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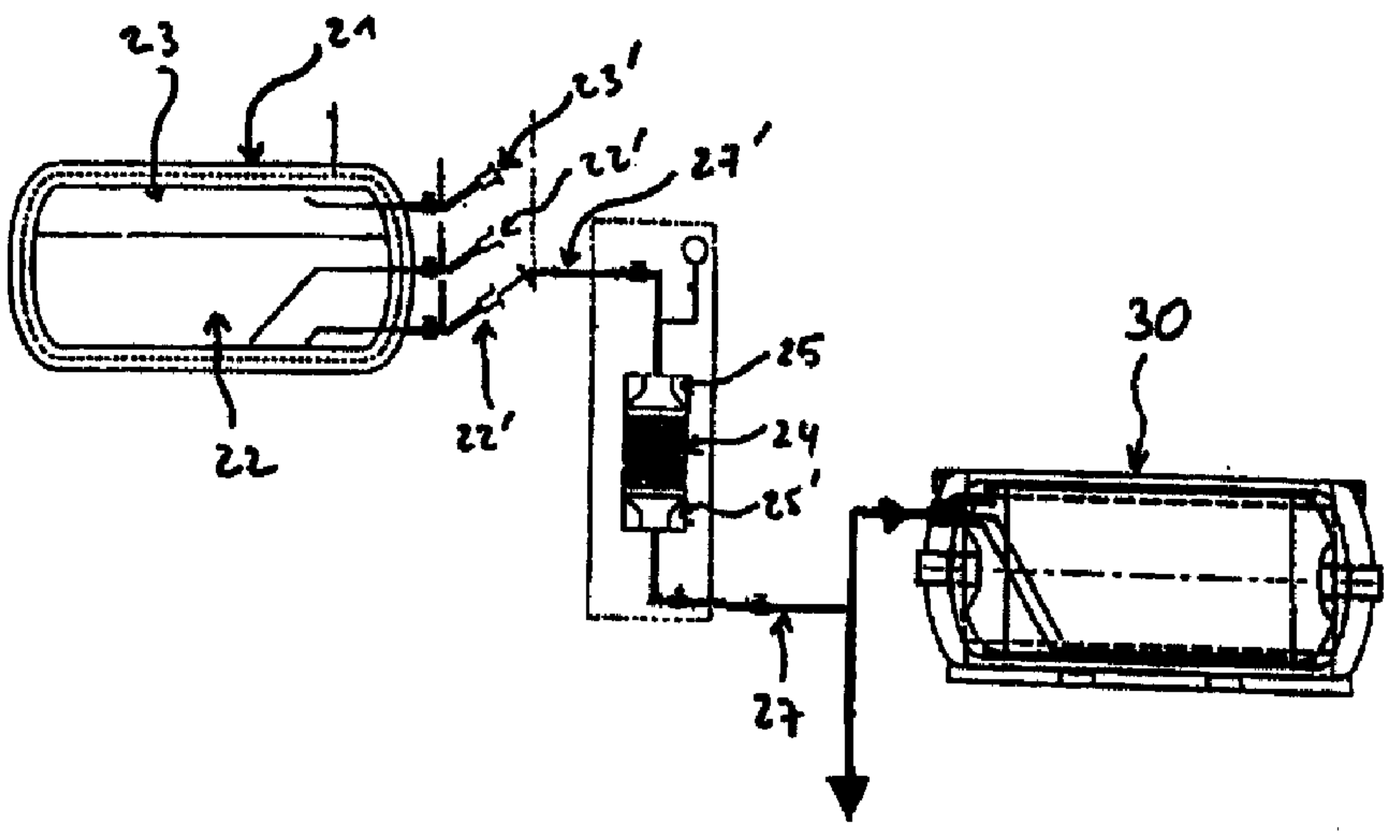
(54) **PROCEDE D'EPURATION D'UN FLUIDE CRYOGENIQUE PAR FILTRATION ET ADSORPTION**

(54) **METHOD FOR PURIFYING A CRYOGENIC FLUID BY FILTRATION AND ADSORPTION**



(57) Procédé de purification d'un fluide cryogénique choisi dans le groupe formé par l'hélium, l'hydrogène, le deutérium, l'argon, le néon, le xénon ou le krypton à l'état liquide, diphasique, gazeux ou supercritique, ayant un point d'ébullition Pe, en l'une au moins de ses impuretés ayant un point d'ébullition Pe', avec Pe' > Pe, comprenant au moins: une étape de filtration d'au moins une impureté à l'état solide au moyen d'un filtre mécanique; et une étape d'adsorption d'au moins une impureté à l'état liquide ou gazeux; et dans lequel on récupère au moins une partie du fluide cryogénique au moins partiellement épuré, ledit fluide contenant au plus environ 1 ppb d'impuretés. Dispositif de mise en oeuvre du procédé.

(57) The invention concerns a method for purifying a cryogenic fluid selected from the group formed by helium, hydrogen, deuterium, argon, neon, xenon or krypton in liquid state, diphase, gaseous or supercritical, having a boiling point Pe, in one at least of its impurities having a boiling point Pe', with Pe' > Pe, comprising at least: a step of filtering at least one impurity in solid state using a mechanical filter; and a step of adsorption of at least one impurity in liquid or gaseous state; and in which at least part of the cryogenic fluid at least partially purified is recuperated, said fluid containing not more than 1 ppb of impurities. The invention also concerns a device for implementing the method.

