

Jan. 20, 1970

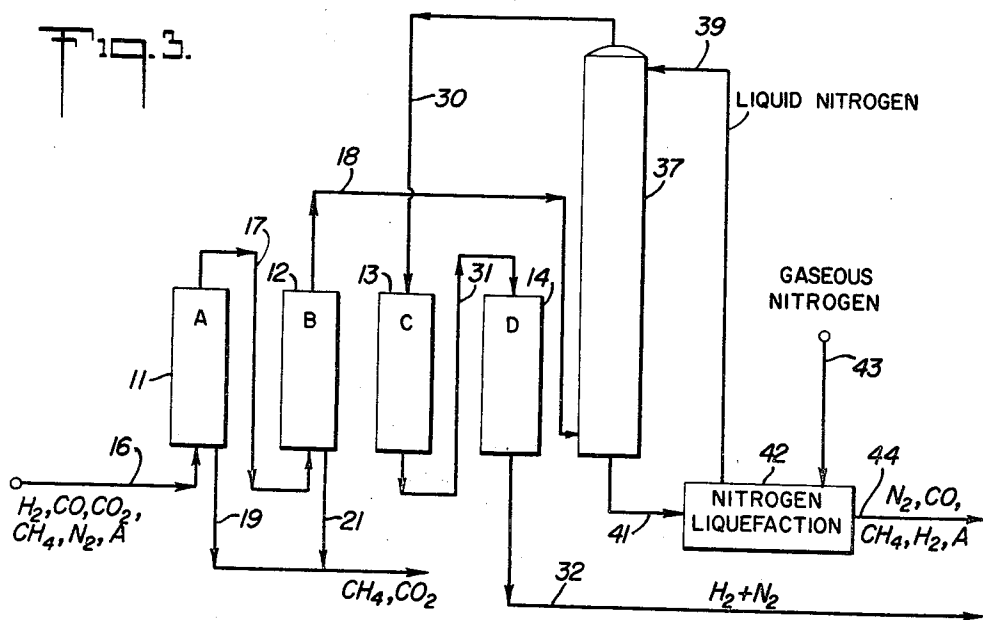
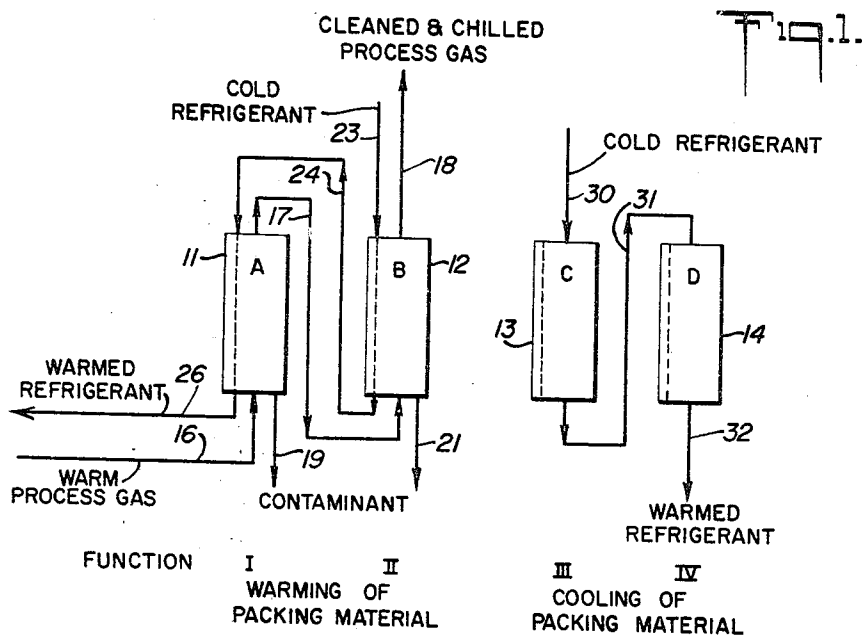
J. R. MUENGER ET AL

