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HEAT EXCHANGE

2,499,043

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2 Sheets-Sheet 1

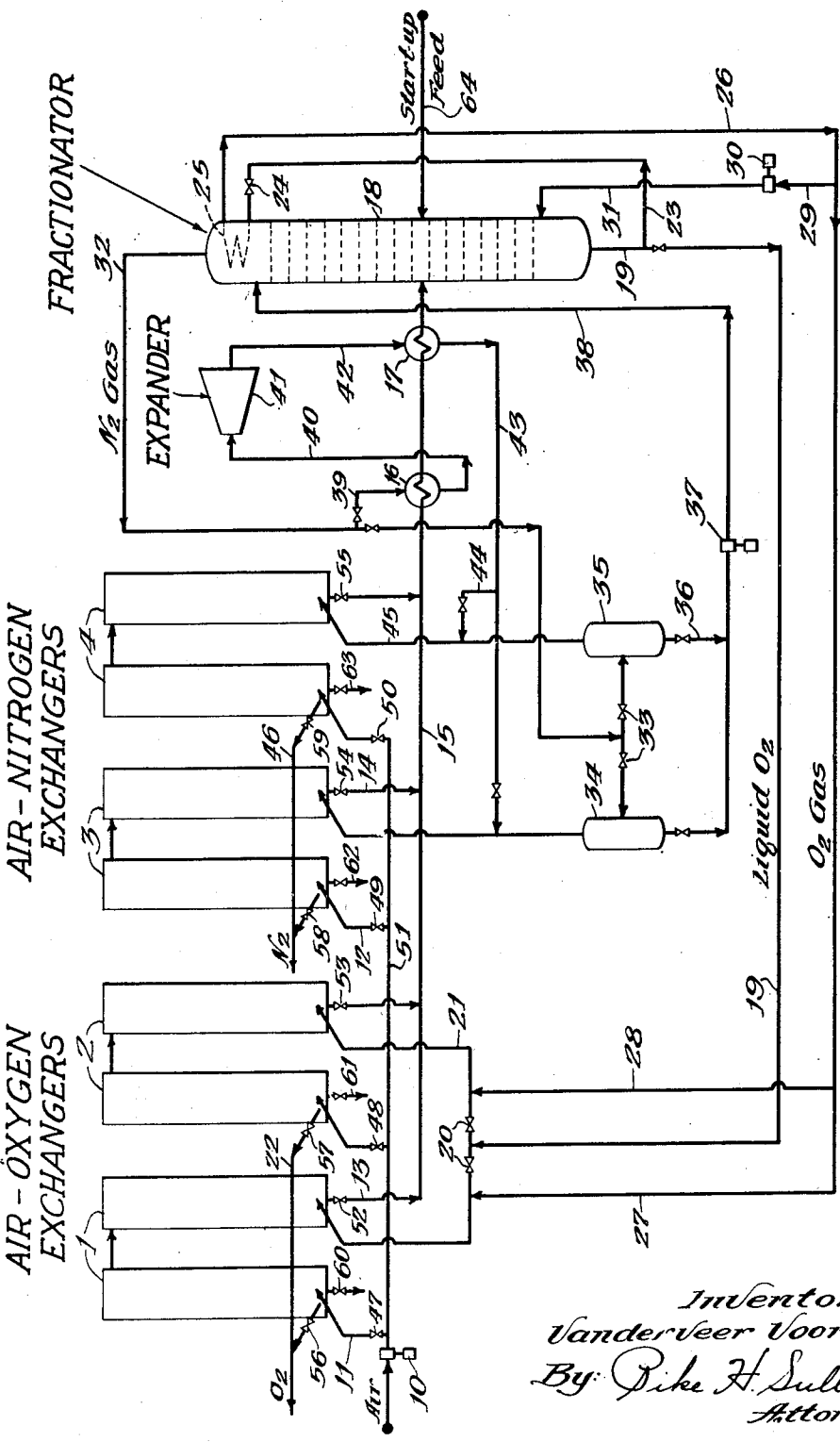


Fig. 1.