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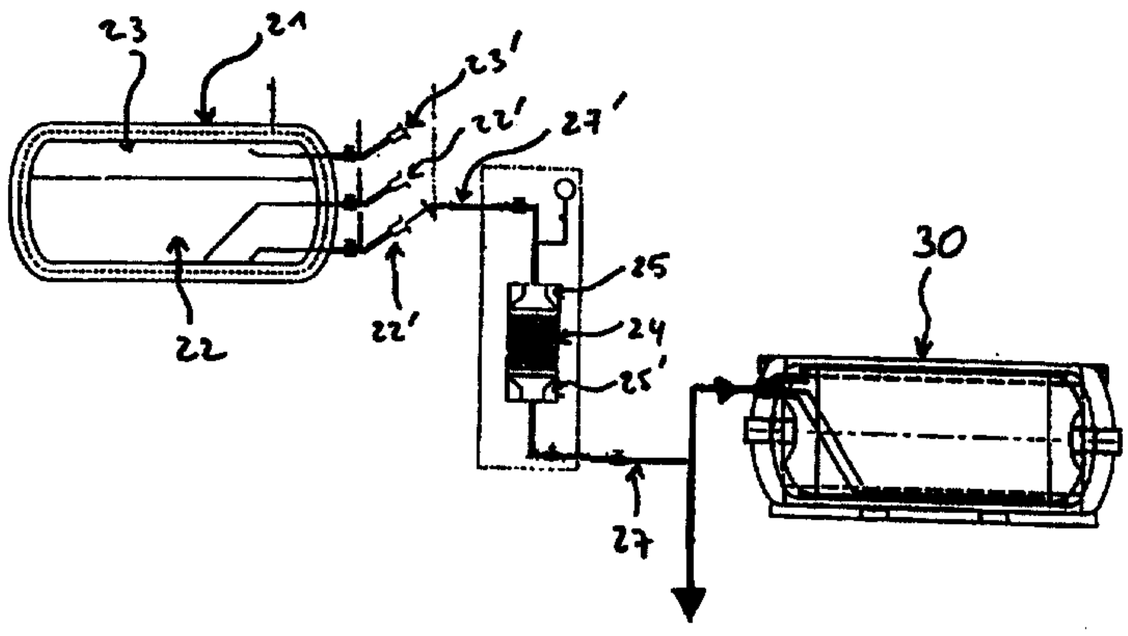

(57) Abstract

The invention concerns a method for purifying a cryogenic fluid selected from the group formed by helium, hydrogen, deuterium, argon, neon, xenon or krypton in liquid state, diphase, gaseous or supercritical, having a boiling point Pe, in one at least of its impurities having a boiling point Pe', with Pe' > Pe, comprising at least: a step of filtering at least one impurity in solid state using a mechanical filter; and a step of adsorption of at least one impurity in liquid or gaseous state; and in which at least part of the cryogenic fluid at least partially purified is recuperated, said fluid containing not more than 1 ppb of impurities. The invention also concerns a device for implementing the method.

(57) Abrégé

Procédé de purification d'un fluide cryogénique choisi dans le groupe formé par l'hélium, l'hydrogène, le deutérium, l'argon, le néon, le xénon ou le krypton à l'état liquide, diphasique, gazeux ou supercritique, ayant un point d'ébullition Pe, en l'une au moins de ses impuretés ayant un point d'ébullition Pe', avec Pe' >Pe, comprenant au moins: une étape de filtration d'au moins une impureté à l'état solide au moyen d'un filtre mécanique; et une étape d'adsorption d'au moins une impureté à l'état liquide ou gazeux; et dans lequel on récupère au moins une partie du fluide cryogénique au moins partiellement épuré, ledit fluide contenant au plus environ 1 ppb d'impuretés. Dispositif de mise en oeuvre du procédé.

WO 98/28226 PCT/FR97/02345

METHOD FOR PURIFYING A CRYOGENIC FLUID BY FILTERING AND ADSORPTION

The present invention relates to the field of purifying cryogenic fluids and, more particularly, to a method and to a device for purifying a cryogenic fluid in the liquid, gas, supercritical or diphasic state with respect to at least one of the impurities in the solid and/or liquid and/or gas state which it contains.

Cryogenic fluids are currently employed in a large number and variety of industrial fields. For example, nitrogen, helium, neon, argon, deuterium, krypton and xenon are commonly used in the field of electronics.

This field very particularly requires these compounds which are as pure as possible, that is to say free from their major impurities, in order to avoid subsequent damage to the electronic components by reaction with the said impurities. One example which may be mentioned is the use of ultra pure helium as an inert gas which can be used in keeping at a constant temperature the chips carrying integrated circuits forming memories or processors, or in the cooling of wafers.

There is also an increasing demand in the electronics field as regards the provision of ultra pure hydrogen.

A large number of methods for purifying cryogenic fluids, such as the inert fluids, are known from the prior art, but these generally have several drawbacks or disadvantages, namely:

- they are not suitable for purification of cryogenic fluids whatever their state, namely liquid, gas, supercritical and/or diphasic, and therefore require heating and/or cooling steps, depending on the case, in order to bring the cryogenic fluid to be purified to a given temperature at which the removal of the impurities will need to be carried out;

- they require the use of expensive adsorbents, for example of the getter type;

- the adsorbents used are only effective when "hot", that is to say at temperatures above 0°C, or even 100°C;

- they are limited in terms of the amount of cryogenic fluid which can be processed in a given period of time;

- they are limited to one type of cryogenic fluid, for example argon or helium, that is to say the same method and/or the same device cannot be used to purify different kinds of cryogenic fluids;

- they have limitations in terms of the impurities which can be removed through the use of adsorbents or catalysts which react only selectively, that is to say with some impurities but not with others, which results in a cryogenic fluid that is only partially purified; for example, conventional catalysts or adsorbents do not make it possible to remove the nitrogen impurities contained in helium;

- they also comprise one or more oxidative catalysis steps in order to convert, in particular, the hydrogen and/or carbon monoxide impurities into water and/or carbon dioxide.

