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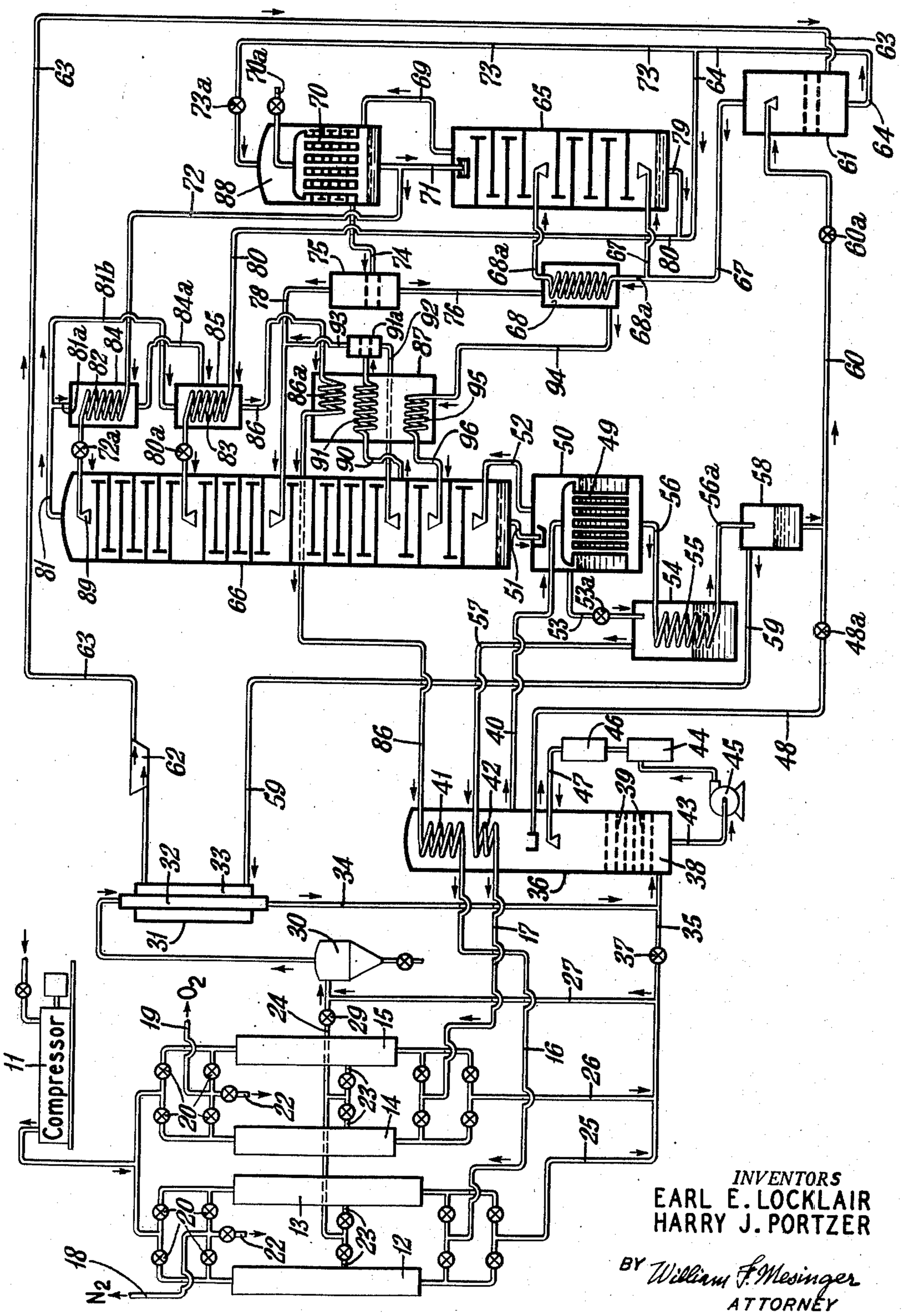

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PROCESS AND APPARATUS FOR SEPARATING GAS MIXTURES

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This invention relates to an air separation cycle for producing gaseous oxygen and more specifically concerns a method and apparatus for fractionating air in a low pressure air separation cycle to produce gaseous oxygen in a state of substantial purity with high oxygen recovery and reduced power requirement.

Heretofore there have been two common methods of air separation which have been generally designated as the single stage or column and the two stage or double column cycles. In the single column cycle all of the rectification trays are located in a single column operating at about 6 p. s. i. g. Air is fed to a condenser in the base or reboiler portion of the column at a pressure which is generally sufficient for total condensation of the air by heat exchange with the oxygen bath of the reboiler, the minimum necessary air pressure being about 51 p. s. i. g. The single column cannot separate the air completely and operates with a relatively low oxygen recovery. In the customary double column cycle an upper or second stage rectifying column operates at about 6 p. s. i. g. and a lower or first stage rectifying column operates at a sufficient pressure to condense pure nitrogen by heat exchange with boiling oxygen in the reboiler at the base of the upper column, the required pressure being about 67 p. s. i. g. The major portion of the air supply is fed to this first stage or lower column and is rectified to pure nitrogen vapor for condensation, and an oxygen-enriched liquid for transfer as feeds to the upper column. The double column devices can separate the air completely into nitrogen and oxygen and are the preferred types in general commercial use. In some instances a minor portion of the air supply is fed as saturated vapor directly into the upper column, but the higher recovery of oxygen is accompanied by the higher power cost of compressing the air to at least 67 p. s. i. g.

A principal object of the present invention is to obtain substantially complete separation of oxygen from air with reduced power consumption by combining the lower air supply pressure requirement of the single column cycle with the air separating ability of the double column type of cycle. To achieve such object according to the invention, the pure oxygen bath is reboiled by a heat exchange that condenses a fraction of cooled supply air as in the single column cycle, but the pure nitrogen that is needed as a feed for the final stage of rectification is condensed at a pressure below that at which the supply air is condensed, by a heat exchange which evaporates at a lower pressure a portion of the fraction of the supply air which was condensed by heat exchange with the reboiling oxygen. The condensation of nitrogen in heat exchange with boiling pure oxygen which characterizes the customary double column cycle is thus avoided.