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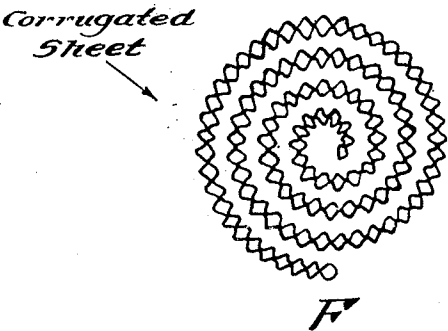
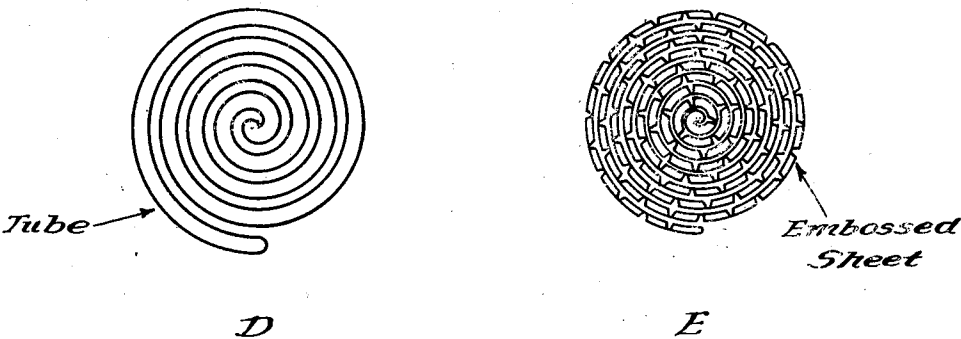
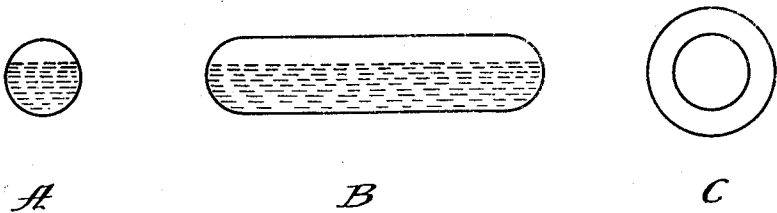


Fig. 2.

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UNITED STATES PATENT OFFICE

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HEAT EXCHANGE

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4 Claims. (Cl. 62—175.5)

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This invention relates to improved heat exchangers for cooling fluids and more particularly to an apparatus and method for separating oxygen from air by the use of improved heat exchange means. Still more particularly the invention relates to a packing for a regenerative-type heat exchanger which provides a heat exchanger operation giving a substantially constant outlet temperature.

The invention is illustrated by drawings which show in Figure 1 a schematic diagram of an oxygen recovery apparatus and in Figure 2 a detail of the heat-exchanger packing material employed in the process.

The separation of oxygen and air has heretofore been accomplished chiefly by two rather closely related processes wherein the oxygen and the nitrogen of the air are separated by fractionation in liquefied form. One of these processes, the Linde process, has employed high pressure heat exchangers in cooling the air to liquefaction temperature, whereas the other process, the Frankl modification of the Linde process, has employed regenerative heat exchangers operating intermittently and reversibly to cool the air to liquefaction temperature. In the latter process, the heat exchangers are packed with a heat-retaining packing material presenting an extensive surface, the temperature of the packing material rising and falling between cycles of charging and discharging through the exchanger, heat being transferred from the charge air to the packing material during the charging cycle and heat being absorbed by the packing material from the cold gases when discharging through the regenerator. For packing, it has been the practice to employ metallic foil, e. g. aluminum foil, suitably crimped and rolled to provide extensive heat exchanger surface.

