

PROCESS FOR PURIFYING A CRYOGENIC FLUID CONTAINING

N_2O , C_nH_m AND/OR NO_x IMPURITIES

The present invention relates to a process for purifying a cryogenic fluid, such as nitrogen, oxygen, helium, hydrogen or argon, of in particular its N_2O , C_nH_m and/or NO_x impurities.

Cryogenic fluids such as oxygen, nitrogen, helium, hydrogen or argon are of great industrial importance, especially in the electronics field.

Thus, it is common practice to use nitrogen for inerting or cooling printed circuits during their manufacturing process and helium is often employed for cooling hot optical fibres.

At the present time, the various cryogenic fluids are obtained by cryogenic distillation from ambient air or from gas mixtures containing them or by non-cryogenic separation techniques, for example by pressure swing adsorption processes, usually called PSA processes, or by membrane permeation.

However, for some applications, especially in the electronics field, the cryogenic fluid must be of high purity, that is to say it must contain minimal amounts of impurities and other undesirable contaminants, in order to prevent these impurities from causing undesirable physico-chemical reactions or reactions incompatible with the intended aim.

Thus, it is usual to purify the cryogenic fluids very thoroughly, that is to say down to purity levels of less than a few tens of ppb (parts per billion) or even to 1 ppb.

Up to the present time, many methods of purifying cryogenic fluids have already been proposed.

Thus, mention may be made of document EP-A-662,595 which describes a process for preparing high-purity liquid nitrogen, in which process the carbon monoxide, oxygen and hydrogen impurities present in the liquid nitrogen are removed by adsorption on a zeolitic material or a material of the porous metal oxide type.

Furthermore, document US-A-4,746,332 describes the removal of carbon monoxide present in liquid nitrogen by adsorption on a type 5A zeolite.

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Moreover, EP-A-590,946 teaches prepurification, using a TSA (Temperature Swing Adsorption) type process, of carbon monoxide present in gaseous nitrogen at a temperature of 90 K to 150 K, followed by ultrapurification by subsequent distillation of the nitrogen thus prepurified.

Document EP-A-750,933, for its part, relates to removal of carbon monoxide and oxygen which are present in liquid or gaseous nitrogen or argon by adsorption on a transition metal oxide or oxides, for example a hopcalite.

Moreover, document US-A-4,717,406 teaches the purification of a stream by mechanical filtration and adsorption on an adsorbent, especially of the molecular-sieve, activated-charcoal or silica type.

Document WO-A-98/28226 recommends purifying a cryogenic fluid, such as helium, hydrogen or argon, of its impurities by mechanical filtration of the impurities in the form of crystals and adsorption of the impurities in dissolved or gaseous form, so as to obtain a purified fluid containing less than 1 ppb of impurities.

Furthermore document US-A-4,425,143 describes a zeolite having enhanced adsorption performance and being characterized by a high Si/Al ratio in order to withstand acids, this zeolite being free of Fe_2O_3 .

Document EP-A-747,118 teaches the removal of oxygen impurities from an inert gas by means of a support impregnated with an alkali or alkaline-earth metal oxide.

Finally, document US-A-3,597,169 relates to a process for removing methane impurities contained in liquid oxygen by employing a zeolite X highly exchanged with calcium or silver cations.

In practice, the adsorbent particles used in these various processes usually have an average size of about 2 mm to 5 mm.

However, although these processes allow certain impurities contained in the cryogenic fluids,

especially such as carbon monoxide, carbon dioxide or oxygen impurities, to be removed relatively well, it appears that the problem of effective removal of certain other impurities likely to be present in relatively large amounts in cryogenic fluids have not been solved hitherto, or have only been solved incompletely.

The object of the present invention is therefore to improve the existing processes by proposing a cryogenic-fluid purification process allowing effective removal of, in particular, N_2O , C_nH_m and/or NO_x impurities liable to be present in a cryogenic fluid, such as nitrogen, oxygen, helium, hydrogen or argon.

Within the context of the present invention, NO_x should be understood to mean NO and/or NO_2 and C_nH_m should be understood to mean one or more hydrocarbons, such as molecules with a saturated or unsaturated carbon backbone.

The present invention therefore relates to a process for purifying a cryogenic fluid containing impurities chosen from N_2O , C_nH_m (hydrocarbons) and NO_x , in which process:

(a) at least some of the impurities contained in the cryogenic fluid to be purified are removed by bringing the said cryogenic fluid to be purified into contact with particles of at least one adsorbent, the said particles having an average size of less than or equal to 1.5 μm ; and

(b) a purified cryogenic fluid is recovered which contains less than 100 ppb of the said impurities, preferably less than 10 ppb of the said impurities.

