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SEPARATION OF AIR

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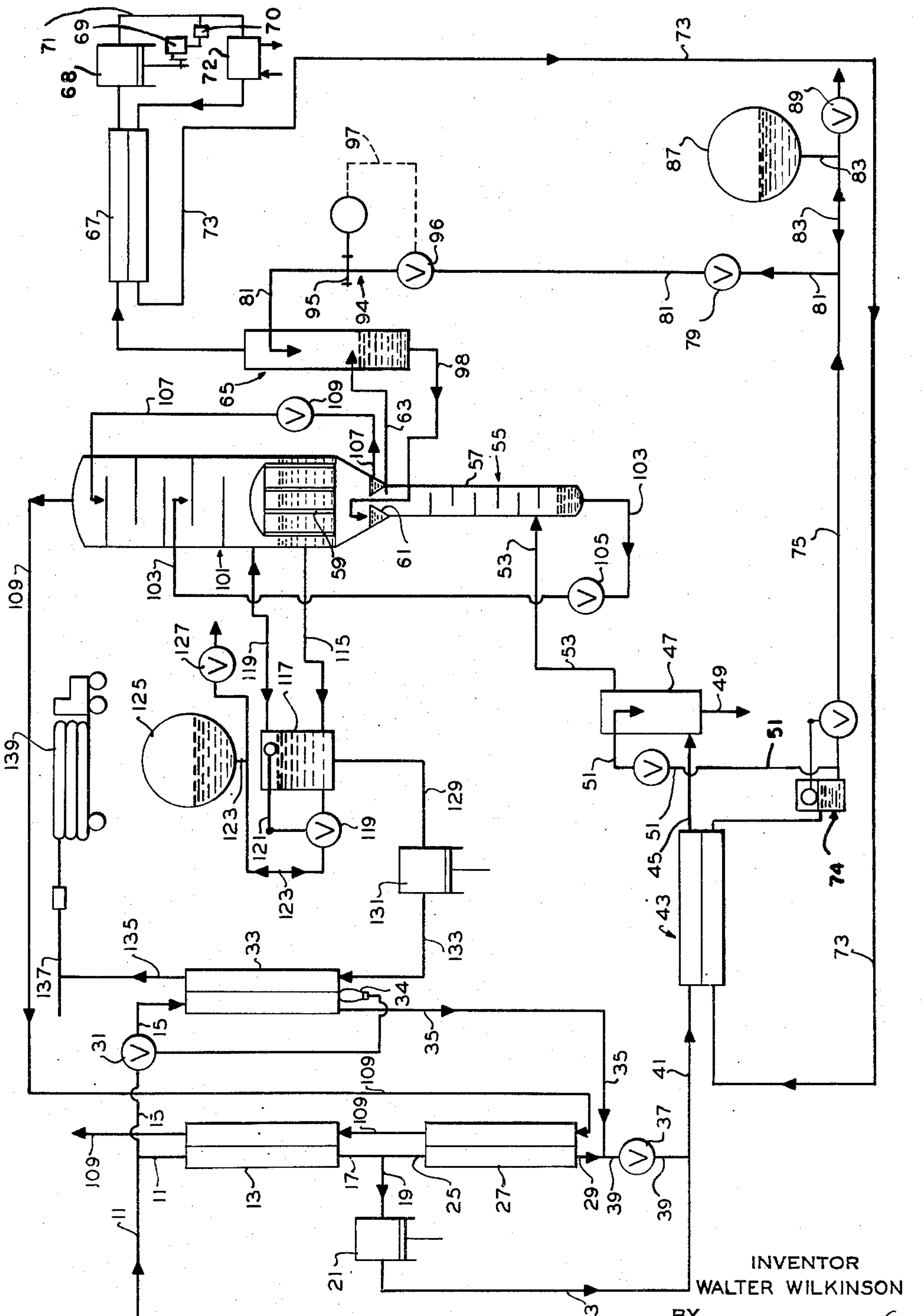


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## SEPARATION OF AIR

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This invention relates to the liquefaction and separation of air and more particularly to such a process in which part of the produced liquid oxygen is pumped and gasified by heat exchange with incoming air.

It is an object of this invention to provide a method and apparatus for the improved operation of an air separation process in which refrigeration is obtained by gasifying the liquid oxygen product by heat exchange with warm incoming air so that the variation in the refrigeration which is obtained does not affect, in an appreciable manner, the rate of liquid oxygen production.

It is another object to provide an air separation system whereby high purity liquid nitrogen is produced in limited quantities and in such a manner that the system does not become unbalanced and that the recovery of oxygen does not suffier during operations which include filling of cylinders with gaseous oxygen obtained by vaporizing pumped liquid oxygen.

The production of gaseous oxygen by a process in which the column first produces a liquid oxygen product and thereafter pumps at a constant rate some of this liquid oxygen through an exchanger system for gasification by heat exchange with warm, high-pressure incoming air so that the gasified oxygen can be filled at high storage pressure into containers, has long been known. Among the advantages of such a process is the fact that the refrigerative effect from the conversion of the liquid oxygen to gaseous oxygen is used in effecting the separation of air. There are, however, certain disadvantages which are inherent with such processes which have been previously in operation.

At the beginning of the filling of oxygen containers, such as high-pressure cylinders or horizontal-tube truck trailers, the pressure in the containers is about 500 p. s. i. g. or somewhat below. During this initial, low pressure period, a large transfer of heat occurs as the liquid oxygen evaporates to relatively low pressures while absorbing heat from the incoming air. At the end of the operation when the pressures approach 2700 p. s. i. g., of course, less heat is transferred from the incoming air to the oxygen being gasified and forced into containers. This can also be thought of as a recovery of cold or refrigeration which was produced in the separation process since the cold of the liquid oxygen being gasified is transferred to the warm incoming air, thus cooling it toward its liquefaction point which is necessary for its subsequent separation. Considering the gasification step in terms of recovery of cold or refrigeration, it is obvious that the amount of refrigeration recovered varies as the pressure on the liquid oxygen being gasified varies. The recovery of cold is largest when the container pressure is low, and smallest when the container pressure is high.

