to deliquescence can in short be termed in the way that at the actual temperatures no risk is allowed that the substance spontaneously becomes dissolved when it is exposed to an to unlimited amount of water vapour.

[0076] For heat pumps for other applications naturally all of the criteria listed above are not applicable even though in many cases corresponding criteria can be used having adapted boundary values within the temperature ranges valid for such heat pumps.

[0077] A large number of different metal salts which can absorb water of crystallization have been studied in regard of the different characteristics mentioned above. Primarily the characteristics according to the points 1 and 2 have been studied. Secondarily, the conditions of not too low melting points and chemical stability according to the points 3, 4 and 5 have been observed. Thirdly, the condition including not too small energy contents according to point 9 has been studied. Thereupon the condition of the reaction kinetics according to point 8 has been studied. Data for different substances in regard of the characteristics according to the points 1-5 partly exist in the literature. A comparison to the desired characteristics leaves a small number of substances which fulfils the conditions and for which supplementing measurements have been made in the sequential order mentioned.

[0078] Among the known substances, sodium sulphide is eliminated to be used in a solar driven heat pump both due a too high ΔT of 58° C. (characteristic 1), and due to a lacking chemical stability (characteristic 5). In a reaction with water vapour the equilibrium is displaced so that production of hydrogen sulphide H_2S cannot be avoided. This gas will then permanently exist in the system and be accumulated so that an intermittent pumping away of the gas becomes necessary. If the vapour pressure of this gas which is not desired in the reaction becomes too high, the reaction speed of the water vapour with the substance in the discharging process (when the substance absorbs water) is affected and similarly the reaction speed of the water vapour in the charging process (when the substance emits water). Calcium chloride is eliminated due to a too low melting point (characteristic **3**). Magnesium chloride is eliminated due to the fact that it has a too high ΔT (54° C.) in the primarily possible phase transition from 4 to 6 water molecules per molecule chloride.

[0079] The following substances which could be imagined to have the characteristics 1-10 according to the discussion above were found after literature studies:

[0080] CrF_2, FeF_2, FeF_3, CoF_2, CoF_3, Ni_2, LiCl, $MgCl_2$, $SrCl_2$, $BaCl_2$, $CoCl_2$, $SrBr_2$, $BaBr_2$, NaI, BaI_2, MnI_2, FeI_2, LiOH, NaOH, KOH, $Sr(OH)_2$, $Ba(OH)_2$, Na_2CO_3, K_2CO_3, Li_2S, $MgSO_3$, $CaSO_3$, $CoSO_3$, $NiSO_4$, $FeSO_4$, Li_2SO_4, $MgSO_4$, $MnSO_4$, $CoSO_4$, $Mg(NO_3)_2$, $NiCl_2$, $NH_4Al(SO_4)_2$, $KAl(SO_4)_2$.

[0081] Strontium chloride $SrCl_2$ and cobalt chloride $CoCl_2$ could be determined to have the characteristics 1-9 from literature studies. However, strontium chloride is eliminated since the literature data proved to be erroneous. The indicated value of ΔT of 20° C. is instead in the vicinity of 15° C.

[0082] Magnesium sulphate $MgSO_4$ could be determined to have all characteristics except 8. In tests it proved to have a reduced reaction speed in discharging, i.e. in absorbing water. This fact later appeared to be generally valid for all tested sulphates beside lithium sulphate.

[0083] Several of these remaining substances were eliminated for different reasons in tests performed therewith:

[0084] The fluorides of chrome, iron and cobalt thus turned out to have large reductions of reaction speeds, i.e. the interesting processes of absorbing water of crystallization occur very slowly.

[0085] $MgCl_2$ has a too high ΔT and $SrCl_2$ as a too low ΔT in the interesting phase transitions as has already been mentioned.

[0086] $BaCl_2$ has a suitable ΔT in phase transitions of 0-1 H_2O and 1-2 H_2O but it has a too small energy content due to the large molecular weight of barium.

[0087] $BaBr_2$ has a too small energy content in the interesting phase transition I - **2** H_2**0**.

[0088] For BaI_2 the corresponding condition is valid in the transition of 1-2.5 H_2O.

[0089] MnI_2 in the transition of 4-6 H_2O has an unknown melting point and a suitable ΔT=27° C. has never been tested. However, manganese is costly, the energy content is theoretically too small and iodides generally are not stable since they emit iodine gas.

[0090] FeI_2 in the transition of 2-4 bonded water molecules has a melting point of 98° C. and its ΔT is unknown. However, it has never been tested since it follows from general reasons that its energy content is too small. In addition, as has been mentioned, iodides are not chemically stable.

[0091] NaOH has a suitable ΔT but has a too small melting point of about 60° C. and deliquesces extremely easily.

[0092] The corresponding facts are valid for KOH.

[0093] Na_2CO_3 and K_2C0_3 have a too low and a suitable ΔT respectively but they have too small energy contents and an extremely large risk of deliquescing.

[0094] Sulphites of Mg, Ca and Co have large reductions of reaction speeds.

[0095] Sulphates of Ni, Fe, Mg, Mn and Co have very large reductions of reaction speeds in the same way as most sulphates as has been mentioned above.

[0096] Li_2SO_4 is a good substance in most respects having a melting point exceeding 100° C. and a ΔT of 20° C. but it has a too small energy content in the interesting phase transition of 0-1 bonded water molecules.

