June 24, 1952 P. C. KEITH 2,601,298

COOLING GASES CONTAINING CONDENSIBLE MATERIAL

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Fig. 2

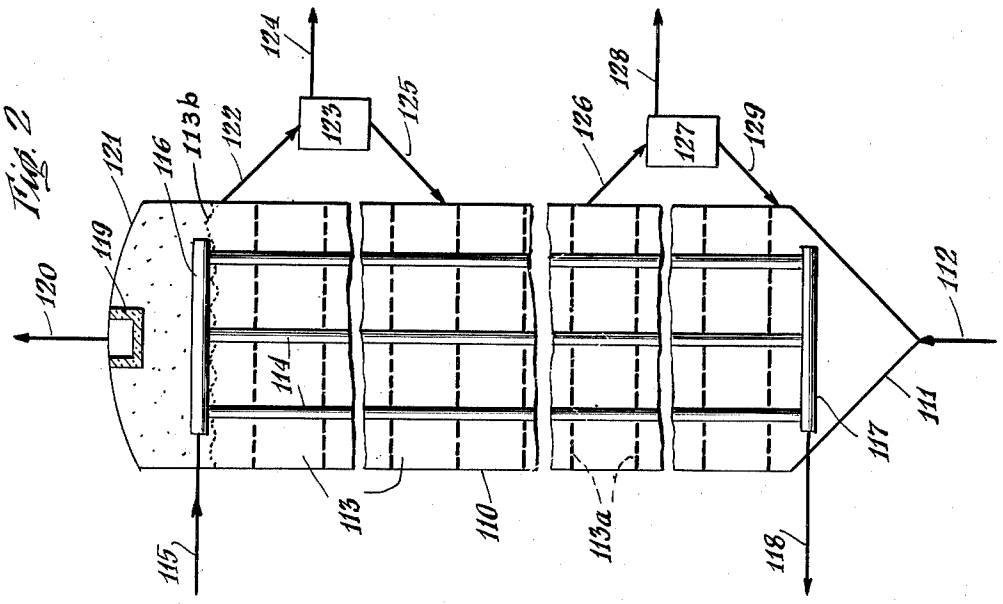
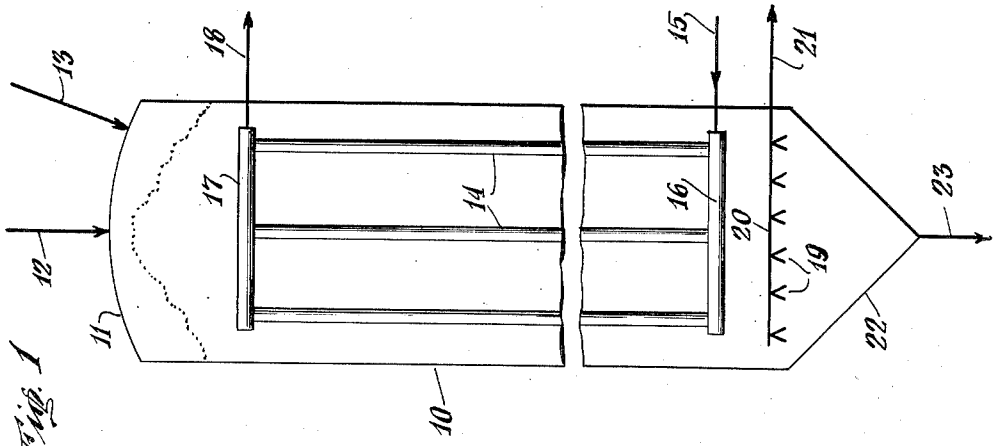


Fig. 1



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COOLING GASES CONTAINING CONDENSIBLE MATERIAL

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This invention relates to processes involving heat exchange and more particularly to processes for cooling gaseous streams in which condensation occurs during the contact of the gaseous stream with the cooling surfaces.

In heat exchange procedures, condensible components of a gaseous stream are deposited on the surfaces of the cooling means when the gaseous stream is cooled below the condensation point of the condensible components. Often the cooling surface is cold enough to cause freezing or solidification of the condensed material so that there is a progressive building-up of condensed material on the cooling surfaces with the result that the heat transfer rate decreases and the heat exchange apparatus is stopped up or choked with the solidified deposits. Several proposals have been made to prevent or remove such solidified deposits.

