PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to the Regeneration of ~~Absorbent~~ Adsorbent Materials Charged With Impurities

We, L'AIR LIQUIDE S.A. ~~POUR~~ L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE, a French body corporate, of 75, Quai d'Orsay, Paris 7e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to the regeneration of an adsorbent material, which has been charged with impurities during the purification of an impure gas or mixture of gases.

It is known that one of the most efficient processes for the removal of carbon dioxide from air consists in causing the air to contact an adsorbent material, such as silica gel or activated alumina, this operation generally taking place at a relatively low temperature, for example in the region of −130°C. When the adsorbent material is too heavily charged with carbon dioxide gas to effect a sufficient purification of the air, it is taken out of circuit and regenerated, while the air to be purified is conducted over another quantity of the adsorbent material, the regeneration of which has been effected during the operational period of the first quantity of adsorbent material. The most frequently employed method of regenerating the adsorbent material consists in flushing or scavenging the adsorbent material with a gas free from carbon dioxide gas and/or any other adsorbable impurities and sufficiently hot to bring about the desorption of the carbon dioxide gas and/or other impurity present in the adsorbent material, this latter then being entrained by the flushing gas. The adsorbent material freed from carbon dioxide is then brought to its operational temperature by direct contact with a cold gas which is also free from impurity. One process of this type, which limits the cold losses occurring during regeneration to a minimum is described in the U.S. Patent Specification No. 2,882,998.

However, the known regeneration processes have certain disadvantages which occur as a result of the large volumes of the flushing and cooling gases required. For this purpose, for example in the purification of air, the general procedure is to use the nitrogen originating from the separation of the air when oxygen is the only gas required to be separated in the pure state. But there is now an increasing demand for separated nitrogen in a high state of purity which is incompatible with its use as a gas for regenerating adsorbent materials charged with carbon dioxide gas. Hence, the quantity of nitrogen available for the regeneration of the adsorbent materials is limited to that fraction of the gas for which there does not exist a strict purity standard, and this quantity is sometimes insufficient. It has then been necessary to replace the process of extracting the carbon dioxide from the air by adsorption by a process of extracting carbon dioxide by chemical means (washing with caustic soda), although such a process necessitates large equipment and results in a lower degree of air purity being obtained.

According to the present invention there is provided, in a process for purifying an impure gas or mixture of gases in which the adsorbable impurities present in said impure gas or mixture of gases are adsorbed by a bed of adsorbent material, the steps which comprise regenerating said bed of adsorbent material by passing therethrough a gas or mixture of gases which has the same or substantially the same composition as said impure gas or mixture of gases and which is hotter than said impure gas or mixture of gases, and thereafter cooling the hot bed of adsorbent material to its operational temperature, said cooling being effected by passing through said hot bed of adsorbent material a cold gas or mixture of gases, which is free or substantially free from

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adsorbable impurities, until a portion of said bed of adsorbent material has been cooled to the temperature of said impure gas or mixture of gases and completing the cooling of said bed of adsorbent material by passing through said portion and then through the remainder of said bed of adsorbent material a stream of the impure gas or mixture of gases to be purified.

The process according to the invention enables the disadvantages of the known processes to be substantially obviated and the adsorbent bed charged with impurities to be regenerated without however contaminating a large volume of pure gas.

It also makes it possible for air to be simultaneously subjected to a drying and to the elimination of traces of hydrocarbons, such as acetylene, as well as to the extraction of carbon dioxide, whereas in the known processes the drying at least was generally effected independently of the extraction of carbon dioxide.

The cold gas or mixture of gases used for the cooling of part of the adsorbent bed may be (i) any available pure gas, for example a component of a purified mixture of gases eg nitrogen which is readily available when the gas to be purified is air, or (ii) a gas or mixture of gases which, for example, may have been purified by passage over another quantity of the adsorbent material; or (iii) a limited quantity of an initially impure gas circulating through a closed system comprising a cooling arrangement for the impure gas. In the second case, it is preferred to carry out the process using at least three adsorbent beds, the adsorbent bed to be cooled being arranged after an adsorbent bed which is in operation in the circuit of a gas or mixture of gases to be purified; the bed of adsorbent material in operation ensures an efficient purification of the gas to be purified until a sufficient portion of the regenerated adsorbent bed, close to the inlet for the gas, has been cooled to its operational temperature.

