

June 9, 1953

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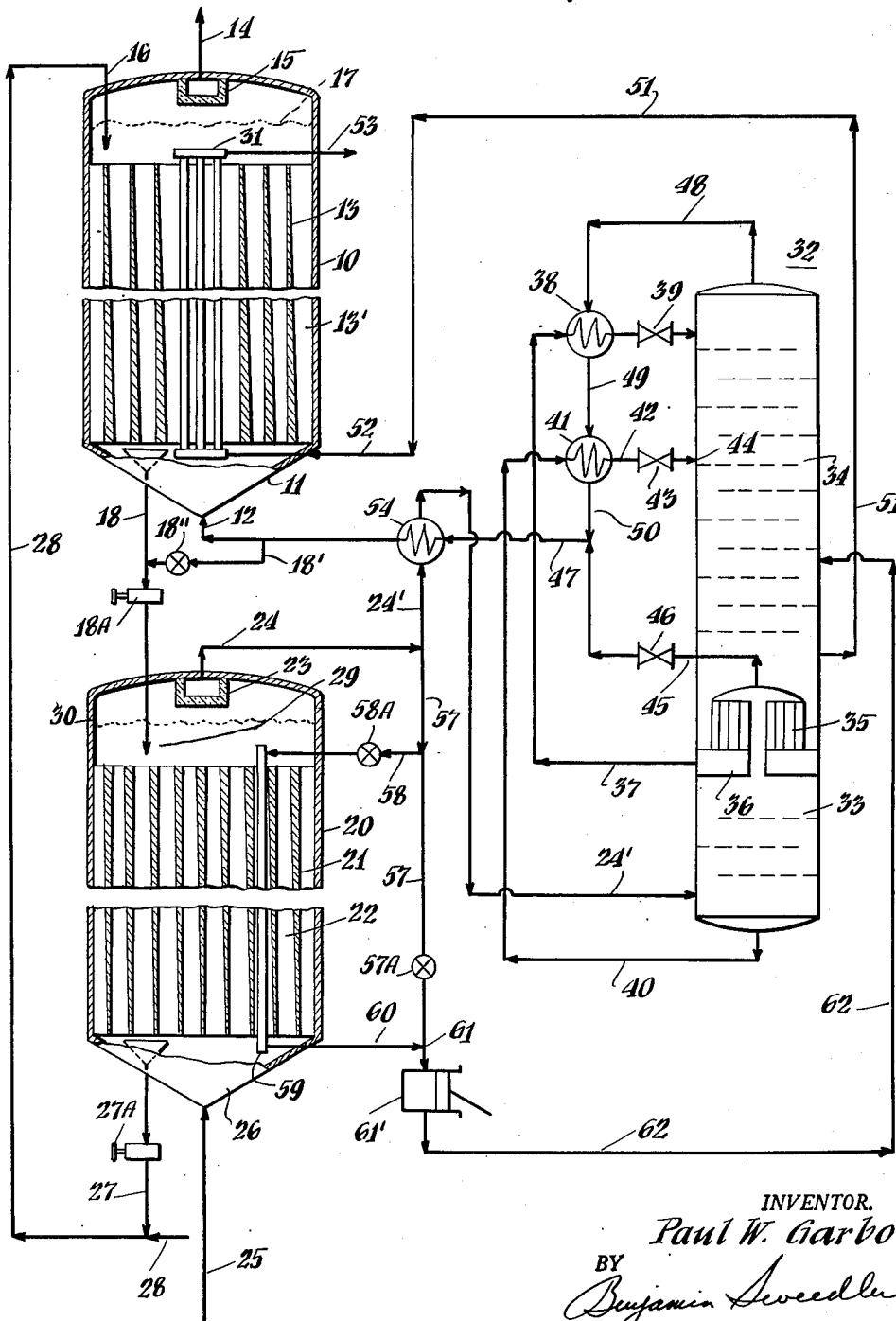
2,641,450