The variation in recovery of refrigeration restricts many previously known plants from obtaining the maximum production of oxygen of the proper purity from the incoming air since the varying recovery of refrigeration necessarily alters the quantity of liquefaction-point air which enters the rectification column and hence the quantity of produced liquid oxygen from the incoming air, since the oxygen production is dependent on the total quantity of refrigeration. Of course, the total quantity of refrigeration could be varied by increasing or decreasing the amount of refrigeration which is produced by the conventional methods used for expansion of air. However, in the operation of a commercial plant, it is not desired to vary continuously the factors which will give increased refrigeration from the expansion of air. In many plants the method of operation preferably is to set the air pressure on the unit at a fixed pressure and to maintain a constant flow. By so doing, the available refrigeration from the expansion engine and the Joule-Thompson effect of liquid passing through the expansion valve is almost constant even if the quantities respectively so handled is varied somewhat. However, the oxygen being gasified in the exchanger system, due to the increase in pressure, effects less refrigeration and hence causes the production of a smaller quantity of liquid oxygen during the terminal portion of the trailer filling operation because some of the liquid oxygen in the separation column will be evaporated to offset the decrease in the quantity of refrigeration. This operation in effect gives less than substantially 100% recovery of oxygen from the air entering the separation column which, of course, is undesirable.

The above described condition which occurs during cylinder filling is, of course, greatly accentuated when there are temporarily no cylinders or trailers available. In many plants, continuous operation is not possible due to the unavailability of cylinders during certain periods of time. To compensate for the temporary absence of refrigeration recovered from gasifying liquid oxygen, of course, even greater adjustments in the factors which give refrigeration from the expansion of air would be required if the full recovery of oxygen is to be effected. As above mentioned, these adjustments are not desired.

The problem, then, is to recover the variable quantity of refrigeration from the liquid oxygen being gasified and to operate during temporary absences of cylinders and yet to maintain the maximum production of oxygen at all times by an economical process which does not require continuous adjustment of the expansion of air in order to maintain a balanced process.

The instant invention solves the foregoing problem and accomplishes the above-mentioned objects by providing the step of supplying a fixed quantity of liquid nitrogen fed into the separation system in relation to a fixed air flow so that the production of liquid oxygen at the proper purity in desired quantity occurs at all times. This regulation is accomplished in the preferred embodiment by modifying a basically conventional air separation system which produces liquid oxygen as a product and has an arrangement for pumping at least some of this oxygen product and then gasifying it by heat exchange with incoming air. A nitrogen recycle, liquid nitrogen storage means, an air-nitrogen exchanger and constant flow means in the liquid recycle nitrogen piping are preferably added to the basic system in such a manner that a proper flow of nitrogen of the nitrogen recycle is brought into heat exchange with cold incoming air which has been, in part, cooled in proportion to the gasification of the liquid oxygen product. With this arrangement and with a predetermined air pressure and flow, it is possible to produce a reserve of liquid nitrogen and, by withdrawing recycle nitrogen at a proper point, to avoid interfering with the purity of oxygen. This reserve of liquid nitrogen re-enters the separation process by means of the constant flow arrangement in the nitrogen recycle and occurs when the quantity of cold absorbed by the incoming air from the liquid oxygen being gasified is less than the amount of cold necessary to provide the desired constant quantity of liquid nitrogen which is necessary for refrigeration and proper operation of the separation process. The system is operated at a constant pressure which is higher than that necessary to balance the system when cylinder filling is being done at lower pressures, and lower than that pressure required to produce 100 per cent liquid oxygen at all times without recovery of any refrigeration therefrom. In this manner and with above arrangement, a reserve quantity of liquid recycle nitrogen is produced during filling at lower and intermediate pressures. Thus, during cylinder filling at lower pressures reserve liquid nitrogen will be produced in a quantity depending upon the pressure in the cylinders; yet, during the terminal filling with no reserve production, the amount of liquid nitrogen passing to the rectification unit will remain constant since the previously produced liquid nitrogen reserve is utilized. This reserve of liquid nitrogen does not have to be very large for normal operation.

When cylinder filling is temporarily not possible, the regular oxygen production which is intended to be gasified is transferred to suitable storage means and, when filling is possible, this stored liquid oxygen can be added to the regular liquid oxygen production going to the vaporizing exchanger in order to effect the production of an increased reserve of liquid nitrogen. In this manner, the reserve of liquid nitrogen will have approached the quantity of liquid nitrogen which, in terms of refrigeration, is necessary for balanced operation when subsequently no cylinders are available temporarily.

This instant process also has a further feature incorporated therein including a suitably arranged nitrogen rectifier in order to produce, when the system is balanced at upper intermediate filling pressures, high purity nitrogen which will be condensed in the nitrogen recycle and can be used for various purposes, such as scrubbing impurities from the incoming air.

The advantages and features of the invention will be more readily apparent by reference to the following description and the accompanying drawing which illustrates diagrammatically the preferred embodiment.

Referring now to the drawing, it can be seen that the dried, compressed air to be separated by the liquid oxygen process of the instant invention is shown entering the system via main conduit **11** and flows towards heat exchanger **13** which can be one of several commercially-available types. Since the illustrated preferred embodiment is designed to produce a large quantity of liquid oxygen for distribution as a liquid, in addition to gaseous oxygen, the air pressure is preferably about 170 atmospheres. Just prior to the heat exchanger **13**, a branch pipe **15** connects to main conduit **11**. When some of the liquid oxygen product of the system is being vaporized, a minor portion of the high pressure air enters pipe **15** for a purpose which will be described subsequently. The major portion of the high pressure incoming air flows through exchanger **13** and is cooled by a cold outgoing process stream of waste nitrogen which enters exchanger **13** at an intermediate temperature. This waste nitrogen is derived in a manner that will be described hereinafter. In exchanger **13**, this major portion of air is cooled to a temperature in the neighborhood of −30° C. This cooled air then flows from exchanger **13** by means of pipe **17** and is divided at the point where conduit **19** joins pipe **17**. One part of this divided air flow passes through pipe **17** to expansion engine **21** where it is expanded to a pressure of approximately 75 p. s. i. g. with the performance of external work as is conventional. This provides refrigeration for the process and, of course, the air leaving the expander **21** in conduit **23** is at a much lower temperature than −30° C.

