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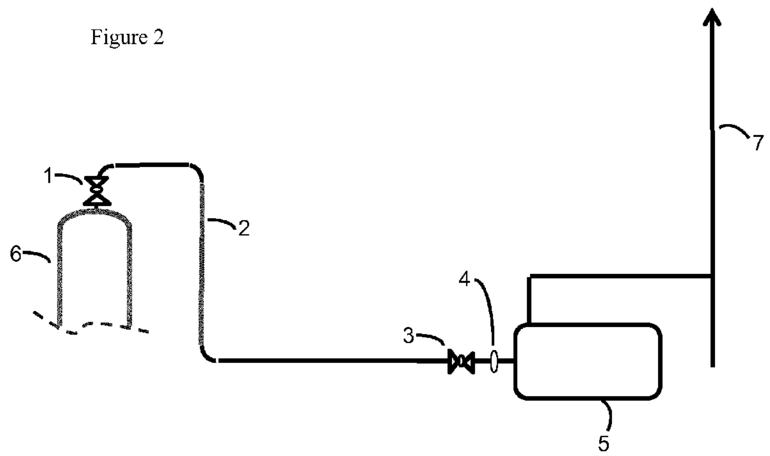
(54) **Title**: PROCESS FOR DEPRESSURIZING A GAS MIXTURE COMPRISING FREEZABLE SPECIES

Figure 2



(57) **Abstract**: The invention relates to a process for depressurizing a gas G1 from a pressure P1 to pressure P2, said gas G1 comprising freezable species and being contained in a capacity (6), said process comprising the following steps: 1) Providing said capacity (6) with a depressurization system which can be fed with said gas G1, said depressurization system comprising in the direction of flow a first automatic valve (1) in closed position, a line (2) comprising a gas G2 free of freezable species at a pressure P1, a second automatic valve (3) in closed position, and a restriction orifice (4), 10 2) Opening the first automatic valve (1) so that gas G1 and G2 come into contact at pressure P1, 3) Opening the second automatic valve (3) so that gas G1 and G2 flow through the restriction orifice (4), thereby recovering the gas G1 whose pressure is lowered to a pressure P2.1 The invention also relates to the depressurization system for implementing the process of the invention.

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PROCESS FOR DEPRESSURIZING A GAS MIXTURE COMPRISING FREEZABLE SPECIES

Field of the invention

The invention relates to a process for preventing the blockage of a line during depressurization of a gas mixture comprising freezable species in emergency situation. Furthermore, the invention relates to a depressurization system for implementing such a process.

The invention is aimed in particular to address the problems due to crystallization of CO2 during depressurization in emergency situation of a pressurized capacity containing a gas having a high percentage of CO2. The invention is particularly useful where the depressurization conditions are favorable to the formation of CO2 crystals, and where the formation of such crystals presents a risk of blocking or plugging the depressurization line due to deposition, adhesion and/or agglomeration of said crystals onto said line. The invention applies in particular to any gaseous mixtures having a certain content of CO2 which are subjected to pressure and temperature conditions below the triple point of the gaseous CO2. In such conditions, any temperature loss due to decompression is likely to cause crystallization of a part of the CO2 contained in the gas mixture. The invention can also be extended to any gas containing compound(s) which may pass from the gaseous phase to the solid phase during depressurization of said gas.

Background

When a gas mixture containing a high percentage of CO2 is depressurized, the temperature of the gas decreases. As a result, the gas may pass in the zone of CO2 solid phase, and crystals of CO2 may appear (see Figure 1).

Initially, the gas phase pressure and temperature is below the CO2 triple point. Thus, during depressurization, as soon as the temperature and pressure gas conditions enter in the zone of CO2 solid phase, uncontrolled risk of blockage exists, depending on the depressurization time, gas flow rate, gas composition, initial and transient temperature of the pipe wall, etc…

During depressurization, the pressure and temperature conditions can become favorable to the formation of a certain quantity of crystals for a certain period for a certain system. It has been shown during experiments that even when the pressure and temperature come back to gas phase position in the phase diagram, the crystals do not disappear instantaneously, and that disappearance can take longer when crystals are agglomerated. The risk of accumulation up to blockage of the depressurization line is therefore obvious as soon as a sufficient quantity of crystals is formed during the depressurization, according to the characteristics of said line (size, metallurgy, roughness, temperature, etc…). The evaluation and the prevention of the plugging risk are not presently possible, and so a solution to suppress said risk and to guarantee the safe depressurization in an emergency situation is needed.