METHOD OF TRANSFERRING HEAT BY A POWDERED THERMOPHORE
IN A STATE OF DENSE PHASE FLUIDIZATION

Filed Oct. 19, 1946

2 Sheets-Sheet 1

Fig. 1



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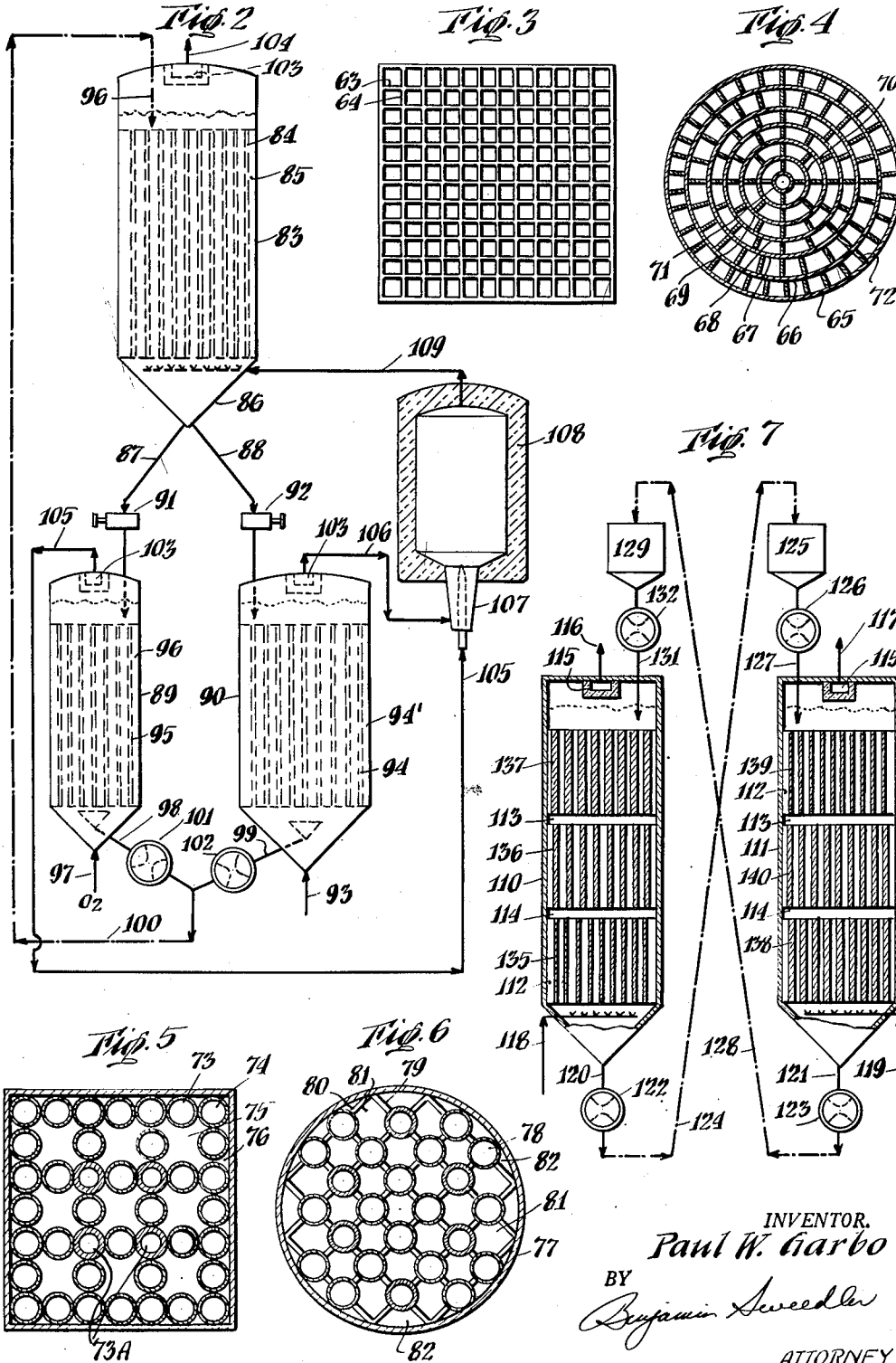
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METHOD OF TRANSFERRING HEAT BY A
POWDERED THERMOPHORE IN A STATE
OF DENSE PHASE FLUIDIZATION

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Application October 19, 1946, Serial No. 704,416

13 Claims. (Cl. 257—55)

1

This invention relates to a novel process of transferring heat or cold from one gaseous medium to another. The term "gaseous medium" is used in a broad sense, to include gases and vapors.

Two procedures have heretofore been chiefly used for the transfer of heat or cold from one gaseous medium to another. One procedure involves the alternate flow of the two gaseous media over a stationary bed of heat or cold absorbing material; during one period of operation this bed is either heated or chilled by the gaseous medium flowing thereover, and during a succeeding period of operation the heat or cold content of the stationary bed is removed therefrom by the other gaseous medium flowing thereover. The well-known regenerator exemplifies this method of transferring heat or cold from one gaseous medium to another. The other conventional method involves the simultaneous flow in indirect heat exchange relationship of the two gaseous media to effect a transfer of heat or cold from one to the other. The well-known recuperator exemplifies this method of transferring heat or cold from one gaseous medium to another.

In both of these methods, in order to obtain relatively high heat or cold transfer efficiencies, it is important to use a maximum of heat or cold absorbing surface area per unit of volume through which the gaseous media flow. Thus, for example, in one type of cold exchanger suggested for recovering the cold content of the outgoing oxygen and nitrogen products of rectification formed in the liquefaction of air to produce oxygen, which products may be at a temperature of about -280°F. , it has been found desirable to use passages, through which the oxygen, nitrogen and air flow in cold exchange relationship, of relatively small cross-sectional area, which passages are provided with closely spaced fins of foil-like metal of high heat conductivity to provide a high surface area of cold exchanger surface per unit of volume of exchanger space.

It is an object of this invention to provide a method of transferring heat or cold from one gaseous medium to another, in which the effective heat or cold exchanger surface area per unit of volume of exchanger is materially greater than in prior known procedures.

Another object is to provide such process of exceptionally high heat or cold transfer efficiency and which process requires relatively simple equipment for its practice.

Other objects and advantages of this invention

2

will be apparent from the following detailed description thereof.

In accordance with this invention, a stream of powdered thermophore is passed through a multiplicity of longitudinally extending channels in one zone in a generally downward direction and in a state of dense phase fluidization, countercurrent to a stream of gaseous medium from which heat or cold is to be abstracted, the gaseous medium maintaining the thermophore in the aforesaid state of dense phase fluidization, so that, in effect, each solid particle of thermophore is vigorously agitated by the gaseous medium, thereby insuring intimate contact between the powdered thermophore particle and the gaseous medium and promoting maximum heat or cold exchange therebetween while maintaining temperature gradients in opposite directions throughout the streams of gaseous medium and thermophore. Thus, for example, if the temperature gradient in the thermophore stream ascends, the temperature gradient in the gas stream descends, and vice versa. From this first zone, the thermophore stream is passed through a multiplicity of longitudinally extending channels in a second zone, countercurrent to a second gaseous medium, while maintaining temperature gradients in opposite directions in the two streams and maintaining the thermophore stream in a state of dense phase fluidization.

The character of the temperature gradient, i. e., whether ascending or descending, in each of the two zones will depend on whether the process is used to abstract heat or cold from one fluid medium and transfer it to another medium. All references herein to the character of the gradient are in terms of the direction of flow of the medium in question. For example, in the practice of this invention for recovering the cold content of the oxygen and nitrogen products of rectification in the liquefaction of air to produce oxygen, nitrogen or oxygen or both may be passed upwardly through the first zone in cold exchange relationship with a down flowing stream of thermophore in a state of dense phase fluidization, so as to maintain an ascending temperature gradient in the gas stream and a descending temperature gradient in the thermophore stream, and the thus chilled thermophore passed downwardly in a state of dense phase fluidization in countercurrent relationship to an up-flowing air stream in the second zone so as to maintain an ascending temperature gradient in the thermophore stream and a descending temperature gradient in the air stream. On the other hand,

3

when employing the invention to abstract heat from one gaseous medium and transfer it to another, a descending temperature gradient is maintained in the hot gaseous stream passing through the first zone and an ascending temperature gradient in the thermophore stream passing through this zone and an ascending temperature gradient maintained in the gaseous stream passing through the second zone and a descending temperature gradient in the thermophore stream passing through the second zone.