The other part of the cooled air at the high entrance pressure, resulting from the division at the juncture of pipes **17** and **19**, flows in pipe **25** to air liquefier **27** in which this part of the air is cooled down to a very low temperature by the previously mentioned waste nitrogen stream at a low temperature. This cold high-pressure air then flows from air liquefier **27** in pipe **29** and is joined by the minor portion of high-pressure air in pipe **35** which was divided off from the incoming air and entered pipe **15**. Prior to this juncture this minor portion of air has passed through pipe **15** and the temperature responsive valve **31** to the oxygen vaporizing or gasifying exchanger **33** in which liquid oxygen produced in the process was gasified by heat exchange with the relatively warm minor portion of air. This heat exchange cooled the minor air portion since its heat was transferred to the liquid oxygen which was being gasified. Valve **31** is responsive, by means of the temperature responsive element **34** and its piping, to the temperature in conduit **35** through which the minor air portion flows after being cooled in vaporizing exchanger **33**. The amount, or lack of, heat exchange in gasifying exchanger **33**, for the reasons previously noted, precipitates the problem towards which the instant invention is directed and will be subsequently considered in greater detail.

As above mentioned after the minor portion of air has been cooled in vaporizing exchanger **33**, it leaves this exchanger by means of conduit **35** and then joins the cold part of the major portion of air from liquefier **27** at the juncture of pipes **35** and **29**. This combined stream of air which is above its critical pressure but at a very low temperature is then expanded through expansion valve **37** in conduit **39** to a pressure of approximately 75 p. s. i. g. After this expansion down to 75 p. s. i. g., the expanded combined stream joins by means of a juncture between pipe **39** and pipe **23** the other part of the major portion of the incoming air which has passed through expansion engine **21**. The combination of the air exhausted from expander **21**, the air from the liquid oxygen gasifying exchanger **33**, and the air from air liquefier **27** constitutes a mixture which contains some liquid air and can be thought of as a reunited air stream. This reunited mixed-phase air next passes through conduit **41** which extends from the juncture of pipes **23** and **39** to recycle nitrogen liquefier **43** in which the liquid-phase portion of the air is evaporated by indirect heat exchange with recycle nitrogen at a suitable pressure with nitrogen being consequently condensed. This treatment of the mixed-phase air in recycle nitrogen liquefier **43** produces air in a dry saturated condition which next flows in pipe **45** to scrubber **47**.

In scrubber **47**, the air is intimately contacted by means of conventional liquid-tray bubble-cap-construction (not shown) with liquid nitrogen for the purpose of removing hydrocarbons, oil, acetylene, residual solid carbon dioxide, etc. which substances can be referred to as high boiling point impurities or contaminants. The contaminants are carried along with a small quantity of liquid which leaves the bottom of the scrubber **47** through pipe **49**. This liquid contains a small portion of the oxygen which is contained in the incoming air and a portion of the liquid nitrogen which was fed into the top of the scrubber **47** by valved pipe **51**. The scrubbing liquid is obtained in manner which will be subsequently described.

The purified air, leaving the top of the scrubber **47** by pipe **53**, contains all of the nitrogen in the incoming air stream and the major portion of the oxygen in the incoming air stream. The purified air next flows in pipe **53** to a conventional double column **55** for air separation and enters the lower part of the column, high pressure, rectifier section **57** which contains conventional means shown schematically for assuring intimate contact between an upwardly-flowing gas and a downwardly-flowing liquid, such as trays with bubble caps.

In rectifier section **57**, the incoming air at about 75 p. s. i. g. is partially rectified by contact with liquid nitrogen passing downwardly which tends to condense more of the lower boiling point oxygen than the higher boiling point nitrogen in the incoming air. This operation results in gaseous nitrogen flowing upwardly into the condenser **59** where it condenses because the tubes of the condenser **59** are cooled by the evaporation of the liquid oxygen at a lower pressure around the tubes. Part of the condensed nitrogen then returns to the bubble-capped trays or other means and part is collected in the annular trough **61**, extending beneath some of the condenser tubes, at the top of rectifier section **57**. By this well-known preliminary rectification of air, liquid which is enriched with oxygen (about 40 per cent) collects in the bottom of section **57** which in the top, nitrogen including principally small amounts of oxygen collects.

Some nitrogen gas at about 75 p. s. i. g. is withdrawn from the top part of rectifier **57** by pipe **63** which extends into rectifier **57** below the annular trough **61** and is introduced into nitrogen rectifier **65** for further purification. In rectifier **65**, the nitrogen is separated from small amounts of oxygen which are carried over. The high purity gaseous nitrogen flows from the top of rectifier **65** through heat interchanger **67** where it is warmed to approximately atmospheric temperature. Next the nitrogen is compressed from about 75 p. s. i. g. to about 120 p. s. i. g. in nitrogen recycle compressor **68** having a variable speed motor **69** which is controlled by a pressure responsive device **70** connected into conduit **71**. After compression, the nitrogen is cooled in water-cooled aftercooler **72** to about atmospheric temperature. The nitrogen is then further cooled in nitrogen interchanger **67** by warming the nitrogen from the top of nitrogen rectifier **65**. From the interchanger **67**, the cooled compressed nitrogen passes by means of conduit **73** to recycle nitrogen liquefier **43** where the nitrogen is liquefied by giving up heat indirectly to evaporate liquid in the mixed-phase air passing through the liquefier **43** on its way to the double column **55**. This nitrogen passes through float control chamber **74** and then is divided with one portion flowing in valved pipe **51** with a reduction in pressure to about 75 p. s. i. g. to scrubber **47** to provide the liquid nitrogen used in the previously described scrubbing of incoming air.