Prior attempts to provide a lower pressure cycle which will recover substantially all the oxygen in the air have been characterized by condensing pure nitrogen at the pressure at which the supply air is condensed by using an intermediate purity reflux liquid for the refrigerating medium. The cycle of the present invention, however,

is distinguished in that after a first fraction of air is partially liquefied by heat exchange with boiling oxygen, the uncondensed portion thereof is turbine expanded and the turbine exhaust is rectified to form pure nitrogen which is condensed to form the required pure nitrogen liquid.

According to the general features of the present invention, compressed air at a relatively lower pressure than is customary for two-stage cycles, is cooled to near-saturation temperature and atmospheric impurities such as water and carbon dioxide are removed. This may be accomplished by any well known method, and the specific main heat exchange and impurity removal system described herein is merely illustrative. In the illustrative example, the air is cooled in regenerators which are unbalanced for self-cleaning by a side bleed stream as taught by M. Frankl in United States Patent 2,002,941. This side bleed air stream may be used for turbine preheat as shown by P. K. Rice in United States Patent 2,619,810. The nearly saturated air leaving the cold ends of the regenerators and the turbine preheat coil may be given a final impurity removal cleanup by a recirculating scrubber-filter-adsorber system as shown by R. W. Houvener in United States Patent 2,572,933. The regenerators are cooled by the separation products which are previously warmed to nearly the feed air dew point by heat exchange with scrubbed air as taught in the above mentioned Rice patent. A small fraction of clean liquid air is withdrawn from the scrubber to maintain a constant liquid level therein.

According to the invention a cold clean air vapor stream obtained from any suitable cooling and cleaning means, which according to the example is the air vapor stream after the scrubber treatment, is partially liquefied and the liquid and vapor phases are separated into vapor and liquid streams in a first separator. This vapor stream fraction is warmed slightly and expanded in a turbine with production of external work to produce the low temperature refrigeration required to operate the plant. The turbine exhaust is led to a second separator. The liquid stream fraction of the first separation is throttled into the second separator together with the small fraction of clean liquid air taken from the scrubber. The purpose of this second separator is to provide a vapor feed for a lower column which is as rich in nitrogen as possible, and an oxygen-enriched liquid air fraction that is divided into two parts.

The lower column is fed below its trays with the nitrogen-enriched vapor from the second separator, is fed intermediate the trays with a nitrogen-enriched liquid formed by totally condensing a portion of the nitrogen-enriched vapor from the second separator, and is fed above its trays with a nitrogen reflux liquid which is part of the condensed vapor product of the rectification effected by the lower column. The feeds to the lower column are rectified therein to form an oxygen-enriched liquid product which leaves the bottom of the lower column and the nitrogen vapor which is condensed by heat exchange with one part of the previously mentioned oxygen-enriched liquid air fraction of the second separator. The surplus portion of the condensed nitrogen not returned to the top of the lower column is drawn off for use as top feed to a final rectification stage which is effected by a low pressure upper column.

The upper column is fed at the top with the surplus portion of nitrogen liquid after the latter has been subcooled and throttled. At a slightly lower level, this upper column is fed with an oxygen-enriched liquid stream obtained by joining the oxygen-enriched liquid product of the lower column with a second portion of the oxygen-enriched liquid air from the second separator. At a still lower level a vapor stream is fed to the column which is characterized by having an oxygen to nitrogen ratio

suitable for the point of admission but which contains more argon than exists in the column vapor at this feed point. Considerably lower in the column is a level from which vapor is withdrawn, partially liquefied, and to which the liquid fraction thereof is returned. The vapor fraction remaining after such partial condensation is enriched in argon, and is used to increase the argon content of the next higher vapor feed. The next lower feed to the column is an oxygen-rich vapor which is relatively low in argon when compared to the amount of argon present in the column at this feed point. The lowest feed is high purity oxygen vapor from the main condenser.

An actual plant requires additional heat exchangers as will be explained in greater detail below. In summarizing the above description the chief characteristics of this cycle include the following:

(1) The supply air is compressed to only enough pressure for partial liquefaction of cold air by heat exchange with the boiling oxygen from the bottom of the low pressure stage or upper column.

(2) The unliquefied portion of the supply air stream is expanded in a turbine to an intermediate pressure.

(3) The turbine exhaust vapor is rectified in a lower column at the intermediate pressure to form high purity nitgrogen vapor which can be condensed and used in part to provide upper column top reflux liquid.

(4) The upper column is fitted with extra feeds, bypasses, and heat exchangers to aid in moving the argon up the column for ultimate discharge with the effluent or waste nitrogen. This permits the attainment of high oxygen purity at the base of the upper column and reduces the quantity of heat that must be transferred to this oxygen from the condensing air.

Other objects, features and advantages of the present invention will be readily apparent from the following detailed description of a preferred embodiment thereof taken in conjunction with the accompanying drawing, in which:

Fig. 1 is a diagrammatic flowsheet of the operating cycle illustrating principles of the present invention.

As shown in Fig. 1, the low pressure air separating system embodying features of the present invention is provided with air at a relatively low pressure, as for example approximately 3 to 4 atmospheres pressure, by means of a compressor unit **11**. To remove moisture and carbon dioxide from the compressed air, the air is cooled in the usual manner in conventional cold accumulators or regenerators **12**, **13**, **14** and **15**. Reversing heat exchangers can be used instead of regenerators.

As illustrated, separated column products, comprising gaseous nitrogen and oxygen, are passed through conduits **16** and **17** into cold ends of the regenerators **12** and **14**, respectively, and out the warm ends at **18** and **19** in the usual manner to cool and clear the regenerators of frozen deposits of moisture and carbon dioxide while counterflowing compressed air is introduced into the regenerators **13** and **14** by proper operation of the reversing valves **20** to cool and freeze the carbon dioxide and moisture content out of the air. The flows are switched to the opposite regenerators for a subsequent period and by operating the reversing valves **20** in a periodic sequential order, a substantially continuous flow of counterflowing air being cooled, and separated gas products being warmed is assured. The air loss of blowdown may be directed through a blowdown branch connection **22** and discharged into the atmosphere.