The process of the invention is more especially applicable to the regeneration of a bed of an adsorbent material such as is used in the purification of air containing carbon dioxide gas and/or moisture and/or hydrocarbons, the air being purified with a view to the separation thereof into its constituents at low temperature by liquefaction and rectification. The process of the invention, however, can also be applied to the regeneration of adsorbent materials which have been used in the purification by adsorption of other gases containing impurities such as hydrogen, helium or mixtures of hydrocarbons.

The process according to the invention permits the periodic regeneration of beds of adsorbent material used for the extraction of carbon dioxide from the air, whatever may be their operational temperature. It is effective even if this temperature is in the region of the ambient temperature, this making it possible for the extraction of carbon dioxide and the drying of the air to be carried out either at low pressure or at high pressure. It should be noted that when the operational temperature is in the region of ambient temperature, the flushing gas must then be brought to a temperature appreciably higher than the ambient temperature, for example by passing it in contact with a steam coil.

The process of the invention permits the use as adsorbent material of a synthetic crystalline zeolite, such as a 5Å molecular seive.

For a better understanding of the invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings which show diagrammatically various arrangements for regenerating a bed of adsorbent material used in the purification of air.

Figure 1 (a, b, c) shows an apparatus which is arranged so that the flow of cooling nitrogen in contact with the adsorbent material to be cooled is interrupted when a portion of the bed of adsorbent material at the inlet end for the air to be purified, is at its operational temperature, the completion of the cooling being effected by the air to be purified;

Figure 2 (a, b, c) shows an arrangement in which the initial cooling is effected by air, initially unpurified, moving in a closed circuit, the final cooling being effected by the air to be purified;

Figure 3 (a, b, c) shows an arrangement in which the initial cooling is effected by purified air to be separated into N_2 and O_2 and leaving a bed of adsorbent material which is still operating in a purified state, and wherein the final cooling is effected with air not previously purified; and

Figure 4 (a, b, c) shows an arrangement comprising a battery of three adsorbent beds arranged in ternary permutation, the air to be purified successively passing through an operating adsorbent bed and then through an adsorbent bed which is being cooled.

In all the Figures, the portion of the adsorbent beds which are charged with impurities are represented by oblique cross-hatching and the regenerated and cooled portions are represented by horizontal cross-hatching.

The regeneration of the adsorbent material shown in Figure 1 (a, b, c) comprises the three phases *a*, *b* and *c*. In phase *a*, while the adsorbent material 3 is still being used, the bed of adsorbent material 9 is being regenerated by reheating. The air to be purified, compressed by a compressor 1 to about 6 kg/cm^2 and cooled in a water condenser (not shown) passes through a conduit 2 into the operational adsorbent material 3 formed, for example, from activated alumina, and leaves the latter dry and free from carbon dioxide by way of a conduit 4. At the same time, a fan 5 drives

the ambient air not freed from carbon dioxide through a reheater 6 over a steam coil 7, which brings it to about 100°C., and thence through a pipe 8 into the adsorbent material 9 in a direction opposite to the circulation direction of the air to be purified. When the adsorbent material 9 is completely reheated, it is brought to its operational temperature, which is close to ambient temperature, by the initial passage therethrough of cold nitrogen until a stage is reached wherein a zone 18 at the end of the arsorbent material and through which the air to be purified must pass is cooled, and then the remainder of the adsorbent material 9, which has only been slightly cooled or not cooled at all, is cooled by passing through the bed air to be purified (Figure 1c). This air is freed from carbon dioxide and dried while passing through the cooled zone 18, and then brings about the cooling of the layers of adsorbent material further from the inlet. It is as a result strongly reheated; by passing through the coil 10 embedded in a water cooler 11, the recooling thereof to ambient temperature is assured before it leaves by way of the pipe 12 to pass to the liquefaction installation proper. The successive layers of the adsorbent material are thus cooled gradually until all the adsorbent material is restored to its operational temperature. The auxiliary cooling of the treated air in the cooler 11 can then be interrupted. The adsorbent material 3 charged with carbon dioxide gas and steam possibly with a small quantity of hydrocarbons, can be subjected to regeneration by the passage of hot air originating from the fan 5 and the reheater 6.