The other portion of the liquid nitrogen passes through pipe **75** to the juncture of pipe **75** with pipes **81** and **83**. At this juncture the liquid nitrogen will divide depending on conditions to be set forth subsequently. The liquid flowing in pipe **81** will pass through expansion valve **79** and a conventional constant flow means **94** to the nitrogen rectifier **65** where this liquid acts as a reflux in the production of high purity nitrogen. In passing through expansion valve **79**, the pressure of the liquid will be reduced to about that existing in rectifier **65** which is approximately 75 p. s. i. g. By means of pipe **83** which joins pipe **81**, the liquid nitrogen (condensed in liquefier **43**) can either enter liquid nitrogen storage tank **87** or, at other times, liquid nitrogen can be taken from tank **87** and added to the liquid nitrogen in pipe **81** which is flowing to nitrogen rectifier **65**. Tank **87** is maintained at a pressure which is in excess of 75 p. s. i. g. by suitable means (not shown) and yet is suitable in relation to the high pressure side of the nitrogen recycle. When desired, liquid nitrogen can be removed from tank **87** by means of valved pipe **89** which branches from pipe **83**.

The constant flow means **94** in pipe **81** which functions to maintain a constant flow of liquid nitrogen from the nitrogen liquefier **43** or from the nitrogen liquefier **43** and the liquid nitrogen storage tank **87** is comprised of a conventional flow orifice device **95** which measures the flow and an automatic valve **96** which valve is responsive to the flow orifice device **95** by means of connections **97** and is upstream of device **95**. With this automatic arrangement, the flow of liquid nitrogen to rectifier **65** is maintained constant.

In nitrogen rectifier **65**, the previously described rectification to get high purity nitrogen is accomplished with the liquid nitrogen entering through pipe **81** serving as reflux. The liquid nitrogen containing the traces of oxygen which collects in the bottom of rectifier **65** is transferred by conduit **98** to the annular trough **61** in the high pressure, lower rectifying section **57**. As above mentioned, annular trough **61** also collects liquid nitrogen which has been condensed in tubes of condenser **59**.

The low-pressure upper rectifier **101** of column **55** which also has the conventional tray-bubble-cap construction (shown schematically) receives oxygen-enriched liquid and liquid nitrogen from the lower high-pressure rectifier **55**. The oxygen-enriched liquid flows in pipe **103** from the bottom of lower rectifier, expands through the expansion valve **105** from about 75 p. s. i. g. to about atmospheric pressure, and enters the low-pressure rectifier **101** at an intermediate level. Liquid nitrogen from the upper portion of trough **61** in lower rectifier **55** is conveyed by pipe **107** to the expansion valve **109**; and, after expansion therethrough to about atmospheric pressure, flows on through pipe **107** to the top part of the low pressure rectifier **101** for reflux. It is to be noted that the liquid nitrogen collecting in trough **61** is, at certain times, augmented by liquid nitrogen from tank **87** by means of conduit **81**, nitrogen rectifier **65**, and conduit **98**.

In rectifier **101**, the vapor rising up through the descending liquid becomes depleted in oxygen so that the vapor leaving the top of the rectifier **101** is fairly pure nitrogen. This gaseous nitrogen is a waste product of the apparatus except that its cold is recovered by passing it by means of pipe **109** to air liquefier **27** and, thereafter by pipe **111**, to air exchanger **13**. This waste nitrogen stream is the previously-mentioned process stream which effects the cooling of incoming air by indirect heat exchange in exchanger **13** and liquefier **27**. The rectification at atmospheric pressure which occurs in rectifier **101** results, in addition to the waste nitrogen vapor just mentioned, in liquid oxygen collecting in the bottom of rectifier **101** around condenser tubes **59**. This body of liquid oxygen is boiled by the condensation of nitrogen vapors in tubes **59** rising up therein from the rectification in the lower, high-pressure rectifier **55**. This boiling or evaporating results in a body of product liquid oxygen which has a high purity.

The liquid oxygen product is removed from the bottom of rectifier **101** by pipe **115** to float control chamber **117**. The vapor space of float control chamber **117** is connected by pressure-equalizing conduit **119** to the space in the upper rectifier **101** which is just above the level of the liquid oxygen being boiled by the condensation of nitrogen in tubes **59** of the condenser. When the quantity of liquid collected in float control chamber **117** is such as to cause valve **119** to open via the float mechanism **121**, the liquid oxygen flows in pipe **123** to liquid oxygen storage tank **125** or flows in valved pipe **127** which is connected to pipe **123** to any suitable means (not shown) for putting it into a liquid oxygen container, such as a railway tank car.

When the previously-mentioned filling of gaseous oxygen containers occurs, liquid oxygen flows by means of pipe **129** from float control chamber **117** to a suitable liquid oxygen pump **131** where the pressure of the liquid is increased from about atmospheric pressure to about 2700 p. s. i. g. This high-pressure liquid oxygen then moves in pipe **133** to vaporizing exchanger **33** where the liquid oxygen evaporates to a gas at about atmospheric temperature and at the pressure existing in the gaseous oxygen containers by indirectly absorbing heat from warm, high pressure incoming air flowing countercurrently through the exchanger **33**. This gaseous oxygen leaves exchanger **33** in pipe **135** and moves by means of suitable piping **137** into high pressure oxygen containers, such as the horizontal tube truck trailer **139** which is shown on the drawing or suitable oxygen cylinders.

The basic operation of the system in regard to the exchanger **13**, expander **21**, liquefier **27**, expansion valve **37**, scrubber **47** and the double column **55** is well known in the art and it is believed this operation is obvious to one skilled in the art from the foregoing description. However the mode of operation of the liquid oxygen vaporizer **33**, the liquid oxygen storage tank **125** and pump **131**, the nitrogen recycle including nitrogen rectifier **65**, liquid nitrogen storage tank **87** and the constant flow means **94** and other related apparatus embodies operational features of the instant invention and will now be described.

