Jan. 27, 1953 C. J. SCHILLING 2,626,510

AIR FRACTIONATING CYCLE AND APPARATUS

Filed June 18, 1947 2 SHEETS—SHEET 1

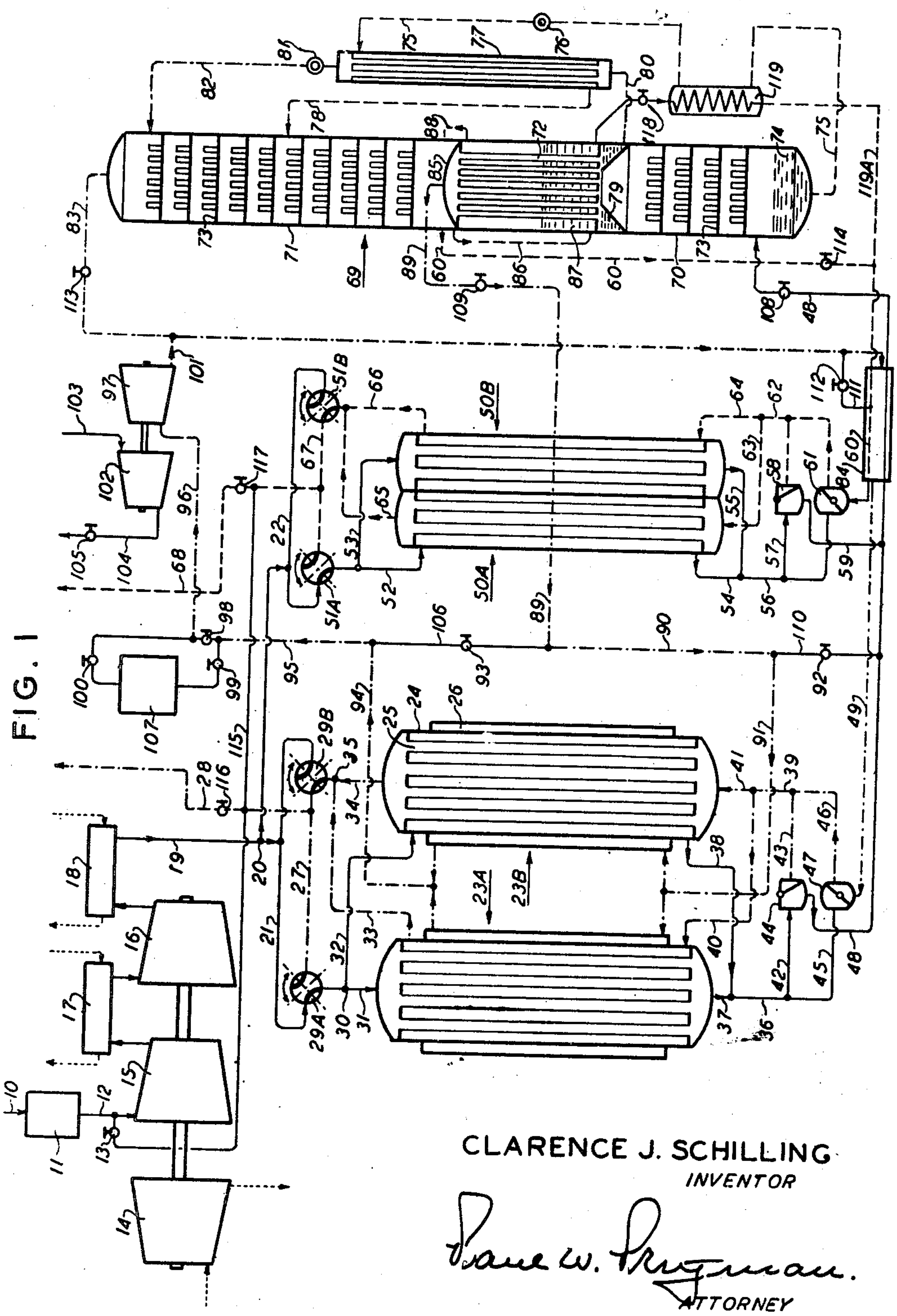

FIG. 1

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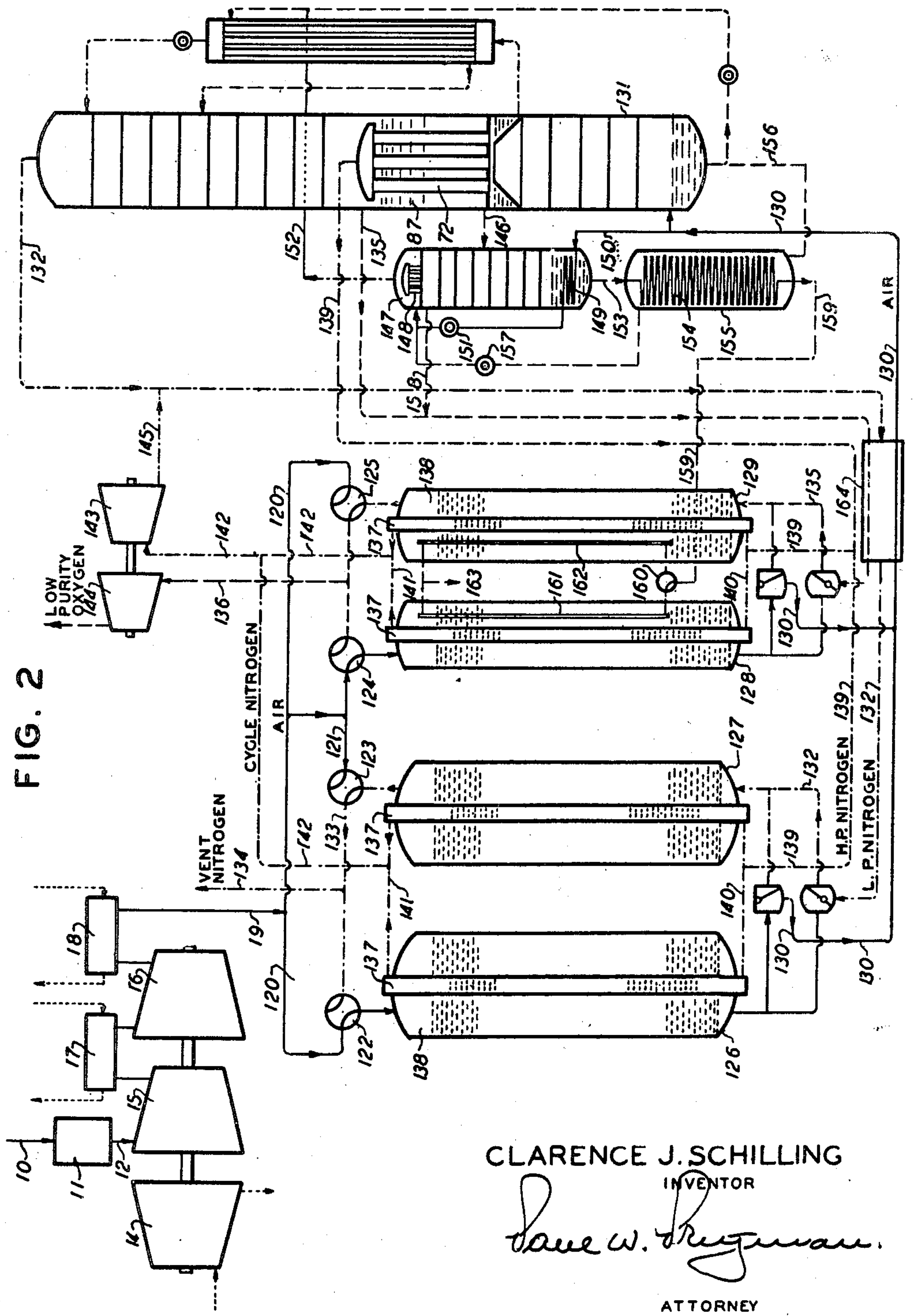

FIG. 2

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AIR FRACTIONATING CYCLE AND APPARATUS

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2 Claims. (Cl. 62—175.5)

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This invention relates to the manufacture of oxygen by the fractionation of atmospheric air and includes an operating cycle and an apparatus adapted to put the cycle into effect.