To assure self cleansing of the regenerator units **12**, **13**, **14** and **15**, the regenerator flows are unbalanced so that only a major portion of the supply air is completely cooled in the colder parts of the regenerators. By this procedure a minor portion of the air being cooled in each regenerator is extracted at points **23** at a temperature below the freezing point of water but slightly above the freezing point of carbon dioxide. This side bleed air enters a bleed line **24** and is mixed with a portion of the colder, substantially carbon dioxide-free air leaving the cold ends of the regenerators through conduits **25** and **26** by means of a branch connection **27**. The proportion of partially cooled air to be combined with the colder air is so balanced as to produce a gas mixture at a temperature below the freezing point of carbon dioxide at the existing air pressure. For example, assuming a withdrawal of about 4.9 cu. ft. per 100 cu. ft. of cooling air in the regenerator at a temperature of about —94° C., upon mixture with about 19.5 cu. ft. of relatively clean air from the cold end of the regenerators at a temperature close to its saturation temperature (about —176° C.), a composite stream at approximately —160° C. is produced. At this temperature practically all of the carbon dioxide in the bleed-off air is precipitated as snow. A valve **29** in bleed line **24** controls the flow of partially cooled air so as to vary the mixture temperature within a reasonable range below the fusion point of carbon dioxide.

As previously described, most of the carbon dioxide in the undiverted air is deposited in the regenerator cold end. Most of the CO_2 in the side bleed air is precipitated by chilling with colder substantially clean air, and the mixture is subjected to a subsequent clean-up step. For this purpose, the carbon dioxide-entrained air is first introduced into a separating device in the form of a whirling or centrifuge apparatus **30** and the carbon dioxide is conveniently and simply separated from the air and removed in the form of snow.

Because the mixture of the streams of air in the bleed line **24** and the connecting line **27** is led directly into separating device **30**, practically all of the carbon dioxide precipitation takes place within the confines of the separating device **30**. In this way only a small percentage of carbon dioxide precipitates outside the separation device **30**, thus reducing to a minimum the possibility of harmful deposit of solid carbon dioxide in the equipment.

The relatively carbon dioxide-free air stream leaving the centrifuge apparatus **30** may possibly contain a small percentage of gaseous carbon dioxide of the order of two or three parts per million. Consequently, further purification of the relatively clean air is carried out in a scrubber circuit. Before being purified, this air is cooled to near-saturation temperature in a turbine preheat coil or heat exchanger **31**. Such heat exchanger may comprise an air flow passage **32** surrounded by a pass **33** containing a counterflowing cooling agent of air vapor. The near-saturated, relatively clean air leaving the pass **32** is passed through conduit **34** leading into a conventional scrubber unit **36**. At the time of entering the scrubber **36**, this air joins conduit **35** carrying the major portion of the relatively clean regenerator cooled air from the conduits **25** and **26**, which remains after diversion through conduit **27** of that required to cool the air in the bleed line **24** to the desired mixture temperature. The conduit **35** is controlled by an adjustable valve **37**. All the supply air thus enters the scrubber **36**.

The scrubber unit **36** comprises an elongated container having a sump or well **38** for holding a bath supply of liquid air and gas and liquid contact trays **39** above the sump. The air vapor, close to its saturation temperature, is delivered into the bath of liquid air in the scrubber sump **38** through the inlet line **35** which communicates with the interior of the scrubber at or near its bottom but below the level of the scrubber liquid, and clean saturated scrubber vapor, free of carbon dioxide contaminants, leaves the scrubber **36** through a scrubber vapor line **40**.

Suitable means are provided for providing the scrubber with make-up liquid. As a means for accomplishing this, the scrubber unit **36** is provided with liquefier coils **41** and **42** containing suitable refrigerated fluids, preferably gaseous nitrogen and product oxygen gas, respectively. These coils **41** and **42** are respectively connected with the conduits **16** and **17** for cooling the regenerators **12**, **13**,

14 and 15 in the manner previously explained hereinabove.

The scrubber liquid in the bottom of the scrubber 36 is withdrawn through a scrubber liquid line 43 and circulated through filters 44 by means of a pump 45 interposed in the scrubber liquid line 43. These filters 44 are usually provided in duplicate so that while one is in use, the other may be replaced or cleaned as by thawing. The filtered liquid is passed through a container 46 having an adsorbent material, such as silica gel, for adsorbing any remaining contaminants from the scrubber liquid which might conceivably impair the functioning of the air separation interchanger equipment. Thereafter, the cleaned liquid air is returned to the scrubber 36 by means of scrubber liquid return line 47 where it may be recycled through the scrubber circuit to perform its washing function on the counterflowing air vapor from line 35.

The liquefied scrubbed air formed by the liquefier coils 41 and 42, in excess of that needed for make-up purposes, may be extracted through a liquid air line 48, and, being free of deleterious substances, can be fed directly into the air separation apparatus. A valve 48*a* is provided to control the excess liquid flow and maintain a desired liquid level in the scrubber.

Thus, only highly purified air vapor and liquefied scrubbed air vapor enter the remainder of the system, contaminated scrubber liquid never being transferred outside the closed scrubber series circuit.

Before the scrubbed vapor is utilized in the separation equipment, it is used as an evaporating agent to gasify the highest purity oxygen liquid product from the final rectification stage of the separation cycle. To this end, the scrubbed air vapor in conduit 40 is passed through a main condenser 49 within an oxygen reboiler chamber 50 where, in heat exchange with liquid oxygen at a low pressure entering the chamber 50 through a conduit 51, part of the air vapor is condensed and flows cocurrently with the remaining vapor from the top of the condenser 49 downwardly, the heat exchange taking place by virtue of the relatively lower boiling temperature of the liquid oxygen at the lower pressure. The gaseous oxygen thus produced leaves chamber 50 upwardly through a conduit 52, and the remaining liquid oxygen leaves through a conduit 53. This liquid oxygen in the conduit 53 is transferred to a side condenser boiling chamber 54 where, in further heat exchange with a coil 55 through which passes the mixture of gaseous and condensed air vapor from the bottom of the main condenser 49 which is connected to coil 55 by conduit 56, the product liquid oxygen is completely evaporated and leaves the side condenser chamber 54 through a product oxygen gas outlet line 57. The heat of evaporation for the liquid oxygen is supplied by the gaseous air in the coil 55 condensing cocurrently as it travels downwardly, the liquid and gas air mixture finally emerging through outlet conduit 56*a* at the bottom of the side condenser coil 55.

After leaving the side condenser 54, the product oxygen gas, which is at a relatively low temperature, is subsequently superheated by connecting it to the liquefier coil 42 in the scrubber 36 and then passing it through the oxygen regenerators 14 and 15 in the manner described hereinabove.