The reason for this is that the inventors of the present invention have demonstrated that the size of the adsorbent particles has a great influence on the performance, that is to say the effectiveness, of the purification process.

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As shown in the examples below, it appears that a beneficial effect on the performance of the process may be obtained by reducing the size of the adsorbent particles used in the purification process, this probably being due to the improvement in the kinetics of impurity adsorption on the adsorbent.

Depending on the case, the process according to the invention comprises one or more of the following characteristics:

- the said particles have an average size of less than or equal to 1.4 mm, preferably less than or equal to 1.3 mm, preferably less than or equal to 1.2 mm and advantageously approximately 0.8 mm to 1.1 mm;

- the cryogenic fluid is chosen from among oxygen, argon, nitrogen, hydrogen and helium;

- the cryogenic fluid is in the liquid and/or gaseous state;

- at least some of the impurities contained in the cryogenic fluid to be purified are removed by adsorption or by chemisorption on the adsorbent particles;

- the removal of the impurities is carried out at a temperature below approximately -120°C , preferably below -150°C ;

- the removal of the impurities is carried out at a pressure of 10^5 Pa to 3×10^6 Pa;

- the contact time between cryogenic fluid and adsorbent particles is less than or equal to 300 s, preferably from 70 to 200 s;

- the adsorbent particles have a pore diameter of 0.5 to 2.5 nm and/or a pore volume of 0.2 to 0.8 ml/g and/or a specific surface area of 100 to $1500 \text{ m}^2/\text{g}$, preferably from 600 to $850 \text{ m}^2/\text{g}$;

- the adsorbent particles are in bead, extruded, crushed or elliptical form;

- the adsorbent particles are made of a material chosen from among silica gel, zeolites, metal oxides, such as hopcalite, and carbon materials;



- a purified cryogenic fluid is recovered which contains at most 1 ppb of impurities;

- the process is of the PSA (Pressure Swing Adsorption) or TSA (Temperature Swing Adsorption), preferably TSA, type;

- the cryogenic fluid possibly contains one or more impurities chosen from the group formed by H_2 , CO , CO_2 and H_2O , which are also removed;

- the adsorbent is of the zeolite type, especially an X, LSX (for Low Silica X) or A zeolite, which is unexchanged or exchanged with metal cations, particularly calcium, silver, copper, cobalt, nickel, palladium or platinum cations.

The invention will now be described in greater detail with the aid of examples and of the appended figures, these being given by way of illustration but implying no limitation.

Examples

The following tests aim to demonstrate the effectiveness of the adsorption purification process according to the present invention.

More specifically, in these various tests, the conditions for carrying out the purification process are as follows:

- fluid to be purified : liquid argon
- impurities to be removed : N_2O
- content of N_2O
impurities (as input) : 1 to 8.5 ppm
- purification temperature : $-185^\circ C$
- purification pressure : 8×10^5 Pa
- contact time : 70 to 200 seconds
- purification throughput : approximately
1 Sm^3/h .

Furthermore, the adsorbent employed has the following characteristics:

- nature of the adsorbent : silica gel

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- shape of the particles : spheres
- average particle sizes : 1.1, 2 or 2.5 mm
- average pore volume : approximately 0.40ml/g
- average pore diameter : 2nm
- specific surface area : 750 m²/g.

Test No. 1: Purification of liquid argon on
2.5 mm particles

The stream of liquid argon to be purified, which contains 8.5 ppm of N₂O impurities, is brought into contact with adsorbent particles having an average size of 2.5 mm.

In this test, the contact time is approximately 130 seconds.

The results obtained are plotted in Figure 1 and clearly show that the N₂O break-through occurs after only 4 hours on 2.5 mm particles.

The break-through stopping capacity is therefore 0.9 Scc/g.

Test No. 2: Purification of liquid argon on
2 mm particles

The stream of liquid argon to be purified, which contains 1 ppm of N₂O impurities, is brought into contact with adsorbent particles having an average size of 2 mm.

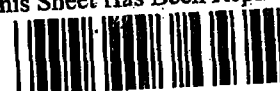
In this test, the contact time is approximately 200 seconds.

The results obtained are plotted in Figure 2 and clearly show that the N₂O break-through occurs after 47 hours on the 2 mm particles.

The break-through stopping capacity is therefore 0.85 Scc/g.