According to some standard norms and rules of the industry, a pressurized vessel is to be provided with a depressurization device. This device is an integral part of the design and safety of the vessel and facility. For instance, the device should be capable of depressurizing down to 7 bar in 15 minutes or half the pressure in 15 minutes according to API 521 (Guide for Pressure-Relieving and Depressuring Systems). This required decompression is an example of cases where the pressure and temperature conditions will be in the zone where CO2 crystallization and particles deposition will occur and crystals will have a high probability to accumulate in the line.

The accumulation of the deposits of CO2 crystals, but also the detachment of adherent deposits afterwards from the walls of the line because of depressurization or vibrations of the line possibly due to the depressurization along with non-instantaneous phase transformation, can block the line and hinder the depressurization. The objective of this invention is to avoid the blockage of the line during depressurization by an innovative system.

The present invention meets all these needs by providing a safe static passive depressurization process and system thereof that does not require any chemical injection or heating device and that is thus intrinsically safe. The process and system of the present invention is particularly suitable in the case of emergency depressurization since it maintains the depressurization flow rate in any case.

Summary

One object of the present invention is a process for depressurizing a gas G1 from a pressure P1 to a pressure P2, said gas G1 comprising freezable species and being contained in a capacity (6), said process comprising the following steps:

1) Providing said capacity (6) with a depressurization system which can be fed with said gas G1, said depressurization system comprising in the direction of flow a first automatic valve (1) in closed position, a line (2) comprising a gas G2 free of freezable species at a pressure P1, a second automatic valve (3) in closed position, and a restriction orifice (4),
2) Opening the first automatic valve (1) so that gas G1 and G2 come into contact at pressure P1,
3) Opening the second automatic valve (2) so that gas G1 and G2 flow through the restriction orifice (4), thereby recovering the gas G1 whose pressure is lowered to a pressure P2.

In one embodiment, the first automatic valve is a full port valve, such as a Blow-Down Valve.

In one embodiment, the second automatic valve is full port valve, such as a Blow-Down Valve.

In one embodiment, the restriction orifice is a perforated plate.

In one embodiment, the freezable species include carbon dioxide.

In one embodiment, the gas G1 originates from a production unit.

In one embodiment, the gas G2 is an inert gas, such as nitrogen.

In one embodiment, the length of the line is at least of 10 m, particularly from 35 m to 300 m, more particularly from 100 m to 250 m, even more particularly from 150 m to 200 m.

In one embodiment, the depressurization system is connected to a dispersion device, in particular a vent or a flare.

In one embodiment, P2 is from atmospheric pressure to 10 bar.

A second object of the present invention is a depressurization system for implementing the process of the invention comprising a first automatic valve connected to a line, in particular with a length of at least 10 m, said line being connected to a second automatic valve, said second automatic valve being connected to a restriction orifice.

In one embodiment, the first automatic valve is a full port valve, such as a Blow-Down Valve.

In one embodiment, the second automatic valve is full port valve, such as a Blow-Down Valve.

In one embodiment, the restriction orifice is a perforated plate.

In one embodiment, the length of the line is from 35 m to 300 m, in particular from 100 m to 250 m, more particularly from 150 m to 200 m.

Brief description of the figures

Figure 1 represents the phase diagram of carbon dioxide.
Figure 2 schematically represents the process and depressurization system of the invention.

Detailed description

One object of the present invention is a process for depressurizing a gas G1 from a pressure P1 to a pressure P2, said gas G1 comprising freezable species and being contained in a capacity, said process comprising the following steps:

(1) Providing said capacity with a depressurization system which can be fed with said gas G1, said depressurization system comprising in the direction of flow a first automatic valve in closed position, a line comprising a gas G2 free of freezable species at a pressure P1, a second automatic valve in closed position and a restriction orifice,

(2) Opening the first automatic valve so that gas G1 and G2 come into contact at pressure P1,

(3) Opening the second automatic valve so that gas G1 and G2 flow through the line and the restriction orifice, thereby recovering the gas G1 whose pressure is lowered to a pressure P2.