3,490,245

SELF-CLEANING REGENERATORS FOR CRYOGENIC SYSTEMS

Filed Dec. 20, 1966

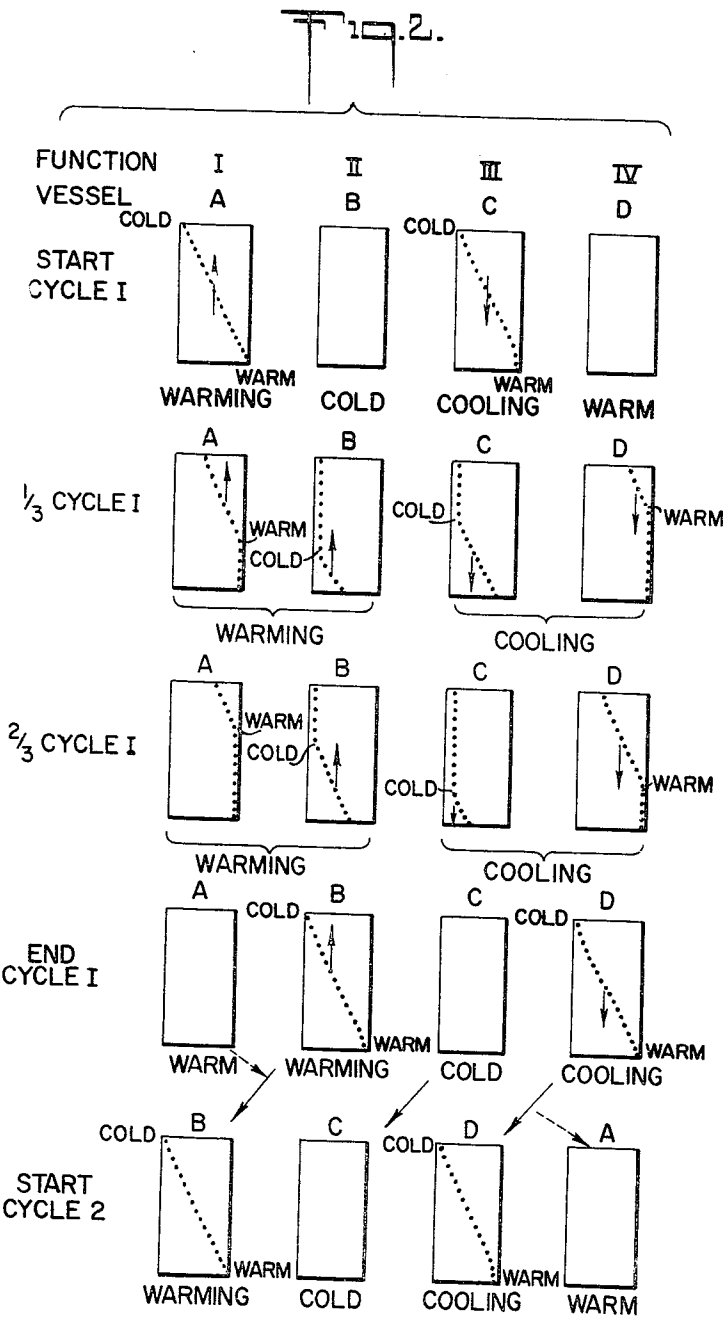
3 Sheets-Sheet 1



SELF-CLEANING REGENERATORS FOR CRYOGENIC SYSTEMS

Filed Dec. 20, 1966

3 Sheets-Sheet 2



Jan. 20, 1970

J. R. MUENGER ET AL

3,490,245

SELF-CLEANING REGENERATORS FOR CRYOGENIC SYSTEMS

Filed Dec. 20, 1966

3 Sheets-Sheet 3

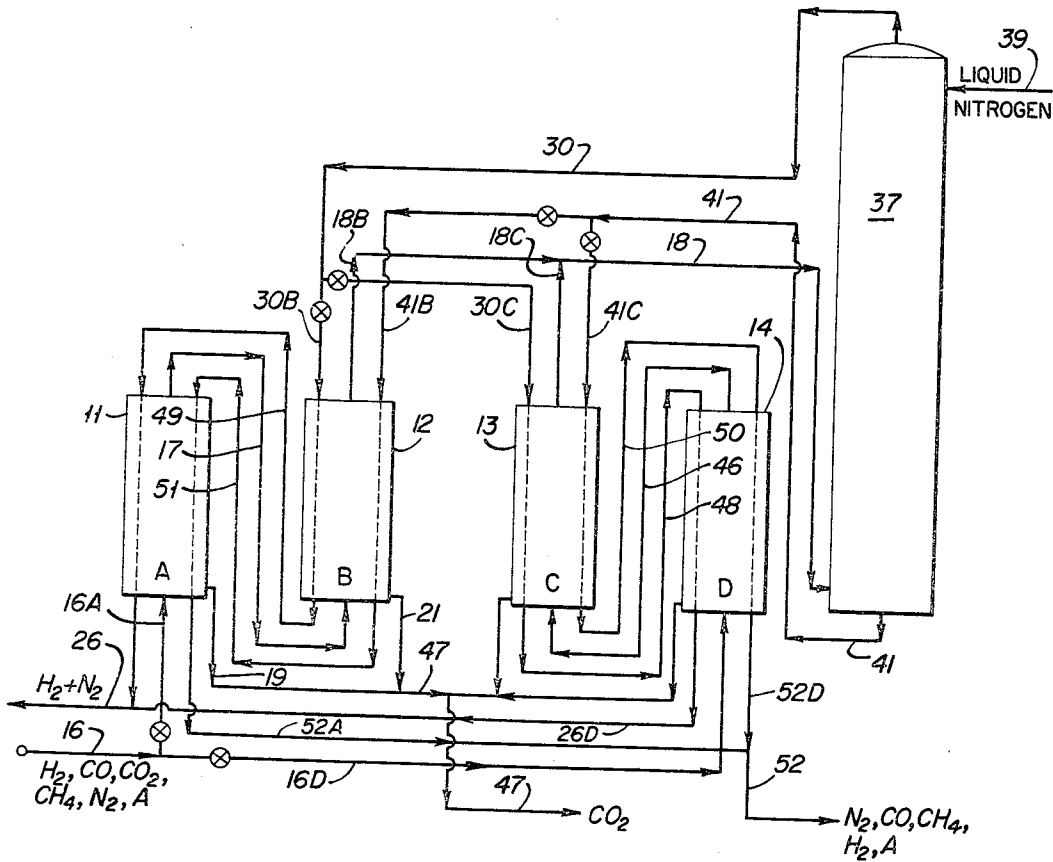


Fig. 4.