It has been suggested that the gaseous stream to be cooled be pretreated to remove condensible components prior to admittance of the gaseous stream into the cooling exchanger. For example, in the production of oxygen by the liquefaction and rectification of air where the air feed is cooled by passage in indirect heat exchange relation with the cold outgoing products of rectification, the air which invariably contains about 0.03% by volume of carbon dioxide and varying quantities of moisture, is pretreated in driers and caustic scrubbers to remove the water and carbon dioxide, respectively, prior to admittance of the air into the heat exchangers. Even with such pretreatment which is costly and cumbersome, the exchangers have to be thawed out periodically to remove solidified deposits of water and carbon dioxide which are present in traces in the pretreated air.

More recently there has been developed the use of reversing exchangers by which the gaseous stream to be cooled and the cooling fluid passed in indirect heat exchange relation therewith are reversed, i. e., the flow paths are switched periodically so that the cooling fluid flows through the path previously traversed by the gaseous stream to be cooled and the gaseous stream to be cooled flows through the path previously traversed by the cooling fluid. By such reversal, the deposited components are re-evaporated or sublimed and carried out of the heat exchanger by the cooling fluid. In other words, the material deposited by the process stream during one period of operation is re-evaporated and purged from the exchanger by the reverse flow of the coolant stream during the succeeding period.

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The use of reversing heat exchangers in a process in which the process gas is compressed to a relatively high pressure results in more costly operation from the standpoint of horsepower requirements because, upon every reversal, the volume of the compressed process gas in the heat exchanger is lost and must be replaced.

It is a primary object of this invention to provide a simple and improved process for cooling a gaseous stream to a temperature at which condensation normally occurs on the cooling surfaces.

Another important object of this invention is to prevent the deposition on cooling surfaces of condensible components of a gaseous stream undergoing cooling.

It is a further object of this invention to provide a truly continuous method of cooling a gaseous stream containing condensible material without pretreatment of the stream.

Other objects and advantages of this invention will become apparent from the description which follows.

In accordance with this invention, adsorptive particles are brought into contact with the cooling surfaces of a heat exchanger to adsorb preferentially the condensible matter of the gaseous stream undergoing cooling in order to prevent the accumulation of condensed material on the cooling surfaces. Adsorption particles laden with the condensible matter are periodically or continuously withdrawn from the heat exchanger and fresh adsorptive particles introduced to replace those withdrawn. The withdrawn adsorptive particles may be regenerated and recycled to the heat exchanger. Since a gaseous stream containing one or more condensible components can be cooled by this invention substantially without condensation on the cooling surfaces, it is evident that the rate of heat transfer will not diminish in the course of operation which, incidentally, does not need to be interrupted because of stoppage of the exchanger or reversal of the streams passing therethrough.

The present invention is particularly applicable in the cooling of a gaseous stream containing at least one condensible component to a temperature at which the condensed material freezes or solidifies on the cooling surfaces.

The process of the invention finds valuable utility especially in the production of oxygen by the liquefaction and rectification of air. For convenience, further description of the invention will be in terms of ordinary air which is cooled for an oxygen plant, but it will be understood that the

invention is not limited to this illustrative application. Other typical applications include the cooling of hot gases containing tarry vapors in which case adsorptive carbon may be used to prevent the deposition of tar on the cooling surfaces, and the cooling of natural gas containing condensible impurities like hydrogen sulfide and carbon dioxide in which case adsorptive bauxite and silica gel may be used, respectively, to obviate the accumulation of these components on the cooling surfaces.

In some cases, it may be advisable to use two or more different adsorbents to remove different condensible components from the gaseous stream undergoing cooling. The different adsorbents may be used as a particulate mixture or separately in different zones of the heat exchanger particularly where the different components are condensed in different temperature ranges. Sometimes, one particulate adsorbent may be used to take up two or more condensible components of a gaseous stream which is being cooled to a temperature below the condensation points of these components.