A purpose of the invention is to provide method and means for the manufacture of oxygen on a very large scale.

A purpose of the invention is to provide an apparatus and an operating cycle of extreme simplicity, with attendant minimization of first cost and operating expense.

The invention will be described with reference to the attached drawings, which will be understood to be flow sheets in which apparatus elements are indicated by symbols and wherein:

Figure 1 is a diagrammatic representation of an air fractionating system illustrating principles of the present invention with switching heat exchangers in which the air supply is refrigerated with returning nitrogen and oxygen components, and

Figure 2 is a diagrammatic representation of a different air system illustrating the principles of the present invention with switching accumulators.

Referring to the drawing, air enters the system at 10 and is substantially freed from dust in an air cleaner 11. This element may be an electrostatic precipitator, a scrubber or a simple air filter. It is not essential to remove the dust completely, but only the coarser particles which might cause abrasion in the compression unit.

The cleaned air passes at 12 (valve 13 being closed) to a compression unit consisting of a steam turbine or other power source 14, a first and a second stage turbo-compressor 15 and 16, a water-cooled intercooler 17 and an aftercooler 18.

The compressed air leaves the aftercooler via conduit 19 at about 100 pounds absolute and at a temperature about 300° Kelvin. This conduit is branched at 20, about 80% of the air supply passing to a header 21 and thence to the nitrogen interchangers and about 20% to header 22 and thence to the oxygen interchangers.

The system includes a pair of "switching" or deriming heat interchangers 23A—23B which are used in parallel for cooling the larger portion of the air supply by heat interchange against the cold gaseous nitrogen produced by the column. Each of these units consists generally of a shell 24, a gaseous nitrogen passage consisting of a plurality of tubes 25 and an auxiliary gas passage illustrated as an external gas jacket 26.

The upper ends of the interchangers communicate with the air inlet manifold 21 and with a nitrogen outlet manifold 27, which in turn is vented from the system through a nitrogen vent pipe 28, through a pair of reversing valves 29A—29B. These valves are reciprocated through quarter turns, in synchronism and at suitable intervals, by means not shown. With these valves in the position shown in the figure, the right end of air manifold 21 is closed and air passes from the left end of the manifold through valve 29A to a conduit which is branched at 30 to deliver air through conduit 31 to the tubes of interchanger 23A and through conduit 32 to the shell of interchanger 23B. In this position the left end of nitrogen manifold 27 is closed and the right end is in communication with the shell of interchanger 23A through conduit 33 and with the tubes of interchanger 23B through conduit 34, these conduits connecting at 35. When the valves are simultaneously reversed in position, as by a quarter turn clockwise, the functions of the described conduits are reversed, conduits 31 and 32 carrying vent nitrogen and conduits 33 and 34 carrying entering air.

The coupling of the interchangers in such manner that each divided stream flows always through the tubes of one interchanger and the shell of the other is important in avoiding variations in resistance to flow of low pressure gaseous nitrogen which often accompany valve reversals when a pair of interchangers are so connected that the flow of nitrogen is directed first through two sets of tubes and then through two shells.

The lower ends of the interchangers are coupled in a similar manner to manifolds which alternately convey air and nitrogen. Thus, manifold 36 is branched at 37 to the tubes of interchanger 23A and at 38 to the shell of interchanger 23B. Manifold 39 is oppositely branched, i. e., at 40 to the shell of interchanger 23A and at 41 to the tubes of interchanger 23B. These manifolds are also branched at 42 and 43 to opposite sides of a flap valve 44, and at 45 and 46 to opposite sides of a flap valve 47.