[0097] $Mg(NO_3)_2$ has a too small ΔT (17° C.) in the interesting phase transition of 4-6 H_2O and in addition a too small energy content.

[0098] Vapour pressure measurements were performed for the following selected substances:

[0099] $Ba(OH)_2$, Li_2S, LiOH, LiCI, NaI, $Sr(OH)_2$, $SrBr_2$, $NiCI_2$, NiF2.

[0100] The vapour pressure measurement was executed by drying the respective substance in glass equipment at about 95° C. in a thermostatic bath using a vacuum pump. After cooling to ambient temperature the substance was allowed to absorb a definite quantity of water vapour and the vapour pressure was measured after an equilibrium had occurred. The temperature was then recorded and the weight of the substance was determined. The procedure was repeated over all of the temperature range which is of interest for a solar driven heat pump according to the discussion above. Among other things curves were obtained which illustrate the temperature as a function of moles of water per mole metal salt.

[0101] Results:

[0102] $Ba(OH)_2$ proved to have three phase transitions: 0-0.5 H_2O having a ΔT>80° C., 0.5-1.5 H_2O having a ΔT=65° C., 1.5-8 H_2O having a ΔT=19° C. Only the last mentioned one of these can be used in a solar driven heat pump.

[0103] Li_2S proved to have three phase transitions: 0-2 H_2O having a ΔT=21° C., 2-3.5 H_2O having a ΔT=15° C., 3.5- X H_2O having a ΔT=11° C., where X is an unknown number larger than 3.5.

[0104] $Li(OH)_2$ proved to have two phase transitions: 0-0.65 H_2O having a ΔT=25° C., 0.65 1-H_2 having a ΔT=15° C.

[0105] LiCl proved to have three phase transitions: 0-1 H_2O having a ΔT60° C., 1-2 H_2O having a ΔT=30° C., 2-3 H_2O having a ΔT=26° C.

[0106] NaI proved to have two phase transitions: 0-1 H_2O having a ΔT=33° C., 1-6 H_2O having a ΔT=13° C.

[0107] $Sr(OH)_2$ proved to have three phase transitions: 0-1 H_2O having a ΔT=33° C., 1-6 H_2O having a ΔT=14° C., 6-8 H_2O having a ΔT=3° C.

[0108] $SrBr_2$ proved to have two phase transitions: 0-1 H_2O having a ΔT=130° C., 1-6 H_2O having a ΔT=35° C.

[0109] $NiCI_2$ has three phase transitions according to literature data: 0-2 H_2O having a non-measured ΔT, 2-4 H_2O having a ΔT=20° C., 4-6 H_2O having a ΔT=10° C. However, in the measurement an eguilibrium could not be obtained within a reasonable time period.

[0110] $NiFl_2$ has a phase transition 0-4 H_2O according to literature data without any measured ΔT. In a measuring process an equilibrium could not be obtained within a reasonable time period.

[0111] From these and other measurements and for different other reasons the following evaluation was obtained:

[0112] Barium hydroxide $Ba(OH)_2$ can according to the discussion above be used in the phase transition 1.5-6.5 H_2O having a ΔT=20° C., However, barium hydroxide is toxic.

[0113] Lithium sulphide Li_2S is impaired by chemical instability and can when absorbing water form lithium hydrogen sulphide LiHS. Lithium hydroxide LiOH can according to the discussion above be used in the phase transition 0-0.65 H_2O and a ΔT=25° C.

[0114] Lithium chloride LiCl proves to become too easily dissolved, i.e. the risk of deliquescence is too high. A transition to liquid state is obtained for 1.7 moles water per mole salt.

[0115] Sodium iodide Nal has an absorption of at most 1 mole water per mole salt in the interesting range. Furthermore Nal deliquesces already for 1 mole water per mole salt, and thus it is not suitable. Furthermore, as has been pointed out above, iodides are chemically instable and can form iodine gas.

[0116] Strontium hydroxide $Sr(OH)_2$ (ΔT=33° C.) has also an absorption of at most 1 mole water per mole salt in the interesting range, which makes it less suitable due to its high mole mass which results in its energy content being too small. In addition $Sr(OM)_2$ has in its phase transition having 1-6 bonded water molecules a too small ΔT.

[0117] Strontium bromide SrBr, can according to the discussion above be used in the phase transition 1-6 H_2O and ΔT35° C. but some risk of deliquescence exists.

[0118] Nickel chloride $NiCl_2$ and nickel fluoride $NiFl_2$ cannot cope with the requirement on reaction velocity.

[0119] Li_2S is eliminated in spite of having a suitable ΔT and a suitable energy content in the transition 0 to 2.5 bonded water molecules due to the risk of forming H_2S and a too low melting point and a risk of deliquescence.

[0120] For the remaining substances barium hydroxide, lithium hydroxide and strontium bromide the energy contents were calculated for the interesting phase transitions. The energy content was determined to be 0.23, 0.15 and 0.25 kWh/l, respectively, without slurry packaging.

[0121] Cobalt chloride CoC_22-6 H_2O having a melting point of 86° C. proved in tests to have very good characteristics with a ΔT of 20-22° C. The melting point can be too low in some applications. Moreover, this substance is very costly.

