July 4, 1950 P. W. GARBO 2,513,306

PROCESS FOR PRODUCING OXYGEN BY THE LIQUEFACTION AND RECTIFICATION OF AIR

Filed Nov. 1, 1947 2 Sheets-Sheet 1

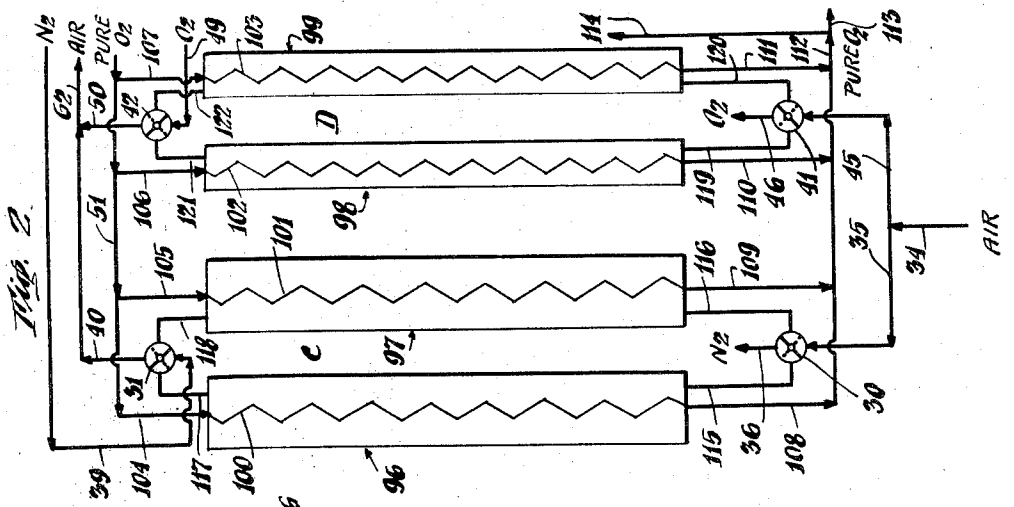


Fig. 2.

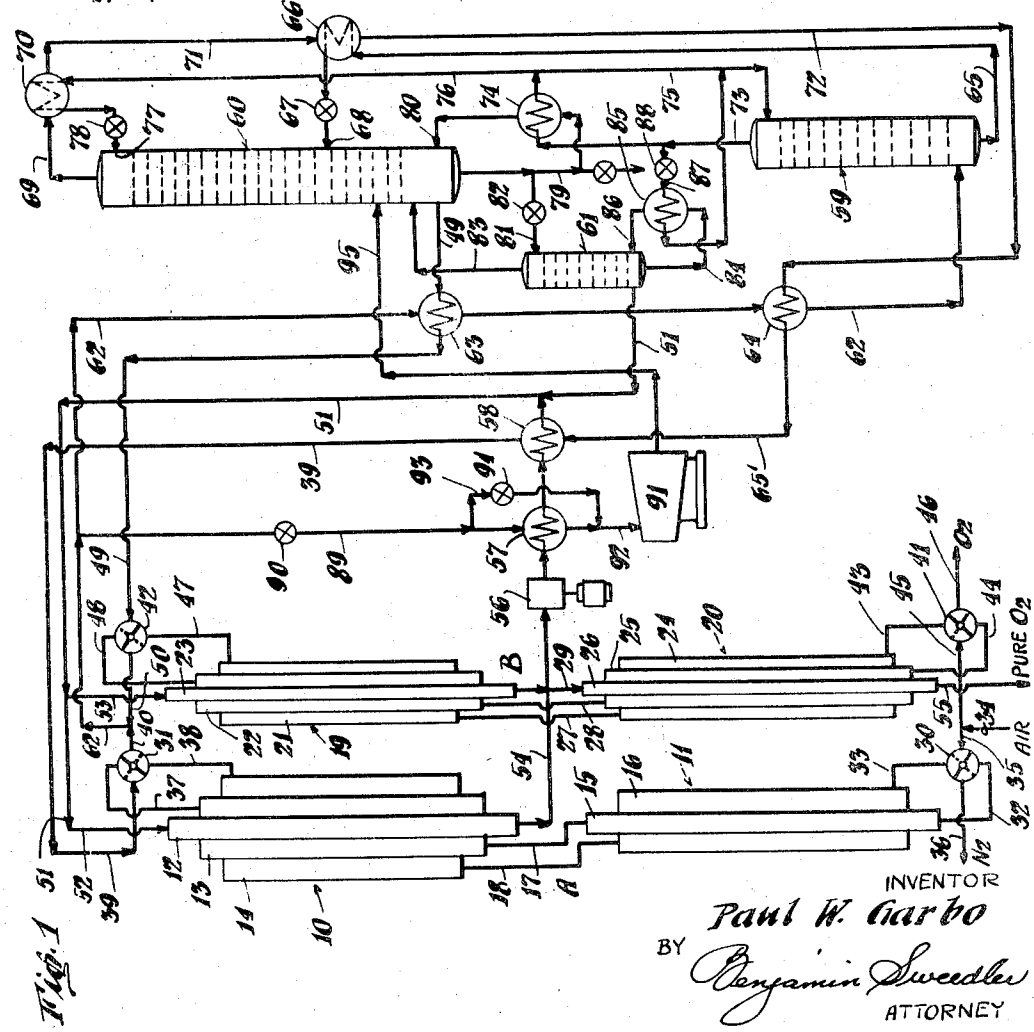


Fig. 1

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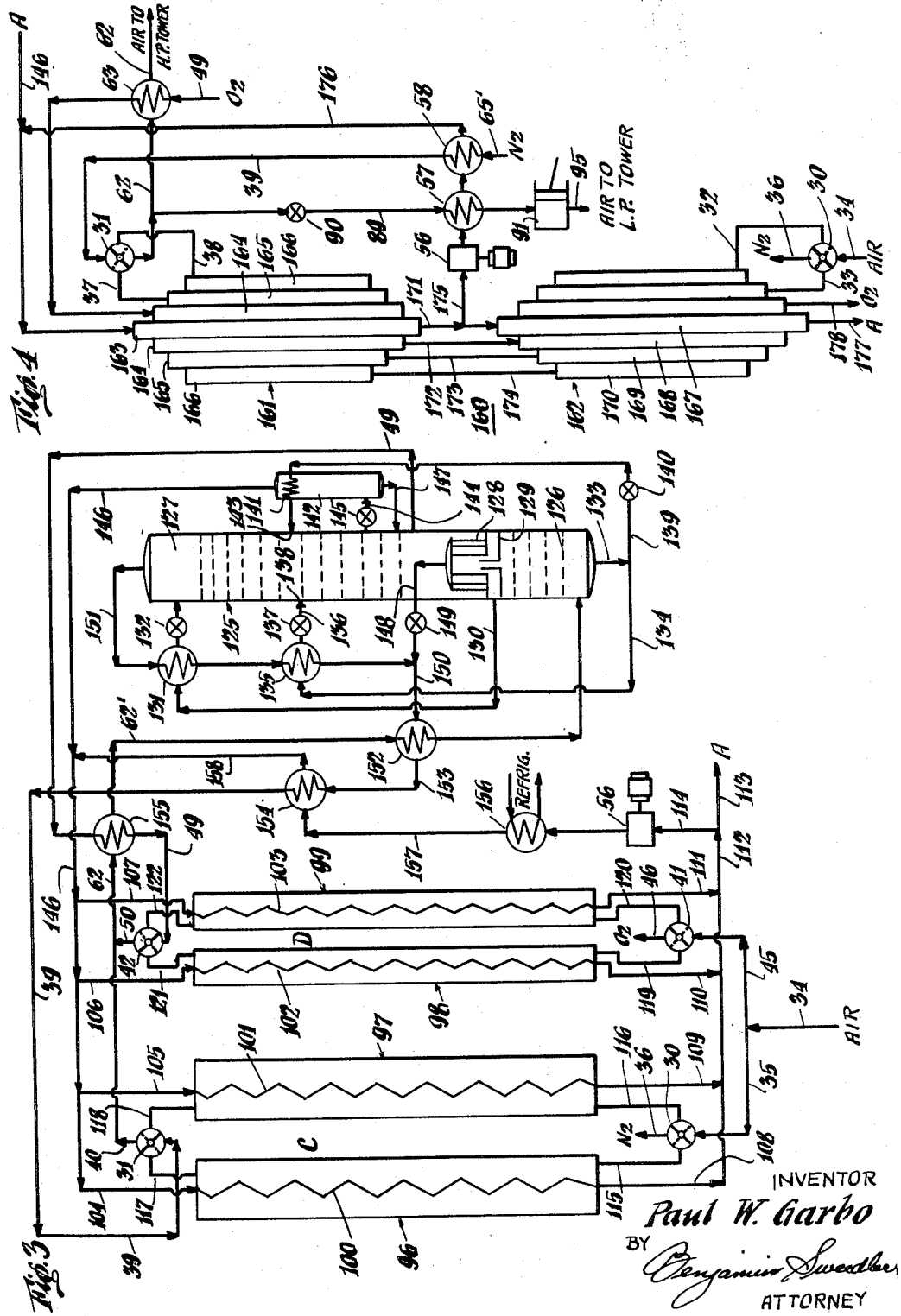


Fig. 4

Fig. 3

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2,513,306

PROCESS FOR PRODUCING OXYGEN BY THE LIQUEFACTION AND RECTIFICATION OF AIR

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Application November 1, 1947, Serial No. 783,552

11 Claims. (Cl. 62—175.5)

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This invention relates to the production of oxygen by the liquefaction and rectification of air, and more particularly to an economical method of obtaining oxygen in high purity and in high yield without the use of chemical reagents to effect the removal of carbon dioxide present in air.