With the reversing valves 29A—29B in the positions shown, manifold 36 is conveying air under relatively high pressure while manifold 39 is conveying nitrogen at a much lower pressure. The overbalancing pressure in branch 42 swings the flap of valve 44 to the right, as illustrated, preventing the air from entering the opposite manifold through branch 43 and directing it into conduit 48 which leads to the fractionating column. The flap in valve 47 being pivoted below its center line, the excess pressure in branch 45 tips it to the right, as illustrated, affording a passage for nitrogen from conduit 49, leading from the fractionating column, into branch 46 and manifold 39 which passes gas upwardly through the interchangers.

The oxygen interchangers 50A—50B are structurally identical with the nitrogen interchangers above described except for the omission of the jackets 26. Air from the compression unit passes from manifold 22 through reversing valve 51A and branch conduits 52 and 53 to the shell of interchanger 50A and to the tubes of interchanger 50B and through bottom connections 54 and 55, manifold 56, branch 57, flap valve 58 and conduit 59 to air conduit 48 leading to the column. Oxygen in gaseous form, withdrawn from the fractionating column through conduit 60, flows through flap valve 61, manifold 62 and branches 63 and 64 to the tubes of interchanger 50A and the shell of interchanger 50B, escaping at the upper ends of the exchangers through conduits 65 and 66 to valve 51B, manifold 67 and product oxygen delivery pipe 68.

The fractionating column generally indicated at 69 may be any conventional or preferred two-stage column. In any case it consists of a high pressure section 70 and a low pressure section 71 separated by a partition plate and a refluxing nitrogen condenser 72. Each of the sections is provided with bubble plates 73.

Liquid crude oxygen collecting in a pool 74 in the base of the high pressure section passes through a conduit 75 and an expansion valve 76 to an interchanger 77 in which it is in counterflow heat interchange with high pressure liquid nitrogen, the expanded crude oxygen then passing through conduit 78 to an intermediate point in the low pressure section.

The high pressure liquid nitrogen collecting in pool 79 below the nitrogen condenser passes through conduit 80 to the opposite side of interchanger 77 in which it is cooled and stabilized by the expanded crude oxygen, flowing thence through expansion valve 81 and conduit 82 to the upper end of the low pressure section.

Gaseous low pressure nitrogen is withdrawn from the top of the column through conduit 83, flowing to a jacket 84 surrounding a part of the air feed line 48, this jacket discharging into conduit 49 above referred to as leading to the nitrogen interchangers.

Oxygen in a desired state of purity, ordinarily 95% or over, collects over the head 85 of condenser 72 and flows through conduit 86 to form a pool 87 surrounding tubes 72. Boiling in this space in condensing high pressure nitrogen vapor within the tubes, the oxygen vapor travels through bypass 88 to the vapor space above head 85, from which it is withdrawn through conduit 60 and the air-nitrogen interchanger 84 to the oxygen interchangers as above described.

The interchangers are operated in the customary manner, the warm air passing through one side of each unit in counterflow to one of the cold product gases until the air passages become sufficiently fouled, by the accumulation of water ice and solid carbon dioxide, to give rise to a high pressure differential or to fall below a predetermined heat transfer efficiency. At this point the reversal of the valves causes the air stream to flow through the passage previously occupied by the cold gas, and which is clean, while the gas stream flows through the passage previously occupied by air, vaporizing and removing the ice and carbon dioxide snow.

It is a well known drawback to this procedure

that the total products of fractionation flowing through a cold accumulator or its functionally equivalent deriming interchanger do not completely and dependably remove the accumulation of carbon dioxide snow and water ice from the surfaces on which they are deposited, and that such substantially complete removal may be effected by passing through the interchanger a quantity of cold gas materially greater than the quantity of air from which these deposits are accumulated.