For a clearer and more detailed understanding of this invention, reference is now made to the drawing forming a part of this specification, of which:

Figures 1 and 2 are schematic elevations in section of different forms of heat exchangers suited for the process of the invention. It is to be understood the invention is not limited to these illustrative embodiments nor to others herein discussed.

The apparatus illustrated in Figure 1 comprises an upright cylindrical or oblong vessel 10 with head 11 to which pipe 12 is attached for the admission of a warm air stream containing carbon dioxide and moisture, these components of air being normally condensible within the operating temperature range of the apparatus. Pipe 13 for the admission of adsorptive particles to adsorb preferentially the condensible components is similarly attached to head 11. Within vessel 10 there is a vertical bundle of cooling conduits 14 to cool the air stream. Coolant flows upwardly through conduits 14, entering at the bottom thereof through inlet 15 and manifold 16 and emptying through manifold 17 and outlet 18 at the upper end thereof. The air stream and adsorptive particles are in direct contact with one another and with the exterior surfaces of cooling conduits 14 and pass downwardly through vessel 10 in countercurrent relation to the upwardly flowing coolant within conduits 14. During the downward passage, the adsorptive particles adsorb the moisture and carbon dioxide from the air and prevent the accumulation of these condensible components on the surfaces of cooling conduits 14, thereby avoiding a decrease in the heat transfer rate and stopping-up of the apparatus. The cooled air stream, now substantially free of moisture and carbon dioxide, becomes separated from the adsorbent particles by entering the inlets 19 of manifold 20 and exits through outlet 21 whence it may flow to a conventional rectification system to produce oxygen. The cold adsorbent particles containing adsorbed carbon dioxide and water are withdrawn from the lower tapered portion 22 of vessel 10 through outlet 23. The withdrawn adsorbent particles may be regenerated and then returned to vessel 10 by way of inlet 12.

Referring to the form of apparatus typified by Figure 2, vessel 110 may be of such shape that its horizontal cross-section is rectangular or circular. Vessel 110 has a tapered bottom 111 to which conduit 112 is connected for the introduction of a warm air stream containing components condensible at the normal operating conditions of the apparatus. Within vessel 110 there is a plurality of vertical coolant-carrying conduits 114 to cool the incoming air stream. Conduits 114 are fed with cooling fluid through inlet 115 to manifold 116 connected to the upper ends of these conduits. The cooling fluid travels countercurrent to the air stream, i. e., in a downwardly direction through conduits 114, and leaves at the bottom thereof through manifold 117 and outlet 118. The adsorptive particles, to prevent accumulation of condensible air constituents on the surfaces of conduits 114, are maintained in contact with these surfaces in a plurality of horizontal zones 113 within vessel 110. These zones are separated from one another by perforated plates, grids or like porous horizontal separators 113*a* permitting the upwardly flowing air stream and suspended adsorptive particles to pass therethrough but preventing the downward passage of the adsorptive particles. The adsorptive particles are of such size that, preferably, a state of dense phase fluidization is readily maintained with an upflowing air stream having a velocity in the range of about 0.2 to 3.0 feet per second, preferably about 0.5 to 1.5 feet per second. Usually, the particle size of the adsorptive particles is not greater than about 20 mesh, and more frequently, not greater than 60 mesh.

The air stream travels upwardly through a plurality of fluidized beds 113 in indirect heat exchange relation with the countercurrently flowing coolant in conduits 114 and the fluidized adsorbent particles adsorb the normally condensible components therefrom. The cooled air stream relatively free of moisture and carbon dioxide emerges from the pseudo-liquid level 113*b* of the uppermost fluidized bed 113 and passes through separating means 119 to keep back any adsorptive particles entrained therewith. The cold air, thus separated from adsorptive particles, leaves vessel 110 through outlet 120 attached to dome 121. The plurality of fluidized beds 113 permit the maintenance of a temperature gradient along the vertical dimension of vessel 110, which gradient is necessary for satisfactory operation of the exchanger. Each bed 113 has a substantially uniform temperature but each succeeding bed has a lower temperature than the adjoining lower bed. Thus, the lowest bed temperature is at the top of vessel 110 adjacent the upper ends of conduits 114 where the cooling fluid enters and the highest bed temperature at the bottom of vessel 110 where the warm air stream enters by way of inlet 112. There is, therefore, a descending temperature gradient in the air stream in the direction of its flow. The fluidized adsorptive particles preferentially adsorb condensible materials from the incoming air stream at different temperature levels of the exchanger, depending on the condensation temperature of these materials, and thereby prevent the accumulation of condensed materials on the surfaces of conduits 114.