The use of the regenerative heat exchanger in the Frankl modification has provided numerous advantages over the Linde exchanger and made it possible to produce oxygen at far lower cost than those obtainable by the Linde method. Theoretically perfect heat exchange cannot be obtained in a regenerator, however, inasmuch as the temperature of the packing must rise and fall substantially between cycles in order for the exchanger to provide the necessary heat capacity in the operation. Shortening the cycle time reduces the temperature fluctuation but introduces other undesirable factors, particularly excessive production of purge gas produced between cycles. It is an object of this invention to increase the heat capacity and the cycle time of a regenerative

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exchanger in a reversible gas-cooling operation. Another object of the invention is to increase the efficiency of a regenerative exchanger by more closely approaching constant temperature conditions between cycles. Still another object of the invention is to simplify the operation of the Linde-Frankl oxygen process by employing an improved exchanger packing material providing uniform gas temperatures for the fractionation operation.

According to my invention, I employ as heat-exchange material fusible solids retained within suitable envelopes or seals to prevent contamination of the gases. The fusible solids employed are selected with fusion temperatures substantially equal to the desired gas temperature at the point in the exchanger in which they are employed. Inasmuch as there is a desirable temperature gradient from end to end of each exchanger, I employ a series of fusible solids with progressively increasing or decreasing melting points. In the preferred arrangement, the fusible solid exchange materials are packed in the exchanger in successive layers and it is further preferred that the heat capacity provided by each layer, i. e. the heat absorbed for a given change in temperature, be substantially the same, and that the fusion points of the solids in each layer be substantially equally spaced on the temperature scale.

Referring to Figure 1, air is compressed in compressor 10 to a pressure of about 50 to 100 pounds per square inch, generally about 75 pounds per square inch, cooled and charged to two of the twin regenerative exchangers 1, 2, 3 and 4. Thus, for example, the air may be charged by lines 11 and 12 to exchangers 1 and 3. In passing through the exchangers, the air is cooled by contact with the packing material therein to a temperature near the liquefying point, e. g. about -175°C . at the pressure used. From the exchangers the air passes by lines 13 and 14 into manifold 15 leading through coolers 16 and 17 and discharging into fractionator 18. A part of the air, mostly oxygen, is liquefied in coolers 16 and 17 and the resulting liquid air is fractionated in the fractionator operating under pressure substantially equal to the pressure supplied by compressor 10 less a small pressure differential resulting from the resistance to flow through the exchangers.

In fractionator 18, the oxygen is separated from the nitrogen in a manner well known in the art with the advantage of the difference in boiling points, oxygen boiling at -183°C . and

nitrogen at -195.8°C . under normal pressure. At a pressure of 75 pounds per square inch, gage, the oxygen and nitrogen boil at about -165 and -175°C ., respectively. Argon which constitutes about 1% of the air charged has a boiling point just below that of oxygen and may be left with the oxygen as a contaminant, unobjectionable for most industrial uses.

From the base of fractionator 18, liquid oxygen, suitably about 85 to 95 percent purity, is withdrawn by line 19 leading to oxygen exchangers 1 and 2 to which it is manifolded through expansion valves 20. On expansion at substantially atmospheric pressure, intense cooling of the oxygen occurs and the resulting cooled mixture of oxygen, gas and liquid, is conducted by line 21 to exchanger 2 through which it flows in a direction reverse to the arrows passing out by line 22 by which it is discharged from the system at substantially atmospheric pressure and slightly below the inlet temperature of the air charged at 11, the regenerating effect of the outflowing gas being transferred to the packing material in the exchanger.

A part or all of the oxygen leaving the base of fractionator 18 is conducted by line 23 to expansion valve 24 where its pressure is reduced to substantially atmospheric and the temperature to that of liquid oxygen boiling at atmospheric pressure, e. g. about -180°C . The cold mixture of liquid and gas flows through reflux coil 25, thereby condensing nitrogen gas in the top of the tower 18 by indirect heat exchange, supplying liquid nitrogen reflux for the fractionation. The maximum amount of reflux which would be obtainable from this coil is about one-fourth the amount of nitrogen produced but this can be augmented as hereinafter described. Expanded oxygen leaving coil 25 is conducted by line 26 and lines 27 and 28 to the low pressure side of expansion valves 20 for discharge from the system through oxygen exchangers 1 and 2.