1

3,490,245

SELF-CLEANING REGENERATORS FOR
CRYOGENIC SYSTEMS

James R. Muenger, Beacon, and David L. Alexander,
Fishkill, N.Y., assignors to Texaco Inc., New York,
N.Y., a corporation of Delaware

Filed Dec. 20, 1966, Ser. No. 603,201

Int. Cl. F25j 5/00

U.S. Cl. 62-12

6 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to an improved heat exchange apparatus and method therefor, to treat a gaseous mixture containing a readily condensible constituent, the latter being condensed or solidified on heat exchanger surfaces during the cooling of the gaseous mixture. The apparatus includes two groups of heat exchangers each being serially connected to form a generally vertically disposed flow path. One of said groups in a chilled condition is provided with a stream of process gas from which the constituent is removed by condensation on cold exchange surfaces. A temperature transitional region is established at the end of each of the heat exchanger flow paths. Said transitional temperature region is thereafter progressed through the entire flow path to effect either a heating or cooling action. Periodically the connection of the heat exchangers within the respective groups are reversed as to permit a sequential actuation of each exchanger in both the condensing and the subsequent cooling cycle.

This invention relates to improvements in heat exchange apparatus and to an improved method of operation of heat exchange apparatus employed in cooling gaseous mixtures containing more readily condensible constituents which condense or solidify on the heat exchanger surfaces during cooling of the gaseous mixture.

In cooling gaseous mixtures to cryogenic temperatures, the problem of frost and ice formation resulting from solidification of higher melting point components of said gaseous mixtures and accumulation of solid deposits or frost on the surfaces of solid heat exchange elements is often encountered. Accumulations of solid deposits on heat transfer surfaces interfere with the flow of heat so that the rate of heat transfer from solid heat exchanger surfaces to the gas stream is reduced, and also tend to restrict the flow of gas through the heat exchanger, even to the point of completely plugging the exchanger with solid deposits.

This invention provides a method by which solid deposits are continuously removed from heat exchanger surfaces without the necessity for reversing, or interchanging, the paths of flow of the process gas or gases. The method of our invention may be applied to either regenerators (heat accumulators) or combination indirect and heat accumulator type heat exchangers, as will be more evident from the detailed description hereinafter.

In the operation of heat accumulators or regenerators commonly employed in air separation systems, solid deposits on the heat exchange surfaces, or packing material, are periodically re-evaporated in a cyclic operation in which the flow of the gaseous mixture undergoing cooling is interrupted and a stream of purge gas is passed over the deposits. The purge gas stream is also the source of refrigeration for the process, so that the purge gas cools the heat exchange surfaces and at the same time effects removal of the deposits. By employing a plurality of regenerators, continuous flow of the gas streams can be maintained. Regenerators of this type are well known and described in the literature, and, therefore, are not further described herein.

2

In normal operation, heat accumulators retain or trap some of the purge gas in the interstices of the packing material which is subsequently picked up by the process gas stream, and similarly some of the process gas is picked up in the purge gas stream each time the streams of process gas and purge gas are interchanged. In addition, vapor from the deposits is picked up by the purge gas stream so that in net effect the more readily condensible components of the process gas stream are transferred to the purge gas stream. The volume rate of flow of the purge gas must be greater than that of the process gas because the temperature of the refrigerant purge gas necessarily must be lower than that of the regenerator packing or heat absorption material at any given point in the regenerator in order to effect heat transfer from the packing to the purge gas whereas the process gas must be warmer than the packing material.

Losses due to stream mixing or contamination of the process gas stream with the purge gas are greater when the system is operated at a high pressure than when operated at a moderate pressure. In other words, as the operating pressure is increased the amount of contamination of process gas with residual purge gas retained on the packing at each cycle is increased. For this reason, the use of regenerators is commonly limited to low-to-moderate pressure applications and to situations in which the contamination of an adequate amount of the chilled gas or purge gas stream can be tolerated.

Reversing heat exchangers, as contrasted with regenerators, also can be used for the transfer of heat from a process gas stream to a colder gas stream to effect cooling of the process gas. The use of reversing exchangers in place of regenerators permits purging of solid deposits from heat exchange surfaces by a minor fraction of the colder gas stream. For example, in the separation of oxygen and nitrogen from air in cryogenic air separation systems, a minor portion of the nitrogen may be passed through the heat exchanger for the removal of solid deposits from the heat exchange surfaces. The major part of the nitrogen is passed over uncontaminated heat exchanger surfaces and delivered as a clean product stream. Even with reversing heat exchangers, losses of product gas or purge gas still occur although these losses normally are usually lower than those of a regenerator type system because the switching frequency is lower.

In the purification of ammonia synthesis feed gas streams, liquid nitrogen is frequently employed as a wash for the final cleanup of the hydrogen-rich gas stream to effect the removal of impurities, such as carbon monoxide, methane and argon, which are condensed from the gas stream and removed in solution in liquid nitrogen. At the same time, liquid nitrogen is evaporated into the hydrogen-rich gas stream, supplying part of the nitrogen required for the ammonia synthesis reaction. Prior to cooling the process gas to a cryogenic temperature suitable for feeding it to the nitrogen wash tower, it is customary to substantially completely remove carbon dioxide, and hydrogen sulfide, carbon disulfide, and carbonyl sulfide, if present, from the gas stream by an absorption system. Absorption in methanol, acetone, polyglycol ethers, sulfanol, water, or in an aqueous solution of mono- or di-ethanolamine or potassium carbonate may be used for removal of various impurities from hydrogen. Alternatively, carbon dioxide may be condensed in part and the liquefied carbon dioxide separated from the hydrogen-rich gas stream, after which carbon dioxide remaining in the gas stream may be removed by absorption.