The gas G1 may be any gas stream obtained from natural gas or a petroleum reservoir. Such gas contains hydrocarbons, primarily methane, and often acid contaminants, such as carbon dioxide or hydrogen sulphide. Carbon dioxide can be present in large amounts up to 70% molar or over. For most of the applications of these gas streams, the contaminants need to be removed, either partially or almost completely, depending on the application and the contaminant. The process of the invention applies to a natural gas before treatment, during treatment or after treatment, in particular during treatment, more particularly during a cryogenic separation treatment.

The gas G1 can comprise from 15 to 99 molar % of carbon dioxide, typically from 20 to 80 molar % of carbon dioxide.

According to the invention, the gas G1 comprising freezable species is contained in a capacity. For instance, the gas G1 may originate from a production unit, such as a cryogenic separation column. The temperature of the gas G1 in the capacity may be typically comprised between – 60 °C and -40 °C. The pressure P1 of the gas G1 in the capacity may be typically comprised between 30 bar and 40 bar.

According to the invention, « freezable species » means any compound which can pass from a gaseous state to a solid state when the gas G1 is subjected to depressurization. Typically, the freezable species include carbon dioxide. Depending on the composition of gas G1, freezable species may also include hydrates. In the following description, it will be referred to carbon dioxide, but the invention can apply to other freezable species which may pass from the gaseous phase to the solid phase during depressurization of the gas G1.

Now referring to figure 2, the depressurization system of the present invention comprises a first automatic valve 1, a line 2, a second automatic valve 3 and a restriction orifice 4.

The gas G1 is contained in a capacity 6 at pressure P1. The capacity 6 is connected to the first automatic valve 1 of the depressurization system.

At the initial time of the process of the invention, the first automatic valve 1 and the second automatic valve 3 are both in closed position. A gas G2 free of freezable species is injected in line 2 at pressure P1. Said gas G2 may be a non-flammable inert gas or a hydrocarbon gas. For safety reasons, the gas G2 is preferably a non-flammable gas inert gas, such as nitrogen.

The first automatic valve 1 and second automatic valve 3 are preferably full flow valves, i.e. valves whose opening is as large as the section of the line 2. Such full flow valves include for instance full port valves, also named full bore ball valves. A full port valve has an over-sized ball so that the hole in the ball is the same size as the line, which results in lower friction loss. In one particular embodiment, the first automatic valve 1 and second automatic valve 3 are Blow-Down Valves (BDV).

According to step (2) of the process of the invention, the first automatic valve 1 is opened so that gas G1 and G2 come into contact at pressure P1 inside line 2. In order to avoid any pressure loss in line 2, the first automatic valve 1 is fully opened. Since they are at the same pressure P1, at this point gas G1 and gas G2 substantially do not form any gaseous mixture.

Then, according to step (3) of the process of the invention, the second automatic valve 3 is opened so that gas G1 and G2 flow through the line 2and the restriction orifice 4. By “restriction orifice”, it is meant any perforated device which allows the control of the flow rate of gas G1 and the depressurization of gas G1. Typically, the restriction orifice 4 is a perforated plate, i.e. a plate perforated with multiple holes. In one embodiment, the restriction orifice 4 is sized to allow a depressurization time of around 15 minutes from P1 to P2, as required by the API 521 (Guide for Pressure-Relieving and Depressuring Systems).

As well known by the person skilled in the art, the depressurization of a gas generally leads to a decrease of the gas temperature. Prior to reaching the restriction orifice 4, the gas G1 flows through line 2 and is heated by heat exchange with the line 2. The dimensions and materials of the line 2 are adjusted so that the temperature of the gas G1 at the restriction orifice 4 is increased to a point where the gas G1 is not under the pressure and temperature conditions which would lead to crystallization of carbon dioxide during depressurization. The calculation of the required dimensions of the line 2 can be made by using a simulation software, such as the BlowDown program from the Imperial College (M.A. Haque, S.M. Richardson, G. Saville: Process Safety and Environmental Protection, Vol 70, 3-17, 1992)

The dimension calculation of line 2 is made from various parameters, including the volume of the gas G1 contained in the capacity 6, the temperature of the air surrounding the line 2 (typically ≥ 15 °C), the temperature and pressure of gas G1 at the inlet of the line 2 (typically from - 60 °C to - 40°C and from 30 to 40 bars) and the material of the line 2.

The line 2 is a conventional line used in gas production units. Typically, the line 2 is made in stainless steel, but any other material able to accumulate heat by contact with the surrounding air may be used.