In the method of regeneration and cooling using the arrangement shown in Figure 2 (a, b, c), the adsorbent mass 9 charged with impurities is first of all heated by passing in contact with air delivered by the fan 5 and reheated in the reheater 6. When the desorption of the impurities is complete, air delivered by the fan 5 into the conduit 13 (Figure 2b) is caused to pass over the same adsorbent mass, but in the opposite direction. This air leaves by way of a conduit 14 at a temperature close to the regeneration temperature of the adsorbent mass; it is then cooled by passing through the coil 16 immersed in a water cooler 17, then recycled by the fan 5 and a conduit 13 towards the adsorbent mass. After a short time, the adsorbent zone 20 near the inlet end 19 is cooled to the region of its operational temperature, and it then fixes in zone 20 the limited quantity of carbon dioxide gas and steam in the circulating air. As soon as the cooled zone has reached a sufficient thickness, the adsorbent mass is again brought into general operation. The air to be purified is freed from its impurities while it is passing through the cooled zone 20, and then cools the still hot layers of the adsorbent mass 9 (Figure 2c). It leaves the adsorbent mass in a strongly heated condition; it is brought to its initial temperature in the coil 10 of the water cooler 11. When the cooling of the adsorbent to its operational temperature is completed, the auxiliary cooling of the air in the water cooler 11 can be interrupted.

In the method employing the arrangement shown in Figure 3 (a, b, c), the adsorbent mass 9 charged with carbon dioxide gas and steam is first of all heated to a temperature permitting the desorption of the adsorbed impurities by a current of hot air from which carbon dioxide has not been removed (Figure 3a). When all of the adsorbent mass 9 reaches this temperature, it is introduced into the circuit of the air to be purified, behind the operating adsorbent mass 3 which is still not saturated with impurities. The air purified in passing through the adsorbent mass 3 cools the mass 9 while being itself reheated and whilst entraining the small quantity of impurities present in the interstices of the grains of adsorbent mass 9; the air is then cooled in the coil 10 immersed in the water cooler 11 before being passed to the oxygen-nitrogen installation through the conduit 12.

When a sufficient zone 21 at the inlet end of the adsorbent mass 9 has been returned to its operational temperature, the air to be purified is caused to pass directly through the adsorbent mass 9, while the regeneration of the ~~new~~ substantially saturated adsorbent mass 3 is started by sending hot air through it in the same manner as described above. The cold zone 21 of the adsorbent mass 9 fixes the carbon dioxide gas and the steam present in the air to be purified at 22 which air then cools at 23 the still hot layers of the adsorbent mass by being reheated on contact therewith. The air is then brought to its initial temperature in the water cooler 11. When the cooling of the adsorbent mass 9 is complete, the auxiliary cooling of the air in the cooler 11 can be stopped.

It will ~~now~~ be noted that in this embodiment, at the moment when the adsorbent mass 9, which is regenerated but still not cooled, is being traversed by the purified air leaving the adsorbent mass 3, this latter air entrains a small quantity of impurities. However, the period of time during which the air leaving contains a small quantity of impurities is quite short; the carbon dioxide gas content of the air leaving, which is for example 70 parts per million (70 p.p.m.) at the start, falls very rapidly to the region of zero. The passage, through the remainder of the installation for separating the air, of this small quantity of impurities does not present any major inconvenience; it can moreover be checked by conventional means, for example filters, at a temperature level where these impurities are solid. This inconvenience can moreover be completely avoided by using a battery of three

adsorbent masses arranged in ternary permutation, as will be described in more detail in connection with Figure 4 (a, b, c).

Referring now to the arrangement shown in Figure 4 (a, b, c), the air compressed in the compressor 1 is introduced during a first period (Figure 4*a*) through the conduit 2 into the operational adsorbent mass 3 (already saturated with impurities in a zone 25), then through a pipe 31 into an adsorbent mass 9 which is being cooled (already cooled in a zone 26); finally, it passes through a conduit 32 into the coil 10 of a water cooler 11, and is passed through the conduit 12 to the cooling exchangers. A third adsorbent mass 24 is regenerated as already described by means of atmospheric air delivered by a fan 5 into a reheater 6 having a steam coil 7, and then through the conduit 8 into the adsorbent mass. When the adsorbent mass 9 is completely cooled, the cooling of the air in the cooler 11 is stopped, this mass remaining in series with the mass 3 and permitting the purification to be completed.