To provide complete deriming for long period operation, it is essential that the cold end temperature difference between incoming air and purging product be 5° C. or less. To accomplish this, it is necessary to compensate for the higher specific heat of air under pressure especially at lower temperature. Adding quantity to the effluent product makes this possible by bringing the temperature-enthalpy curves of the counterflowing gases into approximate parallelism.

It is not necessary that the excess cold gas be in contact with the deposited solids, but only that it be in heat interchange relation with them. In consequence there are numerous ways in which this compensation may be effected, in any interchanger, direct contact or tubular, in which the gas to be cooled and the gas to be heated flow alternately through the same passage.

In the operating cycle here described the oxygen interchangers 50A—50B are provided with an excess of the cold gas by passing through them a smaller quantity of air than that which corresponds to the quantity of oxygen produced, for example, say 20% of the total air supply instead of the 21% to 22% which would correspond with the oxygen yield.

The remainder or say 80% of the air supply passes through the nitrogen interchangers 23A—23B and the excess of cold gas is provided by nitrogen withdrawn in gaseous form from the high pressure section of the column, heated by passing through the nitrogen interchanger, cooled by expansion and returned at low pressure to pass again through the interchanger with the low pressure nitrogen taken from the top of the column, thus passing twice through the step of interchange.

In more detail, a sufficient quantity of gaseous nitrogen, which may for example be perhaps 20% of the total nitrogen content of the air fractionated, is withdrawn from the dome 85 of the column condenser 72, carrying with it any incondensible gases which might otherwise tend to accumulate there. The withdrawn gas, at about 100 pounds absolute and about 100° K., passes through conduits 89, 90 and 91 and is equally divided between the auxiliary gas passages 26 of the nitrogen interchangers, in which its temperature is raised to about 145° K. by interchange with entering warm air. These streams, which flow continuously through the two interchangers in parallel and constantly from the cold to the warm end, are collected in conduit 94 and pass through conduits 95 and 96 to a turbo-expander 97. During normal operation, valve 98 in conduit 95 is open and valves 99 and 100 are closed.

In the expander 97 the pressure is reduced to about 24 pounds absolute in doing work and the temperature is thus reduced to about 110° K. The expanded nitrogen stream then passes through conduit 101 to mix with the colder nitrogen stream passing through conduit 83, the temperature of the mixed nitrogen stream at the cold end of the interchangers being thus raised to about 96° K.

The withdrawal of as much as 20% of the total nitrogen made in this manner does not reduce the quantity of reflux liquid sufficiently to interfere with efficient operation of the low pressure column section, so long as oxygen of the highest purity is not required.

The expander 97 is coupled with a turbo-compressor 102 or other means for applying a power load. The compressor is desirable as providing a steady and readily controllable load. It is illustrated as taking air through conduit 103 and discharging it through a conduit 104 controlled by a valve 105. If the oxygen produced by the column is to be delivered into a pipe line at a pressure above that available at the interchanger outlet, compressor 102 may be utilized for that purpose.

It is desirable to provide a cross-over line 106 to admit a controlled quantity of cold nitrogen into conduit 95 in case the temperature of the high pressure nitrogen passing from the jackets to the expander becomes too high. This quantity is controlled by regulation of valve 93.

It should be noted that the drawing shows only one turbo-expander 97. This unit, expanding the withdrawn high pressure nitrogen, suffices to provide make-up refrigeration for the cycle but when of proper size for that purpose is insufficient to provide refrigeration for starting up a warm apparatus. For this purpose it is desirable to provide the expander in duplicate or even in triplicate to ensure quick starts after a shut-down.

The operating cycle above described is advantageous over previously disclosed methods for controlling the temperature of the cold nitrogen entering the nitrogen interchangers, in doing away with the splitting of the air feed and with the introduction of air into the low pressure stage.