[0122] Example 1a. 598 g barium hydroxide (octahydrate) having a purity of 98%, quality “Puriss”, was mixed with 194 g water, i.e. 5.7 moles H_2O per mole $Ba(OH)_2$-$8H_2O$, so that a sem-liquid or thickly flowing mass, a slurry, was obtained. This means a concentration of 5.7 moles above the most hydrated state of the salt. The mass will thus only be liquified when being stirred or vibrated. It was at ambient temperature applied to an heat exchanger surface of the type shown in **FIG. 2** during a simultaneous vibration obtained from a vibrator which was the same type as being used in moulding concrete but having smaller dimensions and which was held in contact with the heat exchanger. The vibrations had a frequency of 25 to 50 Hz. Then, the substance flew easily and was deposited in the interspaces in the heat exchanger structure. A thin meal plate enclosure was applied around the heat exchanger and it was connected to a vacuum pump. This was allowed to pump air and water away during a simultaneous heating. Typical data was that the pumping was made down to the equilibrium vapour pressure of the substance of about 20 mm Hg at 20° C. for about 240 minutes with a smooth temperature increase from ambient temperature to 80° C. when the pumping away was finished. The tight plate enclosure was removed. The mass was found to be well sintered together and to be rigidly attached to the surface of the heat exchanger. A part of the mass was taken out which was found to contain hydroxide having the formula $Ba(OH)_2$ $1.5H_2O$. The density of the mass was determined to be 861 g/l, which is significantly larger than the density of the correspondingly dryly packed substance, which for this amount of water of crystallization is 619 g/l, see Example 1b. In spite of the high degree of packing as proved by the measured density of **81** gil the porosity is good. The density of crystalline $Ba(OM)_2$ $1.5H_2O$ is 1.37 g/l, and thus the remaining porosity still constitutes 36% of the volume. The heat exchanger including the attached substance was then allowed to execute 10 cycles including absorption of water and heating to 80° C. for eliminating water, placed in a heat pump according to **FIG. 1**. The mass appeared to have no signs of being detached from the surface of the heat exchanger— no cracks or cavities were produced at this surface in the substance. The mass absorbed and emitted water without reductions of the reaction speed as time passed according to the following: completely charged after 4 hours, completely discharged after 30 hours. The reaction speed was maintained without any noticeable chance for all of the cycles. The effective value of the energy content was measured to be 0.32 kWh/l.

[0123] Example 1b. 430 g barium hydroxide (octahydrate) having a purity of 98%, quality "Puriss", was ground to a fine grain powder and was screened through steel cloth of 300 mesh. The screened powder was applied at ambient temperature when being vibrated, in the same way as in Example 1a, to the surface of the heat exchanger according to **FIG. 2**. Then the substance was applied in the interspaces in the heat exchanger structure. The substance was sintered by drying and heating to a mass in the same way as in Example 1a. The mass was thereupon found to be well sintered together and be rigidly attached to the surface of the heat exchanger. A part of the mass was taken out which was found to contain hydroxide having the formula $Ba(OH)_2$-$1.5H_2O$. The density of the mass was determined to be 619 g/l which gives a porosity of 50% of the volume of crystalline $Ba(OH)_2$ $1.5H_2O$. The heat exchanger including the attached substance was then made to execute 10 cycles including absorption of water and heating to 80° C. for eliminating water, placed in a heat pump according to **FIG. 1**. The mass appeared to have indications of being detached from the surface of the heat exchanger. The mass absorbed and emitted water without reduction of the reaction speed but the time for obtaining a complete charging was now prolonged to **6** hours. The time up to a complete discharge was 30-40 hours. The reaction speed was maintained without any noticeable change for all the cycles. The effective value of the energy content was measured to be 0.23 kWh/l.

[0124] Example 2a. 670 g $CoCl_2 \cdot 6H_2O$ having a purity of 99% and a quality "pro analysi" was mixed with 127 g water, i.e. 1.75 moles H_2O per mole $CoCl_2$ $6H_2O$, so that a semi-liquid or thickly flowing mass, a slurry, was obtained, This means a concentration of 1.75 moles above the most hydrated state of the salt. The mass was applied at ambient temperature when being vibrated, in the same way as in Example 1a, to the heat exchanger surface according to **FIG. 2**. Then the substance became easily flowing and was deposited in the interspaces in the heat exchanger structure. The substance was sintered by drying and heating to a solid mass in the same way as in Example 1a. The mass was thereafter found to be well sintered together and to be rigidly attached to the surface of the heat exchanger. A part of the mass was taken out which was found to contain hydrated salt having the formula $CoCl_{2,}$ $2H_2O$. The density of the solid mass was measured to be 900 g/l, which is larger than the density 635 g/l of the corresponding dryly packed substance, see Example 2b. The mass has a porosity of 33% compared to the crystalline form of the corresponding hydrate which has a density of 1.34. The heat exchanger including the attached substance was then made to execute 10 cycles including absorption of water and heating to 80° C. for eliminating water when it was placed in a heat pump according to **FIG. 1**. The mass had no indications of being detached from the surface of the heat exchanger. The mass absorbed and emitted (desorbed) water without any reduction of reaction speed. The effective value of the energy content was measured to be 0.25 kWh/l.