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

Oxygen is commonly produced by liquefaction of air and rectification at low temperatures; preferably rectification is conducted in two stages at different pressures. The refrigeration necessary for liquefaction is supplied to the air, after it has been compressed and water-cooled to approximately room temperature, by indirect heat exchange with the effluent products of rectification. However, an additional amount of refrigeration must be supplied to compensate for cold losses resulting from the differenct in enthalpy between the incoming air and the outgoing products of rectification and for heat leaks into the system. Methods of supplying this refrigeration heretofore used involve compressing at least a portion of incoming air to pressures as high as 3000 pounds and expanding with or without the performance of work to produce a temperature drop, or compressing all the incoming air to about 600 pounds and after the air has been partially cooled by the products of rectification expanding a portion of the air. These methods are wasteful from the standpoint of compressor energy and require a great deal of equipment in the form of extra compressors, intercoolers and expanders.

For economical operation it is essential to recover the cold content of the outgoing products of rectification. This is usually accomplished by passing these products in heat transfer relationship with the incoming air. In older systems, in order to avoid deposition of frost and solid carbon dioxide in the tubular countercurrent heat exchangers through which the air is passed in indirect heat exchange relation with the outgoing products of rectification, the air is treated in driers and caustic scrubbers to remove water and carbon dioxide prior to admittance of the air into the heat exchangers. Even with this treatment the exchangers had to be thawed out regularly to remove the frost (which term is used in a generic sense to include both snow and ice) which caused stopping up of the apparatus.

More recently it has been suggested to use cold accumulators or regenerators (hereinafter referred to as heat exchangers) of large cold absorbing capacity through which the warm incoming air and the cold products of rectification are alternately passed with periodically reversed operation so that streams of warm air are flowed through the same packing-filled spaces that the cold separated oxygen and nitrogen traversed during the previous step in the process, the high boiling impurities deposited in these spaces during the passage of air therethrough being removed by sublimation during the subsequent flow in a reverse direction of the products of rectification. The use of these reversing heat exchangers in a process in which the air is compressed to relatively high pressure results in more costly operation from the standpoint of horsepower requirements because upon every reversal, which may take place every three minutes, the volume of compressed air in the heat exchangers is lost and must be again replaced. Moreover, in the operation of such reversing heat exchangers it is important not to let the temperature at the exit end of the exchangers drop to a point where a part of the air becomes liquid because this liquid adheres to the surface of the exchangers and is wasted upon reversal of flow.

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Among the objects of this invention is to provide a process for producing oxygen by the liquefaction and rectification of air, which process results in the production of an additional rectification product, such as oxygen of over 99% purity suitable for welding purposes, high purity nitrogen or fractions rich in krypton, argon or xenon, in addition to the usual oxygen of commerce of about 90% to 95% purity, and notwithstanding the utilization of such additional rectification product or products to improve the efficiency of the purging of the heat exchange zone, such additional rectification product or products may be withdrawn in substantially uncontaminated condition, i. e., not contaminated with condensible constituents removed from the air; and in which process the carbon dioxide, and preferably also the moisture, are removed from the air without the use of chemical reagents by flow through reversing heat exchangers of the regenerator or recuperator type operated at relatively low pressures, of the order of about 60 to 100 pounds, so that the loss of compressed air in the exchangers upon each reversal is small and under conditions such that the carbon dioxide deposited therein is efficiently removed to permit continuous operation.

Other objects and advantages of this invention will be apparent from the following detailed description.

In accordance with this invention, the rectification system is operated to produce a main oxygen product stream having an oxygen content of from 90% to 95% suitable for many commercial uses and a main nitrogen rectification product stream containing usually over 95% nitrogen, the rest being chiefly rare gases such as krypton, argon or xenon, and in addition a pure oxygen of say over 99% purity suitable for welding uses, purer nitrogen than the main nitrogen stream, fractions rich in krypton, argon, xenon, or two or more of these additional rectification products which are herein referred to as "additional rectification products" to distinguish them from the main oxygen and nitrogen rectification product streams. In this specification, where reference is made to oxygen and nitrogen streams, the main oxygen and nitrogen rectification product streams are meant. The nitrogen and oxygen streams are passed through a heat exchange zone and a stream of air passed therethrough to recover the cold content of these rectification products. The air is thus cooled to a temperature close to its condensation point at the pressure existing in its flow path through the heat exchange zone, thereby substantially completely removing all carbon dioxide present in the air. The flow of the nitrogen stream, and if desired, also of the oxygen stream, and that of the air, is periodically reversed so that the air flows through a path through which had previously flowed the nitrogen or oxygen and the oxygen or nitrogen or both flow through a path or paths through which had previously flowed the air, these rectification products or product effecting removal of carbon dioxide deposited in the heat exchange zone during the preceding step of the process. A non-reversing stream of additional rectification product is passed through this heat exchange zone in indirect heat exchange relation with the air and the reversing stream or streams of rectification product. This additional stream of rectification product is thus warmed.

A portion of this additional stream of rectification product is withdrawn uncontaminated by carbon dioxide or other condensible constituents deposited in the heat exchange zone from the air stream passing therethrough. The remainder of the thus warmed additional rectification product is recirculated through its flow path in the heat exchange zone augmented by more of the additional rectification product from the rectification system. The flow path for the additional rectification product extends through at least the cold end of the heat exchange zone. By circulating a stream of additional rectification product through a fixed path extending through at least the colder portion of the heat exchange zone the temperature conditions within this colder portion are maintained such that efficient purging takes place during each reversal period. Further, since the additional rectification product stream flows through a fixed path through which the air never passes, efficient purging is effected without contaminating this additional rectification product stream with air.

More specifically, in accordance with this invention a stream of air at about 60 to 100 pounds and at a temperature of about 70° to about 110° F. is passed through a heat exchange zone in heat exchange relation with a stream of nitrogen and a stream of oxygen. The flow of the air and the nitrogen and, if desired, also of the oxygen is periodically reversed so that the nitrogen and also the oxygen, if desired, flows through the path

or paths through which had previously flowed the air, thereby effecting removal of carbon dioxide and moisture, if any, deposited in the heat exchange zone during the preceding step of the process. A non-reversing stream of additional rectification product, preferably oxygen suitable for welding purposes, is passed through at least the cold end of the heat exchange zone where deposition of carbon dioxide takes place in indirect heat exchange relation with the air, oxygen and nitrogen; the additional rectification product is thus warmed. A portion of this additional rectification product is withdrawn as product uncontaminated by carbon dioxide or other condensibles removed from the air stream. The remainder is recirculated through the heat exchange zone.

The stream of air leaves the heat exchange zone at a temperature below about —270° F. but above its condensation point. This stream is divided into two streams; one comprising the major portion of the air flows to the rectification system, the other comprising the remaining minor portion, say 15% to 35% by volume of the total air introduced into the process, is warmed to a temperature such that upon subsequent expansion little or no liquid air is formed in the expander; the warming is preferably achieved by heat exchange with the non-reversing stream of additional rectification product which is recirculated within the heat exchange zone. The non-reversing rectification product stream also desirably flows in heat exchange relation with a reversing rectification product stream, preferably the nitrogen, to heat this stream to a temperature within 5° to 10° F., preferably 6° to 8° F., below the temperature of the exiting air stream, thereby conditioning the reversing rectification product stream so that it effects more efficient removal of carbon dioxide deposited in the exchanger during the preceding step of the process. The minor portion of the air stream which is warmed is then expanded to produce the refrigeration necessary to compensate for cold losses resulting from the difference in enthalpy between the incoming air and the outgoing products of rectification and for heat leaks into the system. The expanded air is introduced into the low pressure stage of the rectification system where its oxygen content is recovered.

In the rectification system the air is rectified to produce the usual oxygen and nitrogen streams and an additional rectification product, such as high purity oxygen, e. g., welding grade oxygen, high purity nitrogen, or a fraction rich in one or more of the rare gases including argon, neon, krypton and xenon, which additional rectification product, as hereinabove described, is recirculated through at least the cold end of the heat exchange zone in indirect heat exchange relation with the air, oxygen and nitrogen passing therethrough, a portion of the recirculated additional rectification product being continuously withdrawn as product uncontaminated by condensibles removed from the air stream.

Thus, when operating in accordance with this invention, in addition to the usual oxygen and nitrogen rectification products an additional rectification product, desirably welding grade oxygen, is produced, and this product is recirculated through a flow path in the heat exchange zone through which path the air never passes so that it is not contaminated by carbon dioxide and other condensibles removed from the air, the recirculating stream of additional rectification

product improving the efficiency of the periodic purging of the heat exchange zone.