For example, document US-A-3,996,082 describes a method for purifying argon gas with respect to its oxygen impurity using a type A synthetic zeolite.

For its part, document US-A-2,874,030 describes a method for purifying argon gas with respect to its oxygen impurity, in which the oxygen is converted into water by catalytic reaction with excess hydrogen; the water which is formed is then removed by dehydration.

Furthermore, document EP-A-0350656 describes a method for purifying an inert gas with respect to its oxygen, carbon monoxide and hydrogen impurities, in which the carbon monoxide and the hydrogen are removed by catalytic oxidation at a temperature of between 150°C and 250°C in the presence of a first catalyst based on reduced copper, then by a second catalyst

based on oxidized copper, giving carbon dioxide and water which are then removed by adsorption at ambient temperature on an adsorbent of the molecular sieve type.

In addition, document FR 9604955 describes a method for supplying ultra pure helium to a line where it is used, in which helium in liquid or supercritical form is taken from a storage tank, the helium is filtered using a steel fabric in order to trap the solid impurities, the filtered helium is vaporized and the resulting helium gas is returned to the user line. It is indicated in this document that the hydrogen and/or neon impurities dissolved in the liquid or supercritical helium are not trapped.

For its part, document FR 9507943 describes a method for purifying inert gases, such as nitrogen and rare gases, with respect to their oxygen and carbon monoxide impurities by adsorption at a temperature below 30°C on a specific adsorbent of the porous metal oxide type; the hydrogen impurity is subsidiarily removed by distillation.

Furthermore, document FR 9611271 relates to the purification of a cryogenic fluid, such as liquid nitrogen, liquid argon or liquid helium with respect to its hydrogen, carbon monoxide and/or oxygen impurities by adsorption on a support of the following type: alumina, silica, zeolite or titanium oxide supporting a metal, such as platinum, palladium, rhodium or iridium.

In addition, document US-A-4,659,351 describes a two-step method for obtaining liquid helium, in which a gas flow consisting essentially of helium and nitrogen with a few minor impurities is subjected to a cooling step in order to condense the said minor impurities and the nitrogen, which are then removed; the helium-enriched gas flow is then subjected to a process of the PSA type (Pressure Swing Adsorption), which results in a relatively pure helium gas flow, which helium is then condensed to form liquid helium. It will be readily understood that this method has many

disadvantages and drawbacks, both in terms of energy costs and in terms of the purity of the helium obtained. Specifically, the need to employ steps of vaporizing/liquefying helium is a great burden from the point of view of energy and economics, and although the helium obtained is relatively pure, it contains amounts of impurities which are much too high for it to be used for electronics applications, in particular.

The object of the present invention is therefore to provide a method and a device for purifying cryogenic fluids whatever their state, namely liquid, diphasic, gas or supercritical, which is less of a burden in terms of economics and energy than currently existing methods and devices, which can be adapted for the purification of different cryogenic fluids, and which makes it possible to obtain pure cryogenic fluids, that is to say ones which are free at least from their main solid and/or liquid and/or gas impurities.

The invention therefore relates to a method for purifying a cryogenic fluid selected from the group formed by helium, hydrogen, deuterium (D2), krypton, xenon, neon and argon (the term helium being intended to mean : helium and its isotopes He^3 and He^4) in the liquid, diphasic, gas or supercritical state, having a boiling point Pe, with respect to at least one of its impurities having a boiling point Pe', with Pe' > Pe, comprising at least:

- a step of filtering at least one impurity in the solid state using a mechanical filter;
- and a step of adsorption of at least one impurity in the liquid or gas state;
- and in which at least part of the at least partially purified cryogenic fluid is recovered, the said fluid containing at most about 1 ppb of the said impurities.

In other words, the impurities in the solid state (crystals) contained in the cryogenic fluid to be purified are trapped by mechanical filtering, whereas

the impurities in the liquid state or in the gas state are adsorbed using at least one adsorbent material.

Depending on the case, the method of the invention may furthermore comprise one or more of the following characteristics:

- the cryogenic fluid is such that its boiling point Pe is below -100°C, preferably below -150°C, preferably below -240°C (at a pressure of 10^5 Pa);

- the cryogenic fluid to be purified is helium and the impurities removed belong to the group formed by neon, nitrogen, carbon monoxide, carbon dioxide, oxygen, argon, xenon, krypton, hydrocarbons and water;

- the cryogenic fluid is to be purified hydrogen and the impurities belong to the group formed by neon, nitrogen, carbon monoxide, carbon dioxide, oxygen, argon, xenon, krypton, hydrocarbons and water;

- the cryogenic fluid to be purified is neon and the impurities belong to the group formed by nitrogen, carbon monoxide, carbon dioxide, oxygen, argon, xenon, krypton, hydrocarbons and water;

- the mechanical filtering is carried out using a metal or ceramic filter, or using the adsorbent material employed for removing the impurities in the liquid state or in the gas state. It is actually possible for the said adsorbent material to be used as a filter as well in order to trap the particles and the solid impurities (crystals) contained in the cryogenic fluid to be purified; in this case, the filtration and adsorption steps will be referred to as "simultaneous".