Adsorptive particles containing adsorbed material are periodically or continuously withdrawn from vessel 110, regenerated in any of the conventional ways to eliminate the adsorbed material and returned to vessel 110 to adsorb again condensible components of the air stream undergoing cooling. For instance, as shown diagram-

matically, adsorptive particles carrying carbon dioxide are withdrawn from the coldest (uppermost) fluidized bed 113 through line 122, heated in chamber 123 to drive off the adsorbed carbon dioxide which is eliminated through vent 124, and the purged adsorptive particles returned by way of line 125 to a lower fluidized bed 113 which is at a temperature above that at which carbon dioxide would normally begin to condense, i. e., generally a temperature above about —180° F. It is advisable to bring the regenerated adsorptive particles to the approximate temperature of the fluidized bed 113 into which they are to be introduced before their entry into the bed. Similarly, adsorptive particles containing adsorbed moisture are withdrawn through line 126 from a fluidized bed 113 at a temperature below that at which substantially no water vapor is found in the upflowing air stream, say below about 0° F., heated in chamber 127 to eliminate the adsorbed moisture which is discarded through line 128, and the regenerated particles returned by line 129 to the lowermost fluidized bed 113. If desired, chambers 123 and 127 may be replaced by a single chamber in which the adsorptive particles may be purged of both adsorbed moisture and carbon dioxide.

The present invention may be carried out using various other types of heat exchanging apparatus and procedures. For example, the adsorptive particles may be rapidly swept through an exchanger by suspension in the air stream to be cooled. Deposition of carbon dioxide and moisture in the air on the cooling surfaces of the exchanger would be substantially avoided by the entrained adsorptive particles which take up these condensible components of air. The adsorptive particles carrying the condensible components would be separated from the chilled air upon leaving the exchanger, would be regenerated and then would be resuspended in the warm air stream entering the exchanger to adsorb additional quantities of condensible components.

For further clarification of the invention and its advantages, a specific example will now be presented illustrating one embodiment of the invention as conducted in the heat exchanger of Figure 2.

In the production of oxygen by the liquefaction of air and its rectification at low temperatures, the rectification is preferably conducted in two stages at different pressures. The refrigeration necessary for liquefaction is supplied to the air, after it has been compressed and water-cooled to approximately room temperature, by indirect heat exchange with the cold effluent products of rectification. An additional amount of refrigeration is usually supplied to compensate for cold losses resulting from the difference in enthalpy between the incoming air and the outgoing products of rectification and for heat leaks in the system.

Cold nitrogen from the low-pressure stage of the rectification system enters heat exchanger conduits 114 through inlet 115 and manifold 116. At inlet 115, the nitrogen stream usually has a temperature in the range of about —270° F. to about —290° F. and is at a gauge pressure of about 2 to 6 pounds per square inch. The incoming air stream containing moisture and carbon dioxide is introduced into the lower portion of the exchanger through conduit 112 and flows countercurrently in indirect heat exchange relation to the nitrogen while fluidizing adsorptive particles in a plurality of beds 113.

At inlet 112, the air stream generally is at a temperature in the range of about 30° to 70° F. and at a gauge pressure of about 60 to 150 pounds per square inch. As the air stream flows up through vessel 110, moisture is removed from the stream by the fluidized adsorptive particles in the lower portion of vessel 110 and carbon dioxide is removed by the adsorptive particles in the upper portion of vessel 110. Thus, in its upward flow, the air stream is cooled and freed of its condensible components which are taken up by the fluidized adsorptive particles; consequently, the external surfaces of the cooling conduits 114 are maintained substantially free of deposits of these condensible components and a relatively high rate of heat transfer through the walls of conduits 114 is realized. The cooled air stream leaves vessel 110 by way of outlet 120 after passing through filter 119 for the removal of entrained adsorptive particles. The cooled air stream exiting from outlet 120 is generally at a temperature of about 5° to 15° F. above the temperature of the nitrogen entering inlet 115 and thence flows to the high-pressure stage of the rectification system wherein the air is separated into oxygen and nitrogen product streams. Similarly, the nitrogen which is warmed in its passage through conduits 114 discharges from outlet 118 at a temperature close to that of the air entering at inlet 112; usually the nitrogen exit temperature is about 5° to 15° F. below the air inlet temperature.