In order to provide reboiling in the base of fractionator 18, a part of the cold oxygen gas from line 26 is conducted by line 29 to compressor 30 whereby it is recompressed to fractionator pressure, e. g. 75 pounds per square inch, and introduced into the base of the fractionator by line 31. The temperature of the gas is substantially increased by the work of compression and this heat is employed to reboil the oxygen in the base of the fractionator supplying additional vapor for fractionation. Furthermore, the amount of oxygen recycled in this way serves to augment the amount of liquid oxygen available for the reflux coil 25, thereby increasing the nitrogen reflux ratio in a desired manner. Heat of compression of oxygen in line 31 may be removed by heat exchange with cold oxygen in lines 19 or 26, or with other suitable cold stream available at about the temperature of the base of the fractionator, thereby serving to further increase the amount of oxygen which may be recycled to the fractionator in this manner.

Nitrogen gas is withdrawn from the top of the fractionator 18 by line 32 leading to expansion valves 33 where pressure is reduced to substantially atmospheric. On expansion of the cold gas, a portion of the nitrogen is liquefied by the Joule-Thompson effect and is collected in one of the separators 34 and 35. Thus liquid nitrogen is withdrawn from the base of separator 35 by valved line 36 leading to pump 37 and thence by line 38 the liquid nitrogen is returned to the top of fractionator 18 to supply additional reflux

therein. In order to obtain further refrigeration for the system, a part of the nitrogen in line 32, for example one-third to two-thirds, is conducted through by-pass line 39 leading through heat exchanger 16 and thence by line 40 to expansion turbine 41 in which the gas is expanded down to substantially atmospheric pressure, the expanded gas flowing by line 42 through exchanger 17 and thence by line 43 to one of the nitrogen exchangers 3 or 4, depending on which one is employed for outgoing nitrogen at the moment. Thus, it may pass through valved line 44 and line 45 through exchanger 4 in a reverse direction and thence be discharged by line 46 which may lead to the atmosphere if no use is made of the nitrogen, or to suitable storage if the process is being operated to recover nitrogen. In line 45 the nitrogen stream is augmented by nitrogen gas from separator 35.

In the operation of expansion engine 41, the temperature of the nitrogen in line 39 is increased, e. g. 5 to 25°C ., by passage through exchanger 16, in order to avoid liquefaction in expander 41. The expander may be a multistage turbine providing useful power for the process, e. g. for compressing air by compressor 10. It is desirable to control the operation of the expander, and particularly the temperature of the inlet nitrogen in line 40 so that the outlet nitrogen in line 42 is at about its liquefaction temperature, e. g. about -195°C .

The cold nitrogen gas passing through exchanger 4 cools the heat-absorbing elements therein as will be hereinafter described. After operating for a brief interval, the flow of gases through the exchangers 1 to 4 is reversed in order to balance the refrigeration of the outflowing gas with the heating effect of the incoming air. To facilitate this reversal valves 47, 48, 49 and 50 leading from the air manifold 51 can be automatically operable by a cycle timer. Likewise valves 52, 53, 54 and 55 leading to the cold air manifold 15 are automatically operable. Also valves 56 and 57 leading to the oxygen outlet are automatically controllable as well as valves 58 and 59 leading to the nitrogen outlet line. By means of an electric or pneumatic controller or other device operating on a time cycle, valves 47, 49, 52, 54, 57 and 59 are in the open position while valves 48, 50, 53, 55, 56 and 58 are in the closed position, valves 20 and 33 being set to pass outflowing oxygen and nitrogen through lines 21 and 45, respectively. At the end of the next time interval, the position of these valves is instantly reversed, thereby reversing the flow of gases through the exchangers. If desired, means may be provided for purging air from the oxygen exchangers. The cycle time, heretofore about 5 minutes, can be increased with the use of my crystallizing packing to 10 or 20 minutes or even more, depending on the mode of application of the material.