By the method and apparatus of the present invention the absorption systems may be eliminated or substantially reduced in size effecting substantial economies in the cost of installation of equipment and operating costs for the process. The relatively large amounts of carbon dioxide

present in the usual feed gas streams, the high process gas pressure desirable for the gas production system and the necessity of keeping the refrigeration gas stream clean, i.e. the purified hydrogen-nitrogen mixture, all make impractical the use of conventional regenerators or heat exchangers for the combined job of cooling and cleaning the process gas. Generally the process gas comprises large amounts of carbon dioxide which result when a crude synthesis gas mixture such as that produced by the steam hydrocarbon reforming reaction or the partial oxidation of hydrocarbons and which comprises carbon monoxide and hydrogen is subjected to the water gas shift reaction for the conversion of carbon monoxide to carbon dioxide by reaction with steam with the concomitant production of hydrogen.

In the production of oxygen from air by liquefaction and rectification at low temperatures, compressed air is passed in heat transfer relationship with cold products of rectification to cool the air and utilize the refrigeration effect of the cold products. In many plants, moisture and carbon dioxide are carefully removed from the incoming air to prevent the accumulation of solid deposits in heat exchangers in which the compressed air and cold products are passed in indirect countercurrent heat exchange relationship with one another. In others, cold accumulators or regenerators are used, without prior removal of carbon dioxide and all moisture from the incoming air. During the passage of cold product (oxygen and nitrogen) through the regenerators, the packing material is cooled to a low temperature. When warm compressed air is passed over the cold packing material, it absorbs heat from the air and cools the compressed air to a low temperature. Moisture and carbon dioxide contained in the air are deposited as solid deposits on the cold packing material. When the flow of a gaseous product and air are reversed, these deposits are removed from the packing material by sublimation into the cold product gas stream. Usually an impure product gas is used, passing over the packing material in the reverse direction from the direction of flow of air in the preceding step in the process. The product gas stream thus functions as purge and as a refrigerant.

The purge gas stream becomes contaminated or diluted with air remaining in the spaces surrounding the packing through which the gas streams must flow in passing over the packing material. When the compressed air is at high pressure relative to the pressure of the purge gas, relatively larger amounts are lost to the purge gas with each reversal of flow through the packing material than in the case of lower pressure operation. Similarly, the compressed air stream is diluted with purge gas at each reversal, the amount of dilution increasing as the pressure of the purge gas stream is increased relative to the pressure of the compressed air stream.

A number of other cryogenic processes involve heat exchange between a cold gas stream and a warmer stream containing some more readily condensible component or higher melting component which forms solid deposits on heat exchange surfaces as the gas stream is cooled.

As used herein, the term "heat exchanger" is used in a comprehensive sense to include both regenerators or heat accumulators (sometimes called cold accumulators) as well as apparatus for directly effecting heat transfer from a warmer stream to a cooler stream without deliberate and cyclic storage of heat. The term "regenerator" is used herein in the sense commonly employed in this art. The term "condensation" is used herein in a comprehensive sense to include the formation of solid deposits which subsequently melt as well as liquid condensate. The term "more readily condensible component" is used in a comprehensive sense to include higher melting point materials contained in the process gas stream.

The term "process gas" is used to designate a gaseous mixture which is subjected to cooling to a temperature below the solidification temperature of its more readily condensible or higher melting point constituents.

The method of this invention is described herein with reference to the accompanying drawings which illustrate diagrammatically a suitable arrangement of apparatus for carrying out the method and illustrative examples of the application of this method to industrial processes.

FIG. 1 is a flow diagram illustrating the general method of operation of heat accumulators in accordance with the subject invention.

FIG. 2 is a diagram illustrating temperature gradients in the packing material of heat accumulators are illustrated in FIG. 1 during one fourth of a four stage cycle.

FIG. 3 is a flow diagram illustrating the application of the method of this invention to the operation of heat exchanger accumulators in a nitrogen wash operation for purification of hydrogen.

FIG. 4 is a flow diagram illustrating another application of the method of this invention to a nitrogen wash operation for purification of hydrogen.

Referring to FIG. 1 of the drawings, the numerals 11, 12, 13 and 14 designate identical heat accumulators, for example, Frankl-type regenerative heat exchangers, comprising a series of vessels containing packing material of high heat absorptive capacity and a set of passageways not open to the packing material. For convenience in describing the process flow, these vessels are designated also by the letters A, B, C and D, respectively. Flow lines and connections to and from the accumulators A, B, C and D are so constructed and arranged that the paths of flow of warm process gas and cold refrigerant may be shifted from vessel to vessel sequentially as desired while retaining the four vessel functions illustrated in FIG. 1. At the period in the cycle represented in FIG. 1 warm process gas flows in series upwardly through accumulators A and B. At the same time a main stream of cold refrigerant gas is passed downwardly in series through accumulators C and D. A set of four heat accumulators is illustrated in this example, but more may be used if desired. When accumulator A becomes warm from the heat in the process gas, the flow of process gas is switched to flow in series through accumulators B and C, while the cold refrigerant gas is switched to flow in series through accumulators D and A. Similarly when accumulator B becomes warm, the process gas flow is switched to accumulators C and D while the cold refrigerant gas passes serially through A and B. The sequence of operation is described in more detail hereinafter in connection with FIG. 2 and in the Vessel Sequence Table appearing hereinafter.