According to the present invention, the vaporization of the oxygen column product is carried out in the main and the side condensers 50 and 54 at the lowest possible pressure to avoid the excessive power requirements usually associated with high pressures.

It will be noted that the change in composition of the air brought about by condensation causes the condensing temperature to be lower at the bottom of the main condenser 49. As a consequence, the net effect is a much lower temperature driving force at the bottom of condenser, which is a limiting factor in determining the condensing pressure, and hence the initial head pressure of the compressed air.

The side condenser 54 can be similar to the main condenser, the liquid oxygen being expanded to just above 1 atmosphere pressure by a throttle valve 53*a* before introduction into the side condenser, the evaporated oxygen leaving the side condenser at about the same pressure. As the partially condensed air from the main condenser 49 passes through the side condenser coil a further vapor fraction is concurrently condensed by heat exchange with the vaporizing oxygen.

As previously stated, the pressure conditions in the main condenser 49 and chamber 50 largely determine the pressure of the compressed air to be produced by the compressor 11. Thus in the above example, the compressed air would be supplied by compressor 11 at about 3 atmospheres pressure, usually less than 50 p. s. i. g., and the scrubber 36 operates at about the same pressure. In the specific example described, a compressed air supply of 44 p. s. i. g. has been found to give a satisfactory heat balance.

Rectification of the air is brought about in interchanger equipment comprising primarily a first stage or lower column 65 and a second stage or upper column 66, the former being primarily for the purpose of producing reflux liquid for said latter column 66, each column being fitted with customary liquid and gas contact rectifying trays.

The dual phase air mixture is delivered by line 56*a* to a first separator 58 where the air vapor is separated from the liquid air, the air vapor being sent by means of a conduit 59 through the pass 33 of the exchanger 31 for preheating by the warmer side-bleed air in pass 32 prior to work expansion in a turbine 62. The liquid from the separator 58 is joined with the excess scrubber liquid from conduit 48 and the combined stream in conduit 60 is throttled through valve 60*a* into another or second separator 61. The turbo-expanded air also enters this separator through turbine discharge conduit 63. The nitrogen-rich vapor from this second separator passes through conduit 67 connecting to the bottom of the lower column 65 which receives only a major portion of this vapor, the remainder being split off through a branch conduit 68*a* which has interposed a heat exchange passage within the lower column secondary condenser 68. Such remainder is completely cocurrently condensed by heat exchange with cocurrently evaporating liquid air, and is then fed by the upper part of conduit 68*a* into the column 65 at an intermediate point thereof. The oxygen-enriched liquid fraction emerges from the second separator 61 in bottom connected conduit 64, and a minor part of it is joined by the oxygen-enriched liquid product in conduit 79 from the bottom of the lower column 65. Conduits 64 and 79 join in a conduit 80 and the combined stream in conduit 80 at about 16 p. s. i. g. is directed through subcooler heat exchanger 85 for subcooling by effluent nitrogen, and is throttled through valve 80*a* into a high region of the upper column 66 as a reflux liquid feed at about 2 p. s. i. g. This stream is in some respects analogous to the crude oxygen transfer liquid feed in conventional single and double column cycles and the subcooling step minimizes flash-off from throttling.

As previously indicated, the lower column 65 is fed by nitrogen-rich vapor at or near the bottom, and nitrogen-rich liquid at an intermediate point. A nitrogen reflux liquid feed at the top is also required, therefore the dome of the lower column is provided with a nitrogen gas line 69 for transferring the nitrogen gas produced by rectification in the lower column to a reflux condenser 70 where it is condensed into the liquid phase. This liquid nitrogen, constituting the source of supply of nitrogen reflux liquid feeds for the rectifying equipment, is introduced to the upper ends of the lower and upper

columns **65** and **66** through split nitrogen transfer conduits **71** and **72** respectively.

For cooling and liquefying the gaseous nitrogen in the reflux condenser **70**, a major part of the oxygen-rich liquid air fraction in the conduit **64** is diverted by branch conduit **73** into a boiler chamber **88** surrounding condenser **70** after being throttled through an expansion valve **73***a* to a pressure below the pressure in the lower column, the throttling pressure being such as to depress the boiling temperature of the liquid fraction a few degrees below the liquefaction temperature of gaseous nitrogen in the reflux condenser **70**.

As a result, gaseous nitrogen at approximately the same pressure as in the lower column is condensed against a cocurrently evaporating mixture of cooler, relatively lower pressure liquid and gaseous oxygen-rich air fraction. A dome vent line **70***a* in the condenser **70** provides for the escape of non-condensibles into the atmosphere. Cocurrent instead of countercurrent evaporation is preferably used in the reflux condenser to keep the head pressure low. The partially vaporized air formed by this heat exchange transaction leaves the reflux condenser **70** by way of conduit **74**, and enters the separator vessel **75** for separating the liquid and gaseous phases. The liquid portion emerges in conduit **76** connecting to secondary condenser chamber **68** where the relatively higher pressure nitrogen vapor in the line **68***a* is cocurrently condensed. By this heat exchange such liquid portion undergoes partial cocurrent evaporation. The gas from the separator **75** progresses through a flow line **78** for subsequent rectification in the upper column **66**.

The upper column **66** comprises an insulated elongated tower having means for receiving and rectifying the liquid and gaseous feeds of varying compositions and temperatures into their component parts. As illustrated in Fig. 1, the upper column is divided into six sections, a column feed being introduced at each section. In the topmost section, gaseous nitrogen effluent or waste nitrogen resulting from the rectification process in the upper column **66** is removed from the dome of the column via nitrogen gas line **81**. The waste nitrogen stream is split into streams **81***a* and **81***b*, stream **81***a* flowing through a nitrogen heat exchanger **84**, where it subcools the counterflowing, relatively higher pressure nitrogen reflux liquid flowing in coil **82** interposed in the conduit **72**. Stream **81***b* passes through the cold leg of a kettle transfer liquid heat exchanger **85**, which subcools the kettle transfer liquid in a coil **83** interposed in the conduit **80**. The stream **81***a* is recombined with stream **81***b* by a connection **84***a* from exchanger **84** to the warmer leg of exchanger **85** and the combined stream passes through the warmer leg of the kettle transfer heat exchanger **85** for further subcooling of the kettle transfer liquid. Finally, the waste nitrogen in stream **86** from the warm end of exchanger **85** passes through a passage **86***a* extending through the colder part of an upper column secondary condenser **87** and thence to the nitrogen liquefier coil **41**, after which it leaves the system via the regenerators **12** and **13**. The subcooled nitrogen reflux liquid from the nitrogen heat exchanger coil **82** is expanded past throttle valve **72***a* and delivered into the upper column **66** through nitrogen reflux inlet **89**.