- the adsorption of the impurities is carried out using an adsorbent selected from the group formed by active carbon, zeolites exchanged or unexchanged with metal cations, silica gel, alumina or any other porous adsorbent making it possible to stop effectively one or more types of soluble or gas impurities in the cryogenic fluid to be purified, for example, a carbon fabric;

- at least one mechanical filtering step is carried out upstream and/or downstream of at least one

adsorption step, and preferably upstream and downstream of the adsorption step. It is also possible to alternate a plurality of adsorption steps and a plurality of filtration steps while using adsorbent materials and filtration means which are identical, similar or different in the various steps;

- the adsorbent employed in the step of adsorption of the impurities contained in the cryogenic fluid and/or the filter or filters is subjected to at least one regeneration step. The regeneration of the adsorbent material may be carried out, for example, by adopting the following procedure:

- baking the adsorbent material, such as active carbon for a few hours at a temperature of from 100°C to 150°C (only during first use of the adsorbent material);

- flushing or purging the purifier using an inert gas, such as nitrogen, at ambient temperature and at atmospheric pressure;

- and subsequently flushing using the gas to be purified at ambient temperature and at atmospheric pressure.

After this double flushing, the purification system can carry out a new purification phase.

The invention also relates to a device for implementing the method according to the invention, characterized in that it has a purification zone for cryogenic fluid to be purified, which purification zone comprises at least one mechanical filter and at least one adsorbent bed, means for feeding cryogenic fluids to be purified to the said purification zone and means for recovering purified cryogenic fluid containing at most 1 ppb of impurities.

Depending on the case, the device of the invention may furthermore have:

- means for storing the purified cryogenic fluid;

- means for conveying the purified cryogenic fluid on-line to a site where it is used;

- means for regenerating the adsorbent material, making it possible to regenerate the said adsorbent material, for example by adopting the procedure mentioned above.

The method of the invention can therefore advantageously be used to purify a cryogenic fluid, whichever of the following states it is in:

- liquid or supercooled, that is to say at a temperature below its boiling point,

- gas, that is to say at a temperature more than a few degrees above its liquefying temperature or boiling point, for example at a temperature of about 5°C to 20°C above the said boiling point,

- diphasic, that is to say in the form of a liquid/gas mixture, and therefore at a temperature substantially equal to the bubble point or boiling temperature, or fluctuating around the said bubble point,

- or supercritical, for example in the case of helium, at a temperature of about -268°C with a pressure of $2.275.10^5$ Pa.

The advantage of the invention resides in the fact that it allows ultra purification of cryogenic fluids having a boiling temperature, at atmospheric pressure, below -100°C, preferably below -150°C, advantageously below -240°C, such as helium, krypton, xenon, argon, hydrogen, deuterium (D2), or neon, with respect to at least one of their impurities having a boiling point above that of the said cryogenic fluid, whether they are in the solid and/or liquid and/or gas state, using steps of mechanical filtering and/or adsorption of the said impurities.

The method of the invention will advantageously be implemented in a temperature range lying between -273°C and -240°C approximately, and for a pressure range of between 10^5 Pa and 30.10^5 Pa, preferably between 10^5 Pa and 10.10^5 Pa.

By way of indication, the boiling points or temperatures, at atmospheric pressure, of various compounds are given in Table I below:

TABLE I

Compounds	Pe (°C)
Argon	-185.80
Nitrogen	-195.60
Xenon	-108.10
Krypton	-153.35
Neon	-246.05
Oxygen	-182.97
Helium	-268.90
Hydrogen	-252.77
Methane	-161.52
Propane	- 42.04
Ethane	- 88.68
CO_2	- 78.50
NO	-151.75
CF_4	-127.94
D2	-249.58

The present invention is particularly well-suited to the purification of helium, preferably in the liquid state, and of hydrogen.

The present invention will now be explained in more detail with the aid of examples which are given by way of illustration but without limiting the invention in any way, and with reference to the appended figures.

Figure 1 represents a conventional experimental device which can be used to carry out the tests described below.

Figure 2 represents an industrial device for implementing the method according to the invention.

Figure 1 represents a tank 1 which is vacuum-insulated in order to prevent or minimize any entry of heat and contains liquid helium 2 and a helium gas overhead 3. In this experimental device, the zone for

purification of helium contaminated with impurities consists of a cartridge 4 containing an adsorbent material, here active carbon, which is intended to absorb the impurities of liquid or gas type and two mechanical filters 5 and 5', respectively arranged upstream and downstream of the said purification cartridge 4, which filters 5 and 5' are intended to stop the impurities of solid type (crystals).

A mechanical filter is customarily made by compressing a metal powder, such as a powder of a metal or a metal alloy, preferably stainless steel, and forming the compacted structure obtained into a disc. It is possible to vary the geometry of the disc or filter obtained by altering, in particular, its diameter, its thickness and its porosity. By way of example, mention may be made of the metal filters or frits sold by the company PORAL© or the company METAFRAN©. Certain seals may also be equipped with such a metal mechanical filter, for example the seal VCR© (connectors with surface leaktightness using a metal seal) manufactured by the company CAJON™.

The contaminated liquid helium 2 enters the purification zone in the direction indicated by the arrow 6, that is to say upwards. The solid impurities are firstly stopped by the filter 5, then the liquid impurities are adsorbed in the purification cartridge 4 by the adsorbent material, for example active carbon, and lastly the solid particles which may be generated by attrition of the adsorbent material are stopped by the filter 5'.