In the accompanying drawings forming a part of this specification and showing, for purposes of exemplification, preferred layouts of equipment for practicing the process of this invention,

Figure 1 illustrates diagrammatically a preferred layout of apparatus for practicing the process of this invention; the apparatus of this figure involves a heat exchanger of the recuperator type;

Figure 2 illustrates a modified arrangement of heat exchangers of the regenerator type which may be used in lieu of the exchangers of the recuperator type shown in Figure 1;

Figure 3 illustrates diagrammatically another modified arrangement of apparatus for practicing the process of this invention, which modification involves exchangers of the regenerator type; and

Figure 4 illustrates still another modified arrangement of exchangers of the recuperator type.

It will be understood the drawings illustrate diagrammatically preferred apparatus for practicing the process of this invention and that the invention may be carried out in other apparatus. For example, any desired number of reversing exchangers of either the recuperator or regenerator type may be used in lieu of the reversing exchangers shown in the drawings; each of the reversing exchangers of the drawings may be replaced by two or more similar exchangers placed in series and/or parallel if desired; the divided or separate exchangers hereinafter described may be disposed in a single housing or may be constructed as separate and distinct units; other rectification systems may be used in lieu of those shown in Figures 1 and 3; the manner of providing refrigeration 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 as disclosed in Figure 1 may be employed with the exchangers shown in the other figures of the drawings, or conversely the manner of supplying such refrigeration shown in Figure 3 may be used with the exchangers of the other figures of the drawings.

In the drawings, in which like reference characters indicate like parts, referring to Figure 1, A and B indicate a pair of heat exchangers; A is the heat exchanger in which flow of air and nitrogen is reversed and B is the heat exchanger in which the flow of air and oxygen is reversed. Exchanger A comprises two sections 10 and 11, section 10 having three flow paths, namely, internal path 12 and concentric paths 13 and 14 disposed in heat exchange relation with each other. The heat exchanger has in each of these paths suitable fins of heat conducting material such as copper or aluminum for promoting rapid and efficient heat exchange between the gaseous media flowing therethrough. For purposes of illustration and in the interests of simplicity, each flow path in an exchanger is shown on the drawings as being formed by a single tube, the several paths being disposed concentrically. Actually, however, each path in each exchanger may comprise a multiplicity of tubes for flow therethrough. One form of exchanger of the recuperator type shown diagrammatically in Figures 1 and 4, which may be used in practicing the process of this invention, is disclosed in application Serial No. 676,142, filed June 12, 1946.

As the construction of the heat exchanger per se does not form a part of this invention and as it may be of any well known type, it is believed further description thereof is unnecessary.

Exchanger section 11 has two flow paths, 15 and 16. Flow path 15 is connected with path 13 by line 17 and flow path 16 is connected with path 14 by line 18.

Exchanger B is of approximately one-fourth the volumetric capacity of exchanger A. Exchanger B comprises two sections 19 and 20. Section 19 consists of three flow paths, 21, 22, 23, and section 20 consists of three flow paths, 24, 25 and 26 connected with paths 21, 22 and 23 by lines 27, 28 and 29, respectively. The exchanger sections 11, 19 and 20 are of the same construction as section 10 hereinabove described.

Reversal of flow through exchanger A is effected by a pair of reversing valves 30, 31. Valve 30 is connected with flow paths 15 and 16 by lines 32, 33. Air line 34 has a branch 35 leading into valve 30 which is provided with a nitrogen exit line 36. Valve 31 is connected with flow paths 13 and 14 by lines 37 and 38. Valve 31 has a nitrogen line 39 leading thereinto and is provided with an air exit line 40.

Reversal of flow through the exchanger B is effected by a pair of reversing valves 41 and 42. Valve 41 is connected with flow paths 24 and 25 by means of lines 43 and 44. Valve 41 has a branch line 45 leading thereinto from the air line 34 and is provided with an oxygen discharge line 46. Valve 42 is connected with flow paths 21 and 22 by lines 47 and 48. This valve is provided with an oxygen supply line 49 and has leading therefrom an air line 50.

A line 51, through which substantially pure oxygen flows from the rectification system, is provided with branches 52 and 53 leading into the flow paths 12 and 23, respectively. A line 54 leads from the exit end of flow path 12; line 29 connecting the flow paths 23 and 26 communicates with line 54; a portion of the pure oxygen passing through paths 12 and 23 flows through line 54 to a pump or blower 56, the remainder passing through path 26 from which it is withdrawn as product through an exit line 55. Line 54 has therein a blower 56 for circulating the pure oxygen through the circulating system comprising heat exchangers 57, 58 of the non-reversing type, a portion of oxygen line 51, branches 52, 53, flow paths 12, 23 and line 54.

The rectification system comprises three columns 59, 60, 61. Column 59 is operated at a pressure of from about 60 to 100 pounds, preferably at about 75 to 90 pounds; columns 60 and 61 at a pressure of from about 5 pounds to about 12 pounds, preferably at about 7 to 9 pounds. These columns customarily are provided with rectification plates of the bubble cap or other desired type. Air is supplied to the base portion of the high pressure column 59 through air line 62 into which lead the lines 40 and 50 and which passes through non-reversing heat exchangers 63 and 64, hereinafter more fully described. Crude oxygen containing approximately 40% oxygen, the rest being chiefly nitrogen, flows from the base of column 59 through line 65 which passes through a non-reversing heat exchanger 66, has therein an expansion valve 67, and enters column 60 at 68. A nitrogen line 69 leads from the top of column 60 into a non-reversing heat exchanger 70. From this exchanger 70 a line 71 leads to a non-reversing heat exchanger 66. A line 72 leads from this non-reversing heat exchanger through the non-

reversing heat exchanger 64. Thence, line 65' discharges into exchanger 58 from which leads nitrogen line 39.

Line 73 leads from the top of column 59, passes through a non-reversing heat exchanger 74 into a line having one branch 75 for returning liquid reflux comprising chiefly nitrogen to column 59 and another branch 76 passing through a non-reversing heat exchanger 70 and leading into the low pressure column 60 at 77. An expansion valve 78 is disposed in the branch 76.

The base of column 60 is provided with a line 79 passing through the non-reversing heat exchanger 74. This line has a return portion 80 leading into the low pressure column 60 at its base. The lines 79 and 80 and the heat exchanger 74 function as a reboiler; liquid oxygen flows through line 79 through exchanger 74 in indirect heat exchange relation with the gaseous stream comprising chiefly nitrogen passing through line 73 which causes vaporization of the liquid oxygen to take place, the oxygen vapor flowing into column 60 through line 80. Line 79 is provided with a branch line 81 having a valve 82 therein. Through this line a portion of the oxygen of about 90% to 95% purity flowing through line 79 is drawn and passed as reflux down through column 61. Vapors, essentially oxygen, pass from column 61 through line 83 into the base of column 60. Substantially pure oxygen of over 99% purity flows through a line 84 leading from the base of the column 61 through heat exchanger 85 from which a return line 86 leads into the base of column 61. A branch line 87 having a valve 88 therein leads from the nitrogen line 73 through the heat exchanger 85 to the branch 75. The lines 84, 86, and the heat exchanger 85 function as a reboiler; liquid oxygen flowing through line 84 and heat exchanger 85 is vaporized by the nitrogen flowing through the heat exchanger 85 in heat exchange relation therewith. The oxygen vapors flow through line 86 into the column 61 and upwardly therethrough countercurrent to the descending stream of oxygen reflux liquid admitted to column 61 through line 81. A stream of oxygen having a purity of over 99% is withdrawn from column 61 through line 51 leading from the base of this column.

Air line 62 is provided with a branch line 89 having a valve 90 therein; line 89 leads to the non-reversing heat exchanger 57. A minor portion of the air flowing through line 62 is caused to flow through line 89 into and through the exchanger 57 in heat exchange relationship with the stream of pure oxygen passing through this exchanger, the air being thus warmed to a temperature such that no liquefaction thereof takes place on subsequent expansion in expander 91 connected with exchanger 57 by a line 92. A bypass line 93 having a valve 94 therein bypasses the exchanger 57 so that more or less of the air flowing through line 89, depending upon the position of valve 94, may be caused to bypass the heat exchanger 57, thereby controlling the temperature of the air entering the expander 91. A line 95 leads from the expander 91 to the low pressure column 60. The main oxygen stream leaves column 60 by way of line 49 and passes through exchanger 63 before entering reversing valve 42.