It is to be understood that neither the specific arrangement of heat exchangers illustrated in the figure nor the specific number of vessels illustrated is to be taken as a limiting arrangement or number.

In the operation of the heat exchangers of FIG. 1 in accordance with the method of this invention, warm process gas enters the lower part of vessel 11 (accumulator A) through line 16 and is passed upwardly therethrough into contact with packing material. Effluent gas from the upper end of vessel 11 is introduced via line 17 to the lower end of vessel 12 and passed upwardly therethrough previously chilled heat absorbent packing material contained therein. Chilled process gas is discharged from the upper end of regenerator 12 through line 18. In passing over the cold packing material in vessels 11 and 12, the process gas stream is cooled to a temperature below that at which high melting point components of the process gas stream, also referred to herein as contaminants, form solid deposits on the surface of the packing material, i.e. the heat exchanger surfaces. As the process gas stream progressively warms the packing material along its path of flow, a transitional temperature gradient is established over a part of the packing material in vessels 11 and 12 such that part of the packing material is maintained at a temperature above the melting point of the solid deposits of contaminant and another part of the packing material, which is always at a higher elevation than the warm pack-

ing material, is maintained at a temperature below the condensation and solidification temperature of the contaminant. The region of temperature transition of the packing material, from a temperature at which the solidified contaminant melts and that at which the last solid deposits of contaminant are deposited, is termed herein as the transitional temperature region in the accumulator (or accumulators). As the packing material in accumulators A and B is gradually and progressively warmed by the process gas stream, the transitional temperature region progressively moves upwardly through the packing material depositing solid contaminants and melting the solid deposits. As the solid deposits melt, resulting liquid runs down over the warm packing material and is drained from the lower part of the regenerators. In FIG. 1, the liquid is drained from vessel 11 through line 19 and from vessel 12 through line 21.

The warm process gas enters heat exchanger 11 preferably at a temperature between the triple point and the critical point of the contaminant which it is desired to remove. The liquefied contaminant is withdrawn from the heat exchanger at a point along the path of flow of the process gas where the process gas is at a temperature below the boiling point of the liquid, usually at the bottom of the vessel. The vapor pressure of the contaminant at the point of withdrawal must be lower than the process gas total pressure so that as the solid deposit melts and the liquid flows downwardly in the vessel, it does not entirely revaporize into the process gas stream. As the process gas passes through the regenerator, it is cooled and deposits the main contaminant as a solid. Minor contaminants may also be condensed as solids or liquids. As the transitional temperature region moves upwardly through the packing material due to progressive warming by the process gas flow, solid deposits on the packing material are warmed, and the principal deposit melts when its triple point temperature is reached. The resulting liquid flows down over the packing material in the vessel where it serves as a wash, finally running out of the drain. Also, in acting as a wash it serves to dissolve and carry away minor constituent solid deposits the triple points of which may be higher than the entering temperature of the process gas.

While process gas is undergoing cooling and cleaning in passing through accumulators A and B, a minor stream of refrigerant, which may be the same as or different from refrigerant used for chilling accumulators C and D, may be passed in indirect heat exchange relationship therewith downwardly through accumulators B and A, respectively. The cooling available from the minor stream of refrigerant is less than the heat released from the process gas in passing through accumulators A and B so that the transitional temperature region in the packing material moves continuously upwardly through the packing in accumulators A and B as hereinbefore described. Where a countercurrently flowing stream of cold refrigerant is to be used in conjunction with warm process gas stream, the refrigerant is conducted through the heat accumulators in a suitable arrangement of passageways in the accumulators so that there is no mixing between the refrigerant and the process gas. As illustrated in FIG. 1, cold refrigerant is introduced into the upper part of vessel 12 through line 23 and passed downwardly through vessel 12 in indirect heat exchange with packing material contained therein. Effluent refrigerant from the lower end of vessel 12 is passed by line 24 to the upper end of vessel 11 through which it is passed in indirect heat exchange relationship with packing material contained therein. Warmed refrigerant is discharged from the lower end of vessel 11 through line 26.

During the period in which the packing material is undergoing progressive warming in accumulators A and B, the packing material in accumulators C and D undergoes progressive chilling by the passage of cold refrigerant through vessels 13 and 14. The cold refrigerant may

pass in direct contact with packing material contained therein as shown, or the cold refrigerant may be passed through enclosed passageways, illustrated by the dotted lines in vessels C and D, in indirect heat exchange with the packing material. As illustrated in FIG. 1, cold refrigerant is supplied to the top of vessel 13 from line 30 and passed downwardly therethrough in contact with the packing material contained in the vessel. Effluent from the bottom of vessel 13 is conducted by line 31 to the upper part of vessel 14 through which it is passed in direct contact with packing material contained therein. Warmed refrigerant is discharged from the lower end of vessel 14 through line 32. The flow of refrigerant through lines 23 and 30 is balanced against the mass flow of the warm process gas entering the system through line 16 so that the packing material in accumulator C is cooled to approximately the minimum temperature of the cold refrigerant available at approximately the same rate as the packing material in accumulators A and B is warmed to a temperature approximating that of the inlet warm process gas.