When no liquid nitrogen product is desired and after the system is in operation and liquid oxygen is being vaporized in the liquid oxygen vaporizing exchanger **33** and moving to an empty trailer **139**, the minor portion of air flowing through the vaporizer **33** will be absorbing a large quantity of cold. This cold will result in small excess of liquid nitrogen being condensed in recycle nitrogen liquefier **43**. The excess liquid nitrogen thus produced will be diverted into the liquid nitrogen storage tank **87** due to the constant flow means **94**. As the pressure in the trailer **139** and hence in the vaporizer **33** increases, the temperature responsive means **34** at the cold end of the vaporizer and the valve **31** responsive thereto will begin to reduce the flow of incoming air through the vaporizer **33** since recovery of refrigeration has diminished. During this period and until the filling of the trailer is completed, the amount of cold absorbed by the incoming air in vaporizer **33** will be gradually decreased in a small but bothersome amount. This reduction in cold recovery decreases the total refrigeration in the process and would normally affect the recovery of oxygen. However, this smaller quantity of total refrigeration is compensated for by utilizing the small excess or reserve liquid nitrogen which represents an offsetting quantity of refrigeration. This utilization is effected by the constant flow means **94** which is connected to the liquid nitrogen storage means **87**. Thus, when the filling of containers at high pressures is being done, the required quantity of the previously-produced small reserve of liquid nitrogen will flow from storage tank **87** back through pipe **83** into pipe **81**, etc. so that the predetermined flow through constant flow means **94** is maintained. In this manner the flow of liquid nitrogen into nitrogen rectifier, and, as a consequence, the flow of liquid nitrogen through pipe **107** and its valve **109** to the low pressure, upper rectifying section **101** is maintained constant. Considering the system as a whole, it is apparent that liquid oxygen collects at the bottom of the rectifier **101** around condenser tubes **59** in an amount proportionate to the refrigeration effect supplied to the column **55** by means of the cold vapor entering pipe **53** and the liquid nitrogen enter through valve **79**. The consequence of this operation is that the desired full recovery of oxygen is maintained at all times without troublesome adjustments in the compressor, expansion engine **21**, or throttle valve **37**.

It is to be noted that the system during operations when no high purity liquid nitrogen is desired is so operated as to be balanced (that is, when liquid nitrogen is neither flowing to storage or flowing from storage) when oxygen is being filled into containers at an intermediate pressure. The compensation in refrigeration during high pressure filling, when normally the system would become unbalanced due to a lack of refrigeration, is supplied automatically by the introduction of reserve liquid nitrogen from storage. Of course it is obvious that the total refrigeration requirements of the system are in the large part supplied by the expansion of entering high pressure air and that the introduction of the reserve liquid nitrogen when the system would otherwise be under-refrigerated (during high pressure filling) merely provides a minor fraction of the required refrigeration. However this automatic refrigeration compensation is sufficient to avoid the troublesome continuous adjustments which would otherwise be required for the desired full recovery of liquid oxygen.

During the periods when no cylinder or trailer filling is possible due to the absence thereof, no incoming air, of course, is passed through vaporizer **33** and the total quantity of refrigeration is reduced since the refrigeration from the expansion of air in expansion engine **21** and throttle valve **37** remains more-or-less constant. This reduction in refrigeration, of course, tends to be compensated for in the same manner as during the high pressure filling if liquid nitrogen is available in the compensating arrangement. However, the small excess nitrogen made during average low pressure average filling of cylinders when no liquid nitrogen product is desired is primarily intended to offset the lower cold recovery during high pressure filling. If desired, the balancing of the process could be set at an upper intermediate filling pressure so that the liquid nitrogen recovered during low-pressure filling is sufficient to provide refrigeration for some part of a no-filling period. In this manner, short temporary absences of cylinders or trailers would not substantially affect the process since a further secondary reserve of liquid nitrogen would be maintained. This balanced condition of operation when a secondary reserve is not desired is also suitable, in conjunction with the nitrogen rectifier **65**, for the production of a limited quantity of high purity liquid nitrogen, as will be subsequently referred to.

However, the foregoing production of a secondary reserve of liquid nitrogen by producing a larger reserve of liquid nitrogen during average low pressure filling need not be resorted to as a general rule. This is possible because of the oxygen storage and pumping means and the capacities and arrangement of the vaporizer and nitrogen recycle are such that, during the no filling period, the liquid oxygen to be gasified is stored; and, during the time when filling in larger than average quantities can be done, this stored liquid oxygen is added to the average quantity of liquid oxygen to be gasified. In this manner, more cold is absorbed by the incoming air and this increase in cold results in a larger reserve of liquid nitrogen. This larger reserve of liquid nitrogen is stored during these higher-than-average filling periods and then returned to the process during the no-filling periods in the same manner as occurs during the high pressure filling.

The foregoing description does not point out the manner and means for getting the required quantity of nitrogen to the nitrogen liquefier **43**. Obviously this quantity must vary in proportion to the refrigeration, or the lack thereof, transferred to the incoming air from the liquid oxygen being gasified. Assuming the state of operation when the gasified, liquid oxygen in regular production quantity is being filled into containers at high pressures, it is apparent that less refrigeration will be available for transfer in liquefier **43** to the nitrogen recycle than was possible when the gasified oxygen was being filled into containers at low pressure. During this period it is necessary to reduce the quantity of nitrogen passing to liquefier **43**. This is accomplished quite simply and in a satisfactory manner by means of the pressure sensitive device **70** which is connected into the discharge line **71** from the compressor **68** and which is suitably constructed and arranged to control the variable speed motor **70** which operates the compressor. With this arrangement when the refrigeration available at liquefier **43** decreases, the pressure sensitive device will respond promptly to the resulting increase in pressure of the nitrogen in conduit **71** and so the compressor **68** will be operated at a lower speed in order to provide the proper amount of nitrogen for liquefaction in liquefier **43**. It is to be noted that the float control chamber **74** which operates exactly as the previously described float control chamber **117** in the liquid oxygen flow path provides the means for assuring that only liquid nitrogen flows in conduit **81**. Numerous other means, such as throttling the intake to compressor **68** or unloading means, can be used in place of the variable speed motor which has been shown to regulate the volume of compressed nitrogen flowing to liquefier **43**.