In the operation of the equipment of Figure 1, air from the main air line 34 flows through branch lines 35, 45 through the reversing valves 30, 41, lines 33, 43, flow paths 16, 24, lines 18, 27, flow paths 14, 21 of exchangers A and B, respectively, lines 38, 47 and the reversing valves 31, 42, branch lines 40, 50 through the air line 62. In its flow through paths 16, 24, the air is cooled to a temperature sufficient to remove all moisture, if any, present in the air. In its flow through paths 14, 21 the air is cooled to a temperature near its condensation point so that all carbon dioxide is removed from the air and deposited in these two flow paths. The major portion of the air leaving paths 14, 21 flows through line 62, non-reversing heat exchangers 63, 64 into the high pressure column 59 of the rectification system. The remaining minor portion flows through lines 89, 93, that flowing through line 93 bypassing heat exchanger 57 and that flowing through the heat exchanger 57 being warmed as it passes in indirect heat exchange relation with the warm pure oxygen stream flowing through the exchanger 57. The thus warmed air stream mixes in line 92 with the air from line 93 to produce a mixture at a desired temperature such that upon expansion no liquid air is formed in expander 91. The expanded air from expander 91 flows through line 95 and enters the low pressure column 60.

Nitrogen flows from the rectification system through line 39 into valve 31 passing through line 37, flow path 13, line 17, flow path 15, line 32, valve 30 through the nitrogen exit line 36. Simultaneously oxygen flows from the rectification system through line 49 into valve 42, line 48, flow path 22, line 28, flow path 25, line 44, valve 41 into and through the oxygen exit line 46. Substantially pure oxygen flows through line 51, branches 52, 53 and through the flow paths 12, 23 into line 54. A portion of the pure oxygen passes from line 54 into and through line 29 and flow path 26, and is withdrawn as product through line 55. The remainder of the pure oxygen entering line 54 is recirculated by blower 56 through the exchanger 57 where the pure oxygen warmed in its flow through paths 12 and 23 gives up a portion of its heat to the air stream flowing through this exchanger. From the exchanger 57 the pure oxygen stream flows through exchanger 58 where residual heat is given up to the nitrogen stream passing through this exchanger. From this exchanger 58 the pure oxygen stream enters line 51 where it mixes with the pure oxygen flowing through this line from the rectification column 61, the resulting mixed pure oxygen stream flowing through the branches 52, 53 into and through the flow paths 12 and 23 as hereinabove described.

Upon reversal, which may take place every three minutes, the air flows in the case of exchanger A through branch line 35, valve 30, line 32, flow path 15, line 17, flow path 13, line 37, valve 31 into branch 40 communicating with air line 62. In the case of exchanger B the air flows through branch 45, valve 41, line 44, path 25, line 28, path 22, line 48, valve 42, and branch 50 communicating with line 62. From line 62 the flow of the air is the same as hereinabove described in connection with the preceding step. Nitrogen flows from line 39 through valve 31, line 38, flow path 14, line 18, flow path 16, line 33, valve 30, nitrogen exit line 36. Oxygen flows through line 49, valve 42, line 47, flow path 21, line 27, flow path 24, line 43, valve 41 through the oxygen exit line 46. The flow of the pure oxygen is the same as hereinabove described in connection with the preceding step.

The nitrogen, the flow of which is periodically reversed through flow paths 13 and 14 of exchanger section 10 and flow paths 15 and 16 of exchanger section 11, and the oxygen, the flow

of which is periodically reversed through flow paths 21, 22 of exchanger section 19 and flow paths 24, 25 of exchanger section 20 remove from their respective flow paths carbon dioxide and other condensibles deposited therein from the air stream flowing therethrough during the preceding step of the process. The pure oxygen stream flowing through paths 12, 23 is in part withdrawn as product after passing through flow path 26 and is in part recirculated through paths 12, 23. The recirculated pure oxygen stream gives up heat to the minor portion of the air stream fed to the expander 91 and to the nitrogen fed to exchanger A. Since the portion of the pure oxygen withdrawn as product never flows through a path through which the air passes, it is uncontaminated by condensibles removed from the air stream. The portion of the pure oxygen recirculated through the exchanger sections 10 and 19 establishes temperature conditions within the several streams passing therethrough such that the reversing oxygen and nitrogen streams effect most efficient purging of carbon dioxide and other condensibles from the flow paths through which they pass.

The modification of Figure 2 differs from that of Figure 1 chiefly in that (1) two sets of regenerators are used instead of a pair of recuperators, and (2) the recirculated pure oxygen stream passes through the entire extent of the flow paths in the exchangers and not through the colder end only as is the case in exchanger A of Figure 1.

Each of the regenerators of Figure 2 contains material such as copper or aluminum of high heat transfer capacity over which alternate streams of rectification product and air flow, the rectification product imparting its cold content to this material and the air recovering this cold when it flows over this material during the succeeding step of the process as is well known in this art. The two sets shown are C and D; C comprises the regenerators 96, 97, whereas D comprises the regenerators 98, 99. Extending through these regenerators are oxygen flow paths 100, 101, 102 and 103, respectively. Each of these flow paths desirably is in the form of one or more tubes of high heat conducting material, such as copper or aluminum, in indirect heat exchange relationship with the material of high heat transfer capacity in the regenerators 96 to 99.

Pure oxygen line 51 is provided with branches 104, 105, 106 and 107 which communicate with the pure oxygen flow paths 100, 101, 102 and 103, respectively. These flow paths are provided with exit lines 108, 109, 110 and 111, respectively, communicating with a line 112 having branch 113 for withdrawal of pure oxygen as product and a second branch 114 through which the remainder of the pure oxygen is recirculated by a blower corresponding with blower 56 (Figure 1) to the pure oxygen supply line 51 receiving pure oxygen from the rectification system as hereinabove described in connection with Figure 1. Line 114 may pass through heat exchangers corresponding to exchangers 57 and 58 of Figure 1 so that the warm pure oxygen passing through this line 114 gives up heat, say to a minor portion of the air to be expanded in order to supply refrigeration to the process and, if desired, also to the nitrogen stream passing to the exchanger set C.

Reversing valve 30 is connected with regenerator 96 by a line 115 and with regenerator 97 by line 116. Reversing valve 31 is connected with regenerator 96 by a line 117 and with regenerator 97 by line 118. Reversing valve 41 is connected with regenerators 98, 99 by lines 119 and 120, respectively, and reversing valve 42 is connected with regenerators 98, 99 by lines 121, 122, respectively. By means of these reversing valves the flow of air is caused to take place alternately through regenerators 97, 99 while nitrogen flows through regenerator 96 and oxygen through regenerator 98 and upon reversal the air flows through the regenerators 96, 98, while nitrogen flows through regenerator 97 and oxygen flows through regenerator 99.

In the operation of the modification of Figure 2, air at a pressure of 60 to 100 pounds and at a temperature of 70° to 110° F. supplied through line 34 flows through branches 35, 45 into and through the valves 30, 41, lines 116 and 120, regenerators 97, 99, lines 118, 122, valves 31, 42, lines 40 and 50 into the air line 62. The air is thus cooled to a temperature close to its condensation point at the pressure prevailing in these regenerators through which it flows. The thus cooled air flows through line 62 to the rectification system, a minor portion, if desired, being expanded in expander 91 as hereinabove described in connection with the modification of Figure 1 to supply refrigeration to the process.

Simultaneously, nitrogen flows through line 39, valve 31, line 117, regenerator 96, line 115, valve 30 and nitrogen exit line 36, giving up its cold to the heat transfer material in regenerator 96. Oxygen flows through line 49, valve 42, line 121, regenerator 98, giving up its cold to the heat transfer material therein, the oxygen exiting through line 119, valve 41 and oxygen exit line 46. Pure oxygen flows from line 51 through the branches 104 to 107, the oxygen flow paths 100 to 103, lines 108 to 111 into line 112. From this line a portion of the pure oxygen is withdrawn as product through line 113 and the remainder recirculated through line 114 to the pure oxygen supply line 51.

Upon reversal, which may take place every three minutes as indicated by the dotted line valve settings, the air flows through valves 30, 41, lines 115, 119, regenerators 96, 98, lines 117, 121, valves 31, 42, lines 40, 50 into the air line 62 from which the air flows to the rectification system as hereinabove described. Simultaneously, nitrogen flows through line 39, valve 31, line 118, regenerator 97, line 116, valve 30, nitrogen exit line 36. Oxygen flows through line 49, valve 42, line 122, regenerator 99, line 120, valve 41 into the oxygen exit line 46. Pure oxygen flows from line 51 through the same flow paths as hereinabove described in connection with the preceding step of the process.

The nitrogen which alternately flows through one or the other of regenerators 96, 97 and the oxygen which alternately flows through one or the other of regenerators 98, 99 remove therefrom the carbon dioxide and other condensibles deposited therein from air during the preceding step of the process. The efficiency of the purging action of the nitrogen and oxygen is materially improved by the recirculated stream of pure oxygen, which recirculated stream results in temperature conditions within the regenerators optimum for effecting removal of carbon dioxide by the nitrogen and oxygen streams flowing therethrough.

The modification of Figure 3 differs from those hereinabove described chiefly in that (1) a different rectification system is employed, namely a system which results in the production of a rec-

tification product rich in argon instead of a pure oxygen rectification product as in the modification of Figure 1, and (2) the refrigeration to compensate for cold losses resulting from the difference in enthalpy between the incoming air and the outgoing products of rectification and for heat leaks into the system is supplied by a refrigeration system and not by expanding a minor portion of the air as in the modification of Figure 1.