At a point some trays below the nitrogen reflux liquid inlet **89**, the subcooled kettle transfer oxygen-enriched liquid air from the kettle transfer heat exchanger coil **83** is throttled through expansion valve **80***a* and introduced into the upper column **66**.

The vapor in the line **78** from the separator **75** is fed directly into the upper column **66** at an intermediate section thereof below the kettle transfer liquid inlet **80***a*.

Below the vapor inlet line **78**, vapor is extracted from the inside of the upper column **66** through an extraction conduit **90** and passed through a warm-to-cold passage **91** extending completely through the upper column secondary condenser **87** where it is partially cocurrently liquefied. The liquid and gas phases are separated in a vessel **91***a*, the oxygen-enriched and argon-deleted liquid extract being recycled into the upper column **66** as by means of line **92** at approximately the same level as the extraction conduit **90**. The nitrogen and argon-enriched vapor from the separator **91***a* is delivered to the line **78** by means of a branch connection **93** so that the combined vapor stream enters the low pressure column at an intermediate point above the vapor takeoff **90** and below the kettle transfer liquid feed **80***a*. The basir purpose of the previously described partial condensation of column vapor is to transfer a substantial portion of the argon from the lower part to the upper part of the upper column without substantially changing the oxygen content at any point in the column. By so doing, high purity liquid oxygen can be attained at the bottom of this column, and the quantity of heat to be transferred to this boiling oxygen from condensing air is minimized.

The partially evaporated liquid air from the lower column secondary condenser **68** passes through conduit **94** to a passage **95** through the warmer part of the upper column secondary condenser **87** where it is completely cocurrently evaporated. This vapor enters a lower region of the upper column **66** substantially below the conduit **90** through an inlet **96**.

The lowest section of the upper column **66** receives the gaseous oxygen through conduit **52** from the main condenser boiling chamber **50**, and dispenses liquid oxygen separation product through the outlet conduit **51** to the chamber **50** as previously described.

The pressures maintained in the upper column **66** are relatively low, being governed largely by the withdrawal pressure of the liquid oxygen in the conduit **51** and the entering gaseous oxygen pressure in the conduit **52**. Consequently, the pressures in the lower regions of the upper column approximate that of the oxygen in the main condenser **50**, and the pressures in the upper areas of the upper column **66** are of slightly lower order because of the effects of the rectification process operating therein. The pressure at the top of the column must be sufficiently higher than the effluent nitrogen outlet pressure at conduit **18** to effect circulation of the nitrogen through its flow paths at adequate velocity.

Using the above-described apparatus, 99 percent gaseous oxygen may be obtained from the side condenser without employment of the 5 atmosphere air head pressure usually associated with gaseous oxygen plants. It is to be understood that when regenerators or passage exchanging heat exchangers are used for warming the product oxygen, such oxygen product is slightly contaminated by water and carbon dioxide and by nitrogen of residual air of reversing operation for cooling and cleaning the regenerators, so that the end product purity may be 98.5% oxygen. If an uncontaminated oxygen product is required, the product oxygen is not passed through regenerators but may be heated in embedded coils in the air-nitrogen regenerators or in a non-reversing pass in a reversing heat exchanger plant.

From the above description it is believed apparent that the system of this invention constitutes an efficient separation cycle for producing oxygen with a lower air head pressure and smaller power costs than are usually associated with gaseous oxygen production plants. This improvement is obtained by:

(1) Compressing the supply air to only enough pressure for partial liquefaction by heat exchange with the boiling oxygen of product purity from the bottom of the upper column;

(2) Separation of, warming, and turbine expansion of the unliquefied portion of the supply air to an intermediate pressure between the supply pressure and the upper column pressure;

(3) Rectification of the turbine exhaust vapor and the liquid air fractions at the intermediate pressure in a lower column to form high purity nitrogen vapor which

in turn is condensed and used in part as upper column top nitrogen reflux liquid and as top nitrogen reflux liquid for the lower column;

(4) The use of extra feeds, bypasses, and heat exchangers to aid in transferring the argon from the lower part to the upper part of the upper column for ultimate discharge with the waste nitrogen to permit the attainment of a high purity in the oxygen liquid at the base of the upper column and to reduce the quantity of heat needed to be transferred to the boiling oxygen from the condensing air.

The closer approach to reversible cycle conditions resulting in lower power costs has been obtained without sacrifice of operating controllability. When the main air cooling heat exchange is of the regenerator or passage exchanging heat exchanger type there is a need for unbalancing the flows at the cold zones to insure against carbondioxide accumulation. This could be accomplished by passing a diverted portion of air backward through an unbalance coil passage in the regenerators and recooling this diverted air by preheating the turbine air. As illustrated, the unbalance is accomplished by side bleed withdrawal of a portion of air at **23**. The carbon dioxide content of the side bleed is frozen by admixture therewith of cold end diverted air in an amount about four times the amount of the side bleed air. This chilling is found to precipitate substantially all of the carbon dioxide so that it can be readily removed by cyclone type separators or filters or a combination thereof illustrated at **30** and the operating life of the heat exchanger **32** is extremely long. This admixture of a relatively large amount of cold end air with the side bleed air provides a mixture which is closer to the warm end temperature of the turbine air in passage **33** but which is of large enough volume for very efficient heat exchange. A further result is that the slight amount of remaining carbon dioxide is spread over a large heat exchanger surface area which results in long service life of the heat exchanger **32** so that it would be unnecessary and uneconomical to install such heat exchanger unit **31** in duplicate. A further reason for the effective carbon dioxide removal is that the turbine inlet air for this cycle need not have as high a temperature because of the substantially larger volume of air available for expansion in the turbine. The warm end temperature for the heat exchanger unit thus is well below the temperature for effective freezing of carbon dioxide at the air supply pressure.