By "thermophore" is meant a comminuted solid material of high heat absorbing and heat transfer capacity. It is advantageous in the practice of this invention that the thermophore be in the form of a powder, substantially all of which passes a 100 mesh screen. For best results, the powder will usually contain at least 85% of particles passing through a 200 mesh screen and contain particles as small as 400 mesh or smaller. The particle size in any given system will depend upon the density of the material of the particles, the shape of the particles, the density and velocity of the gaseous fluidizing medium, etc.; the optimum particle size for any such system is readily determinable by simple preliminary experiments conducted under conditions simulating those of actual operation.

The material used as the thermophore will depend upon the particular application to which the invention may be put. Thus, for example, in the recovery of the cold content of the oxygen and nitrogen products of rectification in the liquefaction of air to produce oxygen, a material of exceptionally high heat absorbing and transfer capacity should be used. Copper, aluminum and other metals and alloys of high heat absorbing and transfer capacity will be found eminently satisfactory for this purpose. If the process is employed to transfer heat at high temperatures from one gaseous medium to another, materials of high heat absorbing and transfer capacity capable of withstanding such high temperatures should be employed; silica, silicon carbide (Carborundum) and alumina are examples of such materials.

The thermophore is maintained in each of the two zones in a state of dense phase fluidization, i. e. the thermophore in each of the two zones is subjected to a rate of gaseous flow therethrough, such that a bed or mass thereof is maintained in each zone, each of the particles of the bed or mass being suspended in the gas and exhibiting relatively random movement, and so that the upper surface of the bed or mass assumes a level substantially above the normal level of the settled thermophore, which level is commonly known as a pseudo-liquid level.

During the flow of the gaseous medium through the bed or mass of thermophore in each of the zones, the individual particles rise and fall, the general direction of movement of the particles, however, being downwardly so that as the operation of the process progresses, fresh incoming particles of thermophore form the upper surface of the mass and these particles gradually progress downwardly until they reach the exit, where they are withdrawn.

This state of fluidization, in which the particles are maintained in a vigorous and intense state of agitation, i. e., in a condition resembling "boiling," with the upper surface of the mass or bed thereof substantially above the normal level

4

of the settled thermophore, is herein designated as "dense phase" fluidization.

The process of this invention is particularly applicable to the recovery of the cold content of oxygen and nitrogen products of rectification in the liquefaction of air in the production of oxygen. However, the invention is not limited to this application but has numerous other applications, such, for example, as the transfer of heat from one fluid medium to another. Thus, it may be employed to transfer heat from synthesis gas to the gaseous reactants. For example, oxygen and a mixture of steam and natural gas may be heated by the heat removed from the carbon monoxide and hydrogen synthesis gas produced therefrom, or the invention may be employed to abstract heat from flue gases or other products of combustion or waste gases and transfer this heat to any desired medium, for example, to pre-heat air used to support combustion or to super-heat steam.

In the accompanying drawings forming a part of this specification and showing, for purposes of exemplification, preferred forms of apparatus for practicing this invention:

Fig. 1 is a layout of equipment for recovering the cold content of oxygen and nitrogen products of rectification in the liquefaction of air to produce oxygen;

Fig. 2 is a preferred layout of equipment for practicing the process of this invention in effecting transfer of heat from synthesis gas to the gaseous reactants;

Fig. 3 is a horizontal section through a rectangular chamber and shows one arrangement of partitions forming longitudinal passages or cells;

Fig. 4 is a horizontal section through a cylindrical chamber showing a modified arrangement of longitudinally extending passages or cells;

Fig. 5 is a horizontal section through a rectangular chamber showing a third arrangement of longitudinally extending passages or cells;

Fig. 6 is a horizontal section through a cylindrical chamber showing still another arrangement of longitudinally extending passages or cells; and

Fig. 7 is a modified form of apparatus for practicing this invention in which apparatus the chambers are arranged in side by side relationship rather than superimposed relationship as in the modifications of Figs. 1 and 2.

Fig. 1 of the drawing shows a chamber 10, having a conical base 11, the chamber being provided with a gas inlet 12 at the apex of the conical base 11. A plurality of closely spaced partitions 13 are disposed within chamber 10 to divide this chamber into a multiplicity of longitudinally extending passages 13', which substantially prevent top-to-bottom intermingling and mixing of the thermophore, such as would interfere with the maintenance of the desired temperature gradient in the mass of thermophore particles passing through chamber 10, as hereinafter described. As hereinafter more fully disclosed, partitions 13 may be in the form of tubes, parallel partitions or intersecting partitions forming longitudinally extending cells or passages of any desired cross-sectional configuration. These longitudinally extending passages 13' may be elliptical, circular, square or other polygonal shape in cross-section and should be so dimensioned that they have an effective size of a pipe having an internal radius falling within the range of from about $\frac{1}{4}$ " to about 2", preferably from $\frac{1}{2}$ " to about 1". Thus, if a passage has an effective

pipe size corresponding to an internal radius of say $\frac{1}{2}$ ", no thermophore particle will be spaced from a wall by a distance more than $\frac{1}{2}$ " and the distance between a thermophore particle and the wall farthest away will be 1". With the partitions spaced within the range above indicated, and passing a gaseous medium therethrough at a suitable velocity, readily determined by trial, depending on the density and particle size of the thermophore, intermingling of the thermophore particles is prevented from top to bottom of the passages to an extent sufficient to maintain desired temperature gradient conditions.