During periods when an ample number of high pressure oxygen containers is available and more than the normal average production of liquid oxygen (destined for gasification) is being gasified by withdrawing liquid oxygen from storage tank **125**, there is a need for additional nitrogen to flow to the nitrogen passage of liquefier **43** since the additional refrigeration is to be stored by making liquid nitrogen which will pass to liquid nitrogen storage tank **87**. This additional nitrogen is supplied by the same means **69**, **70**, above-described, used for reducing the quantity of nitrogen flowing to liquefier **43**. Thus, when the pressure of the nitrogen in the conduits back from liquefier **43** to compressor **68** begins to decrease, due to the additional refrigeration in the air passing through liquefier **43** derived from gasifying liquid oxygen from storage tank **125**, the pressure sensitive device **70** will function to increase the speed of the compressor motor **69** and hence the proper quantity of nitrogen will flow to liquefier **43**, be liquefied and pass to liquid nitrogen storage tank **87** due to the constant flow means **94**.

When the amount of liquid oxygen being gasified decreases towards the normal average production of liquid oxygen (destined to be gasified) and, as a consequence, the pressure of the nitrogen downstream from compressor **68** increases due to less excess refrigeration, it is apparent that the pressure responsive means **70** will reduce the speed of the compressor motor **69** in the same manner, as abovementioned in regard to filling at high pressures, so that the proper quantity of nitrogen flows to liquefier **43**.

In accordance with the above-mentioned object relating to the production of high purity liquid nitrogen, it is to be noted that the preferred embodiment disclosed herein is adapted to achieve this object in part because of the nitrogen rectifier **65**. With rectifier **65** suitably interposed in the nitrogen recycle which is primarily arranged to provide the previously described compensation by maintaining a constant ratio between the air flow and the liquid nitrogen entering the system and with the operational conditions set as is above-mentioned in relation to a secondary liquid nitrogen reserve, it is possible to produce limited quantities of high purity liquid nitrogen. Thus with the system balanced at an upper intermediate filling pressure, there will be more liquid nitrogen produced during low pressures and during part of the intermediate pressure filling than is required to compensate for the reduced recovery of refrigeration from gasifying liquid oxygen during high pressure filling. This excess of liquid nitrogen will constitute a limited production of liquid nitrogen which, due to the functioning of rectifier **65**, will have the desired high purity.

It is to be noted that the system operates so that, during filling of cylinders with high pressure gaseous oxygen, a variable quantity of liquid oxygen is not produced in the rectifier as would normally occur but that, due to the nitrogen cycle which is interposed, the quantity of liquid oxygen produced is maintained constant. This is accomplished by the nitrogen cycle which maintains a constant ratio between the incoming air and the liquid nitrogen reflux since the rate of flow of air is constant and the storage means and constant flow means in the nitrogen cycle maintains a constant flow of liquid nitrogen reflux. Also it can be pointed out that there is ample nitrogen in the air so that the withdrawal of liquid nitrogen for the purpose of absorbing the excess refrigeration does not interfere with the production of oxygen since the liquid nitrogen is withdrawn from a point other than the primary rectification system.

From the foregoing it is apparent that the instant method and apparatus provides a means for operating an air system which pumps liquid oxygen for vaporization without the undesired continuous changing of the amount of refrigeration produced by the expansion of the air entering the system so that the production of liquid oxygen does not vary during the cylinder filling cycle, including temporary periods when no filling can be done. It is also apparent that, in conjunction with the foregoing, means have been provided for producing limited quantities of high purity liquid nitrogen.

It is to be understood that various changes in the disclosed preferred embodiment can be made by one skilled in the art without departing from the invention as defined in the following claims.

I claim:

1. In an air separation process which produces liquid oxygen from air using liquid nitrogen reflux and then pumps and gasifies liquid oxygen to high pressures by heat exchange with a process stream, the improvement which comprises utilizing the refrigeration recovered in gasifying more than the regular production of liquid oxygen which is to be gasified to produce a reserve of liquid nitrogen and subsequently maintaining a constant ratio between the air flow and the liquid nitrogen reflux by adding liquid nitrogen from said reserve to the liquid nitrogen reflux when less than the regular production of liquid oxygen is being gasified.

2. In a process which produces liquid oxygen from air using liquid nitrogen reflux and then pumps and gasifies liquid oxygen to high pressures, the improvement which comprises utilizing the refrigeration recovered in gasifying the liquid oxygen at low pressures to produce a reserve of liquid nitrogen and maintaining a constant ratio between the air flow and the liquid nitrogen reflux by using the reserve of liquid nitrogen when the amount of refrigeration recovered is appreciably less than the amount which is recoverable by gasifying liquid oxygen at low pressures.

3. A method for separating gaseous mixtures by a liquefaction and rectification system having means for gasifying a liquid product comprising separating the gaseous mixture into a high boiling point gaseous fraction and a regular production of low boiling point liquid fraction for gasification, storing at least part of said low boiling point liquid during periods when the entire quantity of said regular production is not being gasified, adding said stored high boiling point liquid to the regular production when gasification thereof is possible, transferring the refrigeration derived from the gasification of said stored low boiling point liquid to a suitable medium in such a manner as to liquefy said medium, and utilizing the liquid medium for refrigeration by bringing it into heat exchange relation with said system where said separating step occurs when no gasification of the low boiling point liquid is being done.