[0125] Example 2b. 473 g $CoCl_2 \cdot 6H_2O$ (hexahydrate) having a purity of 99% and of quality "pro analysi" was ground to a fine grain powder and was screened through a steel cloth of 300 mesh. The screened powder was applied at ambient temperature when being vibrated, in the same way as in Example 1a, to the surface of the heat exchanger according to **FIG. 2**. Then the substance was deposited in the interspaces in the heat exchanger structure. The substance was sintered by drying and heating to a solid mass in the same way as in Example 1a. The mass was then found to be well sintered together and to be rigidly attached to the surface of the heat exchanger. A part of the mass was taken out which was found to contain hydrated salt having the formula $CoCl_2 \cdot 2H_2O$. The density of the solid mass was measured to be 635 g/l. The mass has a porosity of 33% compared to the crystalline form of the corresponding hydrate which has a density of 1.34. The heat exchanger including the attached substance was then made to perform 10 cycles including absorption of water and heating to 80° C. for removing water when it was placed in a heat pump according to **FIG. 1**. The mass proved to have indications of being detached from the surface of the heat exchanger. The mass absorbed and emitted water without any reduction of the reaction speed. The effective value of the energy content was measured to be 0.21 kWh/l. Example 3a. 302 g LiH-$0.65H_2O$ having a purity of 98% and of quality "purum" was mixed with 167 g water, which corresponds to 1.1 moles H_2O above the most hydrated state of the salt, so that a semi-liquid or thickly flowing mass, a slurry, was obtained. The mass was applied at ambient temperature when being vibrated, in the same way as in Example la, to the surface of the heat exchanger according to **FIG. 2**. Then the substance became easily flowing and was deposited in the interspaces in the heat exchanger structure, The substance was sintered by drying and heating to a solid mass in the same way as in Example 1a. The mass was then found to be well sintered together and to be rigidly attached to the surface of the heat exchanger. A part of the mass was taken out which was found to contain the salt LiOH without any water of crystallization. The density of the solid mass was measured to be 513 g/l which is larger than the density 487 g/l of the correspondingly dryly packed substance, see Example 3b. The mass then has a volume porosity of 67% compared to the crystalline form of the salt, which has a density of 1.46. The heat exchanger including the attached substance was then made to execute 10 cycles including absorption of water and heating to 80° C. for emitting water when it was placed in a heat pump according to **FIG. 1**. The time for a complete charging process amounted to 4 hours whereas a complete discharging lasted 24 hours. The mass proved to have no indications of being detached from the surface of the heat exchanger. The mass absorbed and emitted water without any reductions of the reaction speed. The effective value of the energy content was measured to be 0.16 kWh/l.

[0126] Example 3b. 287 g $LiH-0.65H_2O$ having a purity of 98% and of quality "purum" was ground to a fine grain powder and was screened through a steel cloth of 300 mesh. The screened powder was applied at ambient temperature when being vibrated, in the same way as in Example 1a, to the surface of the heat exchanger according to **FIG. 2**. Then the substance was deposited in the interspaces in the heat exchanger structure. The substance was sintered by drying and heating to a solid mass in the same way as in Example 1a. The mass was then found to be well sintered together and be rigidly attached to the surface of the heat exchanger. A part of the mass was taken out which was found to contain the salt LiOH having no water of crystallization. The density of the solid mass was measured to be 487 g/l, which corresponds to a volume porosity of 71% compared to the crystalline form of the salt. The heat exchanger including the attached substance was then made to perform 10 cycles including absorption of water and heating to 80° C. for removing water when it was placed in a heat pump according to **FIG. 1**. The time for a complete charging process comprised like the salt applied in a slurry shape 4 hours whereas the time for complete discharging was increased to 27 hours. The mass proved to have very weak indications of being detached from the surface of the heat exchanger. The mass absorbed and emitted water without any reduction of reduction speed. The effective value of the energy content was measured to be 0.15 kWh/l.

[0127] Example 4a. 883 g $SrBr_2-6H_2O$ having a purity of 99% and of quality "puriss.p.a." was mixed with 132 g water which corresponds to 2.48 moles H_2O above the most hydrated state of the salt so that a semi-liquid or thickly flowing mass, a slurry, was obtained. The mass was applied at ambient temperature when being vibrated, in the same way as in Example la, to the surface of the heat exchanger according to **FIG. 2**. Then the substance became easily flowing and was deposited in the interspaces in the heat exchanger structure. The substance was sintered by drying and heating to a solid mass in the same way as in Example 1a. The mass was then found to be well Sintered together and be rigidly attached to the surface of the heat exchanger. A part of the mass was taken out which was found to contain the hydrated salt $SrBr_2-H_2O$. The density of the solid mass was measured to be 1492 g/l which is larger than the density 1044 g/l of the corresponding dryly packed substance, see Example 4b. The mass then has a volume porosity of 17% compared to the crystalline form of the salt which has a density of 1.79. The heat exchanger including the attached substance was then made to perform 10 cycles including absorption of water and heating to 80° C. for emitting water when it was placed in a heat pump according to **FIG. 1**. The time for a complete charging process comprised 4 hours whereas a complete discharging lasted 16 hours. The mass proved to have no indications of being detached from the surface of the heat exchanger. The mass absorbed and desorbed water without any reduction of the reaction speed. The effective value of the energy content was measured to be 0.32 kWh/l.