Although all the exchangers are shown in the drawing as about the same size, it is advisable that the capacity of the nitrogen exchangers be about four times that of the oxygen exchangers which may be effected by building them about twice the diameter. Likewise, the volume of air admitted through valves 47 and 48 should be about one-fourth the amount which is admitted through valves 49 and 50. This division, however, may be varied somewhat in order to best balance the refrigeration load on the different exchangers.

In operation, the air charged to the process will

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usually contain considerable moisture and about .03% CO₂. On cooling in the exchangers, water is initially condensed and provision is made for collecting it and discarding it from the system, for example by valved drain lines 60, 61, 62 and 63. These lines preferably connect with a water pan located at that point in the exchanger where the liquid water first condenses, for example at a point part way up in the exchanger. After the air is cooled to still lower temperature, the water vapor contained in it separates in the form of ice on the heat-exchange packing material. Finally when the temperature is reduced to about -90° C. and below, CO₂ separates on the packing material in solid form. On the reverse blow the dry oxygen and nitrogen passing in reverse direction evaporates CO₂ and H₂O by a process of sublimation, thus preventing clogging of the passages through the packing material. From time to time at intervals of a few weeks or months, it is advisable to either shut down the entire plant and completely purge the exchangers of CO₂ and H₂O. or by providing standby exchangers cut out of the system one exchanger at a time for complete purging.

When starting up the process, it may be desirable to cool the fractionator 18 and associated equipment to the working temperature by introducing liquid air therein from an outside source, using line 64 for the purpose.

Referring to Figure 2 of the drawing showing detail of the crystallizing packing material, a fusible solid is contained within a spherical shell as shown at A, the shell being constructed of metal. Suitable dimension of the shell is about one-fourth of an inch to one inch in diameter. Instead of enclosing the fusible solid in a sphere, I may alternatively employ a sealed tube of varying length or shape as shown at B, or a coiled tube or torus as shown at C. Spiral tubular coils as shown at D may also be employed providing extensive surface and free passage for gases between the spirals. These spirals may have a gross diameter equal to the diameter of the exchanger and successive spirals may be placed one upon the other with provision, e. g. by spacers, for free passage of gases therebetween.

Another structure for the packing element shown at E is a coil or spiral of flattened tube or hollow ribbon presenting a more extensive surface to the gases. A cross-section of one form of the hollow ribbon construction shown in E is illustrated in F, the walls of the ribbon being formed of embossed, crimped or corrugated sheets, and the space enclosed within the sheets being filled with the desired freezing liquid. If tubular spirals D are employed, these may be made of quite small diameter, thin-walled copper tubing, e. g. one-eighth inch diameter wound into relatively small flat spirals which are filled with the desired freezing liquid, sealed and placed haphazardly in the exchanger shell. Any of the structures described may be provided with fins to increase the surface area for contact with gases. Copper, silver or aluminum are suitable metals for construction of seals for fusible solids employed in this invention because of the high heat conductivity of these metals. It is understood that the apparatus shown in the drawings, particularly in Figure 1, is adequately heat insulated.

As freezing liquids for use in the packing material, I prefer to employ liquids having a high heat of fusion. For maximum efficiency it is desirable to employ a series of liquids having fusion temperatures evenly spaced through the

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temperature range of the exchanger. Thus in the case of the oxygen exchangers, it is desirable to divide the temperature range of +20 to about -165° C. into about eighteen stages employing eighteen different substances having fusion temperatures spaced about 10 degrees apart, the lowest melting substance being at the outlet or cold end of the exchanger.