Chamber 10 is provided with an exit pipe 14 communicating with a filter, cyclone separator or other dust-removing device 15, through which the gaseous medium passes, the device 15 removing substantially all entrained thermophore particles carried by the gaseous stream. This chamber is also provided with an inlet pipe 16 extending below the pseudo-liquid level 17 of the thermophore particles and a standpipe 18 flow through which is controlled by slide valve 18A or its equivalent. A line 18' leads from the main nitrogen line 47 into standpipe 18. Valve 18'' regulates the flow of nitrogen through pipe 18'; this valve being adjusted to provide a nitrogen flow sufficient to maintain the thermophore particles passing through 18 in a free flowing condition.

In the embodiment of the invention shown in the drawing, the partitions 13 are desirably tapered in cross-section to form channels 13' also tapered in cross-section, i. e., channels 13' have a varying cross-sectional area, the cross-sectional area at the top being greater than that at the bottom. Hence, the volumetric space of the channels per unit length thereof progressively increases from bottom to top, thereby compensating for gas expansion with increase in the temperature of the gas stream flowing upwardly therethrough. If chamber 10 were used as the heating zone for the thermophore, the taper of the partitions would be reversed so that the channels defined thereby would have their greatest cross-sectional areas at their bases.

A second chamber 20 is provided similar in construction to chamber 10, except that the partitions 21 therein taper from top to bottom rather than from bottom to top, so that the cross-sectional area of the cells or longitudinal passages 22 formed by these partitions decreases from bottom to top to compensate for the decrease in volume of the gas stream passing therethrough, due to its decrease in temperature. This chamber is provided with a filter, cyclone separator or other dust-removing member 23 communicating with a gas exit pipe 24. A gas inlet pipe 25 at the base of this chamber communicates with the conical portion 26. A thermophore exit pipe 27 having a regulating valve 27A therein, discharges into a main 28 through which the thermophore is carried in suspension in a high-velocity gas stream, e. g., some of the nitrogen leaving vessel 10 by way of pipe 14 may be used for this purpose, to the inlet pipe 16 dipping below the pseudo-liquid level 17 in chamber 10. Pipe 18, supplying the thermophore withdrawn from chamber 10 discharges the thermophore at 29 below the pseudo-liquid level 30.

In the embodiment of the invention shown on the drawings, a bank of tubes 31 is disposed within chamber 10 for flow of oxygen therethrough to recover the cold content of the outgoing oxygen product of rectification, along with the cold con-

tent of the nitrogen product of rectification employing the thermophore circulated through chamber 10 for this purpose. If desired, a separate exchanger may be used for recovering the cold content of the oxygen, in which case the bank of tubes 31 in chamber 10 would not be employed, i. e., a chamber 10, free of such tubes, would be used. The bank of tubes 31, or a similar bank of tubes disposed in chamber 20 may be employed for the purpose of having an external refrigerant, such as ethylene, passed therethrough to introduce into the process an amount of cold adequate to compensate for cold losses resulting from the difference in enthalpy between the air introduced into and the products of rectification withdrawn from the process, and for heat leaks into the system. The bank of tubes 31 is preferably of a metal of high heat conductivity; copper is a satisfactory material of construction.

The rectification system with which the exchanger of this invention may be employed, when used for recovering the cold content of oxygen and nitrogen products of rectification in the liquefaction of air to produce oxygen, comprises, for example, a two-stage rectification column 32, the lower section 33 of which is operated at a pressure of about 72 pounds gauge and the upper section 34 of which is operated at a pressure of from about 4 to about 10 pounds gauge, preferably at about 5 pounds gauge. This column, as is customary, is provided with rectification plates of the bubble cap or other desired type. The lower section 33 of the column 32 communicates with a condenser 35 and has a liquid collecting shelf 36 disposed immediately below the condenser 35 for collecting liquid nitrogen. Pipe 37 leads from this shelf 36 to a heat exchanger 38, which in turn communicates through a pressure-reducing valve 39 with the top portion of the upper section 34. Condenser 35 acts as a re-boiler for the upper section 34 of the column 32.

From the base portion of the lower section 33, a pipe line 40 for the flow of crude oxygen (containing approximately 40% oxygen) passes to a heat exchanger 41 which communicates through pipe line 42 having a pressure-reducing valve 43 therein, with the low-pressure section 34 at an intermediate point 44. A line 45 having a pressure-reducing valve 46 therein leads from condenser 35 to a nitrogen line 47 communicating by way of heat exchanger 54 with the inlet 12 to chamber 10. A line 48 leads from the top of low-pressure section 34 to the heat exchanger 38, the nitrogen flowing through this line passing through the heat exchanger 38, then through line 49 and heat exchanger 41 into line 50 which communicates with line 47. Oxygen line 51 leads from the lower part of the low pressure section 34 to the inlet 52 of the bank of tubes 31 disposed within chamber 10, this bank of tubes being provided with an exit line 53. As above indicated, the bank of tubes in chamber 10 may be omitted, in which case the oxygen line 51 may communicate with an exchanger independent of chamber 10.

Pipe 24 has two branches, one identified as 24' leading through heat exchanger 54 to lower section 33 and the other identified by 57 communicating with branch line 58 having valve 58A therein leading through a tube 59 disposed within chamber 20 and thence through line 60 which joins line 57 having valve 57A therein at 61. From 61, line 57 enters expander 61' which dis-

charges through line 62 into low pressure section 34.

The heat exchangers 38, 41 and 54 and the two-stage fractionating column 32 may be of any conventional type. Two separate fractionating columns suitably interconnected may be used in place of the two-stage column 32 shown. It will be understood that the equipment throughout, including chambers 10 and 20 and all piping connections, is heat insulated to minimize loss of cold.

Chambers 10 and 20 may be square-shaped in section, as shown, for example, in Figs. 3 and 5, or cylindrical as shown in Figs. 4 and 6. The longitudinally extending channels 13' and 22 may be shaped as shown in these figures. In Fig. 3 these channels are defined by partition walls 63, 64 at right angles to each other forming substantially square-shaped channels. Alternatively, the channels or passageways may be defined by a cylindrical outer wall 65 having a plurality of concentric inner walls 66, 67, 68, 69, 70 and 71 defining annular channels. Radial partitions 72 are provided in these annular channels to form longitudinally extending passageways of the desired cross-sectional extent, i. e., having an effective pipe size, the internal radius of which is within the range of from about 1/4" to about 2", preferably from about 1/2" to about 1".