The ultra pure liquid helium thus obtained is conveyed via the line 7 to the analysers 9 and 9' or, when appropriate to an air vent 8.

According to this arrangement, the purification is carried out on helium in the liquid state. However, in order to test the effectiveness of the method of the invention on helium gas, the same procedure was adopted but this time placing the purification zone in the gas overhead 3 so that the orifice 10 for admitting helium

into the filter 5 lies above the level of the liquid helium, and therefore in the gas overhead, where liquid helium to be purified is thus drawn off.

In any case, the helium gas or liquid helium is conveyed successively through the filter 5, the purification cartridge 4, the filter 5' and the tube 7 in the conventional way, by increasing the pressure which is exerted in the tank 1.

This experimental system is connected via the tubes 7 and 7' to a tank 12 containing ultra pure helium for purging, that is to say cleaning, the purification zone comprising the filters 5 and 5' and the purification cartridge 4, in particular before or after a purification step.

Furthermore, another tank 11 contains, for its part, helium contaminated by known amounts of impurities intended to artificially contaminate the liquid helium or helium gas contained in the tank 1 with known amounts of pollutants and, thereby, to test the effectiveness of the purification method of the invention.

Figure 2 represents an industrial device for purifying liquid helium. Liquid helium 22 with a helium gas overhead 23 on top is contained in an insulated tank 21, for example a storage tank or the reservoir of a tanker.

Helium gas 23 or liquid helium 22 is drawn from the insulated tank 21 using tapping means 23' or 22', respectively, and conveyed via a line 27' to a purification zone having a first filter 25, lying upstream of a purification cartridge 24 containing an adsorbent material, such as active carbon or any other suitable porous adsorbent material for adsorbing one or more impurities in the liquid state or in the gas state, which purification cartridge 24 lies upstream of a second filter 25'.

The contaminated helium delivered from the tank 21 is therefore purified in the purification zone and the ultra pure helium obtained is conveyed, via the

line 27, to an insulated tank 30 for ultra pure helium or, when appropriate, to a site where it is used (not shown).

It is clear to see that the handling of cryogenic fluids is a sensitive operation, and that, in order to ensure optimum purification, care must be taken to ensure that all of the device implementing the present invention is correctly insulated so as to avoid, or preferably eliminate, any undesirable heat input, vacuum insulation being preferred.

Furthermore, as we will see in the illustrative examples below, it is also possible, depending on the case, to do without one or the other, or even both filters 25 and 25' and nevertheless to obtain an ultra pure cryogenic fluid meeting the intended specifications, in particular the specifications in the electronics field. In this case, it is the porous adsorbent material which both mechanically filters the solid particles and adsorbs the impurities in the liquid or gas state.

In order to make it possible to regenerate the adsorbent material contained in the purification cartridge and filters for trapping the solid impurities, it is necessary or desirable to subject the purification zone to a regeneration process, for example a conventional method in which the purification zone is returned to ambient temperature by flushing the said purification zone using an inert gas, such as nitrogen, so as to sublime and/or desorb the pollutants adsorbed and/or trapped, followed by "cleaning" that is to say flushing using firstly ultra pure helium gas then ultra pure liquid helium, before any new purification phase.

Examples:

In the examples given below, the amounts of impurities present in the cryogenic fluid to be purified are monitored using commonly sold analysers. Specifically, the amounts of carbon monoxide and

hydrogen impurities are measured using an RGA3 chromatograph marketed by the company TRACE ANALYTICAL, the detection threshold of which is of the order of 1 ppb for carbon monoxide and 5 ppb for hydrogen (ppb = part per billion by volume), and the amount of oxygen impurity is measured using an analyser of the OSK type marketed by the company OSAKA SANSO KOGYO, which has a detection threshold of 1 ppb for oxygen.

For more exhaustive analytical monitoring, the other impurities (nitrogen, neon, carbon dioxide, etc.) can easily be detected using suitable analysers, such as an analyser of the APIMS type (Atmospheric Pressure Ion Mass Spectrometry) whose detection threshold for these impurities is below 1 ppb.

A conventional device which can be used to carry out various tests is represented in Figure 1.

Example 1

In this example, liquid helium was purified with respect to its impurities O_2, CO and H_2 only by mechanical filtering using a frit composed of a VCR seal equipped with a porous metal filter (thickness 2.5 mm, pore size 2 μm) marketed by the company SWAGELOCK.

At the temperature of liquid helium, the impurities other than hydrogen are in solid form, whereas a fraction of the hydrogen is still in liquid form.

Before purification, the liquid helium contains about 1 ppm (part per million by volume) of carbon monoxide, about 5 ppm of oxygen and about 2 ppm of hydrogen, and other solid impurities in trace form, namely carbon dioxide, water, nitrogen and neon.

After purification, the purified helium contains less than 1 ppb of carbon monoxide and less than 1 ppb of oxygen; however, a residue of from 100 ppb to a few hundreds of ppb of hydrogen is detected downstream of the filter (depending on the operating pressure and temperature conditions).

The purification of liquid helium on a mechanical filter is therefore limited in terms of the hydrogen impurity. Nevertheless, such filtering is sufficient when the helium to be purified does not contain impurities such as hydrogen, given that all the other impurities are stopped.

Example 2

This example is in all regards similar to the previous example, apart from the fact that the mechanical filtering (filter or metal frit) is combined with adsorption, in particular of hydrogen on a suitable adsorbent, here active carbon.