Test No. 3: Purification of liquid argon on
1.1 mm particles

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The stream of liquid argon to be purified, which contains 1.5 ppm of N_2O impurities, is brought into contact with adsorbent particles having an average size of 1.1 mm.

In this test, the contact time is approximately 70 seconds.

The results obtained are plotted in Figure 3 and clearly show that the N_2O break-through occurs only after 300 hours on the 1.1 mm particles.

The break-through stopping capacity is therefore, in this Example 3 according to the invention, more than 22 Scc/g. The results of Tests 1 to 3 are summarized in the comparative table below.

Comparative table

Test No.	Particle size	Contact time	Break-through time (in hours)	N_2O stopping capacity (Scc/g)
1	2.5 mm	130 sec	4	0.90
2	2.0 mm	200 sec	47	0.85
3	1.1 mm	70 sec	> 300	> 22

It is apparent from the above tests, that reducing the size of the adsorbent particles (in this case silica gel) has the result of improving the adsorbent kinetics and, surprisingly, of purifying the cryogenic fluid (in this case liquid argon) more effectively.

This is because, by reducing the size of the adsorbent particles it is found that the break-through time increases for the same adsorption capacity, that is to say by using adsorbent particles having a size of less than the sizes conventionally used, the production time is extended, this being so even when the contact time between the fluid to be purified and the adsorbent is reduced.

In addition, it may be seen that reducing the size of the adsorbent by a factor of approximately 2



(cf. Example 3) surprisingly and unpredictably causes the stopping capacity to be increased by a factor of about 25, even though the contact time was, moreover, reduced by a factor of 3 (cf. Example 3).

The purification process according to the present invention, based on the use of small-sized (< 1.5 mm) adsorbent particles, therefore allows the production phase of a purification cycle to be significantly increased, which in turn makes it possible to reduce the overall costs of the process by decreasing the size of the adsorption reactors, the amount of adsorbent to be used, the frequency of adsorbent regeneration and therefore the energy costs and the amount of regeneration fluid used.

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Key to figures

1/3

N₂O input

N₂O content (ppm)

N₂O output

Time (hours)

2/3

N₂O input

N₂O content (ppm)

N₂O output

Time (hours)

3/3

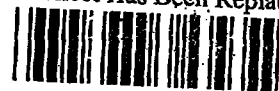
N₂O input

N₂O content (ppm)

N₂O output

Time (hours)

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CLAIMS

1. Process for purifying a cryogenic fluid containing impurities chosen from among N_2O , C_nH_m and NO_x , in which process:

(a) at least some of the impurities contained in the cryogenic fluid to be purified are removed by bringing the said cryogenic fluid to be purified into contact with particles of at least one adsorbent, the said particles having an average size of less than or equal to 1.5 mm; and

(b) a purified cryogenic fluid is recovered which contains less than 100 ppb of the said impurities.

2. Process according to Claim 1, characterized in that the said particles have an average size of less than or equal to 1.3 mm, preferably less than or equal to 1.2 mm and advantageously approximately 0.8 mm to 1.1 mm.

3. Process according to either of Claims 1 and 2, characterized in that the cryogenic fluid is chosen from among oxygen, argon, hydrogen, nitrogen and helium.

4. Process according to one of Claims 1 to 3, characterized in that the cryogenic fluid is in the liquid and/or gaseous state.

5. Process according to one of Claims 1 to 4, characterized in that at least some of the impurities contained in the cryogenic fluid to be purified are removed by adsorption or by chemisorption on the adsorbent particles.

6. Process according to one of Claims 1 to 5, characterized in that the removal of the impurities is carried out at a temperature below -120°C , preferably below -150°C , and/or at a pressure of 10^5 Pa to 3×10^6 Pa.

7. Process according to one of Claims 1 to 6, characterized in that the contact time between





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cryogenic fluid and adsorbent particles is less than or equal to 300 s. preferably from 70 to 200 s.

8. Process according to one of Claims 1 to 7, characterized in that the adsorbent particles have a pore diameter of 0.5 to 2.5 nm and/or a pore volume of 0.2 to 0.8 ml/g and/or a specific surface area of 100 to 1500 m²/g.

9. Process according to one of Claims 1 to 8, characterized in that the adsorbent particles are in bead, extruded, crushed or elliptical form.

10. Process according to one of Claims 1 to 9, characterized in that the adsorbent particles are made of a material chosen from among silica gel, zeolites, metal oxides and carbon materials.

11. Process according to one of Claims 1 to 10, characterized in that a purified cryogenic fluid is recovered which contains at most 10 ppb of impurities, preferably at most 1 ppb of impurities.

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