In methods heretofore proposed, a part of the air cooled in the main interchangers is diverted away from the high pressure section of the column through an interchange against a minor stream of product nitrogen passing to the interchangers or against the incoming air, this minor stream being then expanded and introduced into the low pressure column. This introduction lowers the efficiency of fractionation in the low pressure section and the purity of the oxygen obtainable under given conditions, but is most objectionable in adding greatly to the difficulty experienced in regulating the operation of the column.

By applying the heating effect to a small part of the available high pressure nitrogen and diverting it to the interchangers without entering the column the regulation of nitrogen interchanger temperature is rendered wholly independent of regulation of column operation, and both are simplified without loss of refrigerative effect or interference with the most desirable column operating conditions. A further advantage in the described cycle lies in a material reduction in the size of the column required.

It will be seen from the above description that the air supply to the column is not passed through any step of drying by adsorption, water and carbon dioxide being removed solely by refrigeration. In starting up the apparatus, however, it is necessary to remove water by adsorption until the interchangers have cooled down to the temperature at which they will carry the dehydration load, say to a cold end temperature of 130°/135° K.

To thus dry the entire air supply (thousands of cubic feet per minute) for even the few hours required to obtain interchanger cool-down requires a very large and costly drying installation, but I have devised a system by which the temperature may be reduced with the use of adsorption apparatus of much less size and capacity. This system functions as follows:

In the drawing, 107 indicates any conventional air drier, such unit consisting ordinarily of two shells filled with silica gel or activated alumina, through which the gas to be dried is passed alternately and from which the adsorbed water is driven out by a stream of heated air or other gas. As these drying units are in common use and well known, they are not illustrated but are indicated by a symbol. The adsorptive capacity of the unit may be 1% or less of that which would be required otherwise.

In starting up the warm apparatus, air at about 100 pounds absolute is delivered by the two-stage compressors through the nitrogen and oxygen interchangers. Valve 108 in conduit 48 being closed and valve 92 in conduit 110 open, the air does not enter the column but is directed to expander 97 through conduits 110, 90, 106, 95, and 96. Valves 99 and 100 are now opened and valve 98 is closed to direct all of the air stream through the small drying unit. As the air is to be recycled, the quantity to be dehydrated represents only one volume of the exchangers and piping.

The air expanded in 97 flows through conduit 101 into product nitrogen conduit 83 and into product oxygen conduit 60 through a cross-over 111 and an open valve 112 and is thus divided between the two interchanger units. Valves 113 and 114 may be provided in conduits 83 and 60 to exclude air from the column, though they are not strictly necessary.

In passing through expander 97 the temperature of the air is somewhat reduced and the cold end temperature of the interchangers is gradually lowered. On leaving the interchangers, the dried air, now brought back to atmospheric temperature by interchange with the entering air stream, returns to the intake side of the compression unit through manifolds 27 and 67 and recycling conduit 115, valve 13 in this conduit being open and valves 116 and 117 in the nitrogen and oxygen vents respectively being closed.

Except for make-up due to temperature drop, the same air is thus recirculated continuously through the steps of compression, interchange, drying and expansion. Thus the air within the system will be completely dehydrated before the interchangers come to working temperature, even with the use of a small drying unit. By bypassing the column during the drying-out operation the risk of carrying any solids into it is completely avoided. The removal of water vapor obviates the formation of ice crystals and of attendant risk of damage to the expanders.

As is well known, it is possible for frozen hydrocarbons to accumulate at the bottom of liquid oxygen pool 87, giving rise to risk of explosion. To avoid this risk it is desirable to withdraw continuously a small stream of liquid oxygen from the bottom of the pool, as through valve 118, and pass this liquid downwardly through a vaporizing coil 119 heated by the stream of crude oxygen flowing through conduit 76. The resultant oxygen vapor, carrying the volatilized hydrocarbons, passes through conduit 119A to join the stream of gaseous oxygen flowing through conduit 60.