The rectification system of Figure 3 comprises a two-stage rectification column 125, the lower section 126 of which is operated at a pressure of about 60 to 100 pounds, preferably at about 75 to 90 pounds, and the upper section 127 of which is operated at a pressure of from 5 pounds to 12 pounds, preferably at about 7 to 9 pounds. This column, as is customary, is provided with rectification plates of the bubble cap or other desired type. The lower section 126 communicates with condenser 128 and has a liquid collecting shelf 129 disposed immediately below the condenser for collecting liquid nitrogen. Pipe line 130 leads from shelf 129 to a non-reversing heat exchanger 131 which communicates through a pressure reducing valve 132 with the top portion of low pressure section 127. Condenser 128 acts as a reboiler for the upper section 127.

From the base of the lower section 126 a pipe line 133 for the flow of crude oxygen leads into a branch 134 which passes to a non-reversing heat exchanger 135 which communicates through pipe line 136 having a pressure reducing valve 137 therein with the low pressure section 127 at an intermediate point 138. The other branch 139 has an expansion valve 140 therein and communicates with a condensing coil 141 disposed in the top portion of auxiliary column 142. Coil 141 communicates with the low pressure stage 127 at 143. Column 142 has a line 144 provided with a valve 145 through which a vapor side stream having a maximum concentration of argon flows from stage 127 into column 142. In column 142 this side stream is separated into an argon vapor product which passes off through line 146 and an argon-oxygen liquid fraction which is returned through line 147 to the low pressure stage 127.

A line 148 having a pressure reducing valve 149 therein leads from condenser 128 to a nitrogen line 150. A line 151 leads from the top of the low pressure section 127, passes through heat exchangers 131 and 135 and enters line 150; the nitrogen stream flowing through line 148 enters line 150 where it joins the stream from line 151. Nitrogen line 150 enters a non-reversing heat exchanger 152 which has a nitrogen exit line 153 passing through a non-reversing heat exchanger 154 and communicating with line 39 entering valve 31.

The oxygen line 49 leads from the low pressure section 127 through a non-reversing heat exchanger 155 to reversing valve 42. Line 114 passes through a refrigeration system 156 which may be of any well known construction for supplying a refrigerating medium such as ethylene or methane to cool the recirculating argon stream flowing therethrough. This refrigeration system operates to cause the flow of the refrigerating medium in indirect heat exchange relation with the argon, the rate of flow and the temperature of the various media being so controlled that enough cold is introduced by refrigeration at this point in the process to compensate for cold losses resulting from the difference in enthalpy between the incoming air and the outgoing products of rectification and for heat leaks into the system. Flow of argon through the refrigeration system 156 may be accomplished by pump 56 in line 114. From the refrigeration system 156 a line 157 passes to heat exchanger 154. A line 158 leads from exchanger 154 to the line 146 through which argon is supplied to the argon flow paths 100, 101, 102 and 103 in the regenerators 96, 97, 98 and 99, respectively. These regenerators may be of the same construction as those of Figure 2, differing chiefly in that argon instead of pure oxygen flows through the flow paths 100 to 103 within the regenerators. Hence like parts of the regenerators and associated piping of Figures 2 and 3 are indicated by the same reference characters.

In the operation of the modification of Figure 3 air flows through branches 35, 45, valves 30, 41, lines 116, 120 into the regenerators 97, 99, exiting through lines 118, 122, valves 31, 42, lines 40, 50 and flowing into the air line 62. From this line the air passes through exchanger 155 in heat exchange relation with the oxygen stream flowing through line 49 and passing through this exchanger and then flows through line 62' through the heat exchanger 152, where the air passes in heat exchange relation with nitrogen, into the high pressure section 126 of column 125. The air stream in its flow through the regenerators 97, 99 is cooled to a temperature near its condensation point and substantially all carbon dioxide and moisture, if any, removed therefrom.

Nitrogen flows from the rectification column 125 through line 150, passing through heat exchanger 152, line 153, heat exchanger 154, through line 39 which enters valve 31. From this valve nitrogen passes through line 117, regenerator 96, and gives up its cold content to the heat transfer material within this regenerator, the nitrogen leaving the regenerator through line 115, flowing through valve 30 and exiting through line 36. Simultaneously, oxygen flows from the rectification column 125 through line 49, heat exchanger 155, entering valve 42 and flowing through line 121, regenerator 98, line 119 and valve 41 and exiting through the oxygen exit line 46. Also at the same time a stream rich in argon flows through line 146, enters the branches 104 to 107, flows through the flow paths 100 to 103, respectively, and exits through the branches 108 to 111, respectively, into line 112. From this line a portion of the argon-rich stream is withdrawn through 113 as product. The remainder is recirculated by pump 56 through the refrigeration system 156, line 157, exchanger 154 where it passes in heat exchange relation with the nitrogen, and line 158 into the argon line 146 from which the argon is recirculated through the argon flow paths in regenerators 96 to 99.

Upon reversal, which may take place every three minutes, the air flows through the regenerators 96, 98, the nitrogen through regenerator 97 and the oxygen through regenerator 99. The argon flows through the same flow paths within the regenerators. The nitrogen, flow of which is periodically reversed in regenerators 96, 97, and the oxygen, flow of which is periodically reversed in regenerators 98, 99, remove from their respective flows paths the carbon dioxide and other condensibles deposited therein from the air stream flowing therethrough during the preceding step of the process. The argon-rich stream, withdrawn as product through line 113, since it flows through paths through which the air never passes, is uncontaminated by condensibles removed from the air stream.

The modification of Figure 4 differs from that

of Figure 1, chiefly in that (1) an exchanger of the recuperator type in which the flows of nitrogen and air only are reversed is used instead of the pair of parallel exchangers of Figure 1, and (2) argon, rather than welding grade oxygen, is recirculated through the exchanger. In Figure 4, 160 indicates an exchanger constituted of sections 161 and 162, which sections except as hereinafter noted may be of the same general construction as the sections of the exchangers of Figure 1 hereinabove described. Section 161 comprises four flow paths 163, 164, 165 and 166; 163 is the flow path of the recirculated stream of argon, 164 the flow path for the non-reversing stream of oxygen and 165 and 166 are the flow paths through which flow of air and nitrogen are periodically reversed. Exchanger section 162 is provided with flow paths 167, 168, 169 and 170; a line 171 connects flow paths 163 and 167, a line 172 connects flow paths 164 and 168, a line 173 connects flow paths 165 and 169 and a line 174 connects flow paths 166 and 170. Communicating with line 171 is a line 175 through which a portion of the argon flowing through line 171 is withdrawn and recirculated through the flow path 163 in exchanger section 161. This recirculating system, as in the modification of Figure 1, comprises pump 56, exchanger 57 in which the argon passes in heat exchange relation with a minor portion of the air stream flowing through line 89 to expander 91, an exchanger 58 in which the argon stream flows in heat exchange relation with nitrogen passing through line 65' and a line 176 extending from exchanger 58 to the argon line 146 (Figure 3) which leads into the flow path 163.

Reversal of flow of the nitrogen and air streams is accomplished by reversing valves and connected piping the same as described in connection with Figure 1. Hence these valves and associated piping have been given the same reference characters as the corresponding parts of Figure 1.

In the operation of the modification of Figure 4, air is supplied through line 34 to valve 30 and, as indicated by the full line valve settings, flows through line 32, flow path 170, line 174, flow path 166, line 38 into valve 31 from which the air enters line 62. From this line a minor portion of the air flows through line 89 to exchanger 57 where the air is warmed, the warmed air passing to expander 91 and the expanded air passing through line 95 into the low pressure stage of the rectification system. The remainder of the air passes through heat exchanger 63 where it is further cooled by flowing in heat exchange relation with the oxygen stream passing through line 49. The thus cooled air passes through line 62 into the high pressure stage of the rectification system. In its flow through path 170 the air is cooled to a temperature sufficient to remove all moisture, if any, present in the air. In its flow through path 166 the air is cooled to a temperature near its condensation point and all carbon dioxide is removed therefrom and deposited in flow path 166.

Nitrogen flows through line 65', exchanger 58, line 39, valve 31, line 37, flow path 165, line 173, flow path 169, line 33, valve 30 to the nitrogen exit line 36. Simultaneously oxygen flows through line 49, exchanger 63, flow path 164, line 172, flow path 168 to the oxygen exit line 178 leading from the exit end of the flow path 168. Argon flows from line 146 through flow path 163 into line 171. A portion of the argon flowing through line 171 is recirculated through line 175 by pump 56, flowing as hereinabove described through exchangers 57 and 58, line 176 into line 146 where it mixes with the argon from the rectification system, the resultant stream passing through flow path 163. The remainder of the argon from line 171 flows through flow path 167 and is withdrawn through the argon line 177.