Fig. 5 shows still another arrangement of longitudinally extending passages in which longitudinally extending cylindrical pipes 73 are arranged in the pattern shown within a rectangular housing to provide cylindrical, longitudinally extending passageways 74 defined by the inner walls of the pipes and longitudinally extending passageways 75 of somewhat larger cross-sectional extent, defined by the outer walls of the pipes as well as a series of triangular shaped longitudinally extending passageways 76 defined by the outer walls of a pair of pipes contiguous to the inner wall of the rectangular housing. The modification of Fig. 6 involves a cylindrical housing 77 cooperating with cylindrical pipes 78 disposed therein and longitudinally extending baffles or partitions 79, 80, baffles 79 and 80 being at right angles to each other and cooperating with the pipes 78 to define longitudinally extending passageways 81, 82. It will be understood that Figs. 3 to 6 represent a few of the many possible arrangements of partitions to form longitudinally extending passageways for flow of fluidized thermophore therethrough under conditions such that desired temperature gradient conditions are maintained.

If desired, longitudinally extending passages in any of the modifications hereinabove described may be arranged in two or more groups. Thus, for example, in the modification of Fig. 5, some of the pipes 73, say the corner pipes 73A of each rectangular arrangement of eight pipes, may be used for flow of oxygen therethrough in lieu of the separate bank of tubes corresponding to bank 31 in Fig. 1 while the remaining longitudinally extending passages within the chamber are used for the upward flow of nitrogen and the downward flow of thermophore.

The arrangement of the apparatus of Fig. 2 is particularly designed for recovering the heat content of synthesis gas and imparting this heat to the reacting gases. This equipment involves a chamber 83 having partitions 84 therein to form longitudinally extending passages 85. These longitudinally extending passages may be of any of

the shapes hereinabove disclosed in connection with Figs. 3 to 6 inclusive. Chamber 83 has a conical base 86 from which lines 87, 88 lead to chambers 89, 90. Lines 87 and 88 are provided with slide valves 91, 92, respectively. Chamber 90 has at its base a gas line 93 for introduction therein of a methane and steam mixture; this chamber is of greater volumetric capacity than chamber 89 and has therein partitions 94 forming longitudinally extending passages 94'. Chamber 89 has partitions 95 forming longitudinally extending passages 96 and has at its base an oxygen inlet line 97. These longitudinally extending passages, as hereinabove disclosed, may be of any desired cross-sectional configuration.

Conical base portions of chambers 89 and 90 are provided with thermophore discharge lines 98, 99, respectively, which lead into a common line 100 communicating with the upper portion of chamber 83. Rotary valves 101, 102 are provided in the lines 98, 99, respectively. The rotary valves 101, 102, and the slide valves 91, 92 may be of any well-known type. If desired, all rotary valves may be employed or all slide valves, the function of these valves being to permit flow of thermophore through the lines in which they are disposed without unduly disturbing the pressure conditions in the chambers with which these lines communicate.

Each of the chambers 83, 89 and 90 is provided with a filter or other dust-removing device 103. Filter 103 in chamber 83 has leading therefrom a discharge pipe 104. A line 105 leads from filter element 103 of chamber 89 and line 106 leads from filter element 103 of chamber 90, the lines 105 and 106 entering a reactant nozzle 107 disposed in the base of reaction chamber 108. Synthesis gases leave reaction chamber 108 through line 109 leading into the conical base portion of chamber 83.

The modification of Fig. 7 involves chambers 110, 111 arranged in side-by-side relationship instead of superimposed relationship as in the modifications of Figs. 1 and 2. As in the case of the other modifications hereinabove disclosed, the top of each chamber 110, 111 is provided with a filter or a dust-removing device 115 from which lead the gas exit pipes 116, 117. The conical bases of chamber 110, 111 are provided with gas inlet lines 118, 119 and thermophore withdrawal lines 120, 121 in which rotary valves 122, 123 are disposed. A conveyor 124 leads from the rotary valve 122 for flow of the thermophore into container 125 communicating through rotary valve 126 and line 127 with the chamber 111. Conveyor 128 leads from rotary valve 123 to chamber 129 communicating through a line 131 having a rotary valve 132 therein with chamber 110.

Each chamber 110, 111 has longitudinally extending channels or passageways 112 interrupted laterally at 113, 114 by narrow spaces which should be less than 12" wide, preferably about two inches wide. These lateral spaces function to equalize flow conditions through the several streams of thermophore, each in a state of dense phase fluidization passing through the channels 112. The interrupted channels 112 in chamber 110 are defined by walls 135, 136, 137 of different thickness, the thickest walls being at the top of chamber 110, and the thinnest at the base, so that the cross-sectional area of the channels is smallest at the top and largest at the base, thereby compensating for volume decrease due to temperature decrease of gas flowing upwardly through chamber 110. In chamber 111 the thick-

est wall 138 is at the base, the thinnest wall 139 at the top and the wall 140 of intermediate thickness at an intermediate point of the length of the chamber. Thus the channels each gradually becomes of increasing cross-sectional area in the direction of gas flow upwardly through chamber 111 to accommodate increasing gas volume due to rising temperature. It will be understood any desired number of wall sections in the chamber may be used to define interrupted, longitudinally extending channels having the cross-sectional area thereof gradually increase or decrease to provide for optimum flow conditions. It will be appreciated the arrangement of Fig. 7 provides an alternative method of obtaining substantially the same effect as the tapered walls 13 and 21 in chambers 10 and 20, respectively, and that either of these modifications may be employed in forming the longitudinally extending channels in chambers 83, 89 and 90 of Fig. 2. In heat exchange procedures in which the volume change in the gas flowing through the channels is not large, channels of substantially uniform cross-sectional area from top to bottom of the exchanger may be employed.