Figure 2 illustrates certain alternatives to the procedure and apparatus already described:

(a) in the substitution of direct contact heat interchangers (the so-called cold accumulators) for the switching tubular heat interchangers of Fig. 1, a pair of accumulators being the full equivalent of a single switching interchanger;

(b) in the provision of means for making small quantities of pure oxygen as an adjunct to the described means for withdrawing hydrocarbons from the air fractionating column;

(c) in the application of the unbalancing effect to both the nitrogen and the oxygen interchanger instead of to the nitrogen interchanger only.

These variants may be used in any combination, i. e., either or both interchangers may be unbalanced by the high pressure nitrogen cycle, and either or both may be of the tubular or of the accumulator type.

The modified plant illustrated in Fig. 2 has the same air supplying elements, numbered from 10 to 18 inclusive, as are shown in Fig. 1, and these need not again be described.

The air supply at a preferred pressure, which for example may be about 100# absolute, passes through conduits 120 and 121 to four reversing valves 122—123—124 and 125 which are functionally similar to valves 21 and 51 of Fig. 1 and which control the flow of gases into and out of the upper ends of direct contact heat interchanges ("cold accumulators") 126 and 127 for product nitrogen and 128 and 129 for oxygen, these elements having the customary filling of metal exposing a large surface area.

With the valves in the position shown, air is flowing downwardly through interchangers 126 and 128 into conduit 130 by which it is passed into the high pressure section of two-stage column 131. At the same time gaseous nitrogen flowing from the low pressure section of the column through conduit 132 is passing upwardly through interchanger 127 and through conduit 133 to a vent 134, while oxygen at a desired purity, as for example 95%, flows from the low pressure section of the column through conduit 135, passes upwardly through interchanger 129 and leaves the interchanger by way of conduit 136.

On moving the rotors of the control valves through 90° the gas flows are reversed, air passing downwardly through interchangers 127 and 129 while nitrogen flows upwardly through interchanger 126 and oxygen through interchanger 128. These reversals have already been described in detail in connection with Fig. 1.

The interchangers are provided with secondary gas passages 137—137 which may be simple tubes or, like the primary passages 138—138, may be filled to a desired height with heat conductive metallic elements.

Gaseous nitrogen is withdrawn from the high pressure section of the column through conduit 139 and is distributed by manifolds 140—140 to the four secondary passages 137—137. This flow is constant through the four secondary passages in parallel and in a direction opposite to that of air flow through the primary passages. The nitrogen streams, still at approximately the pressure carried in the high pressure section of the column, are collected in manifolds 141—141 and flow through conduits 142 to an expansion engine 143 which may well be a turbo-expander. This

element is loaded by a compressor 144 which may conveniently be used to raise the oxygen product delivered to it through conduit 136 to pipe line pressure.

In expander 143 the high pressure gaseous nitrogen is reduced to substantially the pressure carried in the low pressure column section, the expanded stream passing through conduit 145 to join the stream of gaseous nitrogen flowing through conduit 132 to the nitrogen interchangers 126 and 127.

Air fractionating columns producing large quantities of oxygen in gaseous form accumulate various hydrocarbons, mainly acetylene, at the bottom of pool 87 of liquid oxygen surrounding the nitrogen condenser.

It is customary to flush out these impurities occasionally, to avoid risk of explosion, but this practice is undesirable as causing wastage of oxygen.

In the structure shown in Fig. 2 the scouring of the liquid oxygen pool is accomplished without loss of oxygen by withdrawing continuously a small proportion of the oxygen output, say from 3% to 5% of the total quantity produced, from the bottom of the liquid pool, as at 146, into a correspondingly small single stage fractionating column 147. This column is provided with packing or plates in the usual manner and also with a refluxing condenser 148 in its upper end and a boiling coil 149 in its lower end.

A stream of high pressure air is drawn from conduit 130 through conduit 150 to the boiling coil and is expanded through valve 151 into the chamber surrounding condenser 148. From this chamber the expanded air passes through conduit 152 to join the stream of crude oxygen passing to the low pressure column.