When the adsorbent mass 3 is saturated with impurities, the three masses are interchanged (Figure 4*b*). While the mass 3 is subjected to the regeneration by reheating, the air to be purified is introduced into the mass 9, and then from thence through a conduit 33 into a regenerated mass 24 to be cooled. As before, a zone 27 saturated with impurities is formed in the mass 9 and a cooled zone 28 is formed in the mass 24, both zones progressing from the inlet end towards the outlet end.

When the adsorbent mass 24 is completely cooled and the mass 9 is saturated with impurities, the three masses are again interchanged. The mass 9 is subjected to the regeneration by reheating, while the air to be purified is introduced into the cooled mass 24, and from thence through a conduit 35 into the regenerated mass 3 which is to be cooled. During this third period, the mass 24 is progressively charged with impurities (zone 29) and the mass 3 is progressively cooled (zone 30). When the mass 3 is completely cooled and the mass 24 is saturated with impurities, the mass 9 being on the other hand regenerated, a fresh interchange restores the adsorbent masses to the arrangement shown in Figure 5*a*.

WHAT WE CLAIM IS:—

1. In a process for purifying an impure gas or mixture of gases in which adsorbable impurities present in said impure gas or mixture of gases are adsorbed by a bed of adsorbent material, the steps which comprise regenerating said bed of adsorbent material by passing therethrough a gas or mixture of gases which has the same or substantially the same composition as said impure gas or mixture of gases and which is hotter than said impure gas or mixture of gases, and thereafter cooling the hot bed of adsorbent material to its operational temperature, said cooling being effected by passing through said hot bed of adsorbent material a cold gas or mixture of gases, which is free or substantially free from adsorbable impurities, until a portion of said bed of adsorbent material has been cooled to the temperature of said impure gas or mixture of gases and completing the cooling of said bed of adsorbent material by passing through said portion and then through the remainder of said bed of adsorbent material a stream of the impure gas or mixture of gases to be purified.

2. A process according to Claim 1, wherein the purified gas or mixture of gases flowing out of the adsorbent bed and originating from the impure gas or mixture of gases used to complete the cooling of said bed of adsorbent material is cooled until such time as the whole of the adsorbent bed has been cooled to substantially the temperature of the impure gas or mixture of gases.

3. A process according to Claim 1 or 2, wherein said cold gas is a component separated out of a purified mixture of gases.

4. A process according to Claim 1 or 2, wherein said cold gas or mixture of gases is a quantity of impure gas or mixture of gases which is passed through said hot bed of regenerated material, cooled and then recycled through said adsorbent bed.

5. A process according to Claim 1 or 2, wherein said cold gas or mixture of gases is a stream of purified gas or ~~mixtures~~ mixture of gases flowing out of an adsorbent bed in operation, and wherein the passage of the impure gas or mixture of gases, from which said purified gas or mixture of gases is obtained, through said adsorbent bed in operation is interrupted when a portion of the hot bed of adsorbent material has been cooled to the temperature of the impure gas or mixture of gases and the impure gas or mixture of gases is used to complete the cooling of the hot bed of adsorbent material.

6. A process according to any one of the preceding claims, wherein the mixture of gases to be purified is air charged with moisture, carbon dioxide and hydrocarbons, the adsorbent material is a silica gel, an activated alumina or a synthetic zeolite, and the purification by adsorption is carried out at room temperature.

7. A process according to Claim 1, substantially as hereinbefore described with reference to Figure 1, 2 or 3, of the accompanying drawings.

8. A process according to Claim 1, sub-

adsorbent masses arranged in ternary permutation, as will be described in more detail in connection with Figure 4 (a, b, c).