In one embodiment, the gas G1 is contained in a cryogenic separation column whose height is from 40 m to 50 m and diameter is 4 m to 6 m including a reflux drum. It contains from 10 to 30 % molar of carbon dioxide, and is at a pressure P1 from 30 to 40 bar and at a temperature from -60 °C to -40 °C. According to this embodiment:

- the length of the line 2 between the first automatic valve 1 and the second automatic valve 3 can be from 10 m to 300 m, in particular from 35 m 100 m to 250 m and, more particularly from 150 m to 200 m,

- the diameter of the line 2 can be from 0.05 m to 1 m, in particular from 0.1 m to 0.9 m, more particularly from 0.2 m to 0.8 m,

- the line 2 can be made of stainless steel.

As an example:

- Gas G1 is contained in a cryogenic separation column of 45m height and 4.6m diameter with a reflux drum of 9 m height and 2.5m diameter,
- P1 is 36 bar,
- Temperature of the head of the column: -54°C
- Diameter of the line 2: 51 cm,

- If the temperature of the air surrounding the line 2 is 20 °C, the required length of the line 2 to avoid crystallization of CO_2 during depressurization of gas G1 to atmospheric pressure is 44 m.
- If the temperature of the air surrounding the line 2 is 0 °C, the required length of the line 2 to avoid crystallization of CO_2 during depressurization of gas G1 to atmospheric pressure is 62 m.

Just as a precautionary measure, the depressurization system of the invention may further comprise a gas/liquid/solid separator 5 for collecting any crystal or liquid which may form during the first minutes of the depressurization of the gas despite line 2. To this end, the gas/liquid/solid separator 5 is preferably connected downstream the restriction orifice 4 in its vicinity. The gas/liquid/solid separator 5 can be any vessel able to separate gas from solids and liquids. If crystallization of CO_2 happens downstream of the depressurization device 4 despite line 2, the crystals will be accumulating in the gas/liquid/solid separator 5. Minimum distance will be maintained between restriction orifice 4 and the gas/ liquid/solid separator 5 or the restriction orifice 4 can be placed directly at the entrance or inside the gas/ liquid/solid separator 5. The gas/ liquid/solid separator 5 can be directly connected to the second automatic valve 3. The gas/ liquid/solid separator 5 is designed to avoid any CO_2 crystal carry-over through the downstream line.

The gas G1 exiting the depressurization system is at pressure P2.

Pressure P2 is lower than P1. In one embodiment, P2 is from atmospheric pressure to 10 bar, more particularly from atmospheric pressure to 5 bar.

In one embodiment, the depressurization system is connected to a dispersion device 7 *via* to the restriction orifice 4 or the gas/liquid/solid separator 5 if applicable.

In one embodiment, the dispersion device 7 is a vent or a flare.

Of course, the process of the invention can be combined with other means such as the heating of the depressurization line 2, for instance if the temperature of air surrounding line 2 is not high enough to ensure enough heating of the gas G1 to avoid crystallization of carbon dioxide, or by a coating of the line to further reduce the risk of crystals adhesion in the line.

A second object of the present invention is a depressurization system for implementing the process of depressurization of the invention as described above, comprising (by referring to Figure 2) a first automatic valve 1 connected to a line 2, in particular with a length of at least 10 m, said line 2 being connected to a second automatic valve 3, said second automatic valve 3 being connected to a restriction orifice 4.

The first automatic valve 1, the line 2, the second automatic valve 3 and the restriction orifice 4 are as described previously.

In one embodiment, the first automatic valve 1 is a full port valve, such as a Blow-Down Valve.

In one embodiment, the second automatic valve 3 is full port valve, such as a Blow-Down Valve.

In one embodiment, the restriction orifice 4 is a perforated plate.

As explained previously, the dimensions and materials of the line 2 are adjusted so that the temperature of the gas G1 at the restriction orifice 4 is increased to a point where the gas G1 is not under the pressure and temperature conditions which would lead to crystallization of carbon dioxide during depressurization.

In one embodiment, the length of the line 2 is from 35 m to 300 m, in particular from 100 m to 250 m, more particularly from 150 m to 200 m, in particular when the line 2 is made of stainless steel.

In one embodiment, the depressurization system may further comprise a gas/liquid/solid separator 5 connected downstream the restriction orifice 4 in its vicinity.