4. In an air separation process in which the produced liquid oxygen is pumped and then gasified by heat exchange with warm incoming air and the incoming air flow is maintained constant, the improvement which comprises producing a reserve of liquid nitrogen due to heat exchange with liquid oxygen being gasified when the gasification of the liquid oxygen is refrigerating the incoming air to a greater extent than is necessary to balance the process and then automatically utilizing said reserve of liquid nitrogen to maintain the total refrigeration in the process about constant when the gasification of the liquid oxygen is not refrigerating the incoming air to the extent necessary to balance the process.

5. The method of operating an air separation system which pumps liquid oxygen and gasifies it by heat exchange with high-pressure incoming warm air for delivery to high pressure containers including the steps of maintaining the air pressure and flow substantially constant, producing a liquid nitrogen reserve by utilizing the refrigeration available when liquid oxygen is being gasified at low pressures, and maintaining the amount of liquid nitrogen which enters the separation system at a constant quantity by utilizing the reserve liquid nitrogen when liquid oxygen is being gasified at high pressure and so less

refrigeration is recovered from liquid oxygen than is possible at low gasifying pressures.

6. A method for separating gaseous mixtures by liquefaction and rectification comprising separating the gaseous mixture into a low boiling point gaseous fraction and a high boiling point liquid fraction by means of a rectification system, gasifying said liquid fraction and filling it into containers to a high pressure whereby a variable amount of refrigeration is produced and transferring the refrigeration from the gasifying step to a suitable medium in such a manner as to assist in liquefying the medium, utilizing the liquid medium for refrigeration and reflux in said separating step, and regulating the utilization of the liquid medium in such a manner that the ratio between the flow of the gaseous mixture and the flow of the liquid medium to the separating step is maintained constant.

7. In an air separation process which produces liquid oxygen and gasifies it intermittently and has a liquid nitrogen reflux system, the improved method of operation which comprises maintaining a predetermined air flow, providing a nitrogen recycle in said process, storing said liquid oxygen when gasification temporarily is not possible, gasifying said stored liquid oxygen when gasification can exceed, due to the availability of gaseous oxygen containers, the normal production of liquid oxygen which is intended to be gasified, transferring the refrigeration produced in said gasifying step to a process air stream and therefrom to a compressed stream of said nitrogen recycle in such a manner that a quantity of liquid nitrogen is produced, storing liquid nitrogen thus produced, returning said stored liquid nitrogen to said liquid nitrogen reflux system when gasification of liquid oxygen is not possible and regulating said return of liquid nitrogen to said reflux system so that the quantity of liquid nitrogen in the reflux is substantially constant in relation to the predetermined air flow.

8. In an air separation system in which a predetermined quantity of liquid oxygen which is produced in a fractionating process is gasified by heat exchange with incoming air, the improvement which comprises adjusting the process so that it is balanced when the recovered amount of refrigeration from gasification of liquid oxygen is less than the amount of refrigeration which is recoverable from the gasification of liquid oxygen at low pressures, incorporating nitrogen recycle flows in the system, transferring the refrigeration recovered from the gasification of the liquid oxygen to nitrogen recycle flow and thus producing a reserve of liquid nitrogen when the recovery of refrigeration from the gasification of liquid oxygen exceeds the amount necessary to balance the system, storing and then utilizing said reserve of liquid nitrogen to help refrigerate the process when the recovery of refrigeration from the gasification of liquid oxygen is less than the amount necessary to balance the process.

9. A process for producing liquid oxygen and liquid nitrogen from an air stream comprising separating the air into a high pressure nitrogen, high pressure oxygen-enriched liquid air, low pressure high purity liquid oxygen, and low pressure gaseous nitrogen by means of a rectification system, gasifying some of said high purity liquid oxygen and filling said high purity gaseous oxygen into containers to a high pressure whereby a variable quantity of refrigeration is produced, by heat exchange with the air stream, rectifying said high pressure nitrogen into high purity gaseous nitrogen and liquid nitrogen, compressing said high purity gaseous nitrogen, liquefying said compressed high purity gaseous nitrogen by heat exchange with said air stream, balancing the process in relation to the refrigeration obtained by gasifying liquid oxygen so that more compressed high purity gaseous nitrogen is liquefied during lower pressure filling than is necessary to compensate for the smaller amount of refrigeration which is recovered from gasifying liquid oxygen during higher pressure filling so that a limited quantity of high purity liquid nitrogen is produced which can be removed from the process.

10. A process for the separation of air which includes the steps of compressing air to about 2500 p. s. i. g., cooling it to about atmospheric temperature, dividing said air into a large flow and small flow, cooling the large flow of said compressed air by heat exchange with waste nitrogen effluent, dividing the compressed, cooled large air flow into a major fraction and a minor fraction, expanding said major fraction to a pressure of about 75 p. s. i. g. with the performance of work, partially liquefying said minor fraction by heat exchange with waste nitrogen effluent, cooling said small flow by gasifying liquid oxygen, regulating the quantity of said small flow being cooled in response to its temperature after gasifying the liquid oxygen, expanding said partially liquefied minor fraction and said cooled small flow with a Joule-Thompson effect to about 75 p. s. i. g. combining all of said expanded air into a reunited flow, warming said full air flow to substantially a dry saturated condition by heat exchange with compressed nitrogen gas, separating said reunited flow by fractionation at pressure of about 75 p. s. i. g. into gaseous nitrogen, condensed nitrogen and oxygen-enriched liquid and at low pressure into high purity liquid oxygen and a gaseous waste nitrogen effluent, utilizing said waste nitrogen effluent in said second mentioned cooling step and said partially liquefying step, removing said high purity liquid oxygen and pumping it to a very high pressure, gasifying said pumped liquid oxygen by absorbing heat from the aforementioned cooling of the small flow, removing some of said high pressure gaseous nitrogen and fractionating it with the use of liquid nitrogen reflux into a rectified nitrogen liquid and a rectified nitrogen gas, compressing and then cooling said rectified gas, liquefying said cooled compressed rectified nitrogen gas by transferring heat from the gas to air in the aforementioned warming of said reunited air flow, collecting said liquefied nitrogen, introducing a constant amount of said collected nitrogen into said nitrogen fractionating step as the reflux, uniting said rectified nitrogen liquid with said high pressure condensed liquid nitrogen, transferring said united liquid nitrogen as reflux and said oxygen-enriched liquid as the mixture to be fractionated to the low pressure fractionating step, adjusting the process so that the liquid nitrogen produced during gasification of liquid oxygen at low pressure exceeds said constant amount of liquid introduced into nitrogen fractionating step and storing the excess liquid nitrogen resulting from the vaporization of liquid oxygen at low pressures in such a manner that it can be added to the constant amount of liquid nitrogen which is introduced into said nitrogen fractionating step.