Referring now to the arrangement shown in Figure 4 (a, b, c), the air compressed in the compressor 1 is introduced during a first period (Figure 4*a*) through the conduit 2 into the operational adsorbent mass 3 (already saturated with impurities in a zone 25), then through a pipe 31 into an adsorbent mass 9 which is being cooled (already cooled in a zone 26); finally, it passes through a conduit 32 into the coil 10 of a water cooler 11, and is passed through the conduit 12 to the cooling exchangers. A third adsorbent mass 24 is regenerated as already described by means of atmospheric air delivered by a fan 5 into a reheater 6 having a steam coil 7, and then through the conduit 8 into the adsorbent mass. When the adsorbent mass 9 is completely cooled, the cooling of the air in the cooler 11 is stopped, this mass remaining in series with the mass 3 and permitting the purification to be completed.

When the adsorbent mass 3 is saturated with impurities, the three masses are interchanged (Figure 4*b*). While the mass 3 is subjected to the regeneration by reheating, the air to be purified is introduced into the mass 9, and then from thence through a conduit 33 into a regenerated mass 24 to be cooled. As before, a zone 27 saturated with impurities is formed in the mass 9 and a cooled zone 28 is formed in the mass 24, both zones progressing from the inlet end towards the outlet end.

When the adsorbent mass 24 is completely cooled and the mass 9 is saturated with impurities, the three masses are again interchanged. The mass 9 is subjected to the regeneration by reheating, while the air to be purified is introduced into the cooled mass 24, and from thence through a conduit 35 into the regenerated mass 3 which is to be cooled. During this third period, the mass 24 is progressively charged with impurities (zone 29) and the mass 3 is progressively cooled (zone 30). When the mass 3 is completely cooled and the mass 24 is saturated with impurities, the mass 9 being on the other hand regenerated, a fresh interchange restores the adsorbent masses to the arrangement shown in Figure 5*a*.

WHAT WE CLAIM IS:—

1. In a process for purifying an impure gas or mixture of gases in which adsorbable impurities present in said impure gas or mixture of gases are adsorbed by a bed of adsorbent material, the steps which comprise regenerating said bed of adsorbent material by passing therethrough a gas or mixture of gases which has the same or substantially the same composition as said impure gas or mixture of gases and which is hotter than said impure gas or mixture of gases, and thereafter cooling the hot bed of adsorbent material to its operational temperature, said cooling being effected by passing through said hot bed of adsorbent material a cold gas or mixture of gases, which is free or substantially free from adsorbable impurities, until a portion of said bed of adsorbent material has been cooled to the temperature of said impure gas or mixture of gases and completing the cooling of said bed of adsorbent material by passing through said portion and then through the remainder of said bed of adsorbent material a stream of the impure gas or mixture of gases to be purified.

2. A process according to Claim 1, wherein the purified gas or mixture of gases flowing out of the adsorbent bed and originating from the impure gas or mixture of gases used to complete the cooling of said bed of adsorbent material is cooled until such time as the whole of the adsorbent bed has been cooled to substantially the temperature of the impure gas or mixture of gases.

3. A process according to Claim 1 or 2, wherein said cold gas is a component separated out of a purified mixture of gases.

4. A process according to Claim 1 or 2, wherein said cold gas or mixture of gases is a quantity of impure gas or mixture of gases which is passed through said hot bed of regenerated material, cooled and then recycled through said adsorbent bed.

5. A process according to Claim 1 or 2, wherein said cold gas or mixture of gases is a stream of purified gas or ~~mixtures~~ of gases flowing out of an adsorbent bed in operation, and wherein the passage of the impure gas or mixture of gases, from which said purified gas or mixture of gases is obtained, through said adsorbent bed in operation is interrupted when a portion of the hot bed of adsorbent material has been cooled to the temperature of the impure gas or mixture of gases and the impure gas or mixture of gases is used to complete the cooling of the hot bed of adsorbent material.

6. A process according to any one of the preceding claims, wherein the mixture of gases to be purified is air charged with moisture, carbon dioxide and hydrocarbons, the adsorbent material is a silica gel, an activated alumina or a synthetic zeolite, and the purification by adsorption is carried out at room temperature.

7. A process according to Claim 1, substantially as hereinbefore described with reference to Figure 1, 2 or 3, of the accompanying drawings.

8. A process according to Claim 1, sub-

stantially as hereinbefore described with reference to Figure 4 of the accompanying drawings.

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I certify this, including the Drawing forming part thereof, to be a True Copy of the Specification as accepted.

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