The low head pressure possible with this invention is attained by condensing only a small amount of the air to make scrubber liquid by coils **41** and **42** and condensing a large fraction of the air by heat exchange with boiling oxygen of product purity in the successive condensers **49** and **55**. The stepwise condensation illustrated is preferred because part of the oxygen can be boiled in reboiler chamber **50** to provide upper column vapor at upper column **66** pressure and the product oxygen can be evaporated in chamber **54** at a slightly lower pressure and temperature so as to effect closer approaches to reversibility and liquefaction of slightly more air. This combined with the operation of the lower column **65** at an intermediate pressure (about 1 atmosphere higher than upper column pressure) and the passage of an oxygen-enriched vapor into the lower part of the upper column through line **94**, reduces the amount of oxygen vapor required to be fed through line **52** to obtain high purity oxygen product.

A second reason for the low head pressure is the provision of the separate nitrogen liquefying condenser **70** that receives nitrogen of the lower column and the refrigeration of the same by the liquid air fraction (separated by second separator **61** after a first throttle expansion through valve **60***a* to intermediate pressure, and passed to the chamber **88** through line **73** after a second throttle expansion through valve **73***a* to the lower column pressure. The nitrogen at intermediate pressure is thus condensed by boiling this liquid air fraction at low pressure so that a nitrogen pressure lower than that of the head pressure is effective to provide all the liquid nitrogen needed for top reflux feeds for both columns.

Another reason why low head pressure suffices is that less oxygen vapor feed through pipe **52** is required because of the provision of the auxiliary condenser system **87** for effectively reducing the argon content in the lower part of the upper column and transferring such argon to upper parts of such column. Thus less condensation need be effected by the oxygen reboiler and the net result is the production of the needed amount of liquid air while leaving an adequate amount of gaseous air fraction to be taken from first separator **58** through line **59** to the expansion turbine **62**. This amount of vapor, when warmed in heat exchange **33** and expanded to the intermediate pressure, is found to be sufficient to provide the low temperature refrigeration requirement. At the same time at least sufficient air vapor is thus available for efficient operation of the lower column to provide the needed amount of nitrogen which when liquefied supplies adequate nitrogen liquid reflux for the upper column.

It is found that in the lower regions of the upper column the equilibrium curve for oxygen-nitrogen-argon includes a region of inflection at high oxygen purities. Since the actual liquid and vapor compositions in the column are in part determined by the ratio of descending liquid to ascending vapor, the liquid-vapor ratio at the bottom of the column must be kept low because of such inflection of the equilibrium. This, due to the argon, is in contrast to an ideal oxygen-nitrogen equilibrium condition which permits high liquid-vapor ratios. Thus above the region of inflection of the equilibrium curve it is found highly desirable to increase the liquid-vapor ratio so that the actual compositions of vapor and liquid may closer approach their equilibrium values.

In this cycle the heat exchange system **87** accomplishes the desired effects by withdrawal at **90** of argon-containing oxygen-rich vapor at a point above the aforesaid inflection zone, subjecting this vapor to a partial condensation (about 70%) in the coil **91**, separating the remaining vapor from the liquid in separator **91***a*, passing the vapor, which contains most of the argon, to a point of the column above the withdrawal point **90** as by joining it with the vapor feed **78** by connection **93**, and returning the liquid, which is very low in argon, back to the column through return connection **92**. The liquid returned helps effectively to maintain desired near-equilibrium compositions above the point of introduction which is preferably at about the same level as the withdrawal point **90**. One effect is to force argon up toward the top of the column; simultaneously nitrogen is forced into the lower zone of the column from the vapor feed line **96**. Both effects are beneficial in increasing the liquid vapor ratio at the lower end which results in a smaller than usual required heat flow in the oxygen reboiler **50** which in turn helps achieve lower initial head pressures as well as making available a larger amount of air vapor for turbine expansion.

In the cycle as previously described, the partial external condensation of column vapor is preferably effected by heat exchange at first with vaporized liquid portion remaining from partial evaporation of the liquid air fraction which was used to condense nitrogen and which is passed through heat exchange passage **95** interposed in conduit **94**; and lastly by heat exchange with effluent nitrogen to the desired extent by coil or passage **86***a* interposed in the effluent nitrogen conduit **86**. However, the improvement may be applied to upper columns in other air separation cycles for similar beneficial effects by effecting the partial condensation of column vapor by heat exchange with other suitable fluids of the cycle, for example expansion of some of the crude oxygen to upper column

pressure and evaporating the liquid portion against the condensing vapor.

The effect of condensing a large amount of high purity oxygen vapor at low pressure reduces by a like amount the quantity of nitrogen which must be condensed at higher pressures for use as reflux liquid at the top of the upper column. Since the pressures at which the several vapors condense are lower, the irreversibility of the cycle is greatly reduced, thus permitting high purity oxygen at a high yield to be produced at a substantial power saving.

It may be noted that oxygen of highest purity can be obtained as a final product by modifications of the initial air cooling heat exchanger system to avoid the use of oxygen-air regenerators 14 and 15. For example, as is known to those skilled in the art, the product oxygen can be warmed by passage through embedded coils in the nitrogen-air regenerators or when passage exchanging heat exchangers are used the oxygen would be passed through a non-reversing passage.

It may be noted that the description mentions cocurrent evaporation and condensation at various points. While cocurrent heat exchange is preferred it is not essential to the invention, nor is the physical separation of the main and side condensers which could be combined in a single device. Also, certain auxiliary equipment shown in the specific embodiment such as kettle transfer heat exchanger 68, nitrogen heat exchanger 84, and the heat exchange system for cooling and conditioning the air and warming the effluent nitrogen and oxygen products which are described for this particular cycle heat balance may be modified or changed to different equipment for cycles having a different heat balance. Thus, such equipment is not to be considered limiting parts of the invention and modifications may be effected without departing from its spirit and scope.

What is claimed is:

1. In a cycle for the low temperature separation of air to produce oxygen of substantial purity by partial liquefaction of compressed air and low temperature rectification of liquid and vapor fractions of the air in stages including a stage of rectification at low pressure wherein an upper effluent comprising mainly nitrogen and a lower product oxygen is produced, the improvements comprising compressing the air to be separated to only that supply pressure at which it, after cooling, will partially condense by heat exchange against boiling liquid product oxygen of the low pressure rectification, effecting such partial condensation of the air, expanding the resultant gas fraction and at least part of the resultant liquid fraction to an intermediate pressure between the supply pressure and said low pressure, effecting a separation at intermediate pressure of the expanded vapor fraction to produce an intermediate nitrogen product, effecting condensation of the intermediate nitrogen product by heat exchange against a portion of said liquid fraction after expansion of same to said low pressure, and utilizing at least part of such condensed nitrogen for top reflux feed to said low pressure rectification.