[0128] Example 4b. 618 g $SrBr_2-6H_2O$ having a purity of 99% and of quality "puriss.p.a." was ground to a fine grain powder and was screened through a steel cloth of 300 mesh. The screened powder. was at ambient temperature when being vibrated applied in the same way as in Examnple 1a to the surface of the heat exchanger according to **FIG. 2**. Then the substance was deposited in the interspaces in the heat exchanger structure. The substance was sintered by drying and heating to a solid mass in the same way as in Example 1a. The mass was then found to be well sintered together and rigidly attached to the surface of the heat exchanger. A part of the mass was taken out which was found to contain the hydrated salt $SrBr_2$ H_2O. The density of the solid mass was measured to be 1044 g/l which corresponds to a volume porosity of 24% compared to the crystalline form of the salt. The heat exchanger including the attached substance was then made to perform 10 cycles including absorption of water and heating to 80° C. for removing (desorbing) water when it was placed in a heat pump according to **FIG. 1**. The time for a complete charging comprised 4 hours whereas the time for complete discharging was prolonged to 20 hours. The mass appeared to have indications of being detached from the surface of the heat exchanger. The mass absorbed and emitted water without any reduction of the reaction speed. The effective value of the energy content was measured to be 0.23 kWh/l.

[0129] $CaCl_2$ is an example of a substance which has suitable ΔT-values and a sufficiently large energy content but which is incapable of forming a slurry. The melting point of the usable phase transitions of this salt is lower than what is required to regenerate the substance after filling the slurry in the heat exchanger structure.

[0130] This is also true for many of the substances which have been sorted away above, such as LiCl, Lirr, $CaBr_2$, $FeCl_3$, NaOH, KOH, etc. It is the sum of all the characteristics required above which makes a substance both to work in the process and to be suited to filling and formation according to the slurry method. Most substances can form a slurry but they cannot be regenerated after applying the slurry.

[0131] In the application for solar driven air conditioning the reactor part and the condenser/evaporator part can suitably be located inside the same physical space or enclosure, see the schematic cross-sectional view of **FIG. 3***a*. The parts can also have a circular or cylindrical geometry or symmetry even though some advantages of the flat structure according to **FIGS. 2***a* and **2***b* cannot be obtained. Thus, a common tank **31** encloses all of the system so that a complete hermetic, evacuated chemical heat pump is obtained therein. The tank **31** is internally partitioned in two separate departments. A first upper department **32** accommodates the accumulator and constitutes the reactor and in a second department **33** located thereunder the condenser/evaporator is provided. In the accumulator part **32** a heat exchanger **34** is placed concentrically along the interior circumference of the tank **31**. The heat exchanger **34** can be single or as is illustrated in **FIG. 3***a* consist of a plurality of concentrc units **34***a*, **34***b* as seen from the centre of the tank so that each unit has the shape of a cylinder ring. Each unit in the heat exchanger **34** is flange type and comprises vertically standing lamellae **35**, see **FIG. 3***b*, which thus are located in planes extending through the axis of the cylindrical shape and are mounted in a fan shape on the heat carrier **36** of the heat exchanger, see the perspective view of **FIG. 3***c*. These heat carriers **36** are constituted of horizontal loops of piping which are coupled in parallel to each other and form circular pipe loops also having the same axis as the other parts of the heat pump. Around the heat exchanger units or packages **34** nets **37** are stretched on both the exterior side and the interior side and over the bottom thereof. Between the net walls **37** the substance **38** has been filled. Furthermore, it is assumed that substance **38** moulded between the lamellae **35** has a free gas flow into it and away from it, respectively, through channels **45** parallel to the lamellae, see **FIG. 3***d*.

[**0132**] The channels **45** can be obtained by a coarse mesh net which on its two opposite surfaces or sides has close mesh nets. The coarse mesh net is bent to a suitable shape and it is applied supported by the flanges **35**. The coarse mesh net forms the channels **45** whereas the close mesh net prevents the substance in slurry shape from flowing into the channels when filling the substance from above.

[**0133**] In this cylindrical heat exchanger the surfaces of the flanges **35** correspond to the large exterior surface **21** of the heat exchanger for the flat case illustrated in **FIG. 2***a*. The heat conduction in the substance is actually so low that the flanges connected to the pipe including the heat carrier in this context can be considered to have the same temperature and the same temperature as the pipe. The substance layer between the flanges and the channel **45** have a thickness of about 10 mm, i.e. in a direction perpendicular to the flanges and circumferentially in all of the heat exchanger ring. A heat conducting structure corresponding to the structure **23** is not provided in the embodiment having cylinder symmetry. Such a structure is required only for very high power. In an application for room conditioning charging can comprise at least **6** hours whereas discharging occurs during perhaps up to 12 hours. Tests show that it in this case is sufficient to have **10** mm thick layers in direct contact with metal surfaces without any extra heat conducting structure and that the metal surfaces do not have to be in direct contact with the heat carrying medium but can be of the type lamellae such as the flanges **35**. An easily obtained compression of the substance by evacuating the tank cannot be obtained in the cylinder symmetrical case.

[**0134**] For a heat exchanger made as a plurality of concentric cylinder rings according to **FIG. 3***a* the central part of the tank cannot be used what gives some dead volume. For a case in which half the radius of the tank is used for the heat exchanger packages it is realized that they take ¾ of the volume of the tank. However, the remaining central space does not have to be filled with a heat exchanger package but this space is used for transport of gras and prevents in an excellent way pressure losses in the system, between the reactor and the condenser/evaporator.