Upon reversal, as indicated by the dotted setting of reversing valves 30 and 31, which reversal may take place every three minutes, air flows through valve 30, line 33, flow path 169, line 173, flow path 165, line 37, valve 31 into line 62. From this line the flow of the air is the same as described above in connection with the preceding step. Nitrogen flows from line 65' through exchanger 58, line 39, valve 31, line 38, flow path 166, line 174, flow path 170, line 32, valve 30 to the nitrogen exit line 36. The nitrogen on each reversal flows through the path through which had previously passed the air and removes from this path carbon dioxide and other condensibles removed from the air stream during the preceding step of the process. The oxygen and argon streams flow through their respective flow paths the same as during the preceding step of the process, i. e., no reversal of flow of either of these streams takes place. Since the argon stream employed to condition the nitrogen stream to effect more efficient purging flows through a path in exchanger 160 through which the air never passes, it is not contaminated by condensibles removed from the air stream.

Instead of argon, streams rich in krypton, xenon, neon or relatively pure nitrogen, produced for example in an auxiliary column associated with the rectification system by rectification of a side stream containing the desired constituent or constituents, may be recirculated through the flow paths 163 in Figure 4 and 100 to 103 of Figure 2, a portion of the recirculating stream being withdrawn as product and the remainder retained in the circulating system. In the modifications of Figures 2 and 3, instead of passing the recirculated additional rectification product through the entire extent of the regenerators, the flow paths through the regenerators may be provided with a take-off line at a point intermediate the ends of the flow paths for withdrawing a portion of the additional rectification product to be recirculated corresponding to the arrangement shown in Figures 1 and 4. Desirably, this point of withdrawal is positioned in the flow path where the temperature is within the range of −120° F. to −175° F. Also the additional rectification product which is recirculated may be caused to pass through the entire extent of the flow paths in the exchangers of Figures 1 and 4 instead of through the colder portion only of certain of these exchangers as shown in Figures 1 and 4.

One example of the operation of the process of this invention in the apparatus shown in Figure 1 is described below. It will be understood this example is given for purposes of exemplification only and the invention is not limited thereto. The example refers to an oxygen plant operating in a locality where the atmospheric pressure is 14.6 pounds per square inch absolute.

Air under pressure of about 90 pounds and a temperature of 70° F. is supplied through line 34, flows through branches 35, 45, valves 30, 41, passing through lines 33, 43, flow paths 16, 24, lines 18, 27, flow paths 14, 21, lines 38, 47, valves 31, 42, lines 40, 50, respectively, into line 62. The air enters line 62 at a temperature of −272° F.

About 28% by volume of the air at this temperature is passed through line 89, flows through exchanger 57 where it passes in heat exchange relation with a recirculating stream of pure oxygen which enters the exchanger at a temperature of −217.5° F.; the temperature of the air is thus increased to −242° F. and the temperature of the oxygen reduced to −256° F. The thus warmed air enters expander 91 where it is expanded to a pressure of approximately 10 pounds and a temperature of −302.2° F., at which temperature and pressure it enters the low pressure column 60 through line 95.

The remaining 72% of the air flows through heat exchanger 63 where its temperature is reduced to −273.8° F. by heat exchange with the oxygen flowing through this exchanger; the oxygen inlet temperature to this exchanger is −288.2° F.; it leaves the exchanger at a temperature of −280° F. The air then flows through exchanger 64 where its temperature is reduced to −274° F. by heat exchange with the nitrogen flowing through this exchanger. The nitrogen enters at a temperature of −292° F. and leaves at −290° F. From exchanger 64 the air at a temperature of −274° F. enters the bottom of high pressure column 59.

High pressure column 59 is operated at a pressure of about 88 pounds. Crude oxygen at a temperature of −275.3° F. is withdrawn through line 65 and passed through the heat exchanger 66 where its temperature is reduced to −277.6° F., at which temperature it flows through expansion valve 67 where it is flashed to a pressure of about 9 pounds and a temperature of about −307° F., at which pressure and temperature it enters the low pressure column 60. The nitrogen stream passing through exchanger 66 enters at a temperature of −294.8° F. and leaves at a temperature of −292° F. Nitrogen at a temperature of −282.4° F. leaves the top of high pressure column 59, part of this nitrogen being recirculated through heat exchanger 85 to supply heat to the oxygen stream passing therethrough. From exchanger 85 the nitrogen flows to branch 75. The remainder of the nitrogen passes through exchanger 74 in heat exchange relation with the oxygen stream passing through this exchanger. The nitrogen stream leaving exchanger 74 is divided so that part flows through branch 75 and this part, along with nitrogen flowing into line 75 from exchanger 85, is returned as reflux to column 59. The other part at a temperature of about −282° F. enters exchanger 70 and leaves at a temperature of −309.4° F. The nitrogen is then expanded through valve 78 to a pressure of about 8 pounds and a temperature of −312.3° F., at which pressure and temperature it enters low pressure column 60 at 77.

Nitrogen rectification product at a temperature of −312.3° F. leaves low pressure column 60 through line 69 and passes through exchanger 70, its temperature thereby being increased to −294.8° F. It then passes through exchanger 66, its temperature thereby being increased to −292° F., thereafter through exchanger 64, its temperature being thereby increased to −290° F., and through exchanger 58, its temperature being thereby increased to about −280° F. At this temperature it flows through reversing valve 31, line 37, flow path 13, line 17, flow path 15, line 32, valve 30 and nitrogen exit line 36, leaving this line at a temperature of 60° F. and a pressure of about 0.1 pound.

Oxygen of approximately 95% purity and at a temperature of −288.2° F. passes through line 81 into the pure oxygen stripping column 61 which is operated at a pressure of approximately 10.5 pounds. From the base of column 61 substantially pure oxygen at a temperature of −287° F. flows through line 84, heat exchanger 85, where it passes in heat exchange relation with the nitrogen stream flowing through exchanger 85, returning to column 61 through line 86 where the oxygen vapors pass countercurrent to the descending stream of reflux liquid oxygen introduced through line 81 as hereinabove described. From the top of column 61 oxygen vapors flow into the base of column 60 through line 83. Substantially pure oxygen (over 99% purity) is withdrawn through line 51 at a temperature of −287° F. This oxygen mixes with the circulating stream of oxygen which leaves exchanger 58 at a temperature of −287° F. and at this temperature enters line 51; the resultant oxygen stream flows through branch lines 52, 53 through the flow paths 12, 23. The oxygen leaves these flow paths at a temperature of about −219° F. Approximately 6% of the oxygen flowing into line 54 continues its flow through flow path 26 and leaves the flow path through line 55 at a temperature of 50° F. and a pressure of about 1 pound. The remainder of the oxygen flowing into line 54 is recirculated by pump 56 through the exchangers 57, 58 into the return line 51; the oxygen enters exchanger 57 at a temperature of −217.5° F. and leaves at −256° F.; it enters exchanger 58 at −256° F. and leaves at −287° F.

Oxygen of approximately 95% concentration flows from column 60 through line 49 at a temperature of −288.2° F. and a pressure of about 10 pounds, passes through heat exchanger 62 where its temperature is increased to about −280° F., at which temperature is enters reversing valve 42, flows through line 48, flow path 22, line 28, flow path 25, leaving this flow path at a temperature of about 50° F. and a pressure of about 1 pound.

Upon reversal, which may take place every three minutes, the air flows through paths 16, 13 in exchanger A and 25, 22 in exchanger B; nitrogen flows through paths 14, 16 of exchanger A and oxygen through paths 21, 24 of exchanger B. The flow of the various streams is otherwise substantially the same as hereinabove described and the temperature and pressure conditions remain the same. The nitrogen and oxygen streams of about 95% concentration in their flow remove by sublimation and evaporation carbon dioxide and moisture, if any, deposited by the air during the preceding step. Thus upon each reversal the reversing nitrogen and oxygen rectification product streams effect removal of the carbon dioxide and frost, if any, deposited in the paths through which the air had passed during the preceding step of the process.

In the operation of the process of this invention it is preferred to effect removal of moisture and carbon dioxide both in accordance with the process of this invention. It will be understood, however, that, if desired, the moisture may be removed from the air by any conventional means and dry air containing carbon dioxide passed through the exchanger or exchangers as hereinabove disclosed. In the event that dry air is supplied to the process and the exchanger system is similar to that of Figure 1, reversing valves 30, 41 may advantageously be moved to the position between exchanger sections 10 and 11 of exchanger A and 19 and 20 of exchanger B so

that reversal of the air and nitrogen streams occurs only in exchanger section 10 and of the air and oxygen streams occurs only in exchanger section 19 wherein the carbon dioxide is deposited by the air stream. The reversing valve 30 of Figure 4 may be similarly positioned when the equipment of these figures is operated with dry air. Operation of such an arrangement is carried out so that the temperature at the warm end of exchanger sections 10 and 19 of Figure 1 and 161 of Figure 4 is at least slightly higher than the temperature at which the carbon dioxide begins to deposit from the air stream. In general, the air entering the warm end of these exchangers should be at a temperature in the range of about −110° to −160° F., the exiting product streams being about 10° to 15° F. colder.