FIG. 2 illustrates graphically the progressive warming of packing material in accumulators A and B and progressive cooling of packing material in accumulators C and D in functions I, II, III and IV, respectively, of FIG. 1. With reference to FIG. 2, at the start of a cycle the packing material at the lowermost portion of accumulator A is warm, i.e., essentially at the temperature of the incoming process gas, whereas the packing material in the upper end of accumulator A is cold, i.e., it has undergone little or no warming as a result of flow of process gas therethrough. The dotted line running diagonally from the upper left corner to the lower right-hand corner of the rectangle representing accumulator A of FIG. 2 indicates the temperature gradient through the packing material therein, ranging from warm to cold, or, in other words, illustrates the transitional temperature region within the heat exchanger at the start of a cycle.

Similarly, in accumulator C at the start of the cycle the packing material at the top of the vessel is cold, i.e. essentially at the temperature of the refrigerant gas stream, whereas the packing material at the bottom of accumulator C is still warm. The transitional temperature region in accumulator C is indicated by the dotted line running diagonally from the upper left to the lower right of the rectangle representing accumulator C. At this point in the cycle, accumulator B is cold, i.e. essentially at the temperature of the refrigerant stream, and accumulator D is warm, i.e. essentially at the same temperature as the process gas stream. As the flow of gases continues through accumulators A and B, the transitional temperature region moves upwardly so that warming of the packing material in the lower part of accumulator B begins to take place as indicated in FIG. 2 at $\frac{1}{3}$ cycle. Similarly, the flow of refrigerant through accumulators C and D cools more of the packing material to the temperature of the refrigerant in accumulator C and begins to cool the packing material in the upper part of accumulator D. At $\frac{2}{3}$ cycle, most of the packing material in accumulator A is warm and most of that in accumulator C is cold, the transitional temperature region extending from the upper part of accumulator A into the lower part of accumulator B and from the lower part of accumulator C into the upper part of accumulator D. At full cycle, accumulator A is warm and accumulator C cold. At this point in the cycle, accumulator A is the equivalent of accumulator D at the start of the cycle, accumulator C is the equivalent of accumulator B at the beginning of the cycle, etc. Now the flow through accumulators A, B, C and D in the flow system are switched as indicated by the legend "Start Cycle 2" in FIG. 2. As each accumulator in function I of the process flow of FIG. 1 becomes fully warmed and each accumulator in function III becomes completely cooled, the flow is switched so that the process gas first enters the partially warmed regenerator and the refrig-

erant first enters the partially cooled regenerator. The sequence of regenerators A, B, C and D in carrying out functions I, II, III and IV are indicated in the following table.

Function.....	Vessel Sequence			
	Warming		Cooling	
	I	II	III	IV
Cycle 1.....	A	B	C	D
Cycle 2.....	B	C	D	A
Cycle 3.....	C	D	A	B
Cycle 4.....	D	A	B	C
Cycle 1.....	A	B	C	D

As an example of the utility of the method of the present invention, its application to a nitrogen wash system for the purification of hydrogen for use as ammonia or hydrazine synthesis feed gas is illustrated in FIG. 3. In this example, the warm process gas stream comprises a mixture of hydrogen, carbon monoxide, methane, carbon dioxide, nitrogen and argon, as in shifted synthesis gas pretreated for removal of most carbon dioxide. The process gas stream is supplied to the lower part of vessel 11 (accumulator A) through line 16 and passed upwardly in series through accumulators A and B (vessels 11 and 12) into direct contact with previously chilled packing material contained therein. During the passage of the feed gas stream over the packing material, carbon dioxide is solidified out of the feed gas stream and deposited as a solid on the packing material as described above in connection with FIGS. 1 and 2. As the transitional temperature region moves upwardly through the packing material in vessels 11 and 12 any solid deposits laid down on the packing material are melted and resulting liquefied carbon dioxide is drained from the lower part of vessels 11 and 12 through lines 19 and 21. (During subsequent switching of the gas streams through functions I, II, III and IV as described in connection with FIGS. 1 and 2, the liquid is drained from those vessels in the I and II functions.)

The resulting chilled product gas discharged from the upper part of vessel 12 comprising hydrogen and containing small amounts of methane, carbon monoxide, nitrogen and argon, is passed through line 18 to the lower part of a nitrogen wash column 37. Liquid nitrogen is supplied to the upper part of the nitrogen wash column 37 through line 39. In the nitrogen wash column, the hydrogen rich feed gas stream is brought into intimate countercurrent contact with liquid nitrogen whereby components in the feed gas stream other than hydrogen and nitrogen are condensed and accumulated in the lower part of tower 37. Liquid nitrogen containing condensed methane, carbon monoxide and argon, typically at a temperature of about -320° F., is discharged from the bottom of the nitrogen wash tower through line 41 and passed to a nitrogen liquefaction unit indicated diagrammatically at 42.

Gaseous nitrogen available at ambient temperature from a suitable source, e.g., from the rectification of air, is supplied to the nitrogen liquefaction unit through line 43. Gaseous nitrogen is liquefied by a mechanical cryogenic system utilizing cooling available from vaporization of the bottoms from nitrogen wash column 37 comprising nitrogen, carbon monoxide, methane, argon and dissolved hydrogen. Gasified nitrogen wash tower bottoms are discharged through line 44.

Purified hydrogen, containing a minor amount of nitrogen, at a temperature of about -325° F. is discharged overhead from the nitrogen wash column to line 30 and passed in series downwardly through vessels 13 and 14 (accumulators C and D) to chill the packing material contained therein, preferably by indirect heat exchange to protect the purity of the overhead product stream. Resulting warmed effluent hydrogen and nitrogen is discharged from the lower end of vessel 14 through line 32 from which it may be passed to an ammonia synthesis reactor.