CLAIMS

1. A process for depressurizing a gas G1 from a pressure P1 to pressure P2, said gas G1 comprising freezable species and being contained in a capacity (6), said process comprising the following steps:
   1) Providing said capacity (6) with a depressurization system which can be fed with said gas G1, said depressurization system comprising in the direction of flow a first automatic valve (1) in closed position, a line (2) comprising a gas G2 free of freezable species at a pressure P1, a second automatic valve (3) in closed position, and a restriction orifice (4),
   2) Opening the first automatic valve (1) so that gas G1 and G2 come into contact at pressure P1,
   3) Opening the second automatic valve (3) so that gas G1 and G2 flow through the restriction orifice (4), thereby recovering the gas G1 whose pressure is lowered to a pressure P2.

2. The process according to claim 1, wherein the first automatic valve (1) is a full port valve, such as a Blow-Down Valve.

3. The process according to claim 1 or 2, wherein the second automatic valve (3) is full port valve, such as a Blow-Down Valve.

4. The process according to any one of claims 1 to 3, wherein the restriction orifice (4) is a perforated plate.

5. The process according to any one of claims 1 to 4, wherein the freezable species of gas G1 include carbon dioxide.

6. The process according to any one of claims 1 to 5, wherein the gas G1 originates from a production unit.

7. The process according to any one of claims 1 to 6, wherein the gas G2 is an inert gas, such as nitrogen.

8. The process according to any one of claims 1 to 7, wherein the length of the line (2) is at least of 10 m, in particular from 35 m to 300 m, more particularly from 100 m to 250 m, even more particularly from 150 m to 200 m.

9. The process according to any one of claims 1 to 8, wherein the depressurization system is connected to a dispersion device (7), in particular a vent or a flare.

10. The process according to any one of claims 1 to 9, wherein P2 is from atmospheric pressure to 10 bars.

11. A depressurization system for implementing the process according to any one of claims 1 to 10, comprising a first automatic valve (1) connected to a line (2), said line (2) being connected to a second automatic valve (3), said second automatic valve (3) being connected to a restriction orifice (4).

12. The depressurization system according to claim 11, wherein the first automatic valve (1) is a full port valve, such as a Blow-Down Valve.

13. The depressurization system according to claim 11 or 12, wherein the second automatic valve (3) is full port valve, such as a Blow-Down Valve.

14. The depressurization system according to any one of claims 11 to 13, wherein the restriction orifice (4) is a perforated plate.

15. The depressurization system according to any one of claims 11 to 14, wherein the length of the line (2) is at least 10 m, in particular from 35 m to 300 m, more particularly from 100m to 250m, even more particularly from 150 to 200m.

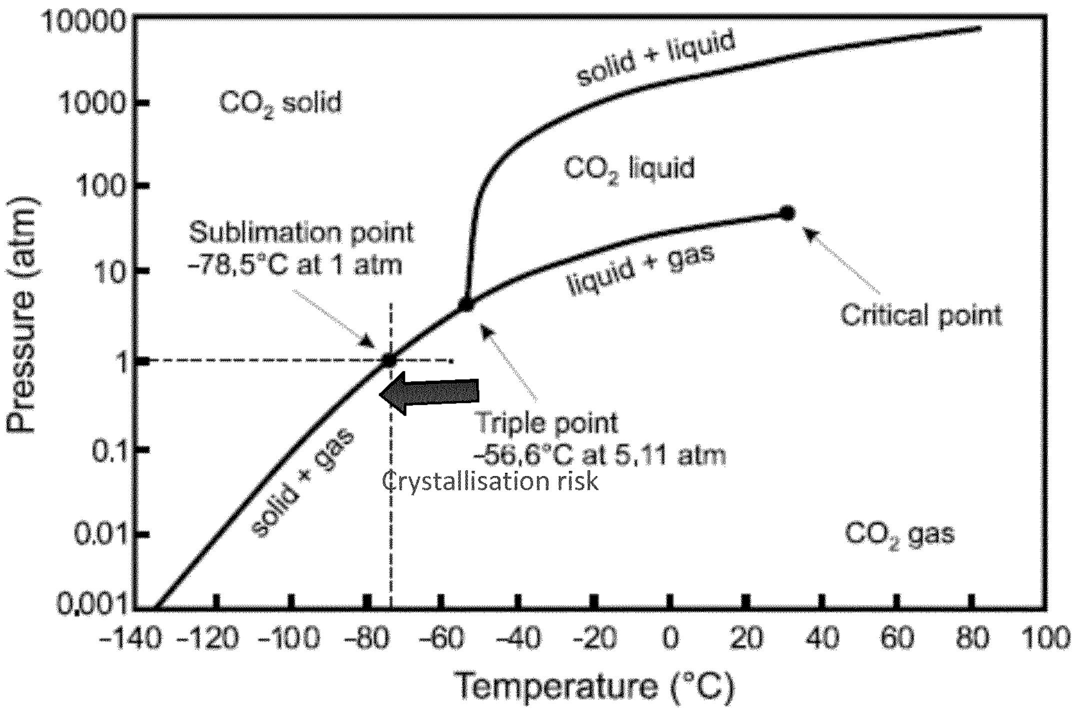
10000
1000
100
10
1
0.1
0.01
0,001
Pressure (atm)
-140 -120 -100 -80 -60 -40 -20 0 20 40 60 80 100
Temperature (°C)
solid + liquid
CO_2 solid
CO_2 liquid
Sublimation point
-78,5°C at 1 atm
liquid + gas
Critical point
Triple point
-56,6°C at 5,11 atm
Crystallisation risk
solid + gas
CO_2 gas