Example 1

The following example is illustrative of the operation of the process of this invention in recovering the cold content of the outgoing nitrogen and oxygen products of rectification in the liquefaction of air employing powdered copper as the thermophore. It is to be understood the invention is not limited to this example.

All temperatures herein given are in degrees F. and pressures are in pounds per square inch gauge.

Air at a pressure of about 75 pounds gauge and a temperature of 100° F. is admitted through line 25 at a rate sufficient to maintain the powdered thermophore circulating through the longitudinally extending channels 22 in chamber 20, constituting zone 2 of the process, in a state of dense phase fluidization. The temperature of the air as it flows countercurrent to the thermophore stream gradually decreases to -273° F. at the point the air leaves the pseudo-liquid level 30. The thermophore stream enters at a temperature of -276° F. and flows downwardly through the longitudinally extending passages 22 in chamber 20 in a state of dense phase fluidization, the temperature thereof gradually increasing to 98° F. at the point where the stream leaves chamber 20 and is passed through main 28 by a suitable conveyor gas, for example, nitrogen, into the chamber 10.

Most of the air (say 80% by volume) from chamber 20 at a temperature of -273° F. flows through heat exchanger 54 in heat exchange relation with nitrogen and enters high pressure section 33 of column 32 at a temperature of -275° F. and a pressure of about 72 pounds.

Crude oxygen at a temperature of -278° F. and pressure of 72 pounds leaves the base of column section 33 through line 40, flows through heat exchanger 41 where its temperature is reduced to -286° F. and upon flow through the pressure-reducing valve 43 is flashed, entering lower pressure column section 34 at a temperature of -310° to -315° F. and a pressure of 5 pounds. Pure oxygen is withdrawn through line 51 at a temperature of -292° F. and a pressure of 5 pounds and flows through bank of tubes 31 in the chamber 10 in heat exchange relation with the thermophore passing thereover, the oxygen leaving the

bank of tubes at a temperature of 90° F. at a pressure of about 1 pound.

Nitrogen at a temperature of about -286° F. and a pressure of 12 pounds is withdrawn through line 45 and passes through valve 46, its temperature being reduced to a temperature of about -315° F. as a result of the expansion through the pressure reducing valve 46. Nitrogen at a temperature of -315° F. and a pressure of 5 pounds is withdrawn through line 48 and flows through heat exchanger 38, where its temperature is raised to about -304° F. The nitrogen flows from heat exchanger 38 through heat exchanger 41 and mixes with that in line 45; the nitrogen stream thus produced at a temperature of -294° F. flows through line 47, into heat exchanger 54 where the temperature of the nitrogen is raised to -278° F. The nitrogen at this temperature and a pressure of about 5 pounds enters inlet 12 to chamber 10.

The nitrogen flows upwardly through the longitudinally extending passages 13 maintaining the thermophore powder in a state of dense phase fluidization, the nitrogen leaving through exit line 14 at a temperature of about 95° F. Thus an ascending temperature gradient is maintained in the nitrogen stream flowing through chamber 10 constituting the first zone of the process. The thermophore particles enter this zone at a temperature of 98° F. and leave through pipe 18 at a temperature of approximately -276° F., a descending temperature gradient in the direction of the thermophore flow being maintained in the stream of thermophore passing through this zone, which temperature gradient it will be noted is in the opposite direction from that maintained in the nitrogen stream passing through this zone.

Any known procedure may be used for compensating for heat leaks and cold losses resulting from the difference in enthalpy between the air introduced into and the products of rectification withdrawn from the system. The preferred method is shown in Fig. 1 and involves the diversion of a minor portion, say 20%, of the cold air from line 24 to pipe 57 controlled by valve 57A and discharging into expansion engine or turbine 61'. A minor portion, say 10%, of the diverted air is warmed by passage through pipe 53 controlled by valve 58A and through heat exchanger 59 disposed in the fluidized mass of vessel 20. This warm air flows through pipe 60 and mixes with the air stream in pipe 57 before it enters expander 61'. In this manner, the air originally at a temperature of -273° F., as discharged into pipe 24, is warmed up to a temperature of about -235° F. before expansion to increase the amount of refrigeration produced. The air expanded from a pressure of about 72 pounds to a pressure of about 5 pounds attains a temperature of about -305° F. and flows through pipe 62 into low-pressure section 34 of column 32.

It will be noted from the above example that the thermophore enters chamber 20 at a temperature of -276° F., while the air stream leaves this chamber at a temperature of -273° F.; thus the temperature approach at the cold end of this chamber is 3° F. The thermophore leaves chamber 10 at a temperature of -276° F., whereas the nitrogen entering this chamber is at a temperature of -278° F., the temperature approach at the cold end of chamber 10 is therefore 2° F.

The air, before introduction into chamber 20, should be treated for removal of moisture and

carbon dioxide to avoid deposition of frost and solid carbon dioxide in the cold exchanging chambers which would interfere with their operation. Any known treatment for effecting removal of moisture and carbon dioxide may be used for this purpose, for example, the air may be scrubbed with caustic soda, or other chemicals, to remove the carbon dioxide.

The production of oxygen may be carried out in equipment of the type disclosed in Figure 2 involving two separate chambers for the flow of oxygen and nitrogen products of rectification, respectively, therethrough in cold exchange relationship with thermophore streams each in a state of dense phase fluidization. Thus the nitrogen stream may be introduced through line 93 and pass upwardly through the longitudinally extending channels in chamber 89, while the oxygen stream is introduced through line 97 and passed upwardly through longitudinal channels in chamber 89, the oxygen stream entering at a temperature of about -292°F. and a pressure of 5 lbs. and the nitrogen stream at a temperature of -278°F. and a pressure of about 5 pounds. Thermophore streams each at a temperature of about 98°F. flow downwardly countercurrent to the rising oxygen and nitrogen streams and leave the base of chambers 89 and 90 at a temperature of approximately -290°F. and -273°F. , respectively. Thus the temperature approach at the base of chambers 89 and 90, where the oxygen and nitrogen streams, respectively, enter and the thermophore is withdrawn, is about 2°F. in case of chamber 89 and about 5°F. in the case of chamber 90. The combined thermophore stream at a temperature of -276°F. flows downwardly in a state of dense phase fluidization through the longitudinal channels 85 in chamber 83 countercurrent to a rising stream of air which may enter at a pressure of about 75 lbs. gauge and a temperature of 100°F. and leave at substantially the same pressure and a temperature of -273°F. through line 104. The temperature approach at the top of chamber 83 where the refrigerated air stream leaves, it will be noted, is approximately 3°F. In chamber 83 an ascending temperature gradient is maintained in the thermophore stream while a descending temperature gradient is maintained in the air stream; in chambers 89 and 90 descending temperature gradients are maintained in the thermophore streams and ascending temperature gradients in the oxygen and nitrogen streams, respectively.