2. A cycle for the low temperature separation of air according to claim 1 in which said gas fraction after partial condensation of the air is warmed by heat exchange with a warmer portion of air prior to expansion and the expansion is effected with production of external work providing low temperature refrigeration for the system.

3. A cycle for the low temperature separation of air according to claim 1 in which said partial condensation of air is effected in successive stages, the first of which is by heat exchange with reboiling liquid oxygen to provide vapor for the low pressure rectification at said low pressure and a subsequent stage is by heat exchange with evaporating product oxygen at slightly lower pressure.

4. A cycle for the low temperature separation of air according to claim 1 in which said liquid fraction is throttle expanded to the intermediate pressure and separated into resulting liquid and gaseous phases, the gaseous phase

is joined with the expanded vapor fraction for the separation providing the intermediate nitrogen product, and the portion of said liquid fraction used for effecting condensation of the intermediate nitrogen product is taken from said resulting liquid phase.

5. A cycle for the low temperature separation of air according to claim 1 in which said separation at intermediate pressure provides also a crude oxygen product which is fed to a zone of said low pressure rectification below the top zone, and including the steps of withdrawing from a zone of rectification substantially below the crude oxygen feed but above the lowest zone a substantial amount of vapor which contains argon, subjecting the withdrawn vapor to partial condensation by heat exchange with colder fluid of the system, separating and returning the liquid so produced to the rectification, and passing the vapor remainder of said partial condensation to a level of said rectification above the point of withdrawal of said substantial amount of vapor.

6. A cycle for the low temperature separation of air according to claim 5 in which said colder fluids of the system includes a vapor enriched in oxygen product by evaporation of the liquid remainder of partial evaporation of said portion of said liquid fraction after the heat exchange with the intermediate nitrogen product.

7. In a cycle for the low temperature separation of air to produce oxygen of substantial purity by partial liquefaction of compressed air and low temperature rectification of liquid and vapor fractions of the air in stages including a stage of rectification at low pressure wherein an upper effluent comprising mainly nitrogen and a lower product oxygen is produced, and in which the air is treated at pressures below about 75 p. s. i. g. by steps including heat exchanges and separations producing several liquid and vapor feeds for said low pressure rectification comprising a liquid nitrogen feed to the upper zone of said rectification, a crude oxygen liquid feed to a zone below said upper zone, and a vapor feed of reboiled product oxygen to the lowest zone of said rectification, the improvement comprising withdrawing from a zone of rectification substantially below the crude oxygen feed but above the lowest zone a substantial amount of vapor which contains argon, subjecting the withdrawn vapor to partial condensation by heat exchange with colder fluid of the system, separating and returning the liquid so produced to the rectification, and passing the vapor remainder of said partial condensation to a level of said rectification above the point of withdrawal of said substantial amount of vapor.

8. A cycle for the low temperature separation of air according to claim 7 in which said colder fluids of the system include a fraction in vapor state at said low pressure and having higher oxygen content than said crude oxygen such colder fluid after the heat exchange being fed to a zone of the rectification below said point of withdrawal of substantial amount of vapor.

9. A cycle for the low temperature separation of air according to claim 7 in which said colder fluid of the system includes at least a portion of said upper effluent comprising nitrogen.

10. A cycle for the low temperature separation of air according to claim 7 in which said vapor feed of reboiled product oxygen is produced by heat exchange of such product oxygen with cold air at the supply pressure for partial condensation of a portion thereof.

11. In a cycle for the low temperature separation of air to produce oxygen of substantial purity by partial liquefaction of compressed air and low temperature rectification of liquid and vapor fractions in at least a stage of rectification at low pressure providing an upper effluent of mainly nitrogen and a bottom product of said oxygen and in which air at a supply pressure below 70 p. s. i. g. is cooled to low temperature by heat exchange with at least the upper effluent, the steps comprising effecting partial condensation of the cooled air at the supply pressure

by heat exchange against boiling liquid oxygen bottom product; separating the resultant liquid and vapor fractions of the air; expanding said vapor fraction to an intermediate pressure which is between the supply pressure and said low pressure; expanding said liquid fraction to said intermediate pressure; effecting a separation including rectification at intermediate pressure of said expanded vapor fraction and said liquid fraction to provide an intermediate nitrogen product and oxygen-enriched liquid portions; effecting condensation of said intermediate nitrogen product at intermediate pressure by heat exchange with at least part of said oxygen-enriched portions after expansion of same to about said low pressure; utilizing part of the condensed intermediate nitrogen for top reflux feed to said rectification at intermediate pressure and the balance for top reflux feed to said low pressure rectification; and utilizing the remainder of said oxygen-enriched liquid portions and the part thereof heat exchanged with said intermediate nitrogen product as feeds to said low pressure rectification.

12. In a cycle for the low temperature separation of air to produce oxygen of substantial purity by partial liquefaction of compressed air and low temperature rectification of liquid and vapor fractions in at least a stage of rectification at low pressure providing an upper effluent of mainly nitrogen and a bottom product of said oxygen and in which air at a supply pressure below 70 p. s. i. g. is cooled to low temperature by heat exchange with at least the upper effluent, the steps comprising effecting partial condensation of the cooled air at the supply pressure by heat exchange against boiling liquid oxygen bottom product; separating the resultant liquid and vapor fractions of the air; expanding said vapor fraction to an intermediate pressure which is between the supply pressure and said low pressure; expanding said liquid fraction to said intermediate pressure; effecting a second separation by separating the liquid which is enriched in oxygen from the vapor flashed off during expansion of said liquid fraction; passing the separated flash-off vapor and the expanded vapor fraction to an intermediate pressure rectification for separation therein providing a top intermediate nitrogen product and a bottom crude oxygen product; condensing said intermediate nitrogen product by heat exchange with at least part of the liquid enriched in oxygen from said second separation after expansion to about said low pressure; using liquefied intermediate nitrogen product in part for feed to the top of the intermediate pressure rectification and in part for top feed to the low pressure rectification; passing said crude oxygen product and a remainder of the liquid enriched in oxygen from said second separation to said low pressure rectification at a zone below the top feed zone; feeding the vaporized portion of the liquid enriched in oxygen employed for condensing intermediate nitrogen product to a zone of said low pressure rectification below the feed of said crude oxygen product; and feeding the unvaporized remainder of the liquid enriched in oxygen employed for condensing intermediate nitrogen product to a zone of said low pressure rectification next above the lowest zone.