Figure 1

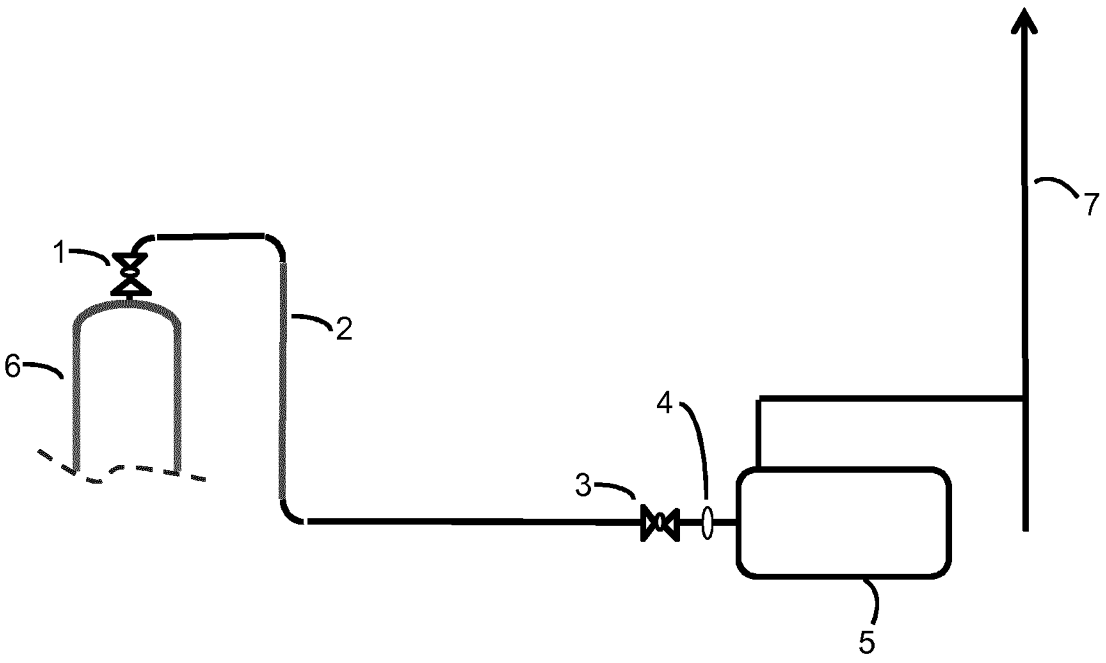

Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/056453

A. CLASSIFICATION OF SUBJECT MATTER
INV. F17C7/02 F17C9/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
F17C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 982 551 A2 (GEN CRYOGENICS [US]) 1 March 2000 (2000-03-01) paragraph [0022] - paragraph [0091]	1-15
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A	JP 2003 028396 A (ITO KOKI KK) 29 January 2003 (2003-01-29) abstract	1-15
A	US 6 182 715 B1 (ZIEGLER ALEX R [US] ET AL) 6 February 2001 (2001-02-06) column 3, line 64 - column 7, line 58	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 June 2013	08/07/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Stängl, Gerhard

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/056453

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