In the operation of the equipment of Figure 7, nitrogen at a temperature of about -278°F. and a pressure of 5 lbs. may be admitted through line 119 and passed upwardly through the longitudinally extending channels 112 in chamber 111, leaving at 117 at a temperature of approximately 95°F. A thermophore stream in a state of dense phase fluidization flows downwardly through channels 112 in chamber 111 entering this chamber at a temperature of 98°F. and leaving at a temperature of approximately -276°F. The thermophore stream at this temperature is withdrawn through valve 123 from which it is elevated through conveyor 128 to compartment 129 communicating through valve 132 with chamber 110. The thermophore stream at a temperature of about -276°F. in a state of dense phase fluidization flows downwardly through the longitudinally interrupted channels 112 countercurrent to a stream of air which enters through line 118 at a temperature of about 100°F.

F. and a pressure of about 75 lbs. and leaves through filter 115 and line 116 at a temperature of about -273°F. and substantially the same pressure. Thus a descending temperature gradient is maintained through the air stream passing upwardly and an ascending temperature gradient through the thermophore stream passing downwardly through chamber 110 and an ascending temperature gradient is maintained in the nitrogen stream passing upwardly and a descending temperature gradient in the thermophore stream passing downwardly through chamber 111.

Example 2

The following example is illustrative of the operation of the process of this invention in recovering the heat content of synthesis gas ($\text{H}_2 + \text{CO}$), using powdered silicon carbide (Carborundum) as the thermophore:

The reactants used in this example are oxygen of 98.5% purity, steam and natural gas having approximate composition by volume as follows: methane 82%; higher hydrocarbons 9%; hydrogen 7%; residuals, nitrogen, carbon dioxide, etc., 2%. A stream of two volumes of natural gas and one volume of steam is introduced through 93, countercurrent to the fluidized thermophore flowing through channels 94' in chamber 90. The oxygen flows through line 97 countercurrent to the thermophore flowing through channels 96. The oxygen and methane-steam mixture are preheated by external means (not shown) to a temperature of about 530°F. at which temperature the gaseous reactants enter chambers 89, 90. They leave these chambers at a temperature close to 2300°F. at which temperature they enter reaction chamber 108, which is under pressure of approximately 200 pounds per square inch gauge. Synthesis gas leaves this reaction chamber at a temperature of about 2300°F. at which temperature it enters base of chamber 83, flowing upwardly through the fluidized thermophore, passing downwardly through the channels 85 therein. The synthesis gas leaves through line 104 at the top of chamber 83 at a temperature of approximately 550°F. The thermophore enters the top of chamber 83 through line 96 at a temperature of approximately 540°F. and leaves the bottom of chamber 83 through lines 87, 88 at a temperature close to 2300°F.

An analysis of the synthesis gas is as follows: 59.2% by volume hydrogen, 29.9% CO , 7.8% CO_2 , 2.1% CH_4 , the remainder being chiefly nitrogen.

It will be noted that the thermophore leaves chamber 20 in the modification of Fig. 1 and the chambers 89, 90 in the modification of Fig. 2, at a temperature closest to atmospheric, at which temperature it is transported to the chamber 10 in the modification of Fig. 1 or chamber 83 in the modification of Fig. 2. Thus the thermophore is moved from one chamber of the process to the other at a temperature closest to atmospheric, with consequent minimization of heat or cold losses.

It will be further noted the process of this invention involves the flow of a fluidized stream of comminuted thermophore through a plurality of heat or cold exchange zones through each of which flows a stream of gaseous medium in a direction countercurrent to the thermophore stream, while maintaining temperature gradients in opposite directions in the thermophore and gaseous streams passing through each zone. The use of a powdered thermophore in a state of

dense phase fluidization provides exceptionally high surface area of heat or cold absorbing material per unit of volume of exchanger space, and exceedingly intimate contact between the gas and the thermophore. The turbulence of the thermophore particles promotes high rates of heat transfer. This insures optimum removal of heat or cold from the gaseous medium passing through one zone and the most efficient transfer thereof to the gaseous medium passing through the second zone. With this invention, it is feasible to maintain a temperature approach between the air leaving, for example, chamber 20 in the modification of Fig. 1 and the nitrogen entering chamber 10 as low as 2° or 3° F.

This compares with a temperature approach of the order of 10° F. or at best 6° to 8° F. obtained in prior processes, and demonstrates the improved efficiency of the process of this invention.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense. Thus, for example, while Fig. 1 of the drawing discloses a single chamber for either heating or cooling the thermophore, it will be understood that two or more of such chambers may be employed in series.