Pure liquid oxygen (containing traces of hydrocarbons) collects in the liquid pool surrounding the boiling coil and passes continuously through conduit 153 into an evaporating coil 154 enclosed in a shell 155. Heat for evaporating the pure liquid oxygen is supplied by a stream of crude oxygen drawn from the high pressure section of the column through conduit 156, the shell being vented into the chamber surrounding condenser 148 through conduit and expansion valve 157.

A mixture of nitrogen and oxygen is vented from the upper part of the small column, at a point below refluxing condenser 148, this product passing through conduit 158 to conduit 135 in which it is blended with the much larger quantity of relatively low purity oxygen passing to the oxygen interchangers 128 and 129.

The substantially nitrogen-free oxygen vapor produced in coil 154 passes through conduit 159 to a switching valve 160 by which it is directed alternately through passages 161 and 162 in heat interchange relation with the air flowing through interchangers 128 and 129. This valve is so timed that the flow of oxygen is through the interchanger through which air is flowing, the opposite passage being shut off. The pure oxygen, returned substantially to atmospheric temperature and pressure, is vented from the system at 163.

It is desirable to pass air conduit 130, nitrogen conduit 132 and oxygen conduit 135 through an interchanger 164 in which the air stream is slightly cooled in imparting a relatively small amount of heat to the streams of product nitrogen and oxygen in advance of the main interchanger.

As in this modification of the operating cycle the unbalancing effect is applied to both pairs of interchangers instead of to the nitrogen interchangers only as in Fig. 1, the warm air supply is divided between the two pairs of interchangers in at least approximately the proportions in which the gaseous products are obtained from the main column.

I claim as my invention:

1. The method of initiating an air fractionating operation which comprises: compressing a stream of air from the atmosphere and removing the heat of compression; adsorbing from said stream a portion of its moisture content; expanding and thereby cooling the partially dehydrated air stream; returning the expanded air stream in heat interchange relation with said compressed air stream and thence to said step of compression as substantially the total air supply thereto; continuing the circulation of said air stream in a cycle through the steps aforesaid until the cold end temperature in said interchange step is sufficiently low substantially to deprive said air stream of moisture and carbon dioxide by congelation, and thereafter discontinuing said step of adsorption, admitting atmospheric air into said step of compression, and introducing said compressed and dehydrated air stream into said fractionating operation.

2. The method of initiating an air fractionating operation which comprises: compressing a stream of air from the atmosphere and removing the heat of compression, adsorbing from said stream a portion of its moisture content; expanding and thereby cooling the partially dehydrated air stream; returning the expanded air stream in heat interchange relation with said compressed air stream and thence to said step of compression as substantially the total air supply thereto; continuing the circulation of said air stream in a cycle through at least the aforesaid steps of compression, heat interchange, expansion, and return heat interchange, until the cold end temperature in the interchange step is sufficiently low substantially to deprive the air stream of moisture and carbon dioxide by congelation; thereafter readmitting air from the atmosphere into the step of compression, and introducing cooled air from which the moisture and carbon dioxide have been substantially completely removed in the heat interchange step into the fractionating operation, the adsorption step being discontinued prior to the readmission of moisure containing air to the step of compression, and passing a product of the fractionating operation to the heat interchange step to cool the air therein.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
727,650	Linde	May 12, 1903
918,468	Place	Apr. 13, 1909
1,264,845	Norton	Apr. 30, 1918
1,539,450	Wilkinson	May 26, 1925
1,717,540	Aubert	June 28, 1929
1,880,981	Pollitzer	Oct. 4, 1932
1,901,389	Hazard-Flamand	Mar. 14, 1933
1,951,183	De Baufre	Mar. 13, 1934
2,048,076	Linde	July 21, 1936
2,084,334	Frankl	June 22, 1937
2,334,632	Koehler	Nov. 16, 1943
2,460,859	Trumpler	Feb. 8, 1949
2,503,939	De Baufre	Apr. 11, 1951
2,553,550	Collins	May 22, 1951