[**0135**] If one instead applies a heat exchanger/substance package having an outer shape like a rectangular block having a square cross-section in a cylindrical tank and thereby maximally uses the central region of the tank one obtains in the same way a filling degree of ¾ of the volume of the tank and the remaining four spaces are good spaces for transport of gas.

[**0136**] An inlet and an outlet **39** of the heat exchanger supplies or removes respectively heat through the outer heat exchanger medium. Between the accumulator part **32** and the condenserlevaporator part **33** a partition wall **40** is provided having a hole located centrally in the tank **41**. The condenserjevaporator part **33** consists of a cylindrical plate heat exchanger **41** connected to inlets or outlets **43** for supplying and removing heat through an exterior medium. The liquid which in this case is water **42** occupies the bottom of the tank **31**. On the surfaces of the heat exchanger **41** at least on one side a capillary sucking material has been applied. When the accumulator is delivered to the user, all of the water is bonded to the substance in the accumulator part **32**. The accumulator is then in a discharged state.

[**0137**] In an application intended for air-conditioning for example at night the function is as follows. Hot water produced in a solar heat exchanger is at day-time supplied to the heat exchanger **34** of the accumulator **32** through the inlet and outlet terminals **39**. At the same time water is supplied for which an exchange of heat with the ambient air is made, to the heat exchanger **41** of the condenserlevaporator **33** through the inlets and outlets **43** respectively thereof for the exterior medium. The vapour pressure of the substance **38** then increases and finally reaches a pressure which is higher than the vapour pressure of the water at the heat exchanger **41** of the condenser/evaporator **33**. Vapour then flows from the substance **38** to the heat exchanger **41** of the condenser/evaporator **33** and condenses to water **42**. The process continues until all of the water of the used substance in the used phase transition has been emitted. All of the water **42** has then been condensed in the condenser/evaporator part **33** and the condensation heat has been removed through the heat exchanger **48** to the outdoor air by the liquid flow through the heat exchanger **41**.

[**0138**] At night the heat exchanger **41** of the condenser part/evaporator part **33** is through the liquid flow therethrough connected to the room heat exchangers of the house at the same time as the heat exchanger **44** of the accumulator part **32** is through its liquid flow coupled to an outdoor heat exchanger. The substance **38** is then kept at the same temperature as the outdoor air, its vapour pressure remalning very low. Owing to the low vapour pressure water vapour now flows from the heat exchanger **41** of the condenser part/evaporator part **33** to the substance **38** of the accumulator part **32**. Vaporization energy is then- consumed in the heat exchanger **41** of the condenser part/evaporator part **33**, which energy is taken from the rooms through the liquid flow between the heat exchanger **41** of the condenser part/evaporator part **33** and the room coolers. The rooms are cooled. The supplied vaporization energy accompanies the vapour and is released together with bonded chemical energy in the substance **38** of the accumulator part **32** and is removed through its heat exchanger **34** to the outdoor air through the liquid flow **39** between the heat exchanger **34** and the outdoor heat exchanger.

[**0139**] In order that the operation of the air conditioning system will be completely understood its method of operation will be further explained with reference to the schematic picture of **FIG. 4**. The chemical heat pump is in **FIG. 4** divided in an accumulator **32** and a condenser/evaporator **33**. External components in the complete air-conditioning system are a solar panel **53**, outdoor heat exchanger **54**, room coolers **55**, accumulator pump **56**, condenser/evaporator pump **57**, accumulator valve **58** and condenser/evaporator valve **59**. In charging at daytime the accumulator valve **58** is set so that the accumulator pump **56** drives the flow from the solar panel **53** to the accumulator **32**. At the same time the condenser/evaporator valve **59** is set so that the condenser/evaporator pump **57** drives the flow from the outdoor heat exchanger **54** through the condenser/evaporator **33**. The substance in the accumulator **32** then supplies water vapour to the condenser/evaporator **33** until the substance is completely charged with absorbed water.

[**0140**] At night the accumulator valve **58** is set so that the accumulator pump **56** drives the flow through the outdoor heat exchanger **54**. At the same time the condenserlevaporator valve **57** is set so that the condenser/evaporator pump **57** drives the flow from the room coolers **55** through the condenser/evaporator **33**. Then the substance in the accumulator **33** is maintained at outdoor temperature and then the vapour pressure over the substance becomes significantly lower than the vapour pressure in the evaporator/condenser **3**, which "is heated" by the air coolers **55**. Water vapour now flows from the condenser/evaporator **33** to the substance in the accumulator **32**. Vaporization energy is then transported from the air coolers **55** to the substance in the accumulator **32** and further on to the outdoor heat exchanger **54**. The rooms are cooled and the process continues until the substance in the accumulator **32** has absorbed all the water in the phase transition used for the used substance.

[**0141**] The fact that the tank which encloses the accumulator and the evaporator/condenser has a cylindrical shape is advantageous from strength reasons. Furthermore, the heat exchangers can advantageously be made as substantially conventional lamella heat exchangers for liquid/gas having a straight pipe loop. This gives heat exchanger packages having an exterior rectangular shape. The heat transfer is in such packages determined by how densely the lamellas are placed. The packages can for example have the dimensions of 400×500×50 mm. The packages are thus thin in order to facilitate gas transport to and from the substance. To some extent in such packages one can deviate from the rule that heat and gas should flow in the same direction. The packages coincide with the cylinder rings according to **FIGS. 3***a*-**3***d* except the pipe **36** being straight, the flanges **35** all being parallel and the channels **45** for gas transport missing. The number of such passages enclosed in nets can be connected in parallel and be filled with substance from above like the embodiment of **FIG. 3***a*.