As examples of liquids suitable for packing material, the following list is illustrative:

Packing Liquid	Melting Point, °C.
Benzene.....	5.5
Water.....	0
Dibromobenzene.....	-7
Acetyl acetone.....	-23
SnCl ₄	-30
Mercury.....	-39
Amyl amine.....	-55
SO ₂	-72
NH ₃	-78
N-butyl alcohol.....	-79
Isopropyl alcohol.....	-86
Toluene.....	-95
Chlorine.....	-101
Cyclohexane.....	-104
Ethyl ether.....	-116
Amylene.....	-124
Dimethylpentane.....	-135
Methylcyclopentane.....	-140
Ketene.....	-151
Ethylene.....	-169
Propane.....	-185

It will be noted that many of the low freezing liquids are gases at ordinary temperature and for this reason it is necessary that they be sealed within containers of sufficient strength to withstand the pressure of the exchange liquid when the exchanger is permitted to come to normal temperature. Considering the need for having the exchange liquid deployed with a low maximum distance between the liquid and the walls of the container, it is readily seen that the container must have a small cross-sectional area and therefore the gross pressure developed within the containers by the vapor of the refrigerating liquid is not large. Accordingly, by making the containers of very small cross-sectional area, the walls may be of quite thin metal and yet be of adequate strength to withstand the high vapor pressure of the filling liquid. Another advantage of thin wall construction lies in the rapid heat transfer through the wall between the gas and the liquid. Rapid heat transfer from the gas to the packing material is facilitated by maintaining relatively high gas velocities and turbulence in the air, nitrogen and oxygen passing through the exchangers.

In order to approach more closely true reversibility in the operation of my regenerative exchangers, I prefer to employ packing liquids which are not entirely pure and which therefore have a spread of crystallizing temperature which suitably equals the difference between the crystallizing temperature of the liquids in adjacent packing zones. Thus in the case of water, I may add a small amount of alcohol to cause the water to freeze over a temperature range of 0 to -23° C., thereby providing a progressive refrigerating effect on the air passing over this section of the exchanger throughout the temperature region of 0 to -23° C. at which point the melting of acetyl acetone, in this example the next adjacent refrigerating liquid, cools the air progressively further. The reverse effect occurs in the reverse flow with cold oxygen or nitrogen.

Having thus described my process, what I claim is:

1. The method of refrigerating gas which com-

prises passing a stream of said gas through a plurality of refrigerating zones packed with refrigerating material of high heat capacity, said high heat capacity being obtained by a plurality of fusible solids, the fusion temperature of said solids being progressively lower in the direction of flow of said gas.

2. The process of claim 1 wherein the fusible solids employed contain sufficient impurity to spread the fusion temperature over a range approximating the difference in fusion temperature between solids in adjacent refrigerating zones.

3. In the process of producing oxygen from air by the liquid air distillation method, whereby streams of compressed air are cooled in regenerative heat exchangers, liquefied, fractionated into nitrogen and oxygen, expanded to lower pressure, and the cold nitrogen and oxygen are discharged through regenerative heat exchangers, the improvement comprising conducting the gases through said heat exchangers in heat exchange relation with a plurality of crystallizable liquids sealed away from said gases, said liquids being arranged in the order of decreasing melting points from the warm end to the cold end of said exchangers, said liquids being selected to have melting points lying within the range of atmos-

pheric temperature on the warm end to liquid air temperature on the cold end.

4. In a regenerative heat-exchanging process for alternatively heating and cooling fluids by reversibly contacting with a heat-exchange agent, the improvement comprising passing said fluid to be heated in successive heat-exchange relation with a plurality of liquid heat-exchange agents in successive zones, the heat-exchange agent in each zone having a crystallizing temperature approximating but slightly above the temperature of the fluid to be heated in that zone, thereby crystallizing said heat-exchange agents during the passage of said fluid to be heated and imparting to said fluid the latent heat of crystallization of said agents, and subsequently conducting thru said zones in the reverse order a fluid to be cooled, said crystallized heat-exchange agents being re-liquefied during the passage of said fluid to be cooled thereby abstracting from said last-mentioned fluid an amount of heat substantially equivalent to the latent heat of fusion of said heat-exchange agents.

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No references cited.