As a desirable operating range the air is admitted to the inlet of the exchangers at a temperature of from 70° to 110° F. and a pressure of 60 to 100 pounds, preferably 75 to 90 pounds. The air in its flow through exchanger sections 11 and 20 of Figure 1 and 162 of Figure 4 is cooled to a temperature of −110° F. to −160° F. and at this temperature enters respectively exchanger sections 10 and 19 of Figure 1 and 161 of Figure 4 and exits therefrom at a temperature within the range of −260° F. to −280° F. In the modification of Figures 2 and 3 the air enters the regenerators at a temperature of from 70° to 110° F. and leaves at a temperature of from −260° to −280° F. In general the oxygen rectification product enters the exchangers at a temperature of from −288° to −293° F., the nitrogen enters at a temperature of from −265° to −285° F., and both the oxygen and nitrogen leave the exchangers at a temperature of from 60° to 100° F. In the modifications involving split or sectional exchangers, e. g., the modifications of Figures 1 to 4, the oxygen leaves exchanger sections 19 and 161 of Figures 1 and 4, respectively, and the nitrogen leaves exchanger sections 10 and 161 of Figures 1 and 4, respectively, at a temperature of from about −120° to −175° F. The high pressure stage of the rectification system is maintained at about 60 to 100 pounds and the low pressure stage at about 5 to 12 pounds. The several streams suffer only a small pressure drop in flowing through the exchangers.

In those modifications involving division of the air stream into two streams with a minor portion of the air passed to the expander to supply refrigeration to the process from 15% to 35% of the total air introduced into the process may thus be expanded.

Operating in accordance with this invention it is found that substantially complete removal of carbon dioxide takes place from the air stream prior to its introduction into the rectification system, permitting efficient rectification of the air to produce oxygen of about 95% purity suitable for most commercial uses and also pure oxygen or other desired rectification product. The air flow paths upon each reversal are purged to remove therefrom the carbon dioxide and frost, if any, thereby permitting continuous operation. This purging is accomplished more efficiently and at the same time pure oxygen or other rectification product stream instrumental in improving the efficiency of the purging is withdrawn as product uncontaminated by condensibles removed from the air.

The expressions "reversing the flow of air and nitrogen" or of air and oxygen and "reversal" are used herein in the sense commonly employed in this art, namely, to mean the switching of the flow of two streams, for example, the air and the nitrogen or oxygen streams, so that upon each "reversal" the air flows through the path through which had previously flowed the nitrogen or oxygen and the nitrogen or oxygen flows through the path through which had previously flowed the air. The term "path" is used herein in a comprehensive sense to include the flow arrangement of Figures 2 and 3 in which the nonreversing recirculating rectification product stream flows through a path consisting of four sections in parallel as well as paths consisting of sections in series as shown, for example, in Figure 1.

Since certain changes may be made in carrying out the above processes 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. This application is directed to species of the generic invention disclosed and claimed in my co-pending application Serial No. 783,551, filed November 1, 1947.

What is claimed is:

1. A process for producing oxygen by the liquefaction and rectification of air, which comprises passing streams of nitrogen and oxygen rectification products through nitrogen and oxygen flow paths respectively in a heat exchange zone, passing a stream of air through another path in said heat exchange zone to recover the cold content of the nitrogen and oxygen rectification products, cooling the air to a temperature close to its condensation point at the pressure prevailing in its flow path through said heat exchange zone and effecting substantially complete removal of carbon dioxide from the air in its passage through said heat exchange zone, subjecting the thus cooled air to rectification to produce said oxygen and nitrogen rectification products and also an additional rectification product, periodically reversing the flow of air and nitrogen through their respective paths in said heat exchange zone, whereby upon each of said reversals the nitrogen substantially completely removes the carbon dioxide deposited during the preceding step of the process in the path through which the nitrogen flows, passing the stream of said additional rectification product through a path extending through at least the colder portion of said heat exchange zone in indirect heat exchange relation with the air and the nitrogen steams passing through their respective paths in said heat exchange zone, removing a portion of said additional rectification product as product uncontaminated by condensibles removed from the air stream and recirculating the remainder through its flow path extending through at least the colder portion of said heat exchange zone.

2. A process for producing oxygen by the liquefaction and rectification of air, which comprises passing streams of nitrogen and oxygen rectification products through nitrogen and oxygen flow paths respectively in a heat exchange zone, passing a stream of air through another path in said heat exchange zone to recover the cold content of the nitrogen and oxygen rectification products, cooling the air to a temperature close to its condensation point at the pressure prevailing in its flow path through said heat exchange zone and effecting substantially complete removal of carbon dioxide from the air in its

passage through said heat exchange zone, subjecting the thus cooled air to rectification to produce said oxygen and nitrogen rectification product streams, rectifying a portion of said oxygen rectification product to produce substantially pure oxygen, periodically reversing the flow of air and nitrogen through their respective paths in said heat exchange zone, whereby upon each of said reversals the nitrogen substantially completely removes the carbon dioxide deposited during the preceding step of the process in the path through which the nitrogen flows, passing a stream of said substantially pure oxygen through a path extending through at least the colder portion of said heat exchange zone in indirect heat exchange relation with the air and the nitrogen stream passing through their respective paths in said heat exchange zone, removing a portion of said substantially pure oxygen as product uncontaminated by condensibles removed from the air stream and recirculating the remainder of said substantially pure oxygen through its flow path extending through at least the colder portion of said heat exchange zone.

3. A process for producing oxygen by the liquefaction and rectification of air, which comprises passing a stream of nitrogen rectification product through a path in a heat exchange zone, passing a stream of air through another path in said heat exchange zone, passing a stream of oxygen rectification product through a path in a second heat exchange zone, passing a second stream of air through another path in said second heat exchange zone, cooling the air during its passage through said first and second heat exchange zones to a temperature close to its condensation point at the pressure prevailing in the air flow paths through said heat exchange zones and effecting substantially complete removal of carbon dioxide from the air in its passage through said heat exchange zones, subjecting the thus cooled air to rectification to produce said oxygen and nitrogen rectification product streams and also an additional rectification product, periodically reversing the flow of air and nitrogen and of the air and oxygen through their respective paths in said heat exchange zones, whereby upon each of said reversals the nitrogen and oxygen substantially completely remove the carbon dioxide deposited during the preceding step of the process in the paths through which the nitrogen and oxygen flows respectively, passing streams of said additional rectification product through a path extending through at least the colder portion of both of said heat exchange zones in indirect heat exchange relation with (1) the air and nitrogen in said first heat exchange zone, and (2) the air and oxygen in said second heat exchange zone, removing a portion of said additional rectification product as product uncontaminated by condensibles removed from the air stream and recirculating the remainder through its flow paths extending through at least the colder portion of said heat exchange zones.

4. A process for producing oxygen by the liquefaction and rectification of air in a rectification system involving high and low pressure stages, which comprises passing streams of nitrogen and oxygen rectification products through nitrogen and oxygen flow paths respectively in a heat exchange zone, passing a stream of air through another path in said heat exchange zone to recover the cold content of the nitrogen and oxygen rectification products, cooling the air to a temperature close to its condensation point at the pressure prevailing in its flow path through said heat exchange zone and effecting substantially complete removal of carbon dioxide from the air in its passage through said heat exchange zone, dividing the air stream into major and minor portions, passing the major portion to the high pressure stage of the rectification system, passing an additional stream of rectification product through a flow path extending through at least the colder portion of said heat exchange zone in heat exchange relation with said streams of nitrogen and oxygen rectification products thereby warming said additional stream of rectification product, dividing said warmed stream into two streams, withdrawing one of said streams as product, recirculating the other of said streams through its flow path in said heat exchange zone, the said recirculated stream flowing in indirect heat exchange relation with (1) said minor portion of the air stream thereby warming said minor portion to a temperature such that said minor portion can thereafter be expanded without substantial liquefaction, and (2) at least a portion of the said nitrogen stream prior to its entry into said heat exchange zone thereby warming said nitrogen stream to a temperature within 5° to 10° F. of the temperature of the air stream leaving said heat exchange zone, expanding said warmed minor portion of the air to produce refrigeration in amount sufficient to compensate for cold losses resulting from the difference in enthalpy between the incoming air and the outgoing products of rectification and for heat leaks into the process, introducing the expanded air into the low pressure stage of the rectification system, rectifying said major and minor portions of air to produce said streams of oxygen, nitrogen and additional rectification products, and periodically reversing the flow of air and nitrogen through their respective paths in said heat exchange zone, whereby upon each of said reversals the nitrogen substantially completely removes the carbon dioxide deposited during the preceding step of the process in the path through which the nitrogen flows.