[**0142**] The chemical heat pump proposed herein can also be used for direct cooling purposes. It is completely possible to cool small spaces like refrigerators or refrigerating boxes for a long time. A cooling box for transport of food or medicine and having a capacity for operating for several nights and days will now be described with reference to **FIG. 5**.

[**0143**] The chemical heat pump illustrated in **FIG. 5** is integrated with a lid of the cooling box, which is constructed in a way similar to the tank **31** of **FIG. 3***a*. The lid thus has a cavity and in the interior space in the upper portion of the lid the accumulator **71** is provided which is attached to the exterior surface of the lid and in the lower part of the interior space the condenser/evaporator **72** is provided and attached to the lower surface facing the cold space of the cooling box. The accumulator **71** and the condenser/evaporator **72** are two flat, low metal containers preferably made of thin stainless steel plate, connected to each other through a centrally located tubular conduit **73** for gas transport between the accumulator **71** and the condenser/evaporator **72**. They are, as to heat, separated from each other by means of a layer of heat isolating material **74** located between the accumulator part and the condenser/evaporator part. Further, the accumulator **71** is divided in two spaces, an upper space containing the substance **75** and a flange heat exchanger **76** and a lower space containing support flanges **77** made of perforated metal plate. The two spaces are separated by a close-meshed net **78**. The flange heat exchanger **76** distributes heat from an electric immersion heater **79** inserted in an heat exchanger pipe **80** connected to the flanges in the flange heat exchanger **76**, and forms together with the support flanges **77** in the lower part of the accumulator a support against the force of the air pressure acting on the structure. The condenser part/evaporator part **72** is filled with perforated support flanges **81** which also have the task of supporting this structure against the force of the air pressure and to conduct heat. Between the support flanges **81** a capillary sucking material **82** has been arranged, for example a cellulose material, in which the water **73** is prevented from moving freely. Evacuation of the interior space of the lid is made through a "tip-off" nipple **84** of the type used for closing for example refrigerator installations.

[**0144**] The structure is made as two low boxes of stainless steel welded to each other through the tubular central connection **73**. The heat exchanger **76**, the net **78** and the support flanges **77**, **81** are placed in the boxes and the substance **75** is filled in the accumulator **71**. Lids **85**, **86** of stainless steel are welded to the two parts by means of welding joints **87**, **88** around the Deripherv, one lid **85** of which faces upwards and forms the uDDer surface of the lid of the cooling box and the other lid **86** of which faces the interior of the cooling box. The lid of the cooling box is charged before use by means of the built-in electric immersion heater **79**. The underside of the lid which faces the space which is to be cooled and which in this case serves as a condenser can preferably be placed for example on a sink in a kitchen. An isolating casing is placed over the accumulator part of the lid in order to reduce heat losses. The charging is intended to be made in a few hours. The lid is after cooling ready to be used and is then placed on the refrigerating box. Since no shut-off valve is provided the lid must be used immediately. In order to keep the lid charged in this case the immersion heater must be connected to a supply of electric current. Of course it is also quite possible to arrange a valve in the connection pipe **73**. Such a valve must then be made with a magnetic forced transfer from the exterior since no normal valves can fulfil the very high requirements on tightness.

[**0145**] Thus, efficient substances have been described. A procedure for producing structures containing a substance and structures have been described which give a very good heat transport and diffusion in an applied layer of the substance, a good mechanical stability in the layer of the substance and a high energy density of the substance. Structures including a chemical heat pump suited for applications like air conditioning, refrigerating boxes and refrigerators respectively have also been described.

1. A chemical heat pump comprising a vessel having an at least partly heat conducting wall or plate and a substance and a sorbate arranged in the vessel, the substance exothermally absorbing and endothermally desorbing the sorbate, characterized in that the substance is arranged on the inner surface as a layer and that a gas transport channel is arranged at an outer surface of the layer which is opposite said inner surface, the layer being configured in such a way that heat conduction through the layer and transport of vapour of the volatile liquid in the layer have substantially the same direction and/or substantially perpendicularly to the gas transport channel and/or to the inner surface.

2. A chemical heat pump according to claim 1, characterized in that the layer has a substantially constant thickness, the thickness being selected so that the sorbate is capable of interacting from the outer surface with all parts of the layer.

3. A chemical heat pump according to claim 1, characterized in that in the layer substantially parallel slot-shaped channels are provided having directions perpendicular to the inner surface in order to allow that the sorbate penetrates in the channels to interact with substance in the layer.

4. A chemical heat pump according to claim 1, characterized in that heat conducting thin or narrow material, in particular thread-shaped or plate-shaped heat conducting material, which is attached to the heat conducting wall, penetrates in the layer.

5. A chemical heat pump according to claim 4, characterized in that the heat conducting thin or narrow material extends substantially perpendicularly to the inner surface.

6. A chemical heat pump according to claim 1, characterized in that the substance is solid and the sorbate is water, which substance has a temperature difference ΔT of substantially 20-40° C. for a pressure equilibrium between the substance and water within a temperature range of substantially 0-100° C.