Another application of the method of this invention to a nitrogen wash system for the purification of hydrogen is illustrated in FIG. 4. In this example; heat exchangers A, B, C and D are heat exchanger-regenerators. Vessels 11, 12, 13 and 14 are provided with heat absorptive packing material and, in addition, with a plurality of indirect heat exchange elements to permit passage of a plurality of separate refrigerants through each vessel in indirect heat exchange with process gas and with packing material in the vessel.

In this example, the feed gas stream supplied to the exchanger-regenerators from line 16 comprises hydrogen containing small amounts of carbon monoxide, carbon dioxide, methane, nitrogen and argon. Such feed gas streams are available from shift converters in which carbon monoxide and hydrogen containing small amounts of methane, nitrogen and argon is subjected to catalytic reaction with steam to convert carbon monoxide to carbon dioxide with concomitant production of hydrogen. In this example, the effluent from the water gas shift reactor has been processed in cryogenic equipment to remove steam and water vapor and to remove most of the carbon dioxide by condensation. The feed gas, available at -62° F., is relatively warm as compared with the available refrigerant streams from a subsequent nitrogen wash column. The feed gas stream is split so that part of the feed gas stream is introduced through line 16A into the lower part of vessel 11 and passed upwardly in series through vessels 11 and 12 (exchanger-regenerators A and B) into direct contact with previously chilled packing material contained therein. The other portion of the feed gas stream is passed through line 16D into the lower part of vessel 14 and passed upwardly in series through vessels 14 and 13, respectively (exchanger-regenerators D and C) into direct contact with packing material contained therein which is undergoing progressive chilling by indirect countercurrent heat exchange with refrigerant streams as explained hereinafter. Chilled and purified gaseous effluent from vessel 12 (exchanger-regenerator B) is discharged through line 18B into line 18 to nitrogen wash column 37. Similarly, chilled and purified effluent gas from vessel 13 (exchanger-regenerator C) is discharged through line 18C into line 18 to the nitrogen wash column.

In passing upwardly through the exchanger-regenerator heat exchange units contained in vessels 11, 12, 13 and 14, carbon dioxide contained in the feed gas stream is solidified and deposited as a solid on the packing material contained in these vessels. The packing material in vessels 11 and 12 is progressively warmed by the process gas stream with the result that the transitional temperature region, as defined hereinabove, moves upwardly through the packing material melting solid deposits of carbon dioxide on the packing material. Resulting liquid carbon dioxide is withdrawn from the vessels 11 and 12 through lines 19 and 21 to a collecting line 47 through which it is discharged as a product of the system. In vessels 14 and 13, on the other hand, the packing material is progressively cooled, with the result that the transitional temperature region moves downwardly through the packing material. Solid carbon dioxide from the process gas stream formed on the packing material remains on the packing material until these exchanger-regenerators are switched in the operating sequence into functions I or II as indicated in the Vessel Sequence Table above. When vessels from functions III and IV in the operating sequence are progressively cycled through functions II and I, solid deposits contained on the packing material are melted together with those laid down on the packing material while the vessels are in functions I and II, as explained hereinabove.

Chilled product gas supplied to nitrogen wash column 37 through line 18 comprises hydrogen containing small amounts of carbon monoxide, methane, nitrogen and argon. Liquid nitrogen from the suitable source of sup-

ply, for example at a temperature of -334°F. , is supplied to the upper part of the nitrogen wash column 37 through line 39. Purified hydrogen containing a small amount of nitrogen is discharged from the upper part of nitrogen wash column through line 30 and split into two streams for use as a refrigerant in heat exchangers A, B, C, and D. One of the streams is passed through line 30C to vessel 13 (exchanger-regenerator C) and passed downwardly therethrough in indirect heat exchange with process gas and packing material contained therein and then conducted by line 48 to the upper end of vessel 14 (exchanger-regenerator D) and passed downwardly therethrough in indirect heat exchange with process gas and packing material contained therein. The other stream of purified hydrogen is passed through line 30B into the upper end of vessel 12 (exchanger-regenerator B) and passed downwardly therethrough in indirect heat exchange with process gas and packing material contained therein, then conducted through line 49 to the upper end of vessel 11 (regenerator-accumulator A) and passed downwardly therethrough in indirect heat exchange with process gas and packing material contained therein. Resulting warmed refrigerant comprising purified hydrogen and nitrogen leaving exchanger-regenerators A and D is discharged through line 26 as product.

A liquid bottoms fraction from the nitrogen wash column, comprising nitrogen, carbon monoxide, methane, hydrogen and argon, is withdrawn through line 41, typically at a temperature of about -316°F. , and split into two streams for use as cold refrigerant in the exchanger-regenerators A, B, C and D. One stream of the bottoms fraction is passed through line 41C into the upper end of vessel 13 (exchanger-regenerator C) and conducted through vessels 13 and 4 in series in indirect heat exchange relationship with process gas and packing material contained therein. Bottoms fraction discharged from the outlet of heat exchange passageways in vessel 13 is conducted to heat exchange passageways in vessel 14 by line 50. Another portion of the bottoms fraction from the nitrogen wash tower is passed through line 41B to the upper part of vessel 12 (exchange-regenerator B) and conducted in series through vessels 12 and 11 (exchanger-regenerators B and A) respectively in indirect heat exchange relationship with process gas and packing material contained therein. Refrigerant bottoms fraction discharged from heat exchange passageways in vessel 12 is conducted to the inlet of heat exchange passageways in vessel 11 by line 51. Resulting warmed gaseous bottoms product is discharged from vessel 14 through line 52D and, from vessel 11, through line 52A to line 52 as product.