In this case, the implementation of mechanical filtering coupled with adsorption makes it possible to obtain ultra pure liquid helium which this time, in contrast to the previous example, no longer contains impurities such as hydrogen. This is because this hydrogen impurity is adsorbed by the active carbon.

The ultra pure helium thus obtained fully complies with the specifications and requirements of an application for electronics purposes, that is to say the purified liquid helium contains less than 1 ppb of its various impurities.

It should be noted that the adsorption of impurities soluble in liquid helium, for example hydrogen, may be carried out upstream and/or downstream of the mechanical filtering. Mechanical filters are preferably placed on each side of the adsorbent material.

Example 3

This example is similar to the previous examples except for the fact that the impurities contained in the liquid helium are removed only using a bed of particles of an adsorbent material, here again an active carbon bed; in other words, the metal mechanical filter(s) have been removed.

Surprisingly, ultra pure liquid helium is obtained as in Example 2, despite the removal of the metal mechanical filter(s). The microporous active carbon therefore makes it possible not only to adsorb the liquid or gas impurities, but also to filter, that is to say mechanically trap, the solid or crystallized impurities (so-called "simultaneous" adsorption and filtering).

Example 4

This example is similar to Example 2, except for the fact that the helium to be purified contains not only the carbon monoxide, hydrogen and oxygen impurities, but also other impurities namely: water, carbon dioxide (1 ppm), nitrogen (1 ppm) and neon (1 ppm).

After purification, the liquid helium here again contains less than 1 ppb of its various pollutants and the impurities H_2O, CO_2, N_2 and Ne are fully removed.

Example 5

This example is similar to Example 2, except for the fact that the adsorbent (active carbon) is replaced by a carbon fabric, for example of the Actitex CS 1501 type marketed by the company ACTITEX©.

The results obtained are identical to those in Example 2.

Here again, ultra purification of liquid helium is obtained when mechanical filtering and adsorption by the carbon fabric are combined.

Example 6

This example is similar to Example 2, except for the fact that the cryogenic fluid to be purified is neon (Te = -246°C) in the liquid state, which is contaminated with the following impurities having boiling points above that of neon: nitrogen (4 ppm),

oxygen (1 ppm), carbon dioxide (2 ppm) and ethane (1 ppm).

After purification, the ultra pure neon obtained contains undetectable amounts of these various impurities (in relation to the analysers used).

The method of the invention is therefore applicable to the purification of neon.

Example 7

This example is similar to Example 2, except for the fact that the cryogenic fluid to be purified is krypton (Te = -153°C) in the liquid state, which is contaminated with the following impurities having boiling points above that of krypton: water (3 ppm), ethane (2 ppm) and carbon dioxide (2 ppm).

After purification, the ultra pure krypton obtained contains undetectable amounts of these various impurities.

The method of the invention is therefore applicable to the purification of krypton.

Example 8

This example is similar to Example 2, except for the fact that the cryogenic fluid to be purified is xenon (Te = -108°C) in the liquid state, which is contaminated with the following impurities having boiling points above that of xenon: water (3 ppm), CO_2 (2 ppm), ethane (1 ppm).

After purification, the ultra pure xenon obtained contains undetectable amounts of these various impurities.

The method of the invention is therefore applicable to the purification of xenon.

Example 9

In this example, which is of the laboratory type, a study is made of the effect of the pore size (pore diameter) of the filter used on the effectiveness of the purification of liquid helium artificially

contaminated with impurities such as hydrogen (H_2), oxygen (O_2) and carbon monoxide (CO) in known amounts. Before purification, the contaminated helium contains of the order of about 1 ppm of CO impurities, about 5 ppm of O_2 impurities and about 2 ppm of H_2 impurities.

Depending on the case, the contaminated helium is purified by filtering alone (tests 1 to 4), or by filtering and adsorption (tests 5 to 10), at a pressure of 1.7 bar absolute and at a rate of 1 m^3 (stp)/h.

The filters used are of the metal or ceramic type and have a pore diameter ranging from 2 to 60 μm. Furthermore, the adsorbent employed is either a carbon fabric (TC) or active carbon (CA).

The results obtained are reported in the table below.

Table

Test No.	Filter	Adsorbent	Residual impurity level (in ppb)		
	Pore size (μm)	Type	H_2	O_2	CO
1	2	/	100 to 200	ND	ND
2	5	/	100 to 200	ND	ND
3	20	/	100 to 200	approx. 50	approx. 50
4	60	/	100 to 200	approx. 100	approx. 100
5	2	CA	ND	ND	ND
6	2	TC	ND	ND	ND
7	5	CA	ND	ND	ND
8	5	TC	ND	ND	ND
9	20	CA	ND	ND	ND
10	60	CA	ND	ND	ND

ND: not detected by the analyser, i.e. amount below the detection threshold of the analyser used (about < 1 ppb for CO and O_2 and about 5 ppb for H_2)

The table above clearly shows that combining at least one filtering step and at least one step of adsorption of the impurities makes it possible to obtain very high-purity helium, i.e. containing less than 1 ppb of impurities.

However, as shown by tests 1 to 4, it is preferable to use a mechanical filter having a pore size smaller than 60 μm, preferably smaller than 20 μm and, if possible, approximately 2 to 5 μm, or even smaller than 2 μm. This is because the smaller the pore size of the filter is, the higher is the effectiveness in removing the solid or crystallized impurities.

It can, however, also be seen that a filtering step alone does not make it possible to remove some of the impurities, in particular the dissolved impurities such as H_2.