11. Apparatus for the separation of air and the filling of gaseous oxygen to high pressures into containers comprising means for rectifying air into a liquid oxygen product, means arranged to pump and to vaporize the liquid oxygen product by heat exchange with incoming air, and means associated with said first and said second mentioned means including a nitrogen recycle having a liquid nitrogen storage tank constructed and arranged to compensate for the decreasing quantity of refrigeration which is recovered when vaporizing the liquid oxygen product at high pressures.

12. Apparatus for separating air and for filling gaseous oxygen into containers to high pressures comprising means for separating air into liquid oxygen, said means including a system for pumping and gasifying the liquid oxygen and a nitrogen recycle having a liquid storage device and a constant flow means, means associated with said first mentioned means in such a manner that refrigeration recoverable from the gasifying of liquid oxygen is transferable to the nitrogen recycle to produce liquid nitrogen, and said storage device, said constant flow means, and said second mentioned means being arranged to deliver a constant quantity of liquid nitrogen into a heat exchange relation with said first-mentioned means for separating air.

13. Apparatus for separating air and for filling gaseous oxygen into containers at high pressures comprising means for placing compressed, incoming air in a partially liquefied state by heat exchange with outgoing gaseous nitrogen and by the expansion of the incoming air, said first-mentioned means including a liquid oxygen vaporizing exchanger, a recycle nitrogen liquefier having an air passage for placing the incoming air in a dry saturated condition by indirect heat exchange, a fractionating column connected to the air passage of said nitrogen liquefier and adapted to produce liquid oxygen and gaseous nitrogen from the incoming air, said column having a liquid nitrogen reflux system, a liquid oxygen pump for delivering liquid oxygen at high pressures arranged to deliver liquid oxygen from said column to said vaporizing exchanger, a nitrogen recycle system operably arranged with said column and said nitrogen liquefier, said recycle system including liquid nitrogen storage means and constant flow means and being arranged to supply liquid nitrogen to the liquid nitrogen reflux system of said column.

14. Apparatus for separating and rectifying air and for producing high pressure gaseous oxygen comprising means for processing air into a partially liquefied state at 75 p. s. i. g., said means including a liquid oxygen vaporizing exchanger which is arranged to automatically assist said means in said processing when liquid oxygen is being vaporized, a nitrogen liquefier having an air passage connected to said first mentioned means for receiving the cold partially liquefied air therefrom and having a nitrogen passage for receiving warm compressed nitrogen, an air rectification device which is adapted to produce a liquid oxygen at atmospheric pressure and gaseous nitrogen at 75 p. s. i. g. connected to the air passage of said nitrogen liquefier, said device having a nitrogen reflux system, a nitrogen recycle including a compressor, the nitrogen passage of said nitrogen liquefier, and expansion valve and a constant flow means suitably connected and arranged to pass nitrogen from said rectification device at the location where gaseous nitrogen is produced at 75 p. s. i. g. through said compressor, said nitrogen passage, said expansion valve, and said constant flow means to the nitrogen reflux system of said rectification device; a liquid nitrogen storage tank arranged and connected into said nitrogen recycle at a point between said nitrogen liquefier and said expansion valve in such a manner that liquid nitrogen can flow to or from said tank as determined by said constant flow means; and oxygen delivery means constructed and arranged to remove liquid oxygen from said rectification device, to increase the pressure thereon to above 2000 p. s. i. g., and to deliver to said liquid oxygen vaporizer exchanger, whereby the vaporization of liquid oxygen produces a reserve of liquid nitrogen at times so that during other times this reserve is used to maintain the flow of liquid nitrogen to the nitrogen reflux system rectification device is maintained constant by the constant flow means.

15. Apparatus for separating and rectifying air and for producing high pressure gaseous oxygen according to claim 14 and including liquid oxygen storage means suitably constructed and arranged in said oxygen delivery means so that liquid oxygen produced can be stored when vaporization thereof is not possible and can be passed through said oxygen delivery means when vaporization is possible.

16. Air separation apparatus for intermittently delivering high pressure gaseous oxygen which is derived from pumped liquid oxygen comprising a rectification column in which a pool of liquid oxygen collects and having a liquid nitrogen reflux system, oxygen delivery means including a liquid oxygen storage tank, liquid oxygen pumping means, and a vaporizing exchanger constructed and arranged to withdraw liquid oxygen from said column and to pump and vaporize said liquid oxygen to high pressure gaseous oxygen, a flow control device arranged in said oxygen delivery means so that, when said liquid oxygen pumping means is not pumping, the liquid oxygen withdrawn from said column will flow into said storage tank, said pumping means and said vaporizing exchanger being constructed and arranged to pump and to vaporize liquid oxygen withdrawn from the column and the storage tank, nitrogen recycle means associated with said column and including a liquid nitrogen storage tank and a constant flow device, heat transfer means associated with said vaporizing exchanger and said nitrogen recycle in such a manner that refrigeration from the vaporization of liquid oxygen produces liquid nitrogen which will flow into said liquid nitrogen reflux system in a constant amount and will flow to, and from, said liquid nitrogen storage tank depending on the liquid nitrogen which is liquefied by the vaporization of liquid oxygen.

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