In one particular design, vessel 110 is about 33 feet high and has eighty-seven beds 113 of fluidized silica gel particles. The air entering at inlet 112 is at a temperature of 32° F. and a gauge pressure of 100 pounds per square inch. Air substantially free of moisture and carbon dioxide leaves vessel 110 by way of outlet 120 at a temperature of —260° F. and a gauge pressure of 90 pounds per square inch. Vessel 110 has two sets of cooling conduits 114, one set for the oxygen rectification product and the other for the nitrogen rectification product. Both rectification product streams enter their respective inlets 115 at a temperature of —275° F. and a gauge pressure of about 5 pounds per square inch and exit from their respective outlets 118 at a temperature of 26° F. and at nearly atmospheric pressure.

Silica gel containing adsorbed moisture is withdrawn by line 126 from a fluidized bed 113 which is at a temperature of about —10° F., is heated in chamber 127 to expel the adsorbed moisture and then returned by line 129 to the lowermost bed 113. The rate of withdrawals of silica gel to eliminate moisture from vessel 110 is of the order of 1 pound of silica gel for each 10 pounds of air entering at inlet 112.

Silica gel containing adsorbed carbon dioxide and traces of acetylene carried into vessel 110 by the air stream is withdrawn from the uppermost fluidized bed 113 by line 122, is heated in chamber 123 to drive off the adsorbed impurities and returned by line 125 to the fluidized bed 113 which is at a temperature of about —100° F. The rate of withdrawal of silica gel to eliminate carbon dioxide and acetylene from vessel 110 is of the order of 0.7 pound of silica gel for each 10 pounds of air entering at inlet 112.

From the foregoing example, it is clear that the invention provides a simple and effective process by which simultaneously a gaseous stream containing condensible components is continuously cooled by contacting cooling surfaces to a temperature below the freezing points of the con-

densible components and the cooling surfaces are kept substantially free of solidified deposits of the condensible components. The adsorptive particles which, pursuant to the invention, contact both the gaseous stream and the cooling surfaces not only make the operation of the heat exchanger very satisfactory since a higher rate of heat transfer is realized and interruptions from choking of the exchanger with solidified deposits of condensible components are greatly minimized but also permit the withdrawal of the chilled gaseous stream in a highly purified state relative to the contaminating condensible components.

The particle size of the solid absorbent selected for a given operation will depend on whether the particles are to be fluidized or carried by gaseous entrainment or moved as a permeable bed. Usually, particle sizes below about 60 mesh are advisable where the particles are to be fluidized or carried in suspension by a gas and coarser particles, say about $\frac{1}{8}$ to $\frac{1}{4}$ inch in diameter, are better suited for forming a permeable bed. In a fluidized operation, it is generally desirable to maintain the fluidizing gas at a linear velocity of about 0.5 to 1.5 feet per second, while linear velocities of about 20 feet per second and higher are frequently employed where the gas sweeps or entrains the adsorptive powder through the heat exchanger.

Various modifications of the invention will occur to those skilled in the art upon consideration of the foregoing disclosure without departing from the spirit or scope thereof. Accordingly, only such limitations should be imposed as are indicated by the appended claims.

What is claimed is:

1. In the method of cooling a gaseous stream comprising condensible material by passage of said stream over cooling surfaces at a temperature which is effective for the deposition of said condensible material in frozen form on said cooling surfaces, the improvement of substantially preventing said deposition of frozen condensible material which comprises moving over said cooling surfaces a particulate adsorbent adapted to adsorb preferentially said condensible material, while passing said stream over said cooling surfaces.