Conversely, combining filtering and adsorption steps makes it possible to obtain helium containing less than 1 ppb of impurities, the said soluble impurities then being effectively removed using a suitable adsorbent, such as active carbon or a carbon fabric. Other adsorbents may be used, in particular exchanged or unexchanged zeolites, activated alumina or silica gel.

Example 10

This pre-industrial example is intended to check the long-term effectiveness of a method for purifying liquid helium employing a step of filtering on a metal mechanical filter having a pore diameter of about 3 μm and a step of adsorption on an adsorbent, such as active carbon, the said method being implemented at a pressure of 1.7 bar absolute and at a flow rate of 2500 m^3 (stp)/h.

The average levels of H_2, CO and O_2 impurities in the helium to be purified are the same as those in Example 9, and those of methane (CH_4) and carbon dioxide (CO_2) impurities are respectively 0.1 ppm and 0.5 ppm.

The results obtained are represented in appended Figure 3 where the concentration (C) of O_2, N_2, CH_4, CO_2 and CO impurities (in ppb) is represented on the ordinate and the purification time T (in hours) is represented on the abscissa. More precisely, it can be seen that after 3 hours, the level of impurities is kept at a value much below 1 ppb; the starting point of the impurity measurement being set as time t_0.

This demonstrates that the method of the invention can be employed on an industrial scale by virtue of its effectiveness both in terms of the quality and the purity of the liquid helium obtained (less than 1 ppb of impurities) and in terms of the operating time of the method, namely several hours without regeneration.

On an industrial scale, however, care will be taken to regenerate the filter and/or the adsorbent before the impurities break through, and this will clearly depend on the flow rates processed and the amount of impurities to be removed.

NEW CLAIMS

1. Method for purifying helium in the liquid, diphasic, gas or supercritical state, having a boiling point Pe, with respect to at least one of its impurities having a boiling point Pe', with Pe' > Pe, the said impurities being selected from the group formed by hydrogen, neon, nitrogen, carbon monoxide, carbon dioxide, oxygen, argon, krypton, xenon, hydrocarbons and water, comprising at least:

- a step of filtering at least one impurity in the solid state using a mechanical filter;
- and a step of adsorption of at least one impurity in the liquid or gas state;
- and in which at least part of the at least partially purified helium is recovered, the said helium containing at most about 1 ppb of impurities in the group formed by hydrogen, neon, nitrogen, carbon monoxide, carbon dioxide, oxygen, argon, krypton, xenon, hydrocarbons and water.

2. Method according to Claim 1, characterized in that the filtering is carried out using at least one filter whose pore diameter is ≤ 60 μm, preferably ≤ 20 μm, preferentially ≤ 5 μm.

3. Method according to one of Claims 1 and 2, characterized in that the filtering is carried out using at least one metal or ceramic filter.

4. Method according to Claim 1, characterized in that the adsorption of at least one impurity is carried out on an adsorbent material selected from the group formed by active carbon, carbon fabric, exchanged or unexchanged zeolites, alumina, silica gel and mixtures thereof.

5. Method according to one of Claims 1 to 4, characterized in that at least one mechanical filtering step is carried out upstream and/or downstream of at least one adsorption step.

6. Method according to one of Claims 1 to 5, characterized in that the purification of the helium is

carried out at a pressure of between 1.10^5 Pa and 30.10^5 Pa, preferably between 1.10^5 Pa and 10.10^5 Pa.

7. Method according to one of Claims 1 to 6, characterized in that the adsorbent and/or the filter is subjected to a regeneration step.

8. Device for implementing a method according to one of Claims 1 to 7, characterized in that it has a purification zone (24, 25, 25') for helium (22, 23), which purification zone comprises at least one mechanical filter (25, 25') and at least one absorbent bed (24), means (21, 22', 23', 27') for feeding helium to be purified to the said purification zone and means (27, 30) for recovering purified helium containing at most 1 ppb of impurities.

9. Device according to Claim 8, characterized in that it has means (30) for storing purified helium, and/or means (27) for conveying the purified helium on-line to a site where it is used, and/or means for regenerating the adsorbent material.