What is claimed is:

1. The method of transferring heat from a stream of air to a stream of a product of rectification in the liquefaction and rectification of air, which comprises circulating a powdered thermophore downwardly through a plurality of longitudinally extending channels arranged in parallel in a first zone countercurrent to said stream of a product of rectification rising at a velocity which maintains said thermophore in said first zone in a state of dense phase fluidization, each of said channels having an effective size of a pipe having an internal radius in the range of about 1/4 inch to about 2 inches which substantially prevents top-to-bottom mixing of said thermophore within the channel, thereby maintaining an ascending temperature gradient in the rectification product stream and a descending temperature gradient in the thermophore stream passing through said first zone whereby the thermophore stream leaves said first zone at substantially the temperature at which the rectification product stream enters said first zone, circulating said thermophore from the lower end of said first zone downwardly through a plurality of longitudinally extending channels arranged in parallel in a second zone countercurrent to said stream of air rising at a velocity which maintains said thermophore in said second zone in a state of dense phase fluidization, each of said channels having an effective size of a pipe having an internal radius in the range of about 1/4 inch to about 2 inches which substantially prevents top-to-bottom mixing of said thermophore within the channel, thereby maintaining a descending temperature gradient in the air stream and an ascending temperature gradient in the thermophore stream passing through said second zone whereby the heat content removed from the air stream in said second zone by said thermophore is imparted to the rectification product stream, and circulating said thermophore from the lower end of said second zone downwardly through said first zone as aforesaid.

2. The method as defined in claim 1, in which the channels have an effective size of a pipe having an internal radius falling within the range of about one-half inch to about an inch.

3. The method as defined in claim 1, in which the rectification product stream is predominantly nitrogen and enters said first zone at a temperature of approximately -230° F., and the air stream enters said second zone at a temperature of approximately 100° F.

4. In the method of transferring heat from one gaseous medium to another wherein one gaseous medium is passed upwardly through a mass of powdered thermophore in a state of dense phase fluidization, another gaseous medium is passed upwardly through another mass of said thermophore in a state of dense phase fluidization, and said thermophore is circulated between the two said masses, the improvement which comprises dividing each of the two said masses in a plurality of longitudinally extending channels arranged in parallel, each of said channels having an effective size of a pipe having an internal radius falling within the range of from about 1/4 inch to about 2 inches, and maintaining temperature gradients in opposite directions along the vertical dimension of the two said masses in a plurality of longitudinally extending channels.

5. The method as defined in claim 4, in which the horizontal cross-section of each of the longitudinally extending channels gradually increases in the direction of increasing temperature.

6. The method as defined in claim 4, in which the powdered thermophore is of a particle size such that substantially all passes through a 100 mesh screen and at least 85% thereof passes through a 200 mesh screen.

7. The method of transferring heat between a single gaseous stream and two separate gaseous streams having substantially the same initial temperature, which comprises circulating a powdered thermophore downwardly through a plurality of longitudinally extending channels arranged in parallel in a first zone countercurrent to said single stream rising at a velocity which maintains said thermophore in said first zone in a state of dense phase fluidization, each of said channels having an effective size of a pipe having an internal radius in the range of about 1/4 inch to about 2 inches, maintaining in said first zone temperature gradients in opposite directions in said thermophore and in said single stream, circulating said thermophore from the lower end of said first zone downwardly through a plurality of longitudinally extending channels arranged in parallel in a second zone countercurrent to one of said two separate streams rising at a velocity which maintains said thermophore in said second zone in a state of dense phase fluidization, each of said channels having an effective size of a pipe having an internal radius in the range of about 1/4 inch to about 2 inches, maintaining in said second zone temperature gradients in opposite directions in said thermophore and in said one of the two separate streams, circulating said thermophore from the lower end of said second zone downwardly through said first zone as aforesaid, and passing the other of said two separate streams in heat transfer relationship with said thermophore while maintaining temperature gradients in said other separate stream and in said thermophore in said relationship.

8. The method as defined in claim 7, in which said heat transfer relationship is effected in a

third zone similar in arrangement and operation to said second zone.

9. The method as defined in claim 8, in which hot synthesis gas is said single stream, and methane and oxygen are said two separate streams.

10. The method as defined in claim 8, in which air is said single stream, and cold nitrogen and oxygen rectification products are said two separate streams.

11. The method as defined in claim 7, in which the horizontal cross-section of each of said channels gradually increases in the direction of increasing temperature.

12. The method of producing synthesis gas comprising essentially carbon monoxide and hydrogen, which comprises passing separate, compressed streams of methane and oxygen upwardly through separate, downwardly moving columns of heated, powdered thermophore maintained in a state of dense phase fluidization while maintaining temperature gradients in opposite directions in said columns and said separate streams, reacting the thus heated streams of methane and oxygen in an unobstructed reaction zone maintained at a gauge pressure of at least 200 pounds per square inch and a temperature of at least 2300° F., passing the resulting hot synthesis gas from said reaction zone upwardly through a third, downwardly moving column of said thermophore maintained in a state of dense phase fluidization while maintaining temperature gradients in opposite directions in said third column and said synthesis gas, discharging cooled synthesis gas from the top of said third column, and moving said thermophore from the bases of the first said separate columns to the top of said third column and from the base of said third column to the tops of the first said separate columns.

13. The method of transferring heat between a single gaseous stream and two separate gaseous streams having substantially the same initial temperature, which comprises circulating a powdered thermophore downwardly through a plurality of longitudinally extending channels arranged in parallel in a first zone countercurrent to said single stream rising at a velocity which maintains said thermophore in said first zone in a state of dense phase fluidization, each of said channels having a limited, horizontal cross-section which substantially prevents top-to-bottom mixing of said thermophore within the channel, thereby maintaining in said first zone

temperature gradients in opposite directions in said thermophore and in said single stream, the limited, horizontal cross-section of each of said channels gradually increasing in the direction of increasing temperature, circulating said thermophore from the lower end of said first zone downwardly through a plurality of longitudinally extending channels arranged in parallel in a second zone countercurrent to one of said two separate streams rising at a velocity which maintains said thermophore in said second zone in a state of dense phase fluidization, each of said channels having a limited, horizontal cross-section which substantially prevents top-to-bottom mixing of said thermophore within the channel, thereby maintaining in said second zone temperature gradients in opposite directions in said thermophore and in said one of the two separate streams, the limited, horizontal cross-section of each of said channels gradually increasing in the direction of increasing temperature, circulating said thermophore from the lower end of said second zone downwardly through said first zone as aforesaid, and passing the other of said two separate streams in heat transfer relationship with said thermophore while maintaining temperature gradients in said other separate stream and in said thermophore in said relationship.

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