7. A chemical heat pump according to claim 6, characterized in that the substance has an energy content counted as energy of evaporation comprising at least 0.15 kWh/l of the substance, preferably at least 0.20 kWh/l of the substance.

8. A chemical heat pump according to claim 6, characterized in that the substance comprises a substance selected among $CoCl_2$, $Ba(OH)_2$, LiOH and $SrBr_2$.

9. A chemical heat pump according to claim 1, characterized in that the layer is a dried slurry-like mixture of the substance and an excess of the volatile liquid, from which slurry-ike mixture at least the excess of the volatile liquid has been removed.

10. A chemical heat pump comprising an active solid substance and a volatile liquid which is absorbed and desorbed by the solid substance, characterized in that as active solid substance a substance is used which has a temperature difference ΔT of substantially 20-40° C. for a pressure equilibrium between active solid substance and the volatile liquid within a temperature range of substantially 0-100° C. for the chemical heat pump.

11. A chemical heat dump according to claim 10, characterized in that the active solid substance within the temperature range reacts with the gaseous phase of the volatile liquid in at least two phase transitions having ΔT:s located close to each other.

12. A chemical heat pump according to claim 10, characterized in that the active solid substance has an energy content counted as energy of evaporation comprising at least 0.15 kWh/l of the active solid substance, preferably at least 0.20 kWh/l of the active solid substance.

13. A chemical heat pump according to claim 10, characterized in that the active substance comprises a substance selected among $CoCl_2$, $Ba(OH)_2$, LiOH and $SrBr_2$.

14. A chemical heat pump according to claim 10, characterized in that the volatile liquid is water.

15. A chemical heat pump according to claim 10, characterized in that the active solid substance exists in a porous state.

16. A chemical heat pump according to claim 10, characterized in that the active solid substance is in a porous state having a volume porosity of at least 15%, preferably 35%, in relation to the active solid substance in a completely compressed state or in a crystal state.

17. A chemical heat pump according to claim 10, characterized by an at least partly heat conducting wall or plate having an inner surface, the active solid substance being applied to the inner surface and being a dried slurry-like mixture of the substance with an excess of the volatile liquid, from which at least the excess of the volatile liquid has been removed.

18. A chemical heat pump according to claim 10, characterized by an at least partly heat conducting wall or plate having an inner surface, the substance being arranged on the inner surface as a layer and a gas transport channel being arranged at a surface of the layer which is not located at said inner surface, the layer being configured in such a way that heat conduction through the layer and transport of vapour of the volatile liquid in the layer have substantially the same direction, substantially perpendicularly to the gas transport channel and/or to the inner surface.

19. A chemical heat pump according to claim 10, characterized by an at least partly heat conducting wall having an inner surface, the substance being arranged on the inner surface as a layer having a substantially constant thickness and having an outer surface opposite said inner surface, the layer having such a thickness and/or such a configuration that the volatile liquid is capable of interacting from the outer surface with all parts of the substance.

20. A method of producing a heat accumulator, the heat accumulator comprising a vessel, an at least partly heat conducting wall arranged in the vessel and having an inner surface, a substance and a sorbate arranged in the vessel, the substance exothermally absorbing and endothermally absorbing the sorbate, characterized by preparing a slurry-like mixture of the substance with an excess of the sorbate, applying the slurry-like mixture to the inner surface and drying the applied slurry-like mixture to remove at least the excess of sorbate.

21. A method according to claim 20, characterized in that the drying of the slurry-like mixture is performed by applying the slurry-like mixture in a closed space from which gas is evacuated.

22. A method according to claim 20, characterized in that,in drying the slurry-like mixture simultaneously a gradual heating of the slurry-like mixture is made.

23. A method according to claim 20, characterized in that in drying the slurry-like mixture pressure forces are applied to the slurry-like mixture to compress the slurry-like mixture.

24. A method according to claim 20, characterized in that in applying the slurry-like mixture at the same time a vibration of the slurry-like mixture is made.

25. A heat accumulator comprising a vessel having an at least partly heat conducting wall, which vessel contains a substance which exothermally absorbs and endothermally desorbs a sorbate, characterized in that the substance is arranged on the at least partly heat conducting wall as a layer having a substantially constant thickness and having an exterior surface, which layer has such a thickness that the sorbate is capable of interacting from the outer surface with all parts of the substance.

26. A heat accumulator according to claim 25, characterized in that the layer has a thickness of at most 10 mm.

27. A heat accumulator according to claim 25, characterized in that the substance in the layer exists in a porous state.

28. A heat accumulator according to claim 25, characterized in that the substance in the layer exists in a porous state having a volume porosity of at least 15%, preferably 35%, in relation to the active solid substance in a completely compressed state or in crystal state.

29. A heat accumulator according to claim 25, characterized in that in the layer substantially parallel slot-shaped channels are provided having directions perpendicular to the heat conducting wall in order to allow that the sorbate penetrates in the channels to interact with the substance.

30. A heat accumulator according to claim 25, characterized in that heat conducting thin or narrow material, in particular thread-shaped or plate-shaped heat conducting material, which is attached to the heat conducting wall, penetrates in the layer.

31. A heat accumulator according to claim **30**, characterized in that the heat conducting thin or narrow material is located substantially perpendicularly to the surface of the heat conducting wall.

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