13. A cycle for the low temperature separation of air according to claim 12 in which an argon containing vapor is withdrawn from said low pressure rectification at a zone above the lowest zone, is fractionally condensed by heat exchange with colder fluids of the system, is separated into liquid and gaseous remainder fractions, the liquid fraction is returned to the same zone, and the gaseous remainder is fed to the low temperature rectification at a higher zone.

14. A cycle for the low temperature separation of air according to claim 11 in which prior to expansion, said vapor fraction of the air is warmed by a heat exchange including cooling at least a part of the supply air and said expansion is with the production of external work.

15. In a cycle for the low temperature separation of air to product oxygen of substantial purity by partial liquefaction of compressed air and low temperature rectification of liquid and vapor fractions in at least a stage of rectification at low pressure providing an upper effluent of mainly nitrogen and a bottom product of said oxygen and in which air at a supply pressure below 70 p. s. i. g. is cooled to low temperature by passage through reversing heat exchange devices cooled and purged by at least the upper effluent, said devices being unbalanced by side bleed withdrawal of a portion of the air, the steps comprising effecting partial condensation of the cooled air at the supply pressure by heat exchange against boiling liquid oxygen bottom product; separating the resultant liquid and vapor fractions of the air; preheating said vapor fraction by heat exchange with at least part of said side bleed portion of air; expanding said vapor fraction to an intermediate pressure which is between the supply pressure and said low pressure; expanding said liquid fraction to said intermediate pressure; effecting a separation including rectification at intermediate pressure of said expanded vapor fraction and said liquid fraction to provide an intermediate nitrogen product and oxygen-enriched liquid portions; effecting condensation of said intermediate nitrogen product at intermediate pressure by heat exchange with at least part of said oxygen-enriched liquid portions after expansion of same to about said low pressure; utilizing part of the condensed intermediate nitrogen for top reflux feed to said rectification at intermediate pressure and the balance for top reflux feed to said low pressure rectification; and utilizing the remainder of said oxygen-enriched liquid portions and the part thereof heat exchanged with said intermediate nitrogen product as feeds to said low pressure rectification.

16. In a cycle for the low temperature separation of air to produce oxygen of substantial purity by partial liquefaction of compresesd air and low temperature rectification of liquid and vapor fractions in at least a stage of rectification at low pressure providing an upper effluent of mainly nitrogen and a bottom product of said oxygen and in which air at a supply pressure below 75 p. s. i. g. is cooled to low temperature by passing through reversing heat exchange devices cooled and purged by at least the upper effluent, said devices being unbalanced by side bleed withdrawal of a portion of the air, the steps comprising mixing with said side bleed portion a portion of colder air diverted from the air subsequent to its passage through the reversing heat exchange devices sufficient to reduce the temperature of the resulting mixture for solidification of substantial amounts of the carbon dioxide impurity in said side bleed air portion; treating the resulting mixture for removal of at least its solidified carbon dioxide impurity content; effecting partial condensation of the cooled air leaving a vapor remainder; preheating such vapor remainder by heat exchange with at least part of the treated side bleed mixture; expanding the preheated vapor remainder with production of external work; and passing the expanded remainder, and the liquid fractions of partial condensation including the treated side bleed mixture to the low temperature rectification for separation.

17. In a system for the low temperature separation of air including means for cooling and cleaning air at a supply pressure below 75 p. s. i. g. in heat exchange with at least the nitrogen effluent product in preparation for treatment in a low pressure rectifying column having an oxygen reboiler associated with the bottom thereof the combination therewith of means for feeding cooled air to the condenser side of said oxygen reboiler for partial liquefaction of the air; means for separating and expanding the vapor remainder to an intermediate pressure between the supply pressure and said low pressure; an intermediate pressure rectifying column connected to receive the expanded vapor; means for expanding the liquid fraction of said partial liquefaction to the intermediate pressure and passing the vapor portion to said intermediate pressure column; an intermediate product nitrogen condenser associated with the upper end of said intermediate

pressure column; means for refrigerating said intermediate nitrogen condenser by oxygen-enriched liquid expanded to about said low pressure; means for passing part of condensed nitrogen from the intermediate nitrogen condenser to the upper part of the intermediate pressure column and the remainder to the upper part of the low pressure column; and means for passing crude oxygen from the lower end of the intermediate pressure column to said low pressure column at a zone below the top.

18. A system for the low temperature separation of air according to claim 17 including heat exchanger means for preheating said vapor remainder prior to expansion with external work by a heat exchange with at least part of the supply air.

19. A system for the low temperature separation of air according to claim 17 including a second separator connected to receive said expanded liquid fraction and the expanded vapor remainder, and connected to the intermediate pressure column to pass separated vapor and expanded vapor thereto and connected by circuit means to pass at least a portion of separated liquid enriched in oxygen to said means for refrigerating said intermediate nitrogen condenser.

20. A system for the low temperature separation of air according to claim 17 which includes a side condenser having a boiling side connected for receiving liquid product oxygen from said reboiler and a condensing side connected to receive air from the condenser side of said reboiler for condensing additional fractions of the air to form the vapor remainder and the liquid fraction.

21. A system for the low temperature separation of air according to claim 17 which includes means for feeding resulting gas material of the oxygen-enriched liquid used for refrigerating said intermediate nitrogen condenser to said low pressure column; means for withdrawing from a lower level of said low pressure column a vapor containing argon, and fractionally condensing same in a heat exchanger cooled by colder fluids of the system; means for separating and returning the liquid so condensed to the low pressure column at about the withdrawal level; and means for passing the remaining vapor to a higher zone of said column.

References Cited in the file of this patent

UNITED STATES PATENTS

2,386,297	Dennis	Oct. 9, 1945
2,423,543	Yendall	July 8, 1947
2,433,508	Dennis	Dec. 30, 1947
2,547,177	Simpson	Apr. 3, 1951
2,626,510	Schilling	Jan. 27, 1953
2,655,796	Rice	Oct. 20, 1953
2,664,718	Rice	Jan. 5, 1954
2,664,719	Rice	Jan. 5, 1954
2,753,698	Jakob	July 10, 1956
2,762,208	Dennis	Sept. 11, 1956