2. The method of claim 1 wherein the moving particulate adsorbent is carried in suspension by said stream.

3. The method of claim 1 wherein the moving particulate adsorbent is maintained in a fluidized state by said stream.

4. The method of claim 3 wherein the particulate adsorbent maintained in a fluidized state is held as a plurality of fluidized, vertically contiguous beds and said cooling surfaces extend through said plurality of fluidized beds.

5. The method of claim 3 wherein the gaseous stream comprising condensible material is an air stream comprising carbon dioxide.

6. The method of chilling air containing moisture and carbon dioxide to a temperature below the freezing points of moisture and carbon dioxide and of separating said moisture and said carbon dioxide from said air, which comprises passing over cooling surfaces said air and adsorptive particles adapted to adsorb preferentially moisture and carbon dioxide to effect simultaneously the chilling of said air to a temperature below the freezing points of moisture and carbon dioxide and the adsorption of said moisture and said carbon dioxide by said adsorptive particles, and separating the chilled air substantially free of said moisture and said carbon dioxide from said adsorptive particles.

7. The method of claim 6 wherein the adsorptive particles are silica gel.

8. The method of recovering the cold content of a product of rectification in the liquefaction and rectification of air to produce oxygen, which comprises passing upwardly a stream of air containing moisture and carbon dioxide through a fluidized mass of adsorptive particles adapted to adsorb preferentially moisture and carbon dioxide, said fluidized mass being in contact with one side of heat transfer surfaces, passing downwardly a stream of rectification product at an initial temperature below about −270° F. in contact with the other side of said heat transfer surfaces, thereby chilling said air to a temperature below the freezing point of carbon dioxide while substantially preventing the deposition of said carbon dioxide and said moisture on said heat transfer surfaces, withdrawing adsorptive particles containing adsorbed moisture and carbon dioxide from said fluidized mass, treating the withdrawn adsorptive particles to effect elimination of said adsorbed moisture and carbon dioxide, and returning the treated adsorptive particles to said fluidized mass.

9. The method of claim 8 wherein the fluidized mass of adsorptive particles is held as a plurality of fluidized, vertically contiguous beds.

10. The method of claim 8 wherein adsorptive particles containing, respectively, adsorbed moisture and carbon dioxide are separately withdrawn from said fluidized mass.

11. The method of recovering the cold content of a product of rectification in the liquefaction and rectification of air to produce oxygen, which comprises passing downwardly in contact with one side of heat transfer surfaces a stream of air containing moisture and carbon dioxide and a moving bed of adsorptive particles effective for the preferential adsorption of moisture and carbon dioxide, passing upwardly in contact with the other side of said heat transfer surfaces a stream of rectification product at an initial temperature below about −270° F., thereby chilling said air to a temperature below the freezing point of carbon dioxide while substantially preventing the deposition of said carbon dioxide and said moisture on said heat transfer surfaces, separating the thus chilled air from said moving bed, withdrawing from said moving bed adsorptive particles containing adsorbed moisture and carbon dioxide, treating the withdrawn adsorptive particles to effect elimination of said adsorbed moisture and carbon dioxide, and returning the treated adsorptive particles to said moving bed.

12. The method of cooling a gaseous stream comprising condensible material to a temperature at which said condensible material freezes, which comprises passing cocurrently said gaseous stream and a particulate adsorbent adapted to adsorb preferentially said condensible material in contact with one side of heat transfer surfaces and along the length of said surfaces, passing in contact with the other side of said surfaces a cooling stream at an initial temperature below the freezing point of said condensible material, said cooling stream flowing countercurrently to said gaseous stream, thereby cooling said gaseous stream to said temperature at which said condensible material freezes while substantially preventing the deposition of said condensible material on said surfaces, separating the thus cooled gaseous stream from said particulate ad-

sorbent containing adsorbed condensible material, treating the separated particulate adsorbent to effect elimination of said adsorbed condensible material, and returning the treated particulate adsorbent to passage in contact with said one side of said surfaces.

13. The method of claim 12 wherein the condensible material comprises carbon dioxide.

14. The method of claim 13 wherein the gaseous stream is air.

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