5. A process for producing oxygen by the liquefaction and rectification of air in a rectification system involving high and low pressure stages, which comprises passing streams of nitrogen and oxygen rectification products through nitrogen and oxygen flow paths respectively in a heat exchange zone, passing a stream of air through another path in said heat exchange zone to recover the cold content of the nitrogen and oxygen rectification products, cooling the air to a temperature close to its condensation point at the pressure prevailing in its flow path through said heat exchange zone, dividing the air stream into major and minor portions, passing the major portion to the high pressure stage of the rectification system, passing a stream of substantially pure oxygen through a flow path extending through at least the colder portion of said heat exchange zone in heat exchange relation with said streams of nitrogen and oxygen rectification products thereby warming said stream of pure oxygen, dividing said warm stream of pure oxygen into two streams, withdrawing one of said streams as product, recirculating the other of said streams through its flow path in said heat exchange zone, the said recirculated stream first flowing in indirect heat exchange relation with (1) said minor portion of the air stream thereby warming said minor portion to a temperature such that said minor portion can thereafter be

expanded without substantial liquefaction, and (2) at least a portion of the said nitrogen stream prior to its entry into said heat exchange zone thereby warming said nitrogen stream to a temperature within 5° to 10° F. of the temperature of the air stream leaving said heat exchange zone, expanding said warmed minor portion of the air to produce refrigeration in amount sufficient to compensate for cold losses resulting from the difference in enthalpy between the incoming air and the outgoing products of rectification and for heat leaks into the process, introducing the expanded air into the low pressure stage of the rectification system, rectifying said major and minor portions of the air to produce said oxygen, nitrogen and pure oxygen streams, and periodically reversing the flow of air and nitrogen through their respective paths in said heat exchange zone, whereby upon each of said reversals the nitrogen substantially completely removes the carbon dioxide deposited during the preceding step of the process in the path through which the nitrogen flows.

6. A process for producing oxygen by the liquefaction and rectification of air, which comprises passing a stream of nitrogen rectification product through a path in a heat exchange zone, passing a stream of air through another path in said heat exchange zone, passing a stream of oxygen rectification product through a path in a second heat exchange zone, passing a second stream of air through another path in said second heat exchange zone, cooling the air during its passage through said first and second heat exchange zones to a temperature close to its condensation point at the pressure prevailing in said flow paths through said heat exchange zones and effecting substantially complete removal of carbon dioxide from the air in its passage through said heat exchange zones, subjecting the thus cooled air to rectification to produce said oxygen and nitrogen rectification product streams and also an additional stream consisting of substantially pure oxygen, periodically reversing the flow of air and nitrogen and of the air and oxygen through their respective paths in said heat exchange zones, whereby upon each of said reversals the nitrogen and oxygen substantially completely remove the carbon dioxide deposited during the preceding step of the process in the paths through which the nitrogen and oxygen flows respectively, passing a stream of said substantially pure oxygen through a path extending through at least the colder portions of both of said heat exchange zones in indirect heat exchange relation with (1) the air and nitrogen in said first heat exchange zone and (2) the air and oxygen in said second heat exchange zone, removing a portion of said substantially pure oxygen as product uncontaminated by condensibles removed from the air stream and recirculating the remainder through its flow paths extending through at least the colder portions of said heat exchange zones.

7. A process for producing oxygen by the liquefaction and rectification of air in a rectification system involving high and low pressure stages, which comprises passing a stream of nitrogen rectification product through a path in a heat exchange zone, passing a stream of air through another path in said heat exchange zone, passing a stream of oxygen rectification product through a path in a second heat exchange zone, passing a second stream of air through another path in said second heat exchange zone, cooling the air during its passage through said first and second heat exchange zones to a temperature close to its condensation point at the pressure prevailing in said flow paths through said heat exchange zones and effecting substantially complete removal of carbon dioxide from the air in its passage through said heat exchange zones, dividing the thus cooled air leaving said first and second heat exchange zones into major and minor portions, passing the major portion to the high pressure stage of the rectification system, passing a stream of substantially pure oxygen through a flow path extending through at least the colder portions of said heat exchange zones in indirect heat exchange relation with the air and nitrogen and the air and oxygen passing therethrough, thereby warming said stream of substantially pure oxygen dividing said warm stream of substantially pure oxygen into two streams, withdrawing one of said streams as product, recirculating the other of said streams through its flow path in said heat exchange zones, the recirculating stream flowing in indirect heat exchange relation with (1) said minor portion of the air stream thereby warming said minor portion to a temperature such that said minor portion can thereafter be expanded without substantial liquefaction and (2) at least a portion of the said nitrogen stream prior to its entry into the first mentioned heat exchange zone thereby warming said nitrogen stream to a temperature within 5° to 10° F. of the temperature of the air stream leaving said first mentioned heat exchange zone, expanding the said warmed minor portion of the air to produce refrigeration in amount sufficient to compensate for cold losses resulting from the difference in enthalpy between the incoming air and the outgoing products of rectification and for heat leaks into the process, introducing the expanded air into the low pressure stage of the rectification system, rectifying said major and minor portions of the air to produce said oxygen, nitrogen and substantially pure oxygen, and periodically reversing the flow of air and nitrogen and of the air and oxygen through their respective paths in said heat exchange zones, whereby upon each of said reversals the nitrogen and oxygen substantially completely remove the carbon dioxide deposited during the preceding step of the process in the paths through which the nitrogen and oxygen flows respectively.

8. A process for producing oxygen by the liquefaction and rectification of air, which comprises passing a stream of nitrogen rectification product through one of a pair of regenerators while simultaneously passing a stream of air through the other of said regenerators, passing a stream of oxygen rectification product through one of a second pair of regenerators while simultaneously passing air through the other of said pair of regenerators, cooling the air passing through said regenerators to a temperature close to its condensation point at the pressure prevailing in its flow path through said regenerators, subjecting the thus cooled air to rectification to produce said oxygen and nitrogen rectification products and an additional rectification product, passing a stream of additional rectification product through at least the colder portions of all of said regenerators in indirect heat exchange relation with the gaseous media passing therethrough, removing a portion of said additional rectification product as product uncontaminated by condensibles removed from the air stream, recirculating the remainder through its flow path

extending through at least the colder portions of said regenerators and periodically reversing the flow of nitrogen and air through the respective regenerators of the first-mentioned pair and the flow of oxygen and air through the respective regenerators of the second-mentioned pair, thereby effecting the substantially complete removal of carbon dioxide from the air in its passage through said regenerators and upon each reversal effecting the substantially complete removal of the carbon dioxide thus deposited in the regenerators during the preceding step of the process.

9. A process for producing oxygen by the liquefaction and rectification of air, which comprises passing a stream of nitrogen rectification product through one of a pair of regenerators while simultaneously passing a stream of air through the other of said regenerators, passing a stream of oxygen rectification product through one of a second pair of regenerators while simultaneously passing air through the other of said pair of regenerators, cooling the air passing through said regenerators to a temperature close to its condensation point at the pressure prevailing in its flow path through said regenerators, subjecting the thus cooled air to rectification to produce said oxygen and nitrogen rectification product, passing the stream of substantially pure oxygen rectification product through at least the colder portions of all of said regenerators in indirect heat exchange relation with the gaseous media passing therethrough, removing a portion of said substantially pure oxygen rectification product as product uncontaminated by condensibles removed from the air stream and recirculating the remainder through its flow path extending through at least the colder portions of said regenerators, and periodically reversing the flow of nitrogen and air through the respective regenerators of the first-mentioned pair and the flow of oxygen and air through the respective regenerators of the second-mentioned pair, thereby effecting the substantially complete removal of carbon dioxide from the air in its passage through said regenerators and upon each reversal effecting the substantially complete removal of the carbon dioxide thus deposited in the regenerators during the preceding step of the process.

10. A process for producing oxygen by the liquefaction and rectification of air, which comprises passing a stream of nitrogen rectification product through one of a pair of regenerators while simultaneously passing a stream of air through the other of said regenerators, passing a stream of oxygen rectification product through one of a second pair of regenerators while simultaneously passing air through the other of said pair of regenerators, cooling the air passing through said regenerators to a temperature close to its condensation point at the pressure prevailing in its flow path through said regenerators, subjecting the thus cooled air to rectification to produce said oxygen and nitrogen rectification products and argon, passing a stream of argon through said regenerators in indirect heat exchange relation with the gaseous media passing therethrough, withdrawing a portion of the argon as product, passing the remainder in heat exchange relation with a refrigerant and also in heat exchange relation with at least a portion of the stream of nitrogen supplied to the first-mentioned pair of regenerators, thereby cooling said argon, recirculating the cooled argon through its flow path in said regenerators and periodically reversing the flow of nitrogen and air through the respective regenerators of the first-mentioned pair and the flow of oxygen and air through the respective regenerators of the second-mentioned pair, thereby effecting the substantially complete removal of the carbon dioxide thus deposited in the regenerators during the preceding step of the process.

11. A process for producing oxygen by the liquefaction and rectification of air, which comprises passing nitrogen and oxygen rectification products through a heat exchange zone, passing a stream of air through said heat exchange zone to recover the cold content of the nitrogen and oxygen rectification products thereby cooling the air to a temperature close to its condensation point at the pressure prevailing in said heat exchange zone and effecting substantially complete removal of carbon dioxide from the air in its passage through said heat exchange zone, subjecting the thus cooled air to rectification to produce said oxygen and nitrogen rectification products and also an additional rectification product, periodically reversing the flow of air and nitrogen through said heat exchange zone, passing the said additional rectification product through at least the colder portion of said heat exchange zone in indirect heat exchange relation with the air and the nitrogen passing through said heat exchange zone, and removing a portion of said additional rectification product as product uncontaminated by condensibles removed from the air stream and recirculating the remainder through at least the colder portion of said heat exchange zone.

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No references cited.