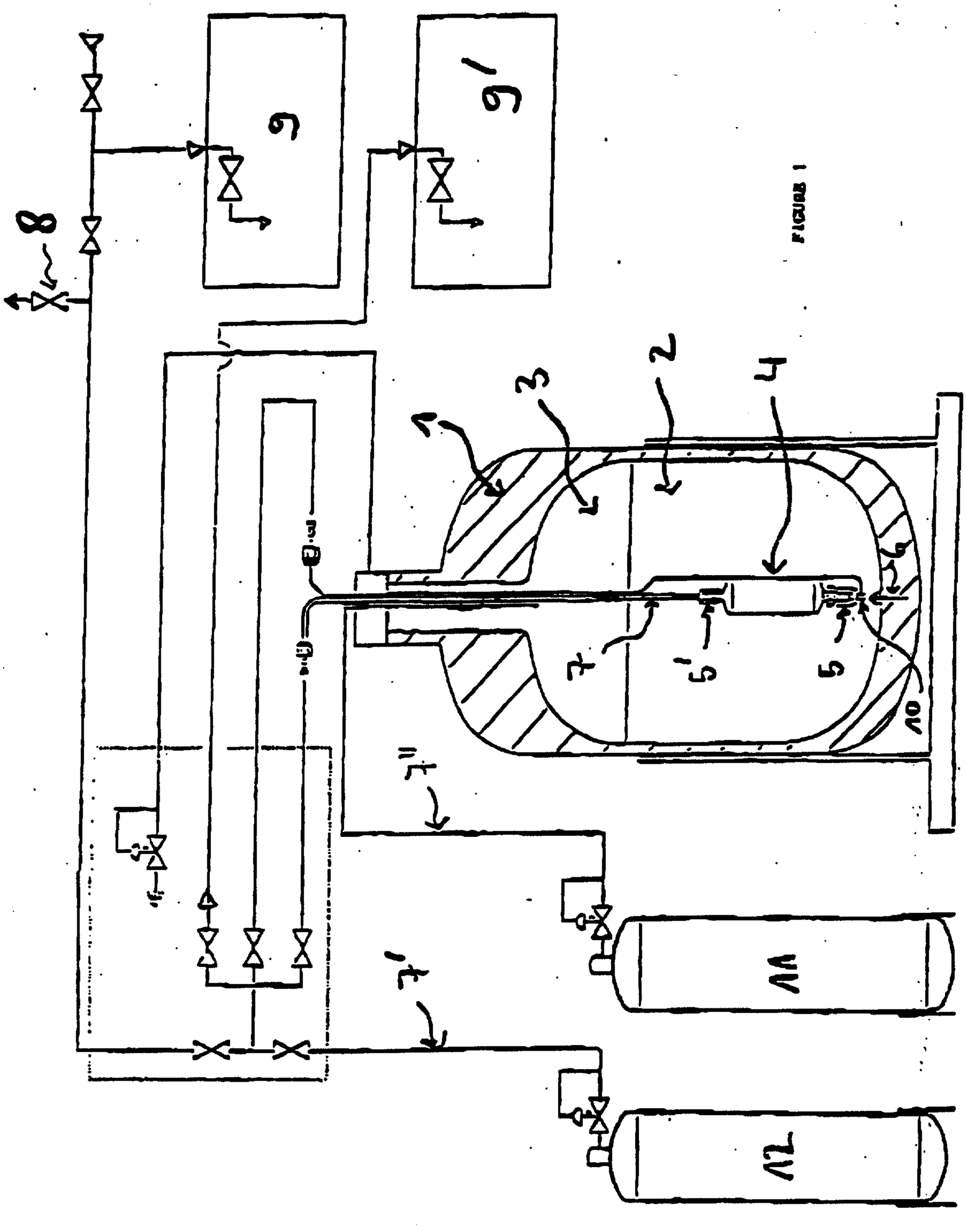

FIGURE 1

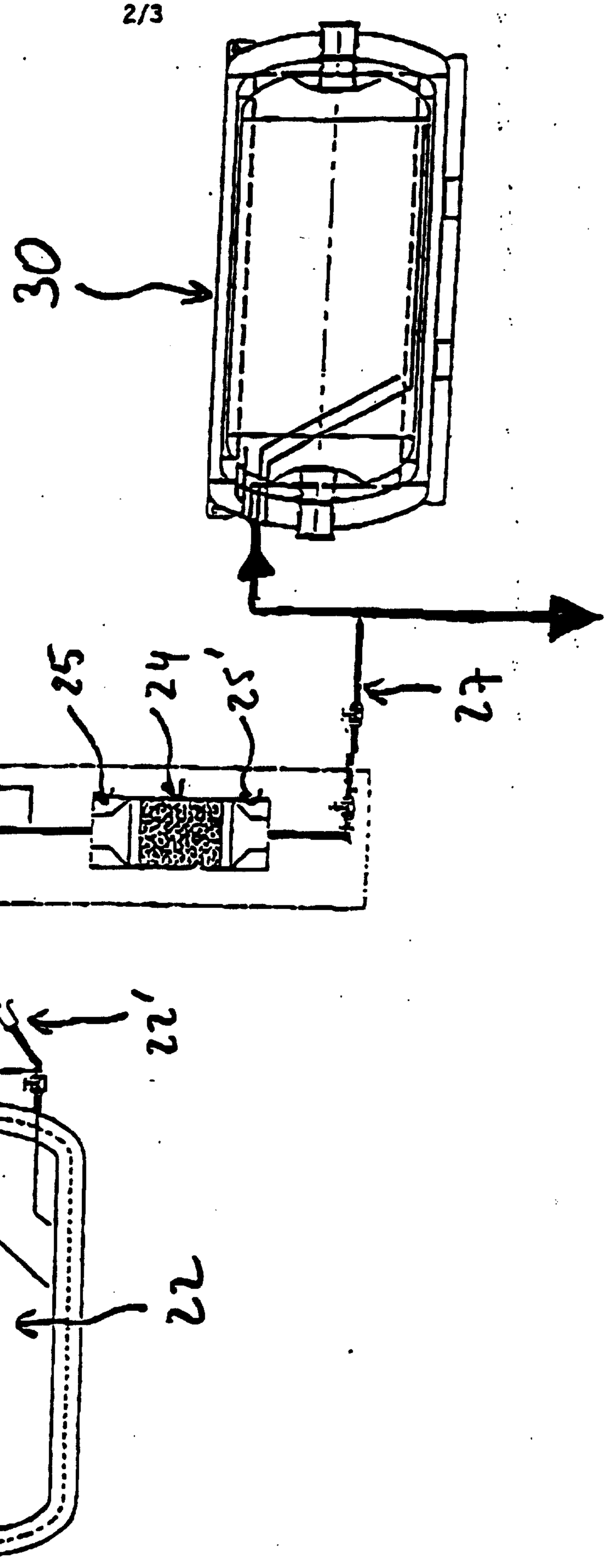

FIGURE 2

FIGURE 3