In the operation of the system of FIG. 4 the volumes of relatively warm process gas to regenerator-exchangers A and D through lines 16A and 16D, respectively are balanced against the volumes of flow of refrigerant from lines 30 and 41 so that an upwardly moving transitional temperature gradient is maintained in vessels 11 and 12 (exchanger-regenerators A and B) while at the same time a downwardly moving transitional temperature gradient is maintained in vessels 13 and 4 (exchanger-regenerators C and D). By proper balance of flow of the various streams distribution of temperature in the vessels remains the same as illustrated in FIG. 2. The switching sequence of exchanger-regenerators A, B, C and D through positions I-IV in the flow scheme remains the same as in FIGS. 1 to 3 and as indicated above in the table of Vessel Sequence.

The terms and expressions employed throughout the above description of the invention are used as terms of description and not of limitation. There is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described, or portions thereof, but it is recognized that various modifications are possible within the scope of the invention as hereinafter claimed.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. Method of treating a hot gaseous stream to remove a higher melting point contaminant therefrom which comprises;

passing said hot gaseous stream upwardly into the first of a plurality of serially connected heat exchange passages, the latter being initially at a temperature less than solidification temperature of said contaminant, whereby to establish a temperature gradient along said serially connected heat exchange passages, said temperature gradient including a transitional temperature region defined by a portion of said heat exchange passages above said region wherein the temperature is less than the solidification temperature of said contaminant whereby to liquefy said contaminant upon contact therewith, and a portion of said passages below said region being at a temperature intermediate the melting and vaporization temperature of said contaminant,

maintaining said upwardly passing hot gaseous stream through said serially connected passages until said transitional temperature region progresses upwardly through the first of said serially connected heat exchanger passages, and

removing said liquid contaminant from the first of said heat exchanger passages,

thereafter discontinuing the flow of hot gaseous stream to said first serially connected heat exchanger, and redirecting said hot gaseous stream from said first of said serially connected heat exchanger passages to another of the latter, and

recooling said first heat exchanger passage to a temperature less than the condensation of said temperature of said contaminant during the period when no hot gaseous stream is being introduced into said first heat exchanger, and

introducing a cooling medium to said plurality of serially connected heat exchangers simultaneously with the introduction of said hot gaseous stream thereto, whereby to regulate the upward progress of said transitional temperature region along said heat exchange passage.

2. In the method as defined in claim 1 wherein; said cooling medium introduced to said plurality of serially connected heat exchangers is introduced in counterflow relation to the passage of said stream of hot gas passing therethrough.

3. In the method as defined in claim 1 including the step of; precooling a second heat exchanger passage to temperature less than the condensation temperature of said contaminant, simultaneously with the passage of said hot gaseous stream through said plurality of serially connected heat exchangers.

4. In the method as defined in claim 3 including the step of; regulating the precooling period of said second heat exchanger passages to reduce the temperature thereof to the condensation temperature of said contaminant during the time period when the said first of said serially connected heat exchangers is receiving said hot gaseous stream.

5. In the method as defined in claim 4 including the step of; connecting said precooled heat exchanger passages to the downstream end of said plurality of said heat exchanger passages subsequent to the discontinuance of said hot gaseous stream to the first of said serially connected heat exchanger passages.

6. Apparatus for removing a contaminant constituent from a warmed process gas which comprises:

(1) a condensing-heating cycle including;

(a) at least two heat exchanger units having fluid

11

- flow paths therein and being serially connected to form a generally vertical flow path, the first of said at least two heat exchange units having an inlet communicated with the lower end of said flow path and being removably connected to a source of said process gas;
- (2) a cooling cycle including;
- (a) at least two other heat exchanger units the first thereof having an inlet communicated with the upper end of said flow path and being removably connected to a source of a refrigerant medium;
- (3) means for simultaneously introducing a stream of warmed process gas and refrigerant medium to the first of said heat exchangers in the condensing-heating, and cooling cycles respectively;
- (4) means for disconnecting said first heat exchanger from said condensing and heating cycle and for reconnecting the same to said source of a refrigerant medium, and for disconnecting said first heat exchanger from said cooling cycle and connecting the same with the downstream side of said cooling cycle.

5

10

15

20

12

References Cited

UNITED STATES PATENTS

1,842,263	1/1932	Gobert	62—12
2,039,889	5/1936	De Baufre	62—13
2,460,859	2/1949	Trumpler	62—14
2,499,043	2/1950	Voorhees	62—13
2,682,157	6/1954	Boling et al.	62—13
2,996,890	8/1961	Baldner et al.	
3,036,439	5/1962	Haringhuizen	62—13
3,097,940	7/1963	Houston	62—12
3,192,729	7/1965	Becker	62—13
2,989,443	6/1961	Martin	203—86

FOREIGN PATENTS

469,943	8/1937	Great Britain.
---------	--------	----------------

WILBUR L. BASCOMB, Jr., Primary Examiner

U.S. Cl. X.R.

62—13; 203—87